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A DISSOLUTION RATE STUDY OF BERYLLIUM
IN HYDROFLUORIC ACID

BY
DONALD LEE MATHIS

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

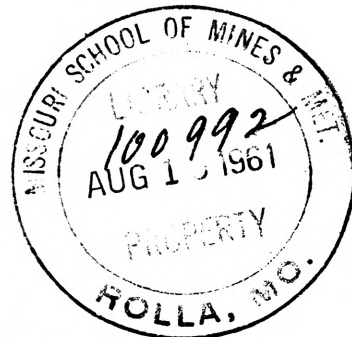
1961

Approved by

J. E. Williams
David E. Zortner

(Advisor)

Wm J. James
H. P. Seigley, Jr.



ABSTRACT

Beryllium was shown to react stoichiometrically with HF, HCl, and H₂SO₄ acids in accordance with a plus two valence. These reactions were investigated by the hydrogen evolution method.

Dissolution rates were determined in five concentrations, 0.01, 0.05, 0.10, 0.50, and 0.75 N, of HF acid at 10, 20, 30, 40 and 50°C. This was accomplished by the hydrogen evolution method and the results were based on the tested stoichiometry. Beryllium has a high dissolution rate in HF acid, which approximates the following under similar conditions: 10 times Al, 4 times Ti, and 1.5 times Zr. A kinetic evaluation of the dissolution results revealed a reaction order of 0.88 and an activation energy of 6.8 Kcal/mole. Unfortunately, due to the existence of complex surface conditions, these values proved to be inadequate to deduce a conclusive mechanism for the reaction. However, a tentative hypothesis is offered which assumes a diffusionally controlled process that is hindered by a BeO film. Future studies involving potential and difference effect measurements should prove effectual in developing an explanation of this reaction.

A preliminary investigation of the HCl dissolution reaction revealed a very different mode of attack which appeared to be primarily electrochemical. A most interesting feature of this reaction was its capacity to exhibit the phenomenon known as the "chunk effect". This resulted in fragments of the beryllium being dislodged into the solution during attack by the dilute acid. Limited dissolution rate data for this reaction indicated it to be more complex than for the

HF acid reaction.

A review of the literature revealed no evidence of previous quantitative corrosion studies on beryllium in the above three acids.

ACKNOWLEDGMENTS

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I. INTRODUCTION

A few heretofore less common metals have become prevalent through their association with the growth of atomic energy. Pure beryllium is definitely one of these metals, which at present has been lowered to an economic level that attracts the attention of non-nuclear interests. Because of its relatively recent availability and the previous limited application of beryllium as a pure metal, there are many potential areas for research that remain unexplored. Accordingly the absence of published work on corrosion in acids suggested the need for the present study.

This study was made possible by the Atomic Energy Commission as a portion of a project devoted to the corrosion of nuclear metals. Its objectives were to provide quantitative information on the corrosion of beryllium in aqueous hydrofluoric, hydrochloric and sulfuric acid solutions with the ultimate goal of explaining the mechanism of dissolution.

A quantitative investigation of the reaction was accomplished through a determination of the dissolution rate of beryllium, under various conditions, by the amount of hydrogen evolved. From these results conclusions as to the controlling reaction mechanism could be drawn from the kinetics of the process; which includes order of the reaction, energy of activation, and the effect on the dissolution rate of noble metal salt additions.

Through necessity portions of this thesis had to be concerned with exploratory investigations and, thereby, act as a basis for future studies in this laboratory.

The results of this study are therefore of a preliminary nature and, as such, are incapable of fully explaining the mechanism of the dissolution process in hydrofluoric acid. In addition, the present state of knowledge of heterogeneous reaction kinetics does not satisfactorily lend itself to a conclusive evaluation of the reaction order and activation energy observed in this study.

II. LITERATURE REVIEW

Since beryllium is a metal which owes its relatively recent prominence and availability to the growth of atomic energy, it is not surprising to note the absence or disagreement of published information regarding its corrosion properties in acids. Especially noteworthy, is the apparent absence of previous quantitative studies aimed specifically at determining the mechanisms involved. The above statements are based upon a review of the Chemical Abstracts and available unclassified literature of the Atomic Energy Commission, plus the most recent texts pertaining to this subject.^(1,2,3)

Inorganic chemistry literature sources state that beryllium metal dissolves vigorously in dilute acids, except dilute nitric acid in which the reaction soon ceases in the cold.^(4,5,6) Besides the lack of detailed information on these dissolution reactions, no mention is made of their stoichiometry. Of the three acids (hydrofluoric, hydrochloric and sulfuric) mentioned in the literature, the least information is reported on the action of hydrofluoric acid toward beryllium metal.

A general summary, as of 1955, of the corrosion resistance of beryllium to air and water at various temperatures was presented at the International Conference on the Peaceful Uses of Atomic Energy by A. R. Kaufmann and B. R. F. Kjellgren.⁽⁷⁾ Almost the same information is also reported in the text "The Metal Beryllium."⁽³⁾

Undoubtedly, the most comprehensive coverage to date, of the overall chemical reactivity of beryllium may be found in the text

"Beryllium" by Darwin and Buddery.⁽²⁾ In fact, they mention the hydrogen evolution method, using hydrochloric acid or potassium hydroxide solution, as a means of determining oxygen content in beryllium over the higher oxygen range.

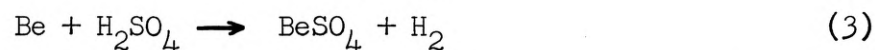
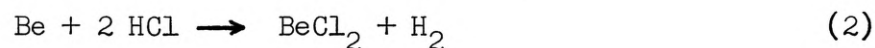
Therefore, a search of the literature reveals many opportunities for original research pertaining to the corrosion of beryllium in acids, with significance being placed upon the mechanism of the attack. Studies of this nature should become of great value as beryllium is more seriously considered as a structural material.

No survey of this metal would be complete without mentioning its toxicity. One should become aware of the hazards involved before contemplating extended contact with beryllium metal or its compounds. A general survey of this subject may be found in either "The Metal Beryllium"⁽³⁾ or "Beryllium."⁽²⁾ More detailed information of great abundance is available in the Chemical or Atomic Energy Commission Abstracts.

III. THE DISSOLUTION REACTION OF BERYLLIUM IN HYDROFLUORIC, HYDROCHLORIC AND SULFURIC ACIDS

This preliminary phase of the research was concerned with the quantitative character of the reaction of beryllium metal with hydrofluoric, hydrochloric and sulfuric acids.

Since beryllium exhibits a stable valence of plus two, it may be expected to react with the above acids as follows:



However, the exactness of these reactions must be known before subsequent dissolution rate studies by the hydrogen evolution method are based upon them.

