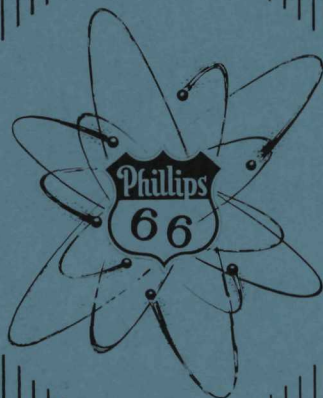MASTER

DISSOLUTION OF ZIRCONIUM AND ZIRCALOY-2
IN NITRIC-HYDROFLUORIC ACID MIXTURES
AT REFLUX TEMPERATURES

E. M. Vander Wall
E. M. Whitener
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September 1959

Chemical Development Section
CPP Technical

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A B S T R A C T

The initial rate constants were obtained for zirconium and Zircaloy-2 dissolution at reflux temperatures in nitric-hydrofluoric acid mixtures. Variation of the nitric acid concentration in these solutions had very little effect on the initial dissolution rate, except for the change in the reflux temperature. However, the nitric acid concentration exhibited an appreciable effect on the average dissolution rate over longer periods of time. An empirical treatment of the rates over extended periods is presented. The maximum attainable rates for zirconium dissolution, adjusted to an initial $1\underline{M}$ hydrofluoric acid concentration, were determined at lower temperatures. Stability of resultant Zircaloy-2 dissolver solutions is reported for both nitric-hydrofluoric acid mixtures and nitric-oxalic-hydrofluoric acid mixtures. Possible reactions and some analyses of off-gases from these dissolutions are given.

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DISSOLUTION OF ZIRCONIUM AND ZIRCALOY-2 IN NITRIC-HYDROFLUORIC ACID MIXTURES AT REFLUX TEMPERATURES

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DISSOLUTION OF ZIRCONIUM AND ZIRCALOY-2
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by

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I. SUMMARY

Economic operation of atomic power reactors requires the recovery of unburned uranium from spent fuel elements. Zirconium and its alloys find considerable usage as structural material in these elements. A suitable reagent mixture for the dissolution of zirconium-uranium alloys of varying composition is a nitric-hydrofluoric acid mixture. The current program was undertaken to determine the mechanism of dissolution in this system.

The initial rates of dissolution of zirconium and Zircaloy-2 at reflux temperatures were found to be first order with respect to the hydrofluoric acid concentration in mixtures of nitric and hydrofluoric acids. The initial rate constants for the first order rate expression,

$$-d\ Zr/dt = k[HF],$$

are 99.6 mg cm^{-2} min^{-1}/moles [HF] $liter^{-1}$ in 8$\underline{M}$ nitric acid and 114.2 in 13$\underline{M}$ nitric acid; for Zircaloy-2 dissolution in 8$\underline{M}$ nitric acid, the rate constant is 96.9. The nitric acid concentration in these solutions has little effect on the initial zirconium dissolution rate, aside from changing the reflux temperature. With Zircaloy-2, the effect is more pronounced.

At lower temperatures the maximum attainable normalized rates (in above units) for zirconium dissolution in 13$\underline{M}$ nitric acid-hydrofluoric acid mixtures are: 9.0 + 0.3 at 16.5°C, 12.1 + 0.3 at 25.5°C, 15.5 + 0.4 at 35.0°C, and 20.3 + 0.3 at 45.0°C. From these data, the activation energy for the dissolution is 5.8 kcal $mole^{-1}$. This low value, plus the fact that 2S aluminum dissolves at the same rate as zirconium and Zircaloy-2 in these solutions, indicates that the dissolution is diffusion controlled.

The nitric acid concentration in the mixed acids has a pronounced effect on the average dissolution rate over extended periods of time ($>1/2$ hr). Since a method for determination of the hydrofluoric acid concentration in these mixtures was not available at the time, an empirical approach was used to evaluate the extended rates. It was assumed that only hydrofluoric acid itself caused zirconium dissolution. On this basis, a rate law for the disappearance of hydrofluoric acid,

$$-d(moles\ HF)/dt = k[HF],$$

was developed. In 2$\underline{M}$ nitric acid, it was necessary to assume that 4 fluorides

were removed per zirconium dissolved, giving a rate constant of

$$3.49 \pm 0.17 \times 10^{-3} \text{ liter cm}^{-2} \text{ min}^{-1};$$

in 5M and 8M nitric acid, 3 fluorides were assumed consumed per zirconium
and the rate constants were

$$2.83 \pm 0.00 \times 10^{-3}$$

and

$$3.33 \pm 0.28 \times 10^{-3},$$

respectively; in 13M nitric acid, only 2 fluorides were assumed to be removed
per zirconium and the rate constant was calculated to be

$$2.21 \pm 0.02 \times 10^{-3}.$$

Similarly, for Zircaloy-2 in 8M nitric acid, 3 fluorides per zirconium were
assumed to be effectively removed and the rate constant found to be

$$3.18 \pm 0.28 \times 10^{-3}.$$

These values were converted, by using the proper constants, to the values
of the rate law for initial zirconium dissolution. The agreement between
the values so calculated and those observed is within 10 per cent.

Equations and results are given which illustrate the variable
stoichiometry caused by the several possible off-gases from the dissolutions.

Experiments were performed with oxalic acid present in addition to the
nitric-hydrofluoric acid mixtures. These experiments were to determine
whether a complexing agent would enhance the stability of resulting
Zircaloy-2 dissolver solutions when the final total fluoride to zirconium
molar ratio was 2 or less. Not only did the presence of oxalic acid
double the average dissolution rate, but it also made it possible to
decrease the nitric acid concentration while achieving the same solution
stability.

II. INTRODUCTION

Economic operation of atomic power reactors requires the recovery of
unburned uranium from spent fuel elements. Zirconium and its alloys are
finding usage as structural material for these elements. A suitable
reagent mixture for the dissolution of zirconium-uranium alloys of
varying composition is a nitric-hydrofluoric acid mixture[1].

This project was undertaken to make a study of the dissolution kinetics
in these acid mixtures at reflux temperatures; however, additional data were
also taken at lower temperatures. Some kinetic data on zirconium dissolu-
tion at lower temperatures have been reported for both dilute nitric-
hydrofluoric acid mixtures[2] and more concentrated mixtures[3] as well as
the initial kinetics of Zircaloy-2 dissolution[4].

III. EXPERIMENTAL

A. Apparatus and Procedure

Because of the corrosive action of the nitric-hydrofluoric acid mixtures on most materials of construction, it was necessary to fabricate the dissolver system from Teflon in order to eliminate any side reactions. In the majority of the dissolutions performed, the dissolver vessel consisted of a machined beaker with a liquid capacity of 300 ml and a press fit lid to prevent vapor escape. The lid was made with a centered neck of one-half inch bore, through which the metal coupons were lowered by means of No. 30 Teflon-covered wire for dissolution. A reflux condenser, which consisted of a thin-walled Teflon tube (3/4 inch ID) surrounded by a glass water jacket, was attached to the neck on the lid.

Since the solutions used in these experiments were ionized to a great extent, it was possible to heat the solutions to reflux temperatures by means of an induction heater. There was no evidence of superheating of the system when the metal coupons were introduced into the dissolver solutions. The rates obtained with the induction heater turned off during the first minute were the same as those obtained while the heater was on.

