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Concentrated Nitric and Dilute Hydrofluoric Acid Mixtures in Dissolution of Zirconium Metal

These acid mixtures hold promise for an aqueous recovery process for zirconium-uranium alloys of variable composition. Rate constants are given for the dissolution rate of zirconium at various temperatures

Zirconium and its alloys will probably be widely used as structural materials for fuel elements in power reactors in the future. However, aqueous processes for recovering uranium from zirconium-containing fuel elements are limited by composition ranges to which they are applicable. One of the most promising methods involves use of nitric and hydrofluoric acid mixtures; however, only certain compositions of product solution are stable with respect to precipitation (1, 2). Because the kinetics of zirconium dissolution in mixtures of mineral acids and hydrofluoric acid have been studied in dilute regions (3), this program was undertaken to study the kinetics in more concentrated regions.

Experimental Procedure

Method. The rates of dissolutions from 40° to 60° C. were measured by
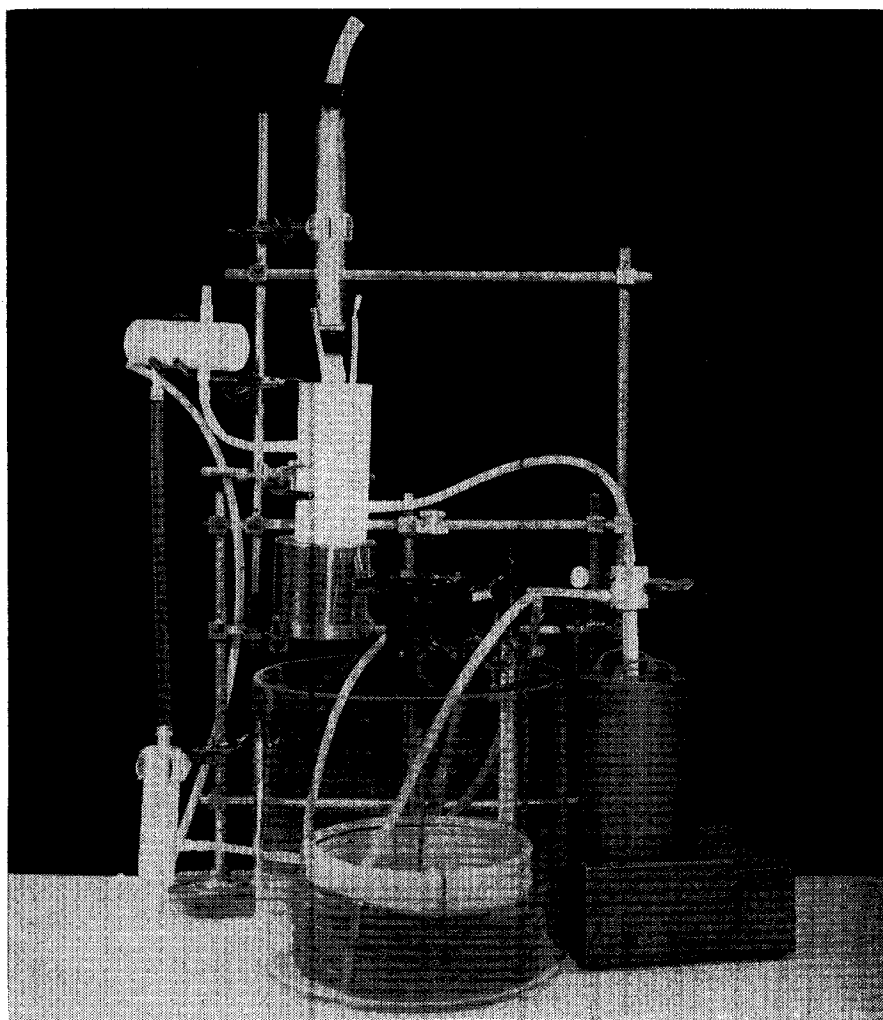

Figure 1. Apparatus was fabricated from Teflon and polyethylene for determination of dissolution rate of zirconium by a radioactive tracer technique

recording, as a function of time, the instantaneous activity of the dissolver solution which resulted from the dissolution of radioactive zirconium coupons. The coupons were weighed before and after dissolution; the total amount dissolved divided by the final specific activity gave the relationship necessary to calculate the amount of zirconium present in solution at any time during the dissolution.