A. MATERIALS

The beryllium was purchased from The Brush Beryllium Company as premium grade vacuum-cast metal lump (lot number Y8918 APQMV). Unfortunately, an exact analysis of this material is unknown; but, if it conforms to specifications it should have a beryllium content of 99.5%.

B. APPARATUS AND PROCEDURE

Use was made of an existing apparatus which had been employed during previous investigations in this laboratory for similar studies.^(8,9) Essentially, it consisted of a constant temperature reaction vessel sealed to a gas burette that was equipped with a leveling bulb. A ground glass rotary seal in the side of the reaction vessel facilitated release of the specimen after the system

approached a constant temperature. Predetermined amounts (approximately 0.028 gms.) were reacted in the apparatus at 36.0°C. and the evolved hydrogen was measured with respect to time until a constant volume was approached. Prior to isolating the system from the surroundings, the atmospheric pressure was recorded. Temperature of the surroundings was recorded with the final volume.

At first, difficulty was experienced in obtaining results of comparable accuracy to previous studies using this apparatus.⁽¹⁰⁾ Since, 0.0001 gm. of beryllium develops approximately 0.25 ml. of hydrogen at STP, more accuracy was required in weighing. An accuracy of ± 0.00001 gm. was achieved with a Gold Balance and a set of class S-1 metric weights, standardized by the Bureau of Standards (NBS Test No. G 18280).

The concentrations of acids listed in Table A were chosen because they gave reaction rates convenient to follow but, yet, not of more than 30 minutes duration. Since the evolved hydrogen was collected in the presence of water, atmospheric pressure readings were corrected for the vapor pressure of water at the recorded temperature; plus, a correction to reduce readings of a mercurial barometer with a brass scale to 0°C. Then the observed volumes were reduced to standard conditions.

Because of the stable valence exhibited by beryllium all of the dissolution reaction determinations were performed in the presence of air.

C. RESULTS

The volumes at STP from the hydrogen evolution experiments and their corresponding theoretical volumes, assuming a purity of 99.5% Be,

are summarized in Table A. Using the theoretical values obtained from equation (1), (2) and (3) as reference, a comparison of the results indicates the deviations to be within experimental limits. Visual examination of the solution remaining in the reaction vessel after each run revealed no evidence of unreacted material; therefore, it was assumed that the reaction with all three acids had been complete.

From this preliminary investigation it was concluded that beryllium reacts with dilute hydrofluoric, hydrochloric and sulphuric acids as anticipated in equations (1), (2) and (3). Also, the purity of the premium grade vacuum-cast beryllium metal lump appears to meet standard specifications.

Table A

The Calculated and Measured Volume of Hydrogen
Evolved from the Complete Dissolution of Beryllium in
Three Acids in the Presence of Air

Acid	Wt. of Be	Vol. of H ₂ Evolved at STP (ml)	Calc. Theor. Vol.(assuming 99.5% Be)	% Deviation From Theor.
HF (3N)	0.02866	71.06	70.91	+ 0.21
"	0.02725	67.51	67.43	+ 0.12
"	0.03042	75.30	75.27	+ 0.04
"	0.02843	70.45	70.35	+ 0.14
			Average	+ 0.13
HCl (2N)	0.02940	72.89	72.75	+ 0.19
"	0.02740	67.68	67.80	- 0.18
"	0.02840	70.38	70.27	+ 0.16
"	0.02818	69.57	69.73	- 0.23
			Average	- 0.02
H ₂ SO ₄ (2N)	0.02831	69.99	70.05	- 0.09
"	0.03105	76.84	76.83	+ 0.01
"	0.02845	70.42	70.40	+ 0.03
			Average	- 0.01

IV. THE RATE OF DISSOLUTION OF BERYLLIUM IN DILUTE
CONCENTRATIONS OF HYDROFLUORIC ACID AT VARIOUS TEMPERATURES

Dissolution rate studies were performed by the hydrogen evolution method for acid concentrations of 0.01 to 0.75 normal. This procedure was repeated at 10, 20, 30, 40 and 50°C in order to determine the activation energy of the reaction.

A. MATERIALS

Because of the irregular shape of the vacuum-cast beryllium metal lump, it was necessary to utilize the less pure QMV structural grade for this phase of the research. This material was also purchased from The Brush Beryllium Company and was certified to conform to specification S-100-B, with the following analysis:

Be (assay)	98.5 %	minimum
BeO	1.2 %	maximum
Al	0.14%	"
C	0.15%	"
Fe	0.16%	"
Mg	0.08%	"
Si	0.10%	"

Any other metallic impurity 0.04% maximum

The specification also stipulated that the beryllium (minimum density 1.84 g/cc) was produced by the "Brush Hot Pressing Process" from -200 mesh virgin powder originating from vacuum-cast billets. Furthermore, the surface should be free of porosity and cracks as detected by dye penetrant inspection.

Reagent grade (assay 48.0-51.0%) hydrofluoric acid was used throughout to prepare solutions of various normalities. The acid solutions were titrated against a standardized carbon dioxide-free

sodium hydroxide solution, using phenolphthalein as indicator. Previously, the sodium hydroxide solution had been titrated against potassium acid phthalate which served as a primary standard. Again phenolphthalein was used as indicator. The primary standard was prepared as outlined in the Handbook of Chemistry and Physics.⁽¹¹⁾ In all the above solutions fresh distilled water was used and the titrations were performed at least three times, producing an average value.

B. APPARATUS

A photograph of the dissolution rate apparatus may be found in Figure 1, with a detailed diagram shown in Figure 2. Basically, it consisted of a spherical reaction vessel to contain the reactants, a stirring mechanism through a mercury seal to keep the specimen in constant motion, a gas burette for measuring the evolved hydrogen and a constant temperature water bath.

The glass reaction flask was of 500 ml. capacity and had three ground glass joint openings. Bees wax covered the portion that came in contact with the hydrofluoric acid. One of the openings contained a valve "h" to the surroundings, the second contained the rotary mercury gas seal and the third an exit to the gas burette. To maintain an even temperature in the reaction flask it was submerged to the base of its openings in the constant temperature water bath.