The nitric-hydrofluoric acid solutions were placed in the dissolver vessel and heated to reflux temperatures. The coupons were then lowered into the refluxing solution and removed periodically for determination of weight and area decrease. The coupons were rinsed with water and carefully dried before weighing.

There was no apparent difference in the rate of dissolution whether the sample was periodically removed for measurement or was retained continuously in the solution. For example, Zircaloy-2 coupons were removed from the dissolution medium ($8\underline{M}$ nitric acid and $1.065\underline{M}$ hydrofluoric acid at reflux) for weighing and measurement at one minute intervals from the second through the fifth minute. Then a coupon was immersed continuously from the second through the fifth minute of dissolution in a fresh solution. The overall rate for the four-minute period was 64.2 ± 4.3 mg cm^{-2} min^{-1} for the coupons removed at minute intervals while the rate for the coupon immersed continuously during the same period in an identical solution was 65.5.

At reflux temperatures, it was found that the rate of dissolution was independent of the stirring rate of the solution. This indicated that sufficient agitation was derived from the boiling motion and dissolution off-gas to obviate any additional agitation supplied by stirring.

At lower temperatures, there is a region in which the dissolution of zirconium is dependent on the stirring rate of the solution[2]. A system was built in which the dissolver solution could be stirred at such a rate, that an increase in the stirring rate no longer altered the dissolution rate. The solutions were stirred at speeds greater than 2000 rpm with a 3-bladed polyethylene propeller (1-3/4 inch diameter). Baffles were placed in the cylindrical polyethylene dissolver vessel in order to prevent cavitation of the

solution when it was stirred. The dissolver system was immersed in a constant temperature bath in order to control the solution temperature to within ± 0.5°C.

B. Materials

The zirconium used in these experiments was obtained as reactor grade plates from the U. S. Bureau of Mines, Albany, Oregon. Emission spectra analyses disclosed only traces of metallic impurities in the zirconium. The tin content of the Zircaloy-2 (2.4 per cent) was appreciably greater than normally expected.

The metal plates were cut into coupons approximately three-eighths of an inch wide in order to facilitate passage through the neck of the lid. The coupon edges were polished and the surfaces milled or etched whenever necessary. A small hole was drilled near one end to permit the coupon to be suspended from the Teflon-covered wire.

The coupon dimensions were determined with a caliper. The apparent calculated area was assumed to be the actual area in the rate calculations; although this assumption is not entirely valid, these quantities should be directly proportional to each other.

The nitric and hydrofluoric acid solutions were prepared by mixing appropriate amounts of duPont C.P. reagent concentrated nitric acid and Fisher reagent 48 per cent hydrofluoric acid in calibrated polyethylene graduates, then diluting to the desired volume with distilled water.

IV. RESULTS AND DISCUSSION

A. Effect of the Hydrofluoric Acid Concentration on the Initial Rate

The dissolution rate of zirconium in mixtures of nitric and hydrofluoric acids at reflux temperatures gradually decreases with time (the first minute being most rapid) if the hydrofluoric acid concentration is initially 0.01M or greater. The gradual decrease in rate is undoubtedly due to the effective removal of hydrofluoric acid from the solution as zirconium fluoride complexes. In the case of Zircaloy-2, the same phenomenon exists, except that the initial hydrofluoric acid concentration must be 0.1M or greater. Below these concentrations there appears to be an inductive effect, possibly due to an existent oxide film.

The initial rate values were obtained from the slope of the tangent to the dissolution curve at zero time. These rate values are expressed in mg cm^{-2} min^{-1}/moles (HF) liter^{-1}.

The initial rates were obtained for zirconium dissolution in 8M and 13M nitric acid with various hydrofluoric acid concentrations (Figures 1 and 2), and for Zircaloy-2 dissolution in 8M nitric acid and various hydrofluoric acid concentrations (Figure 3).