The rates at 115° C. were measured by removal of the zirconium samples from the dissolution vessel at regular intervals for determination of weight loss and area.

Apparatus. The apparatus used for zirconium dissolutions at 40° to 60° C. (Figure 1) is similar to that used by Smith and Hill (3). The dissolver is a cylindrical 200-ml. Teflon vessel with a screw lid closure. The lid has four ports: one for a polyethylene condenser, one for a thermocouple well, one for liquid sampling, and one for control of the metal coupon.

The dissolver vessel has an inlet and outlet to permit external circulation of the dissolver liquid through a polyethylene coil for temperature control. The dissolver liquid was circulated at a rate of 250 to 300 ml. per minute by means of an air lift made from Teflon. Argon instead of air was used for air lift operation, to eliminate possible effects of oxygen. The dissolver contents were stirred at 1200 r.p.m. with a magnetic stirrer to ensure complete mixing.

A Teflon liquid-flow activity monitoring chamber which fits into a well-type scintillation counter was placed between the dissolver vessel and the temperature control coil. This location reduces to a minimum the time lag between actual dissolution and counting.

Approximately 30 feet of $1/4$-inch polyethylene tubing was immersed in a constant temperature bath which permitted the temperature of the dissolver solution to be controlled well within ±0.5° C. The volume of solution remained essentially constant dur-
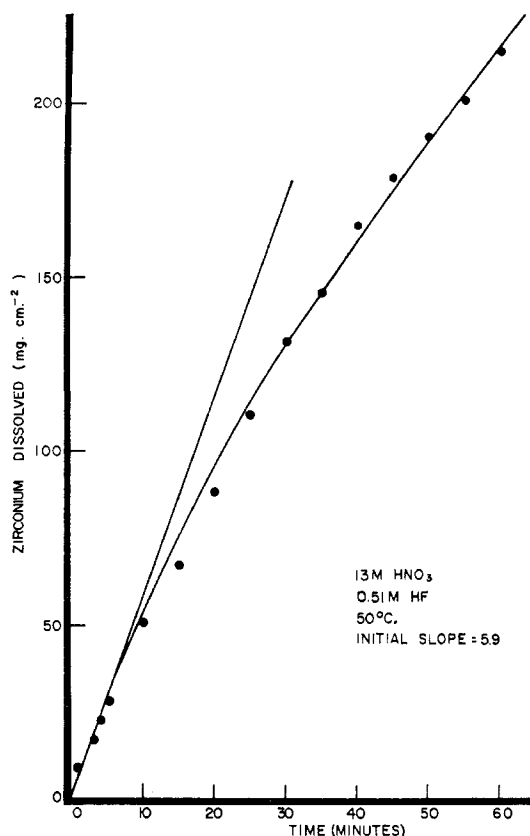
Figure 2. Typical example of determination of initial rate of zirconium dissolution in 13M nitric acid and 0.5M hydrofluoric acid at 50° C.