The stirring mechanism was belt driven by a reduction pulley which in turn was actuated by a variable constant speed motor. Throughout all self dissolution rate determinations the specimen was rotated at 200 r.p.m. and checked by repeated measurement. Motion



Figure 1

Dissolution rate apparatus

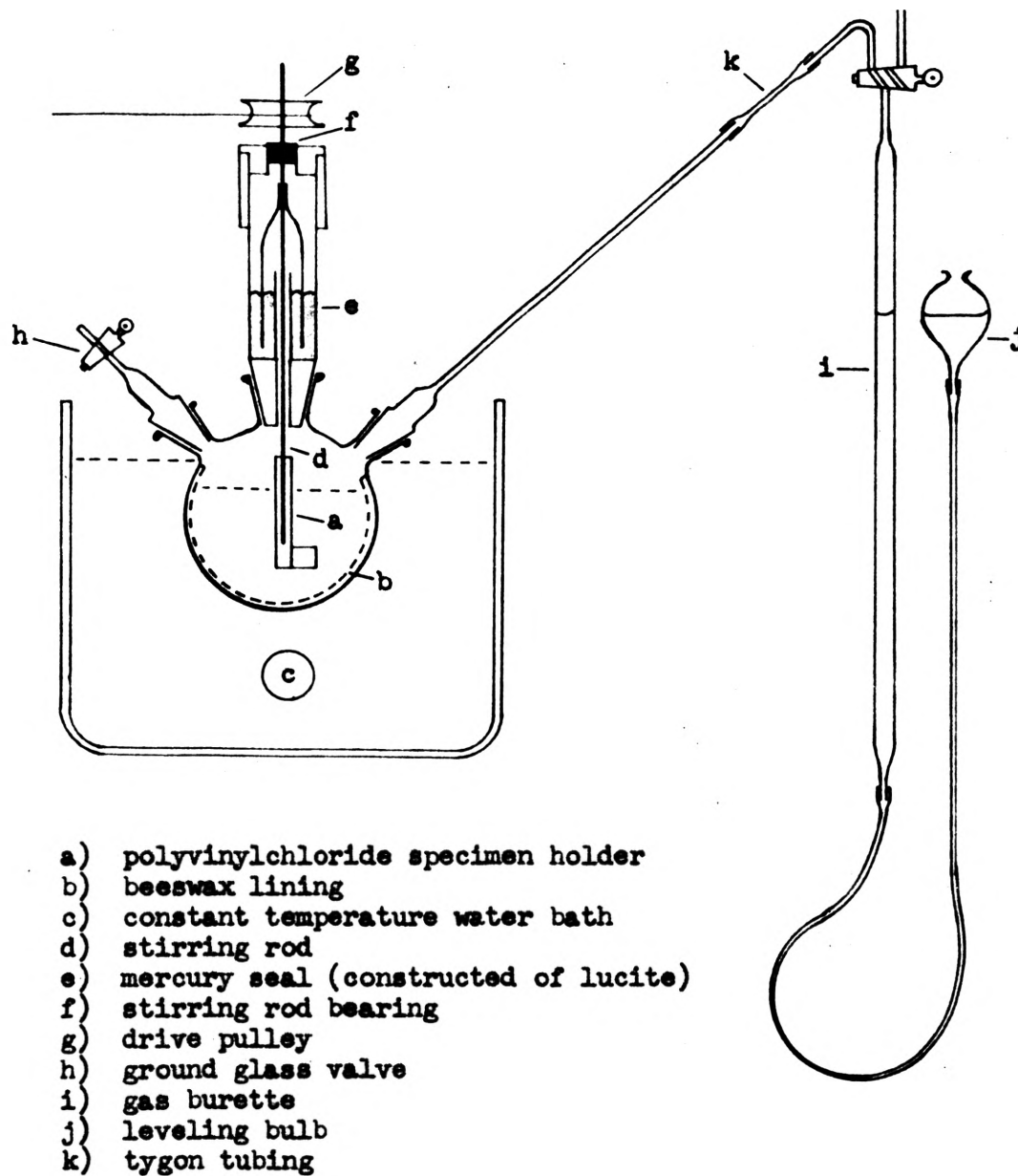


Figure 2

Reaction vessel and volumetric apparatus

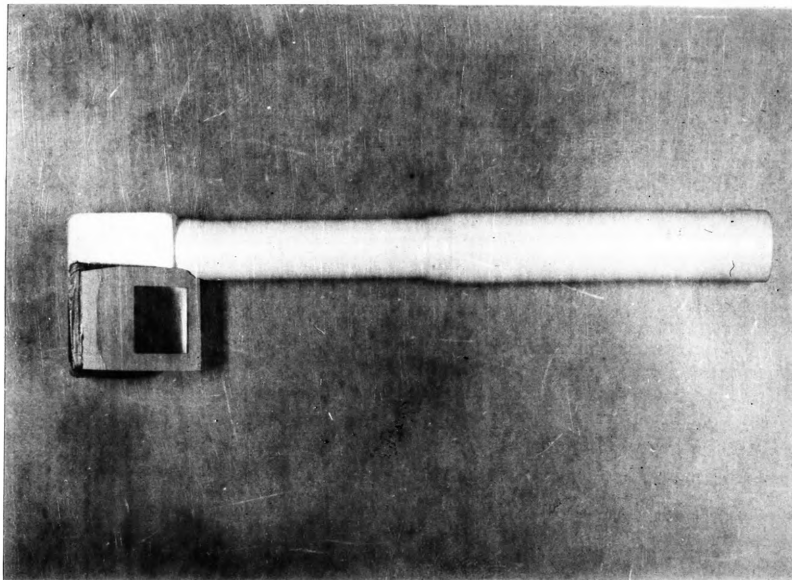


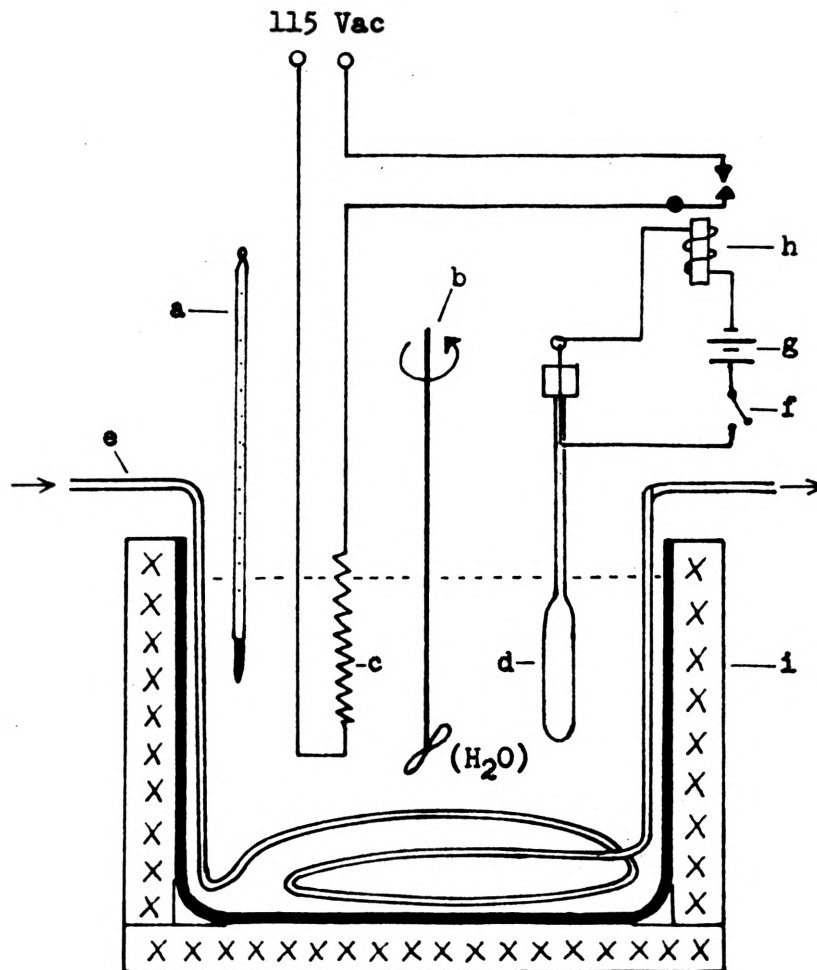
Figure 3

Polyvinylchloride specimen holder.

was transmitted through the mercury seal by a stainless steel rod. The rod was shielded from the acid by firmly slipping into the specimen holder which is shown in Figure 3. The face of the holder was inclined at an angle of 45° and wax was used to fasten the specimen mount to it.

The gas burette had a capacity of 100 milliliters but, if necessary, this could be extended by momentarily closing the entrance valve and expelling the existing hydrogen. Collection of the hydrogen was over distilled water; using atmospheric pressure as a reference since an equal column of water was maintained in an attached leveling bulb.

The constant temperature water bath employed throughout this investigation was capable of maintaining temperatures within $\pm 0.1^\circ\text{C}$. The temperature was automatically controlled by a mercury thermostat which actuated a heating circuit relay as shown in Figure 4. Instead of using the usual metal resistance heater, an infrared type, believed to be an original application of a tubular quartz infrared lamp, was incorporated in the apparatus. It has the inherent advantage of more wattage in less space and much lower mass, which results in a negligible amount of overshoot in temperature. The efficiency of this type of heater is increased if the circulating medium is dyed a dark color. For temperatures below that of the surroundings, cold water was circulated through a cooling coil and in the case of 10°C a chilled brine solution was pumped through a closed system.



- a) thermometer
- b) stirrer
- c) heating element
- d) mercury thermo-regulator
- e) cooling coil
- f) manual switch
- g) battery, 6 volts
- h) electromagnetic switch
- i) fiberglass insulation

Figure 4

Equipment and wiring diagram of the constant
temperature apparatus

C. PROCEDURE

All of the apparatus shown in Figure 1 was constructed and assembled for this dissolution rate study. A minimum of equipment failure was experienced since the apparatus was originally planned as a permanent installation for future studies of this nature.

Preparation of specimens of one centimeter square area necessitates cutting the 2" X 1" X $\frac{1}{4}$ " block of beryllium. This was accomplished with some difficulty by using a hacksaw. Subsequent filing and sanding to final dimensions proved to be similar to working with a hardened steel. All of the above operations were performed with the specimen submerged in a pan of water to preclude the possibility of breathing dust that might otherwise be created. The final dimensions were checked with a micrometer and resulted in the following areas:

Specimen # 1 - 1.000 cm.²
Specimen # 2 - 1.060 cm.²

The specimens were mounted in polyvinylchloride so as to expose one square centimeter of metal to the acid. The mounting was accomplished in a standard metallographic mounting press, except that the mold was heated to about 80°C. This procedure resulted in a cylindrical mount which for convenience was trimmed to the shape shown in Figure 3.