FIGURE I

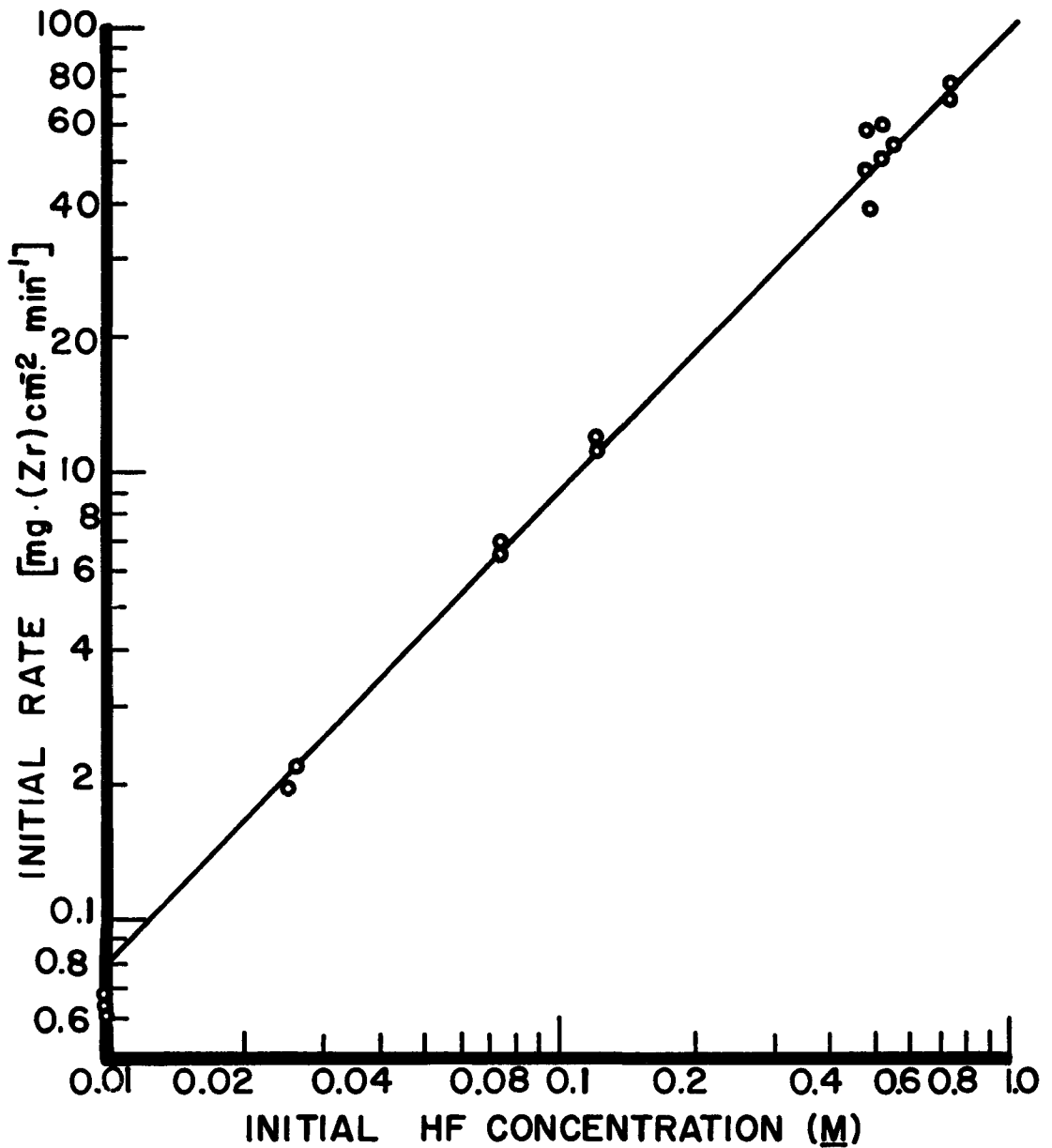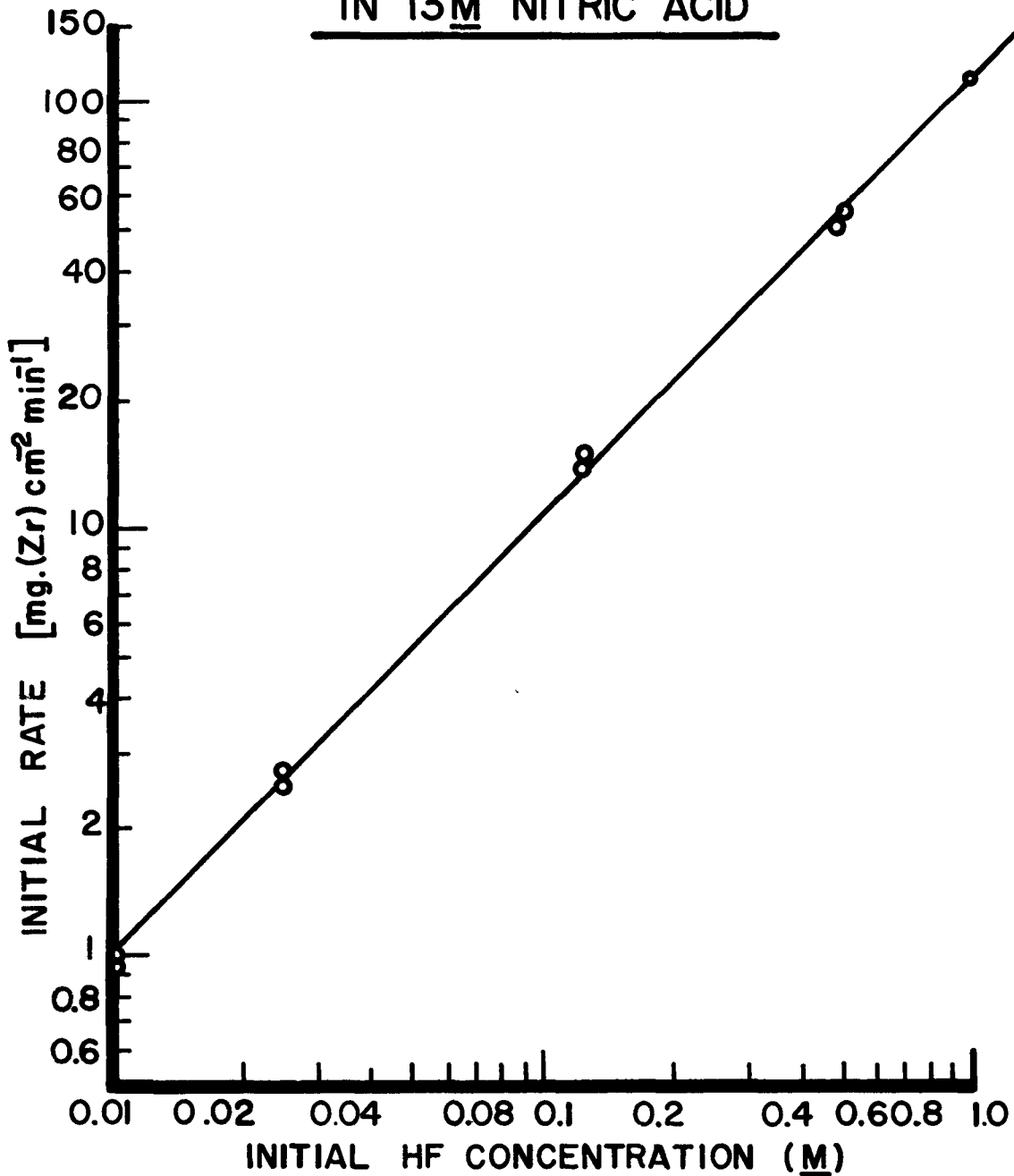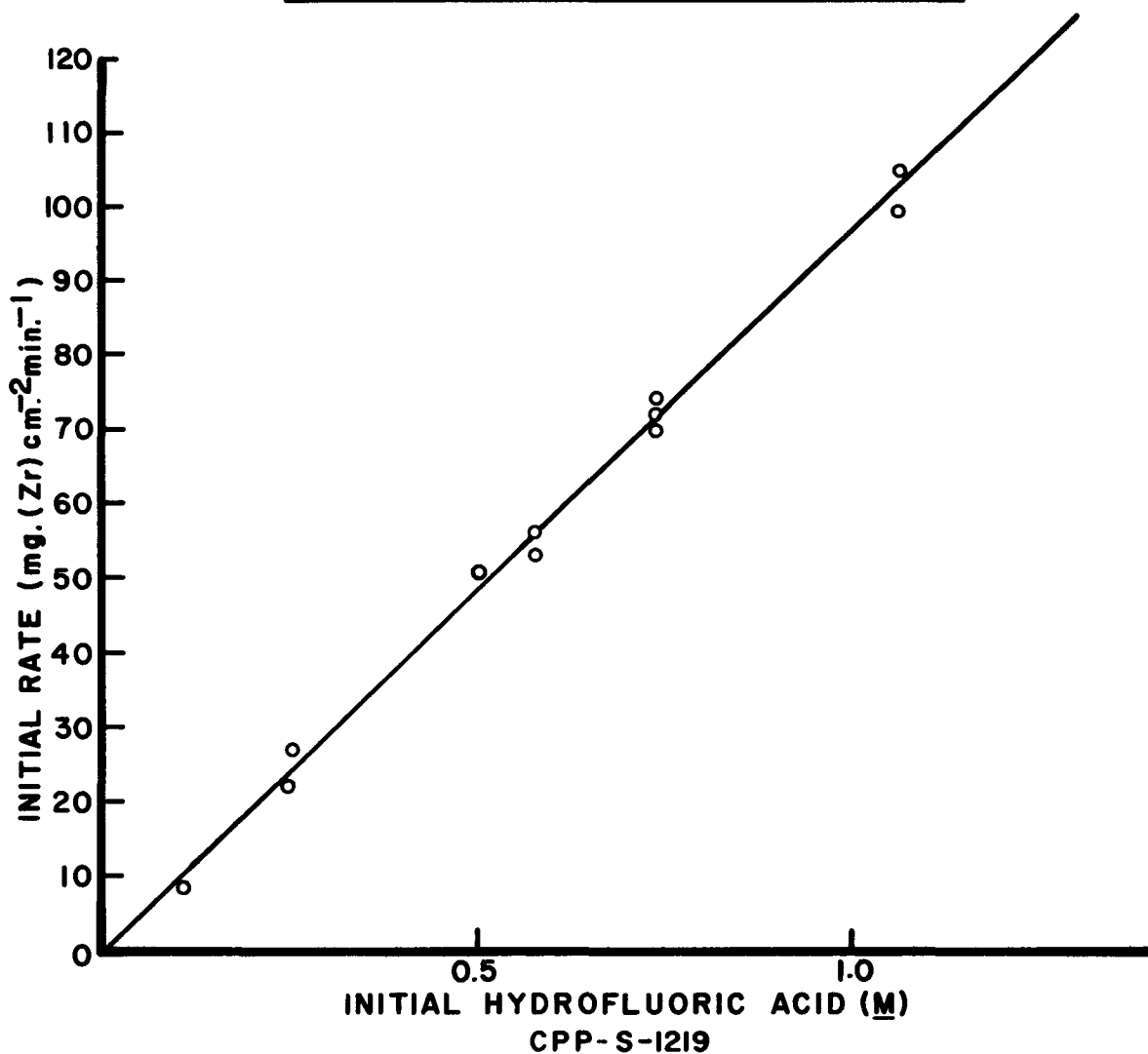## INITIAL DISSOLUTION OF ZIRCONIUM
IN 8M NITRIC ACID