Similar plots were obtained for 40° and 60° C. experiments

Caption on plot:

13M HNO₃
0.51M HF
50°C.
INITIAL SLOPE = 5.9

Axis labels:
ZIRCONIUM DISSOLVED (mg. cm.⁻²)
TIME (MINUTES)

Figure 3. Effect of hydrofluoric acid concentration and temperature on dissolution of zirconium

Initial rate of dissolution is dependent only on initial hydrofluoric concentration

Legend:
60° C. ▲
50° C. ■
40° C. ●

Axis labels:
INITIAL RATE OF DISSOLUTION (mg. cm.⁻² min.⁻¹ OF ZIRCONIUM)
INITIAL HF CONCENTRATION (MOLARITY)
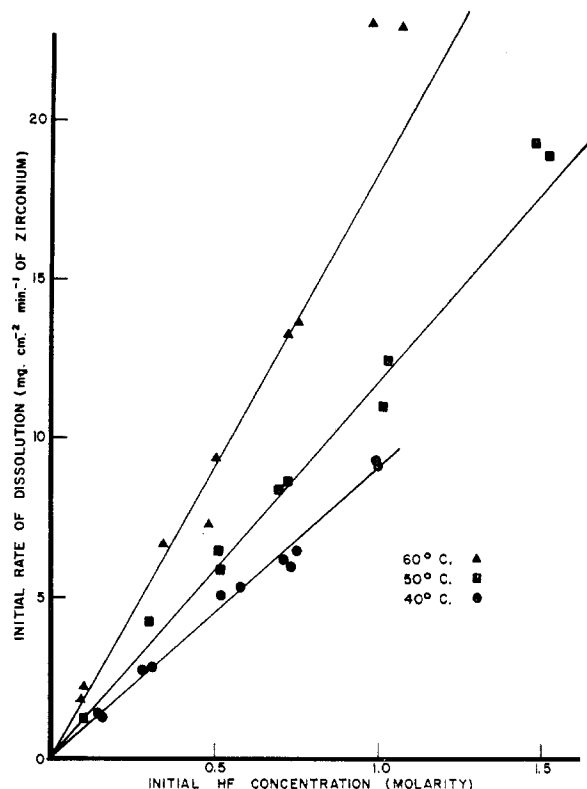
ing dissolution; the total volume required for the system was 575 ml.

The counting system consisted of a sodium iodide–thallium iodide crystal as the gamma detector, a count rate meter, and a recording potentiometer which plotted the instantaneous radioactivity for a permanent record.

The dissolutions performed at 115° C. (reflux temperature of $13M$ nitric acid at atmospheric pressure of 640 mm. of mercury) were conducted in a 1-liter three-necked glass flask. A reflux condenser was inserted in one neck, while the others were used for immersion or removal of zirconium samples and for addition of reagents. The flask was heated with a Glascol heating mantel. The samples were suspended on Teflon tubing from hooks on glass stoppers; one sample was withdrawn and another was immediately immersed, to minimize corrosion of the glassware. The rate of stirring had a negligible effect upon the dissolution rate, because of the vigorous agitation caused by boiling. The total volume of solution used in the dissolutions at 115° C. was 200 ml.

Materials. Two batches of reactor grade zirconium plates were used in these experiments. One source was Westinghouse Atomic Products Division, Pittsburgh, Pa.; the other was the U. S. Bureau of Mines, Albany, Ore. Emission spectra showed only traces of metallic impurities in the zirconium. At the lower temperatures there was a small difference in the dissolution rate of the two batches, but these differences be-

came negligible at the higher temperatures.

Zirconium coupons (approximately $4 \times 16 \times 40$ mm.) were cut from the plates and the edges polished. A small hole was drilled near one end to permit the coupon to be suspended in the solution from a Teflon-coated wire.

The coupons were irradiated in the Materials Testing Reactor at the National Reactor Testing Station, Idaho, from 20 to 60 seconds at approximately 2×10^{14} neutrons per square centimeter per second. The coupons were not used for at least a week after irradiation, to permit the zirconium-97 (17-hour half life) to disappear by decay. As only the 65-day half life zirconium-95 remains, decay corrections need not be applied to the activity in the dissolver solutions. The total activity of the coupons was such that they could be handled directly for short periods without special radiation protection equipment.