Just prior to each dissolution rate determination the specimen was wet sanded until flat and final passes were made on wet 600 grit paper. Then the specimen mount was attached to the polyvinylchloride specimen holder with wax.

Prior to each rate determination fresh 300 milliliter quantities of acid solution were given ample time, at least 30 minutes, to approach thermal equilibrium. This was readily checked by sealing the system and observing the constancy of the water column in the burette. After each rate determination the reaction flask was visually checked for any residue or distinguishing features produced by the reaction. It was then rinsed in distilled water and replaced in the constant temperature bath.

Next the atmospheric pressure, room temperature and initial burette reading were recorded. The specimen holder was slipped on the stirring rod, the stirring assembly was inserted in the reaction flask and the drive belt was connected. Immediately, the constant speed stirring motor was started and valve "h", Figure 2, was closed at test time zero. Thereafter, as hydrogen was evolved from the reaction it was measured by a displacement of the water column. Volumes at regular time intervals were recorded until a noticeable decrease had occurred in the reaction rate. Again, the atmospheric pressure and room temperature were recorded so that an average value for the duration of the test could be used in reducing the volumes to standard conditions.

As the test temperature deviated to either extreme from room temperature, a noticeable effect was observed on the equilibrium of the system. This was caused by inserting the stirring assembly after it had been exposed to room temperature. Thus, producing a temporary differential between the temperature of its entrapped air and that in the reaction vessel. This undesirable situation was corrected by storing the assembly in a container of distilled water

which was in contact with the constant temperature water bath. In this way the differential could be reduced to approximately 1°C and its effect upon the equilibrium of the system was minimized. However, at best, this is only a treatment of the symptom and not a remedy of the cause. In the future, if high reaction rates are encountered, this situation should be corrected by a change in the design of the stirring assembly.

1. Sample Calculation of Reaction Rate

The following calculations pertain to the results reported in Table XII, Run #2 in the Appendix.

Specimen #2

Average barometric pressure: 728.4 mm Hg

Average room temperature: 22.8°C

Pressure corrections:

(1) Correction for vapor pressure of water at 22.8°C = 20.8 mm Hg

(2) Temperature correction to reduce the reading of a mercurial barometer with a brass scale to 0°C = 2.7 mm Hg

Corrected average barometric pressure = 704.9 mm Hg (partial pressure H₂)

Burette reading at 5 minutes = 2.40 ml

Correction of burette reading to standard conditions:

$$\frac{(2.40)(273)(704.9)}{(295.8)(760)} = 2.05 \text{ ml}$$

This same procedure was applied to each burette reading in obtaining corrected volumes at STP. In the Tables of the Appendix the corrected volume is reported with respect to time.

The change in volume, Δ Vol., over a corresponding time interval was obtained by subtracting from each corrected volume the preceding value. As an example, Table XII is repeated on the next page.