CPP-S-1217

FIGURE 2

INITIAL DISSOLUTION OF ZIRCONIUM
IN 13M NITRIC ACID

CPP-S-1218

FIGURE 3
INITIAL DISSOLUTION
OF ZIRCALOY-2 IN 8M NITRIC ACID

CPP-S-1219

The initial rate of dissolution of both zirconium and Zircaloy-2 was directly proportional to the initial hydrofluoric acid concentration. These results confirm earlier reports concerning the first order dependency of the initial dissolution rate on the hydrofluoric acid concentration in these acid mixtures at lower temperatures[2],[3],[4]. The expression for the first order rate law is

$$-d\ Zr/dt = k[HF],$$

where Zr represents either zirconium or Zircaloy-2, and k is expressed in mg cm^{-2} min^{-1}/moles (HF) $liter^{-1}$.

At reflux temperatures the rate constant k has a value of 99.6 in 8M nitric acid and 114.2 in 13M nitric acid for zirconium, while the value is 96.9 for Zircaloy-2 in 8M HNO_3. These rates appear to be the maximum attainable initial rates. There was no increase in dissolution rate when the refluxing solutions were stirred.

At lower temperatures the maximum attainable rates, normalized with respect to hydrofluoric acid concentration and expressed in the same units as above, are: 9.0 + 0.3 at 16.5°C, 12.1 + 0.3 at 25.5°C, 15.5 + 0.4 at 35.0°C, and 20.3 + 0.3 at 45.0°C. These rates were obtained in 13M HNO_3 using the zirconium from the same batch as that used in refluxing solutions. The data are plotted in Figure 4 and give an Arrhenius activation energy of 5.8 kcal $mole^{-1}$. A low value such as this indicates that the dissolution is diffusion controlled.

Further evidence for a diffusion controlled reaction was obtained from the dissolution of a piece of 2S aluminum. In nitric-hydrofluoric acid mixtures, the rate of dissolution of aluminum is directly proportional to the hydrofluoric acid concentration[5]. At reflux temperature in 8M nitric and 0.49M hydrofluoric acid, the initial rate constant for dissolution of aluminum is 1.10 millimoles cm^{-2} min^{-1}/moles (HF) $liter^{-1}$; the corresponding rate constant for zirconium in the same refluxing acid mixture is 1.08. This similarity in values for two different metals tends to substantiate a diffusion controlled reaction. The removal of an oxide film is not a rate controlling step in the dissolution for several reasons. The first evidence is the low value of the activation energy. Secondly, there is no induction period above a certain low concentration of hydrofluoric acid. Finally, exposure of zirconium to air does not appear to affect the dissolution rate.

B. Effect of the Nitric Acid Concentration on the Initial Rate

In this series of experiments, the nitric acid concentration was varied from 2 to 13 molar. The dissolutions were performed at reflux temperatures with an atmospheric pressure of approximately 640 mm of mercury. The data for the dissolution of zirconium are given in Table 1. The rates were normalized with respect to the hydrofluoric acid concentration.

FIGURE 4

ACTIVATION ENERGY FOR DISSOLUTION OF ZIRCONIUM
IN 13M NITRIC AND HYDROFLUORIC ACID MIXTURES

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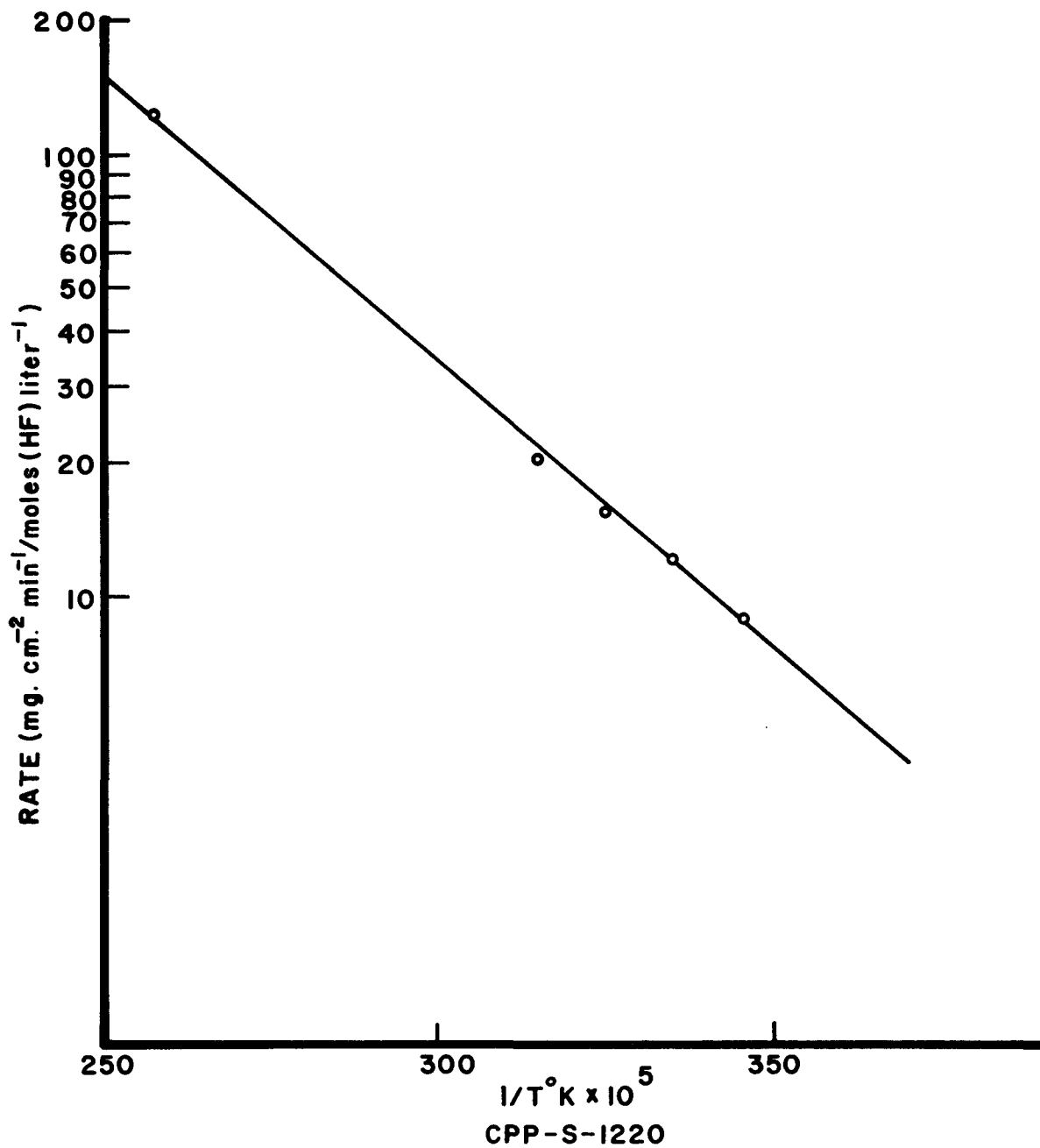
TABLE 1