Coupons which had rough surfaces were etched before the experimental dissolution in a mixture of concentrated nitric acid and dilute hydrofluoric acid, to obtain as smooth a surface as possible. Their dimensions were measured with a caliper. The apparent calculated area was assumed to be the actual area in the rate calculations. Although this assumption is not strictly valid, the actual area should be directly proportional to the apparent area in this instance, because the coupons after dissolution had smooth, uniform surfaces. Etching, prior to the dissolution, in-

creased the precision of the initial rate values.

The hydrofluoric and nitric acid mixtures were prepared by mixing appropriate amounts of Fisher reagent 48% hydrofluoric acid and Du Pont c.p. reagent concentrated nitric acid in calibrated polyethylene graduates and diluting to the desired volume. These mixtures were then circulated in the dissolver apparatus until they reached the desired temperature of the dissolution experiment.

The calcium fluoride and nitric acid mixtures were prepared by adding the desired amount of Baker analyzed reagent calcium fluoride to 200 ml. of $13M$ nitric acid.

Results and Discussion

Effect of Nitric Acid. Dissolution of zirconium metal at reflux temperatures in mixtures of nitric and hydrofluoric acids results in a stable clear solution if the nitric acid concentration is greater than $8M$ and the final total fluoride-zirconium molar ratio is approximately 2 (1). A series of experiments was performed in duplicate at 40.5° ± 0.5° C. using mixtures of 0.5M hydrofluoric acid and various concentrations of nitric acid. Each experiment used irradiated zirconium coupons and was terminated after 25 minutes. If the period of dissolution is extended at this temperature, a precipitate of zirconium tetrafluoride is formed as the total fluoride-zirconium molar ratio approaches 4 to 6. The areas of the coupons were interpolated from the calculated weight
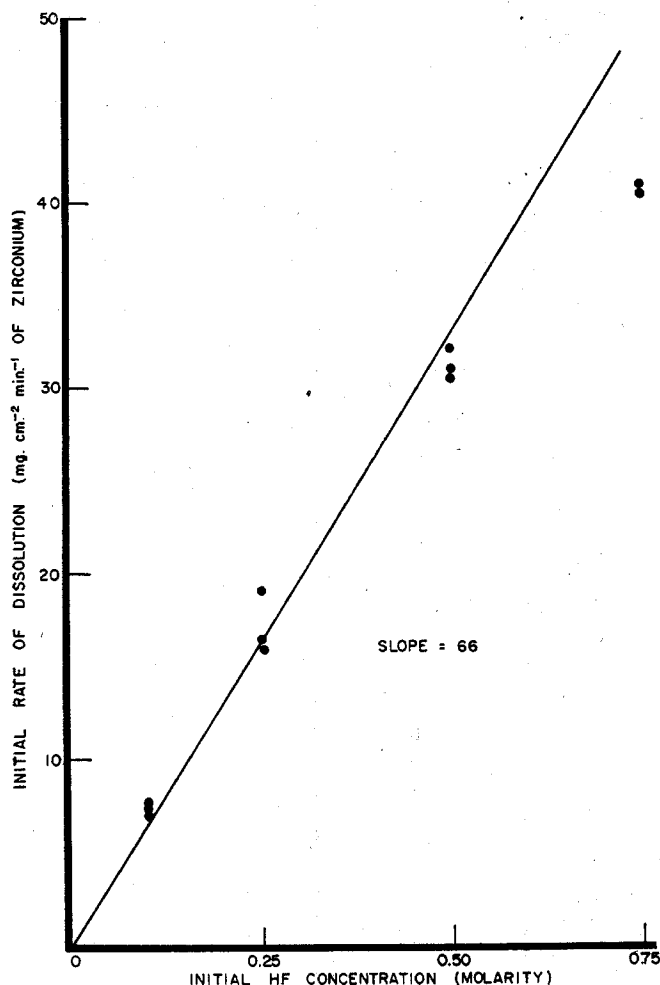
Figure 4. Effect of hydrofluoric acid concentration on dissolution rate of zirconium at 115° C.
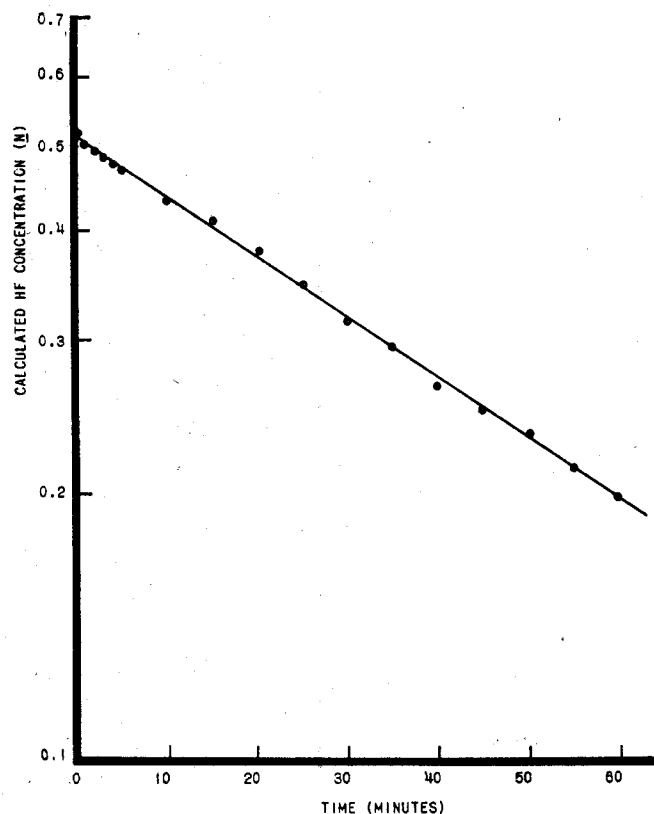