<u>Time</u> (minutes)	<u>Volumes at STP</u> (ml)	<u>Δ Vol.</u> (cm ³)
0	0.00	0.00
5	2.05	2.05*
10	4.11	2.06*
15	6.12	2.01*
20	8.13	2.01*
25	10.10	1.97*
30	12.11	2.01*
35	13.95	1.84
40	15.79	1.84
45	17.63	1.84
50	19.39	1.76

An average maximum value of Δ Vol. can be obtained from a range of values which are practically constant, and is found to be 2.02 cm³. This value may then be converted into rate per unit area by the rate equation

$$R = \frac{(1000)(\Delta V)}{At} \quad (4)$$

where R is the rate expressed in mm³/cm² min.; A is the surface area of the specimen in cm²; and t is the time interval over which the measurement was taken, expressed in minutes. Application of equation (4) to the above example yields

$$R = \frac{(1000)(2.02)}{(1.06)(5)} = 381 \text{ mm}^3/\text{cm}^2 \text{ min.}$$

The rate may also be expressed in terms of the weight lost by the beryllium, according to

$$R = \frac{(0.4016)(\Delta V)}{At} \quad (5)$$

where R is expressed in mg. of Be/cm² min.

At each acid concentration and temperature two rate determinations were performed and their results averaged, so that a more reliable value would be obtained.

D. RESULTS

Dissolution rates at four acid concentrations, 0.05 N, 0.10 N, 0.50 N and 0.75 N, and five temperatures, 10, 20, 30, 40 and 50°C, were investigated. The results are tabulated in Tables I through XXIV in the Appendix and summarized in Table B. One lower concentration, 0.01 N, was also studied at each temperature and reported in the Appendix; however, the results deviated from the higher concentrations and were not included in the calculation of the reaction kinetics. In all the dissolution rate studies with hydrofluoric acid, rates were recorded beyond the times shown in the Tables to definitely ascertain a decrease in the reaction rate. However, in the final analysis, the superfluous rates were omitted.

Beryllium seems to react with all concentrations of hydrofluoric acid. Evidence of this characteristic may be observed in Figure 5, where the relationship of reaction rate to HF acid concentration appears to extrapolate to the origin. Between acid concentrations of 0.10 N to 0.75 N the relationship approaches linearity.

At an HF acid concentration of 0.50 N and at temperatures above 30°C, beryllium does not exhibit a measureable induction period before the maximum dissolution rate is attained. At 20 and 30°C, the induction period appears to be only three minutes and at 10°C, about 10 minutes. For the higher acid concentrations, 0.75 N, the induction periods are about the same, but at lower concentrations they are approximately double the above times. After the dissolution rate reached a maximum, it usually remained constant for a short while, depending upon the acid concentration and temperature,

Table B

Summary of Dissolution Rates of Be in HF Taken from
Tables I through XXIV in the Appendix

Temp. (°C)	Conc. HF (equiv./liter)	Rate (mm ³ /cm ² min)	Avg. Rate (mm ³ /cm ² min)
10.0	0.10	145	
10.0	0.10	171	158
10.0	0.50	815	
10.0	0.50	785	800
10.0	0.75	1111	
10.0	0.75	1116	1114
20.0	0.05	141	
20.0	0.05	144	143
20.0	0.10	284	
20.0	0.10	277	281
20.0	0.50	1118	
20.0	0.50	1133	1126
20.0	0.75	1624	
20.0	0.75	1630	1627
30.0	0.05	188	
30.0	0.05	192	190
30.0	0.10	385	
30.0	0.10	381	383
30.0	0.50	1685	
30.0	0.50	1700	1693
30.0	0.75	2363	
30.0	0.75	2419	2391
40.0	0.05	245	
40.0	0.05	373	309
40.0	0.10	575	
40.0	0.10	569	572
40.0	0.50	2397	
40.0	0.50	2391	2394
40.0	0.75	3504	
40.0	0.75	3392	3448
50.0	0.05	480	
50.0	0.05	475	478
50.0	0.10	920	
50.0	0.10	920	920
50.0	0.50	3608	
50.0	0.50	3576	3592
50.0	0.75	5110	
50.0	0.75	5208	5159