EFFECT OF THE NITRIC ACID CONCENTRATION ON THE RATE OF DISSOLUTION OF ZIRCONIUM IN NITRIC-HYDROFLUORIC ACID MIXTURES

Reflux Temp °C	Initial HNO₃ ($\underline{M}$)	Rate (mg cm^{-2} min^{-1}/moles (HF) liter^{-1})	
		Initial	Overall (30 min)*
99	2	84.5 ± 3.8	20.3 ± 1.2
103	5	88.6 ± 0.7	23.1 ± 0.1
108	8	96.7 ± 1.2	28.8 ± 1.6
111	10	102.9 ± 0.3	30.0 ± 0.6
115	13	109.8 ± 1.7	33.4 ± 0.0

*Since the initial hydrofluoric acid concentration varied ($0.4\underline{M}$ - $0.6\underline{M}$), it was desirable to normalize the overall rates. However the procedure is questionable since the hydrofluoric acid concentration is unknown in later stages.

A plot of the logarithms of these initial rates versus $1/T(°K)$ yields a straight line from which an Arrhenius activation energy of 4.8 kcal mole^{-1} may be calculated. This value is only 1 kcal mole^{-1} less than that determined for dissolution in the $13\underline{M}$ nitric acid system, which indicates that the effect of the nitric acid on the initial zirconium dissolution rate is primarily the alteration of the reflux temperature.

A similar group of dissolutions were performed using Zircaloy-2. The data obtained are given in Table 2.

TABLE 2

EFFECT OF THE NITRIC ACID CONCENTRATION ON THE RATE OF DISSOLUTION OF ZIRCALOY-2 IN NITRIC-HYDROFLUORIC ACID MIXTURES

Reflux Temp °C	Initial HNO₃ ($\underline{M}$)	Initial Rate $\dfrac{\text{mg cm}^{-2}\text{ min}^{-1}}{\text{moles (HF) liter}^{-1}}$	Average Rate (2 hrs; $0.45M$ HF initially) (mg cm^{-2} min^{-1})
99	2	72.8 ± 2.7	2.56 ± 0.10
103	5	85.9 ± 3.0	3.50 ± 0.15
108	8	97.9 ± 7.5	3.90 ± 0.13
111	10	100.4 ± 3.8	4.85 ± 0.07
115	13	114.0 ± 3.7	5.31 ± 0.02

In this case, the initial rates exhibit a larger standard deviation than that observed in pure zirconium dissolution. Some non-homogeneity may have been present in the samples and this would contribute to the increase in deviation. The results from dissolution in 2M nitric acid were erratic and the best values are reported.

The effect of nitric acid on the initial rate is more pronounced in the dissolution of Zircaloy-2 than it is for pure zirconium. The rate change with varying nitric acid concentrations is considerably more than can be predicted from the change in reflux temperature. This effect, however, was not found to be as great as previously reported for the initial rates[6].

C. Empirical Treatment of the Dissolution Rates Following the Initial Period

Since a method for the determination of undissociated hydrofluoric acid in nitric-hydrofluoric acid mixtures with zirconium present was not available concurrently with these experiments, any treatment of the rate data after the initial period must of necessity be of an empirical nature. In an attempt to make this rate data useful, the hydrofluoric acid concentration was deduced in the following manner.

It can be observed from Tables 1 and 2, that the effect of the nitric acid concentration on the dissolution is greater for extended periods of time than it is initially. This phenomenon may certainly be expected. As the zirconium or Zircaloy-2 dissolves, fluoride complexes of zirconium are formed and these may effectively reduce the hydrofluoric acid concentration in the solution. However, in these acid mixtures, the following reaction can also occur:

$$yH^+ + ZrF_x^{(4-x)} \rightleftharpoons ZrF_{(x-y)}^{(4-x-y)} + yHF.$$
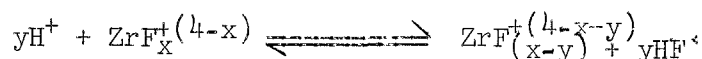
As the hydrogen ion concentration is increased, the reaction should proceed from left to right as written. The net result is then to increase the hydrofluoric acid concentration and simultaneously reduce the average number of fluoride ions in the zirconium fluoride complex.

Since the initial rates of zirconium and Zircaloy-2 dissolutions are found to be dependent only on the initial hydrofluoric acid concentration, it is assumed that throughout the entire dissolution period the only species which causes dissolution is undissociated hydrofluoric acid.

From our dissolution data, only the zirconium concentration of the solution is known after the initial period. In order to estimate the hydrofluoric acid concentration, it is necessary to assume that a certain number of fluoride ions are involved in the zirconium complex. By multiplication with the appropriate constant, the first order rate law, $-dZr/dt = k\,[HF]$ can be converted to

$$-d(moles\ HF)/dt = k'\,[HF].$$

Included in this constant is the number of fluoride ions consumed per zirconium atom dissolved.

A first order rate law requires that a plot of the logarithm of the concentration versus the elapsed time yields a straight line. Thus by assuming the appropriate number of fluoride ions involved in the zirconium fluoride complex, a first order rate law for the rate of disappearance of hydrofluoric acid becomes valid. Only when these values, which are given in Table 3, are used, does a first order relationship remain valid for an extended period of time (Figures 5 and 6). The curves which are obtained by assuming other integral numbers of fluorides used per zirconium atom dissolved are also given in Figures 5 and 6. From the curves it becomes obvious that there is a gradual transition in the number of fluorides used per zirconium as the nitric acid concentration is varied. The minimum total fluoride-to-zirconium molar ratio for which this relationship is valid, as well as the rate constants for the disappearance of hydrofluoric acid, are given in Table 3.

These rate constants k', expressed in liter $cm^{-2} min^{-1}$, can be converted to the original rate constants k of the initial rate law $-dZr/dt = k[HF]$ by multiplication with the following factor:

$$\frac{1000 \text{ (Atomic Weight of Zirconium)}}{\text{(Number of moles of hydrofluoric acid used per mole of zirconium)}}$$

In the case of Zircaloy-2, the hydrofluoric acid concentration was varied from 0.1 to 1.06$\underline{M}$ while the volume of dissolver solution was varied from 150 to 350 ml. There is excellent agreement between the observed initial rate constant and that calculated from the rate of disappearance of hydrofluoric acid.