Figure 5. The rate of fluoride disappearance in zirconium dissolution

A straight line is obtained only if it is assumed that four fluorides are removed per zirconium atom. This relationship is valid only where the total fluoride-zirconium ratio is 6 or greater

Initial concentration. 13N HNO₃, 0.52N HF. 50° C.
Coupon area average 20.11 sq. cm.
Assume reaction. Nitric acid + 4HF + Zr → ZrF₄ + nitric oxides

loss of the coupons. By plotting the milligrams of zirconium per square centimeter against the time, the initial rate was determined from the slope of the dissolution curve for the first few minutes (Figure 2). The over-all rate was obtained by dividing the total amount of zirconium dissolved by the average area for the period; then the result was divided by the total elapsed time (Table I). The standard deviation is given with the values.

The rate of dissolution is not greatly affected by the concentration of the nitric acid over the range used. There is some increase in the initial and over-all rates, if the nitric acid concentration is approximately 7M or less. However, these rates are practically the same for 10 to 13M and comparable to those obtained without nitric acid present. Much of the deviation in the rate values may be caused by variations in the original surface preparation of the samples.

The coupons dissolved in hydrofluoric acid alone were covered with a black film, identified as zirconium hydride (5). In a mixture of 2M nitric acid and 0.5M hydrofluoric acid the coupon had a small amount of this film on one edge

after the dissolution period, but the other mixtures yielded bright shiny surfaces after dissolution.

Therefore, the nitric acid does not appear to be an important factor in the dissolution step, but becomes important in the production of species in solution which are not subject to precipitation when the total fluoride-zirconium molar ratio is approximately 2.

Effect of Hydrofluoric Acid. Because the nitric acid concentration has little effect on dissolution rate, and a high nitric acid concentration is desirable for

Table I. Rate of Dissolution Is Not Greatly Affected by Nitric Acid Concentration

(Temperature, 40.5° ± 0.5° C.)