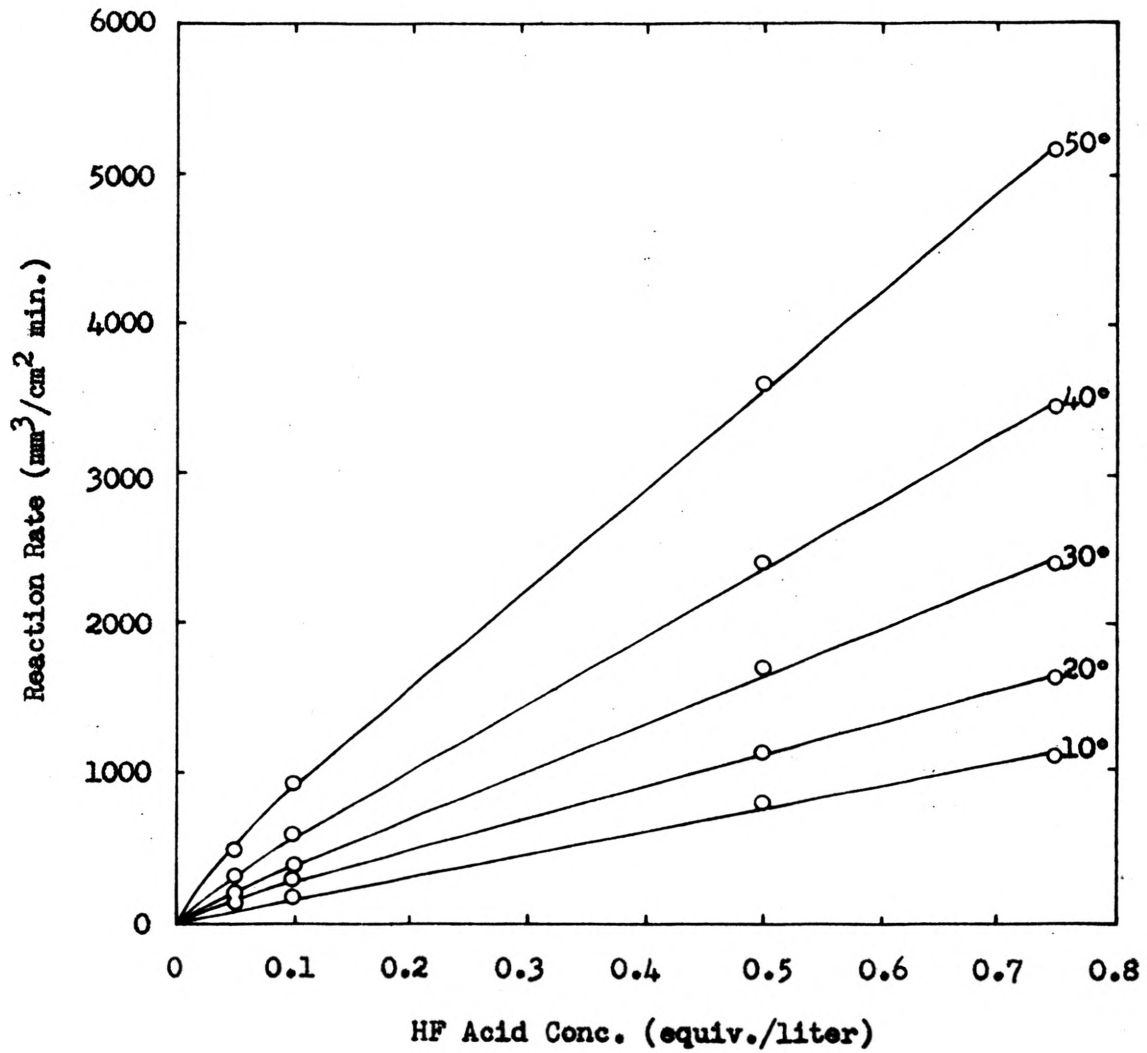


Figure 5

The effect of HF concentration on the rate of dissolution
of beryllium

and then decreased in an orderly manner. These observations are based upon many plots of the hydrogen evolved versus time.

Except for the lowest concentration of acid, a very thin light gray film was observed on the specimen at the end of each dissolution rate determination. The film appeared slightly darker and thicker as the concentration of the acid increased; however, with each set of conditions it seemed to reach an optimum thickness. It did not adhere well to the metal surface and could easily be removed with a camels hair brush before drying. In fact, some of the film could have been dislodged during exposure to the acid by the stirring action. A measure of the thickness of the film was indicated by the fact that it took several samplings to collect sufficient material to prepare a 0.5 millimeter diameter capillary specimen for x-ray examination. The resulting pattern definitely coincided with that of reagent grade beryllium oxide which had been examined by the same technique. The sampling procedure consisted of loosening the film with a camels hair brush, directing a stream of distilled water on the specimen and collecting the solution in a watch glass, from whence the water was later evaporated.

Removal of the beryllium oxide film exposed clean lustrous beryllium metal which had been attacked in an overall even fashion; especially, after attack at 10 and 20°C where the rate was low. Under a binocular microscope slight pitting was observed from exposure to higher rates of dissolution, with the frequency of pits increasing as the rate increased. After the highest rates of dissolution the pitting became so pronounced that the specimen had

a sponge-like appearance; magnification revealed smooth rounded surfaces with concave pits of shallow depth.

With the dissolution rate data obtained from this study, a determination of the reaction order and activation energy should ultimately assist in revealing the rate determining step of this dissolution reaction.

1. Reaction Order

The initial concentration of the acid appeared to be the rate controlling factor.

Thus, the rate equation for the dissolution of beryllium was assumed to be

$$R = k C^n \quad (6)$$

where R is the reaction rate ($\text{mm}^3/\text{cm}^2\text{min.}$), k is the reaction rate constant ($\text{mm}^3/\text{cm}^2\text{min.})(\text{liters/mole})^{1-n}$, C is the acid concentration (moles or equivalent/liter), and n represents the order of the reaction. A more useful form of equation (6) is

$$\ln R = n \ln C + \ln k \quad (7)$$

whereby a plot $\ln R$ versus $\ln C$ should result in a straight line if the reaction is not complicated by additional reactions. This relationship for beryllium in hydrofluoric acid is represented in Figure 6 where the slopes of the curves are equal to n.

By the method of least squares an equation for each temperature was determined as:

$$10^\circ\text{C} \quad \ln R = 0.82 \ln C + 7.25 \quad (8)$$

$$20^\circ\text{C} \quad \ln R = 0.89 \ln C + 7.65 \quad (9)$$

$$30^\circ\text{C} \quad \ln R = 0.93 \ln C + 8.07 \quad (10)$$

$$40^\circ\text{C} \quad \ln R = 0.89 \ln C + 8.40 \quad (11)$$

$$50^\circ\text{C} \quad \ln R = 0.87 \ln C + 8.80 \quad (12)$$

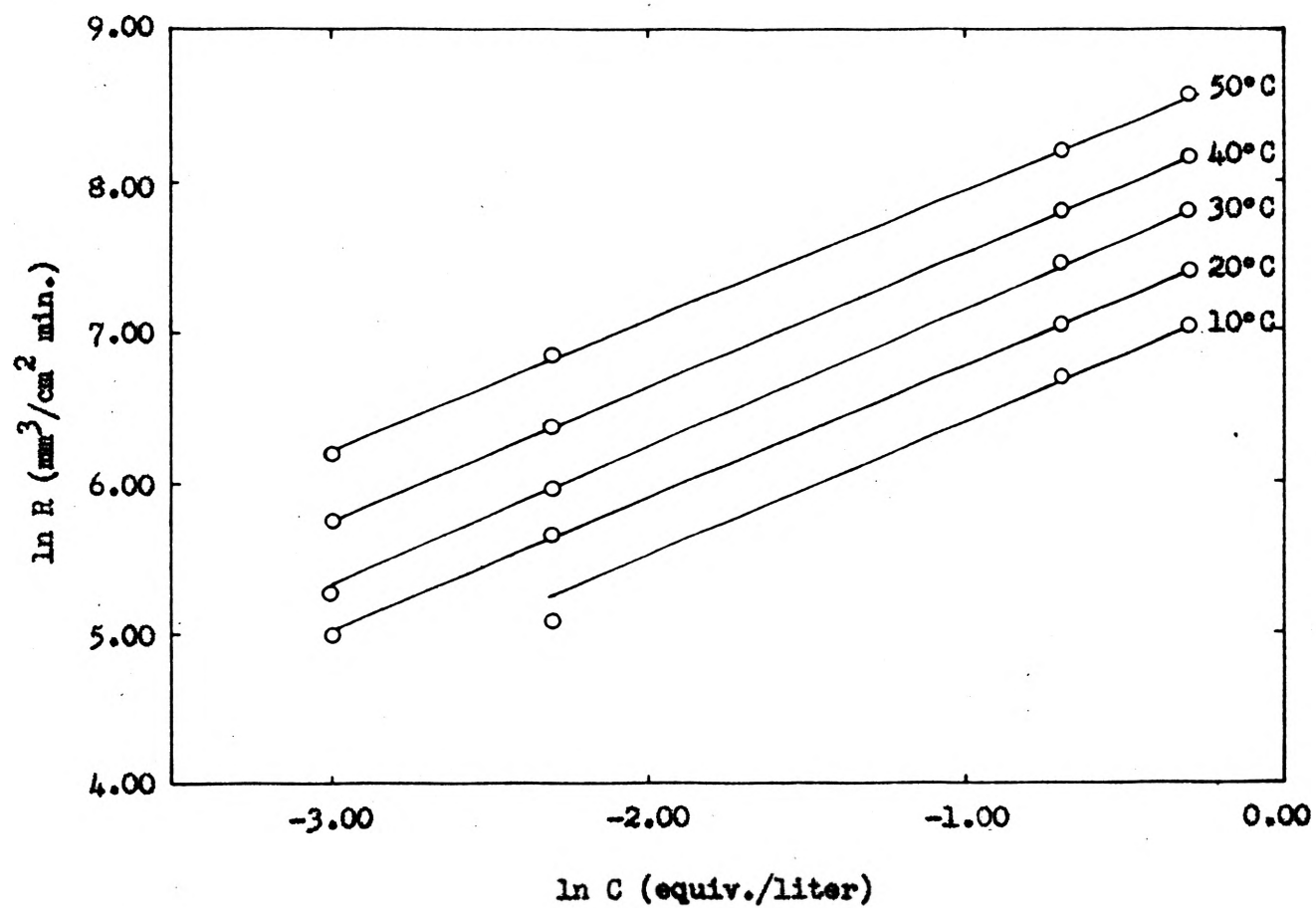


Figure 6

Determination of reaction order over the concentration range

0.05 N - 0.75 N HF

An average of the slopes in the above equations yields a reaction order of 0.88. In addition, an average value for the specific reaction rate constant at each test temperature may be obtained from these equations. The resulting values are reported in Table C.

2. Activation Energy

To account for the effect of temperature on the dissolution rate, use was made of one form of the Arrhenius equation,

$$k = A e^{-E/RT} \quad (13)$$

where k is the reaction rate constant, A the frequency factor, E the energy of activation of the reaction, R the gas constant, and T the absolute temperature. The logarithmic form of equation (13) is usually expressed for this application, as follows:

$$\ln k = -E/R(1/T) + \ln A \quad (14)$$

In this form it is similar to the previous rate equation and a plot of $\ln k$ versus $1/T$ should conform to a straight line, with the slope being related to the activation energy by

$$\text{Slope} = -E/R \quad (15)$$

where E is expressed in cal/mole and R the gas constant in cal/mole deg.

Values for the reaction rate constant, k , were obtained from equations 8 through 12. The resulting curve is shown in Figure 7, which, by the method of least squares conforms to the following equation:

$$\ln k = -3.43 \times 10^3 (1/T) + \ln 19.39$$

Substituting the slope (-3.43×10^3) in equation (15) yields the activation energy for the reaction.

$$E = (-3.43 \times 10^3)(-1.99)$$

$$E = 6.83 \text{ K cal/mole}$$

Table C

Summary of Specific Reaction Rate Constants
for Beryllium in HF Acid

	<u>10°C</u>	<u>20°C</u>	<u>30°C</u>	<u>40°C</u>	<u>50°C</u>
k, (mm ³ /cm ² min)(liters/mole) ¹⁻ⁿ	1410	2100	3200	4450	6630
k, (mg Be/cm ² min)(liters/mole) ¹⁻ⁿ	0.566	0.843	1.285	1.787	2.663

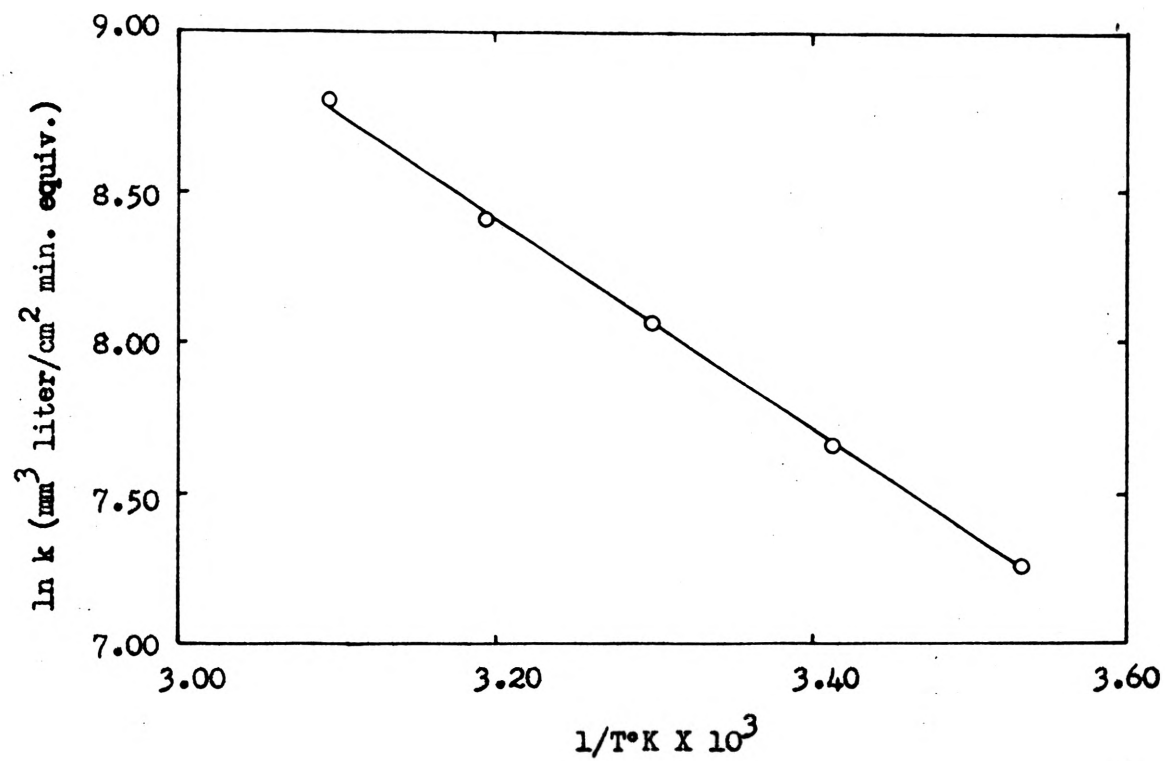


Figure 7

Determination of activation energy over the temperature
range 10°- 50°C in 0.05 N - 0.75 N HF

V. THE EFFECT OF STIRRING SPEED ON THE DISSOLUTION RATE

Often, the influence of stirring speed on the dissolution rate of metals warrants consideration of similar magnitude to that of temperature and concentration of the corrosion medium. This especially applies to reactions where the rate is controlled by the diffusion of reactants to, or products away from, the metals surface.

In this investigation, a determination of the effect of stirring speed will serve as a reference to the particular apparatus and technique employed. Reaction rates from the method used in this study are influenced by the geometry of the corrosion environment. This effect for the apparatus shown in Figure 2 would mainly stem from the size and shape of the reaction vessel and the construction of the specimen holder (Figure 3). Of course it is necessary to assume these environmental factors remain constant throughout the collection of rate data. Therefore, by only varying the stirring speed and attempting to maintain all other conditions constant, the influence of the apparatus on the reaction rate should be reflected in the results.