For zirconium the agreement between the observed initial rate constant and the calculated initial rate constant is within five per cent except in the thirteen molar case, where the agreement is within nine per cent. The reason for the greater discrepancy in the latter case is that the curve resulting from the assumption of 2 fluorides used per zirconium has a slight S shape (Figure 6). This causes the straight line drawn through the points to have a slope which is slightly less than that observed for the first few points.

It must be emphasized that the preceding is an empirical approach and is not valid if a species resulting from the dissolution, other than hydrofluoric acid itself, can effect dissolution of zirconium.

Previous work[3] indicated that four fluorides are consumed per zirconium atom dissolved if the dissolution occurred in a 13$\underline{M}$ nitric acid medium at 40 to 60°C. At reflux temperature (115°C) in 13$\underline{M}$ acid, it appears that approximately two fluorides are consumed per zirconium. A possible explanation for this can be illustrated by the general equation:

$$ZrF_x^{+(4-x)} \underset{\longleftarrow}{\overset{\longrightarrow}{}} ZrF_{(x-y)}^{+(4-x+y)} + yF^-$$
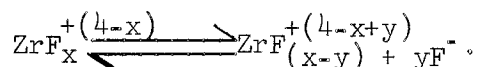
As the temperature increases one may expect the equation to proceed from left to right as written. The average number of fluorides in the zirconium fluoride complexes would therefore decrease with increasing temperature.

TABLE 3

EFFECT OF THE NITRIC ACID CONCENTRATION
ON THE NUMBER OF FLUORIDES
USED PER ZIRCONIUM ATOM DISSOLVED

$HNO_3(\underline{M})$	Reflux Temp $^\circ$C	Material	F/Zr Used	k' for HF Disappearance (liter cm^{-2} min^{-1})	Rate Constants (mg cm^{-2} min^{-1}/mole (HF) liter^{-1}) Calculated	Observed	Valid Until Total F/Zr Drops to
2	99	Zirconium	4	$3.49 \pm 0.17 \times 10^{-3}$	79.6 ± 3.8	84.5 ± 3.8	5
5	103	Zirconium	3	$2.83 \pm 0.00 \times 10^{-3}$	86.0 ± 0.0	86.6 ± 0.7	4
8	108	Zirconium	3	$3.33 \pm 0.28 \times 10^{-3}$	101.2 ± 8.8	96.7 ± 1.2	4
8	108	Zircaloy-2	3	$3.18 \pm 0.28 \times 10^{-3}$	96.7 ± 8.5	97.9 ± 7.5	4
10	111	Zirconium	2.5	-----------------	-----------	102.9 ± 0.3	-
13	115	Zirconium	2	$2.21 \pm 0.02 \times 10^{-3}$	100.8 ± 0.9	109.8 ± 1.1	2.4

FIGURE 5

THE RATE OF DISAPPEARANCE OF HF FROM ACID MIXTURES DURING ZIRCONIUM DISSOLUTION
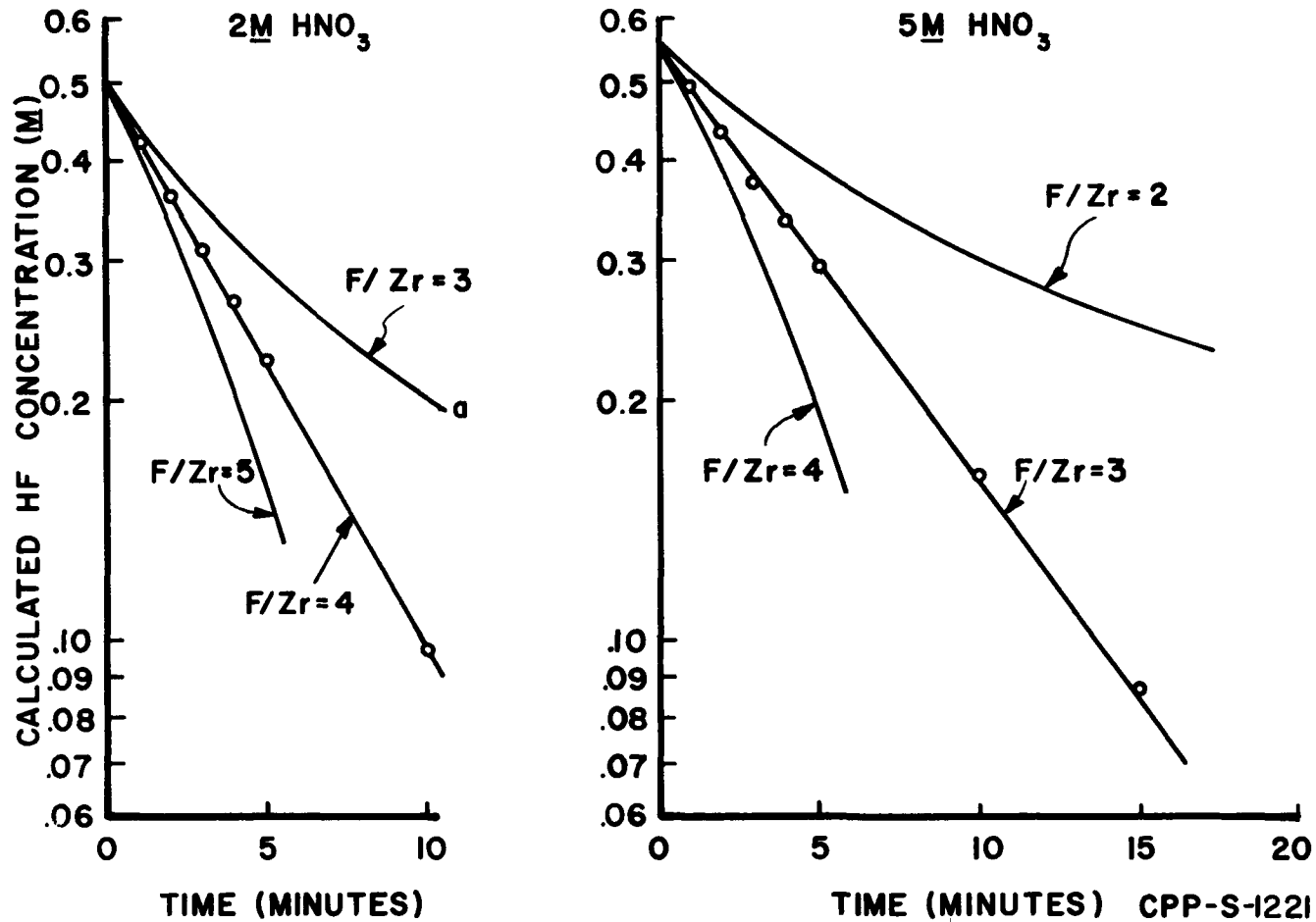
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FIGURE 6