Concentration, M		Rate, Mg./Sq. Cm., Min.⁻¹	
HNO₃	HF	Initial	Over-all (25 min.)
0	0.5	5.8 ± 0.3	4.2 ± 0.2
2	0.5	6.9 ± 0.3	4.8 ± 0.1
5	0.5	6.7 ± 0.1	4.8 ± 0.1
7	0.5	6.2 ± 0.9	4.6 ± 0.4
10	0.5	5.7 ± 0.6	4.1 ± 0.5
11.3	0.5	5.8 ± 0.6	4.5 ± 0.2
13	0.5	5.7 ± 0.3	4.3 ± 0.4

producing a stable product solution, a series of experiments was performed using 13M nitric acid and various concentrations of hydrofluoric acid at 40°, 50°, 60°, and 115° C.

At present, a method for determination of free hydrofluoric acid in the presence of nitric acid and zirconium is not perfected. The hydrofluoric acid concentration is known only before the zirconium is introduced into the solution. Therefore, the amount of zirconium dissolved, expressed in milligrams per square centimeter, was plotted against time. The slope of the line during the initial stages of dissolution was then evaluated as being the initial rate of dissolution expressed in milligrams per square centimeter of zirconium per minute (Figure 2). These initial rates of dissolution were then plotted against the initial hydrofluoric acid concentration (Figures 3 and 4).

These plots yield a straight line passing through the origin, which indicates that the initial rate of dissolution is dependent only on the initial hydrofluoric acid concentration in these mixtures. The rate equation which expresses the dissolution of zirconium in these mixtures is:

$$d\,\mathrm{Zr}/dt = k(\mathrm{HF})$$

The values of k are expressed as mg. cm.$^{-2}$(Zr)min.$^{-1}$/moles(HF) liter^{-1}:

At 40° C.	$k = 8.9$
At 50° C.	$k = 11.6$
At 60° C.	$k = 17.9$
At 115° C.	$k = 66.0$

When the logarithms of the rate constants are plotted against $1/T°$ K., the activation energy obtained from the slope over the range from 40° to 115° C. is 6.4 kcal. mole^{-1}.

Temperature control of the system was inadequate in the case of $1M$ hydrofluoric acid at 60° C. and $1.5M$ hydrofluoric acid at 50° C. This accounts for the deviation of these points from the straight-line relationship obtained at lower concentrations. At 115° C. the dissolution of the glassware became appreciable above $0.25M$ hydrofluoric acid. There is some deviation from a linear relationship at higher concentrations.

Since presentation of this paper data have been obtained for dissolution of zirconium at 115° C. at 1-minute intervals during the initial period. The value of the rate constant is increased to 82 for experiments conducted in glassware and much less deviation from linearity is observed. Experiments conducted in Teflon equipment at 115° C. gave a rate constant of 94, showing that the hydrofluoric acid was reacting with the glassware to an appreciable extent. These values increase the activation energy to approximately 7.5 kcal. mole^{-1}.

The rate of dissolution of zirconium in $1M$ potassium fluoride solution or $1M$ potassium fluoride and $13M$ potassium nitrate solution was negligible. However, a mixture of $1M$ potassium fluoride and $13M$ nitric acid produces a very vigorous dissolution. This confirms the necessity for undissociated hydrofluoric acid for dissolution.

The phenomenon of the initial rate being greatest in the case of zirconium dissolution is plausible, if one considers the induction period to be very small. Undoubtedly, the zirconium surface is oxidized as is the case with active metals, but this film is removed so rapidly that the induction period is negligible. As the dissolution proceeds, the hydrogen fluoride concentration, necessary for the dissolution, is effectively reduced by the complexing action of the increasing zirconium in solution, and this causes a gradual reduction in the dissolution rate.

The value of the activation energy is approximately twice that obtained by Smith and Hill (3). However, both values occur in the region where the reaction can be transport-controlled.

Dissolutions performed in the 40° to 60° C. range produced a precipitate if the reaction was allowed to continue until the total fluoride-zirconium molar ratio approached 4. (This precipitation did not occur if the dissolution was performed at 115° C.) Because of this precipitation, the dissolutions were performed in the region from a very high total fluoride-zirconium molar ratio to one of approximately 6.