THE RATE OF DISAPPEARANCE OF HF FROM ACID MIXTURES DURING ZIRCONIUM DISSOLUTION

D. Gaseous Products from the Dissolution

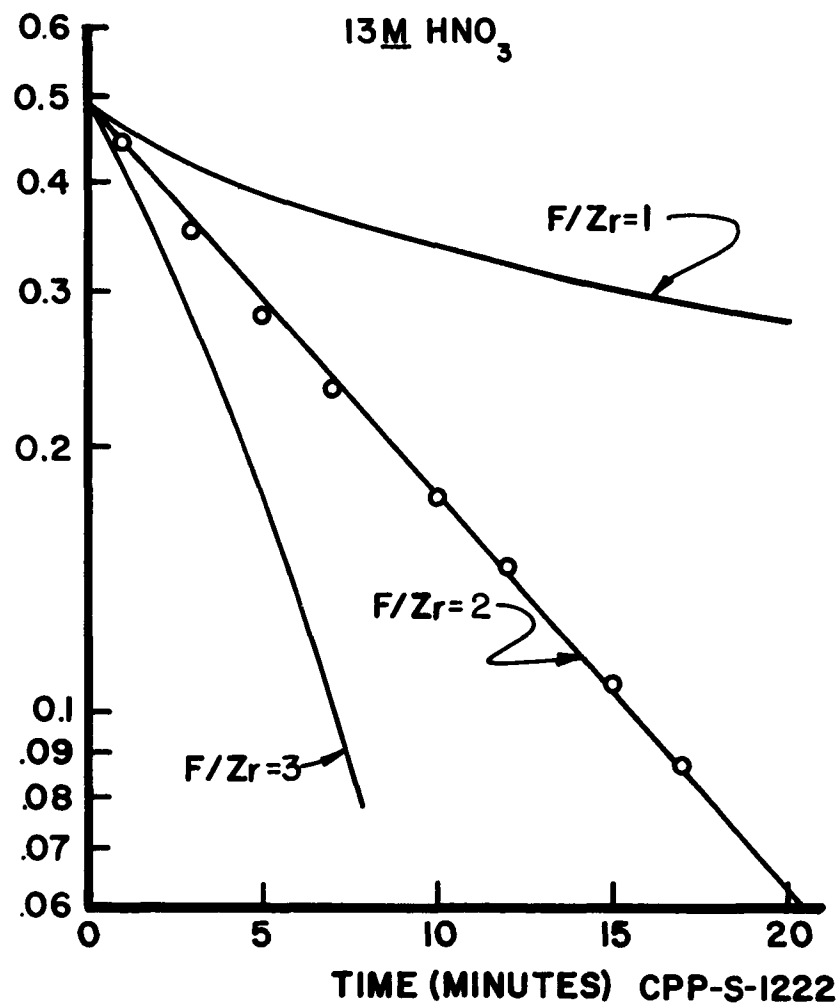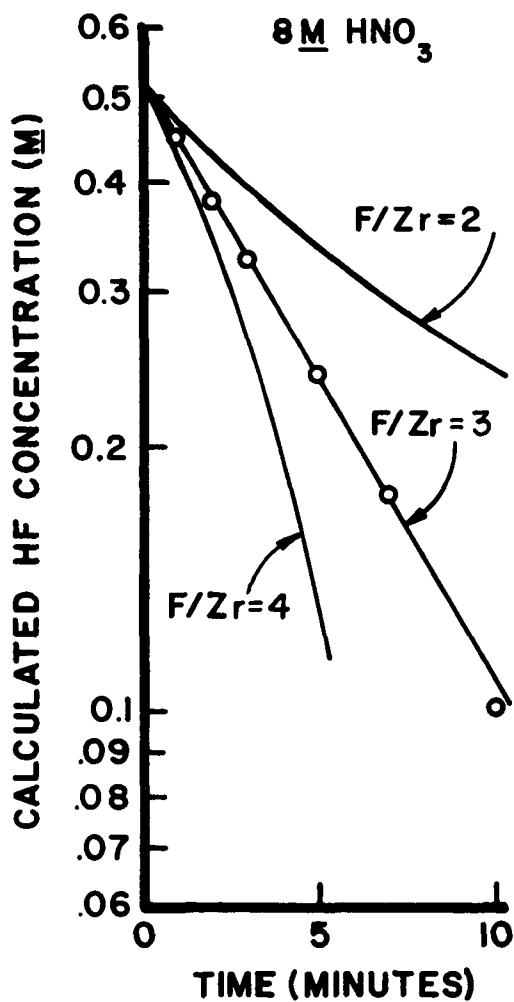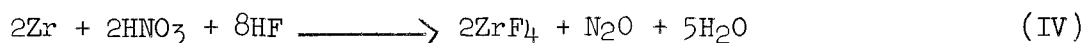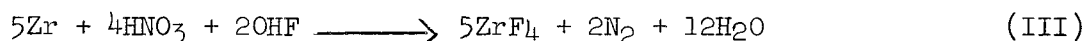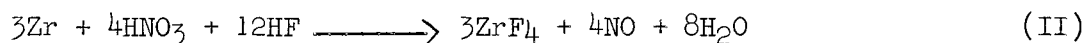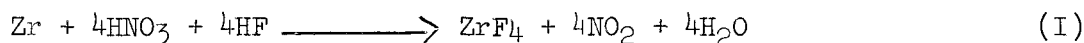Gaseous products of the dissolution were collected and analyzed. The gas collection system was initially purged with argon to prevent any oxidation of nitric oxide to nitrogen dioxide, and the gases were passed through a tube of "Drierite" to remove any water present. The dissolver solutions were refluxed for a short period before dissolution, to allow the system to reach equilibrium. Typical analyses of the off-gases are given in Table 4.

TABLE 4

ANALYSES OF OFF-GAS FROM DISSOLUTION OF ZIRCONIUM IN NITRIC-HYDROFLUORIC ACID MIXTURES

$HNO_3(\underline{M})$	Initial $HF(\underline{M})$	NO_2	NO	N_2	N_2O	H_2	O_2
5	0.5	0.0	83.7	5.5	2.8	8.0	<0.1
8	1	5.1	91.4	0.3	2.9	2.9	<0.1
13	2	54.0	41.9	1.9	0.7	0.7	<0.1

The results indicate that the off-gas products vary according to the nitric acid concentration in the nitric-hydrofluoric acid mixtures. The following equations indicate possible reactions:

$$Zr + 4HNO_3 + 4HF \longrightarrow ZrF_4 + 4NO_2 + 4H_2O \tag{I}$$

$$3Zr + 4HNO_3 + 12HF \longrightarrow 3ZrF_4 + 4NO + 8H_2O \tag{II}$$

$$5Zr + 4HNO_3 + 20HF \longrightarrow 5ZrF_4 + 2N_2 + 12H_2O \tag{III}$$

$$2Zr + 2HNO_3 + 8HF \longrightarrow 2ZrF_4 + N_2O + 5H_2O \tag{IV}$$

$$Zr + 4HF \longrightarrow ZrF_4 + 2H_2 \tag{V}$$

The formation of zirconium tetrafluoride as a product species is hypothetical and it is used only in order to simplify the equations.

The analytical results indicate that reactions (I) and (II) are predominant with 13M nitric acid; reaction (II) appears to be predominant in 8M nitric acid; and in 5M nitric acid reaction (II) is predominant, but reaction (V) is becoming appreciable. Due to the various possible reaction paths, it is difficult to establish a strict stoichiometry during the dissolutions.

E. Stability of Solutions Resulting from the Dissolution of Zircaloy-2

When pure zirconium metal is dissolved in mixtures of 13M nitric acid and various concentrations of hydrofluoric acid, the resulting dissolver solutions are stable with respect to precipitation provided that the total fluoride-to-zirconium molar ratio is two or less. However, when Zircaloy-2 is substituted for pure zirconium, a precipitate occurs in this region.

This precipitate contains both zirconium and tin; the zirconium is possibly co-precipitated. In order to minimize tin precipitation, it is necessary to decrease the initial nitric acid concentration. However, an excessive decrease causes the zirconium itself to precipitate. Therefore, only a narrow range of stability is available when the final fluoride to zirconium ratio is two. Several experiments were performed in order to determine the limits of stability. The data obtained are given in Table 5.

TABLE 5

EFFECT OF NITRIC ACID CONCENTRATION ON THE STABILITY
OF FINAL DISSOLVER SOLUTION FROM ZIRCALOY-2

Temperature During Dissolution: Reflux
Initial Volume of Solution: 200 ml.

Initial Dissolver Solution Composition		Resultant Dissolver Solution		
Nitric Acid M	Hydrofluoric Acid M	Zirconium Conc. M	Solution Condition	Mole Ratio F^-/Zr
2	0.5	0.20	Ppt	2.5
2	0.5	0.19	Ppt	2.5
5	0.5	0.23	Clear	2.2
5	0.5	0.24	Clear	2.1
5	1.0	0.57	Ppt	1.9
8	0.5	0.20	Slightly Turbid	1.7
8	0.5	0.31	Slightly Turbid	1.6
8	1.0	0.55	Clear	1.8
8	1.0	0.56	Clear	1.8
8	1.0	0.62	Ppt	1.6
8	1.0	0.63	Turbid	1.6
8	2.0	0.98	Ppt	2.0
10	0.5	0.31	Turbid	1.6
10	0.5	0.32	Turbid	1.6
10	1.5	1.10	Ppt	1.4
10	2.0	0.82	Turbid	2.4
13	0.5	0.36	Turbid	1.4
13	0.5	0.36	Ppt	1.4

The data indicate that, in the region where the total fluoride to zirconium ratio is approximately 2, the optimum stability is achieved when the initial nitric acid concentration is between 5M and 8M and the initial hydrofluoric acid concentration is 1/2M to 1M. This stability can be maintained until the total fluoride to zirconium ratio drops to 1.8 in the case of 8M nitric acid and 1M hydrofluoric acid.

The amount of precipitate formed in the unstable solutions is a
relatively small amount. In an initially 10M nitric and 1.5M hydrofluoric
acid solution, dissolution to 1.1M zirconium caused 2.5 per cent of the
dissolved Zircaloy-2 to precipitate; while in an initially 5M nitric and
1M hydrofluoric acid solution, dissolution to 0.57M zirconium caused 3.7
per cent of the dissolved Zircaloy-2 to precipitate. The solids obtained
in both cases were approximately 25 per cent tin and 30 per cent zirconium.
No analysis was made for the anions present.

F.   Effect of Oxalic Acid on the Dissolution of Zircaloy-2 in Mixtures
     of Nitric and Hydrofluoric Acids

A series of experiments was conducted in which oxalic acid was added
to mixtures of nitric and hydrofluoric acids for Zircaloy-2 dissolution.
Since oxalate is a complexing agent for zirconium, it was thought that the
addition of oxalic acid would enhance the stability of the resulting dis-
solver solutions. It had previously been reported that the presence of
oxalic acid in these mixtures increased the rate of dissolution markedly[7].
The experiments were performed using 1M to 2M nitric acid to avoid any
decomposition of the oxalate. The data are given in Table 6.

The average rate of dissolution at least doubled in the presence of
oxalic acid, and there was also an accompanying increase in stability with
respect to precipitation from the resultant solutions. Undoubtedly the
oxalate complexes the zirconium to such an extent that considerable
fluoride is released and made available as hydrofluoric acid for further
dissolution. However, the maximum zirconium concentration compatible with
stable solutions appeared to be approximately the same, whether 8M nitric
and 1M hydrofluoric acid was used, or 1M nitric, 1M hydrofluoric and 1M
oxalic acid was used.

V. CONCLUSIONS

1.   The initial rate of dissolution of both zirconium and Zircaloy-2
at reflux temperatures, exhibits a first-order dependency on the hydro-
fluoric acid concentration in nitric-hydrofluoric acid mixtures.

2.   In these acid mixtures, the nitric acid concentration has small
effect on the initial zirconium dissolution rate, other than changing the
reflux temperature; the effect is more pronounced in the case of Zircaloy-2.

3.   The activation energy for the dissolution of zirconium when the
nitric acid concentration is 13 molar in these mixtures, is 5.8 kcal mole^{-1}.
The rate-controlling step during the dissolution appears to be the transport
of hydrofluoric acid to the metal surface.

4.   The nitric acid concentration has a pronounced effect on the average
rate of dissolution over periods of greater than one-half hour. An empirical
treatment shows that whereas 4 fluorides are consumed per zirconium atom dis-
solved in 2M nitric acid, only 2 are used in 13M nitric acid. Therefore,
relatively more free hydrofluoric acid is available for further dissolution
in the more concentrated nitric acid solutions and a higher average rate of
dissolution occurs than would be expected on the basis of reflux temperature
alteration alone.

TABLE 6

EFFECT OF OXALIC ACID ON THE DISSOLUTION
OF ZIRCALOY-2 IN MIXTURES
OF NITRIC AND HYDROFLUORIC ACIDS

Temperature: Reflux $(97-99^\circ C)$
Initial Volume: 200 ml

Nitric Acid $\underline{M}$	Oxalic Acid $\underline{M}$	Hydrofluoric Acid, $\underline{M}$	Length of Dissolution (Hrs)	Average Rate of Dissolution (mg cm^{-2} min^{-1})	Zirconium Conc., $\underline{M}$	Solution Condition
2	0	0.5	1	4.5	0.16	--------
2	0	0.5	1	4.4	0.18	--------
2	0	0.5	1-1/2	3.3	0.18	--------
2	0	0.5	1-1/2	3.1	0.19	--------
2	0	0.5	2	2.6	0.19	ppt
2	0	0.5	2	2.5	0.20	ppt
2	2	0.5	2	6.1	0.54	ppt
2	1	1.0	1	12.1	0.45	turbid
1	1	1.0	1	11.2	0.45	clear
1	0.5	0.5	1-1/2	4.1	0.27	ppt
1	1	0.5	1	7.8	0.32	clear
1	1	0.5	1	7.5	0.32	clear
1	1	0.5	1-1/2	6.2	0.36	turbid
1	1	0.5	1-1/2	5.8	0.36	ppt
1	1	0.5	2	5.0	0.38	ppt
1	1	0.25	1	5.6	0.22	clear
1	1	2.0	1-1/2	11.6	0.68	ppt

5.   In order to minimize tin and zirconium precipitation during Zircaloy-2 dissolution at a total fluoride to zirconium molar ratio of 2, the nitric acid concentration should be in the range from 5 to 8 molar.

6.   Due to the number of possible reaction paths for formation of gaseous products, it is not possible to ascribe a strict stoichiometry to these dissolutions.

7.   A solution initially 1$\underline{M}$ nitric, 1$\underline{M}$ oxalic, and 1$\underline{M}$ hydrofluoric acid produces a Zircaloy-2 dissolver solution which exhibits good stability, equivalent to that achieved with a solution initially 8$\underline{M}$ nitric and 1$\underline{M}$ hydrofluoric acid.

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