The principal off-gases, if $13M$ nitric acid is used, are oxides of nitrogen. Nitrogen dioxide is the major component; the remainder is chiefly nitric oxide, with 1% of hydrogen.

The precipitate which forms, if dissolution is continued at these temperatures, is zirconium tetrafluoride monohydrate (4).

From this information, the following reaction is postulated:

Nitric acid + 4HF + Zr →
$$\mathrm{ZrF_4} + \mathrm{H_2O} + \text{nitrogen oxides}$$
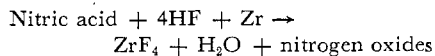
On the basis of this equation, if the amount of hydrofluoric acid remaining in solution is calculated and plotted vs. time on a semilogarithmic plot, a straight-line relationship is obtained, which indicates a first-order dependency on hydrofluoric acid concentration. This relationship occurs only if it is assumed that four fluorides are effectively removed per zirconium atom and is valid in the region where the total fluoride-zirconium molar ratio is 6 or greater. The rate equation for the disappearance of hydrofluoric acid during the dissolution of zirconium is:

$$-d\,(\text{moles HF})/dt = k(\mathrm{HF})$$

The rate constants, expressed in liter cm.$^{-2}$(Zr)min.$^{-1}$, are:

At 40° C.	$k = 3.97 \pm 0.61 \times 10^{-4}$
At 50° C.	$k = 5.05 \pm 0.67 \times 10^{-4}$
At 60° C.	$k = 7.45 \pm 0.88 \times 10^{-4}$

These constant values can be converted to the equivalent units of those found for the initial rate of dissolution of zirconium by multiplying by 2.28×10^4. The values of the two sets of rate constants agree to within 6%.

Use of Calcium Fluoride–Nitric Acid Mixtures. As the hydrofluoric acid species appears necessary for the dissolution of zirconium, any substance which can produce hydrofluoric acid in concentrated nitric acid should effect dissolution. Also, a fluoride-containing compound which is only partially soluble in concentrated nitric acid should provide a chemical means for controlling the rate of dissolution as well as reducing corrosion of the dissolver equipment. As a typical case, calcium fluoride was selected. This mixture of calcium fluoride and nitric acid proved effective as a dissolving agent at 115° C.

The maximum average rate of dissolution was 8 to 9 mg. per sq. cm. per minute and was accomplished when 0.3 to 0.4 mole of total fluoride was added to 200 ml. of $13M$ nitric acid at 115° C. The initial rate for the first 3 minutes was approximately 21 mg. per sq. cm. per minute; this rate dropped rapidly to a constant value of 8 to 9, where it remained until the total fluoride-zirconium molar ratio reached 5. At this point the rate began to decrease gradually and when the solution clarified at a fluoride-zirconium ratio of approximately 2, the rate was 4 mg. per sq. cm. per minute.

Summary and Conclusions

In mixtures of nitric and hydrofluoric acids, the rate of dissolution of zirconium metal is first-order with respect to the hydrofluoric acid. Varying the nitric acid concentration from 0 to $13M$ causes a small change in the initial rate of dissolution, which indicates that nitric acid is not necessary for dissolution. However, the presence of $13M$ nitric acid produces stable solutions which have a final total fluoride-zirconium molar ratio of 2.

Rate constants are given for the initial rate of dissolution of zirconium at 40°, 50°, 60°, and 115° C., and for the disappearance of hydrofluoric acid during dissolution at 40°, 50°, and 60° C. in the region where the total fluoride-zirconium molar ratio is 6 or greater.

Evidence confirms the necessity of the hydrofluoric acid species itself for dissolution, rather than the fluoride ion species.

The activation energy for the dissolution of zirconium in the nitric-hydrofluoric acid system is 6.4 kcal. per mole for the temperature range 40° to 115° C.

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