The effect of stirring speed may be of value in the future if a comparison is desired with results of a duplicate study which were obtained by a similar method.

To investigate the effect of stirring speed, use was made of the same apparatus, procedure and specimen that was described in Chapter IV. A concentration of 0.10 N hydrofluoric acid was

arbitrarily chosen, as was the test temperature of 30°C, and one determination of reaction rate was made at each speed of rotation. The results are reported in Table XXV through XXVIII in the Appendix and summarized in Table D. A plot of reaction rate versus stirring speed is shown in Figure 8.

Table D

Summary of the Effect of Stirring Speed
on the Dissolution Rate
(0.10 N HF at 30°C)

<u>Stirring Speed</u> (rpm)	<u>Reaction Rate</u> (mm ³ /cm ² min.)
75	239
150	316
200	373
250	416
300	448
400	508
525	595

The dissolution rate at zero stirring speed was determined as 170 mm³/cm²min. which is slightly above the value of approximately 160 mm³/cm²min. obtained by extrapolating the curve of Figure 8 to zero stirring speed. However, this is to be expected since the evolution of hydrogen tends to create a slight stirring effect in the stagnant solution.

Observation of Figure 8 indicates that the reaction rate increases less rapidly at speeds above 200 rpm. In reality this is not necessarily true; for the reaction flask was spherical and this would allow the solution itself to rotate. Thereby, having the effect of lowering the rotation speed of the specimen with respect to the solution and reflecting a reaction rate that would correspond to a lower rpm than indicated. Under more ideal conditions it is

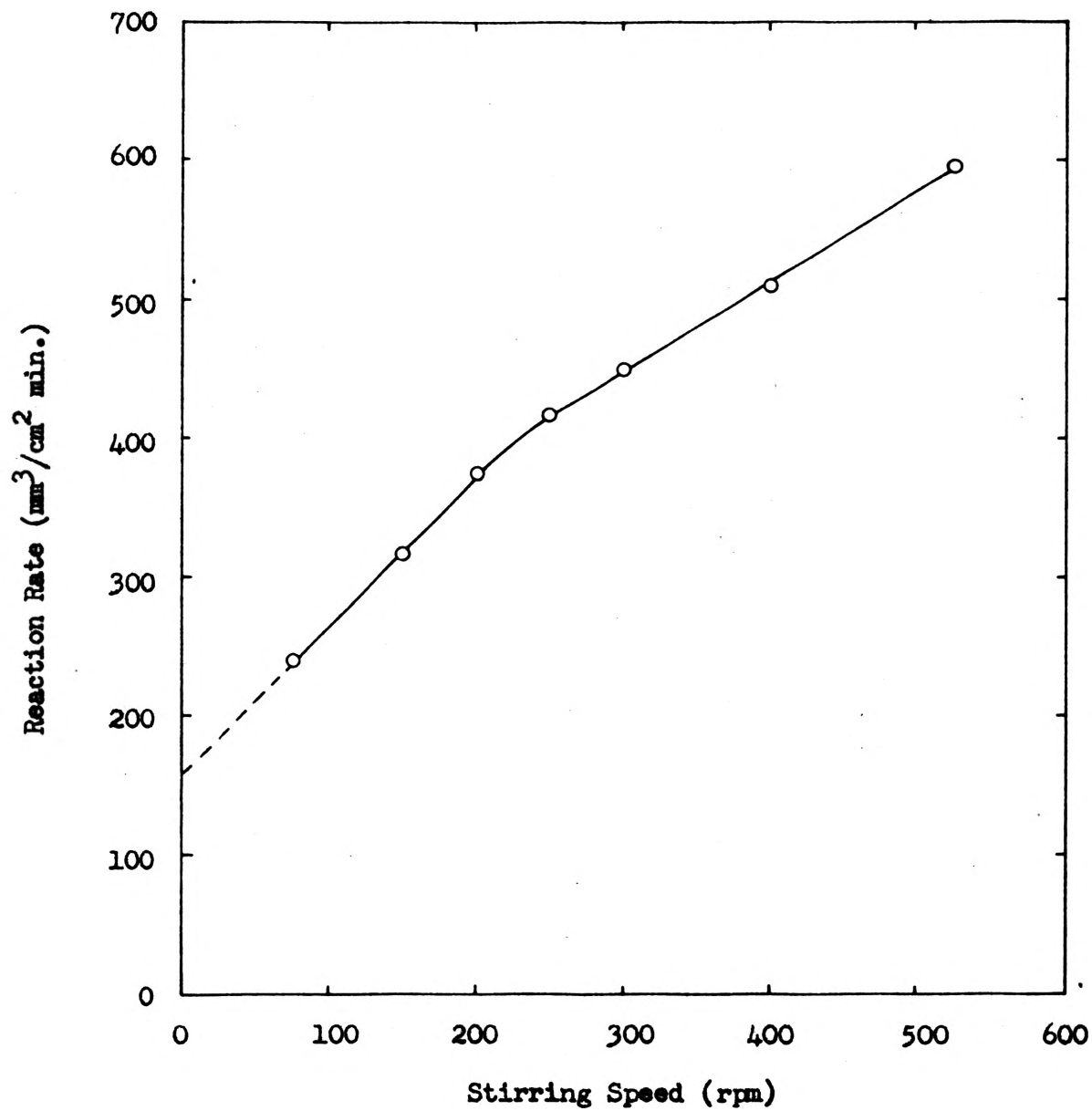


Figure 8

The effect of stirring speed on the dissolution rate of beryllium
in 0.10 N HF at 30.0°C

possible that this relationship would become linear.

The influence of the speed of motion of a corrosion medium on the rate of corrosion is discussed at some length by I. N. Putilova, S.A. Balezin and V.P. Baronnik,⁽¹²⁾ where they mention several cases in which investigators have observed a relationship which approached linearity. Another case in which a linear relationship with stirring speed was observed, is reported in a study of the reaction kinetics of zirconium in hydrofluoric acid.⁽¹³⁾

VI. THE INFLUENCE OF SALTS OF NOBLER METALS ON THE RATE OF DISSOLUTION

This investigation dealt with the effect on the dissolution rate of adding small amounts of six salt solutions, AgNO_3 , $\text{Pb}(\text{NO}_3)_2$, CuSO_4 , NiCl_2 , PtCl_4 , and HAuCl_4 , separately to 0.10 N HF acid at 30°C . The apparatus, procedure and calculations were essentially the same as described in Chapter IV, section B and C. In addition, arrangement was made to add the noble metal salt solution through a funnel which was attached to the exit valve ("h" in Figure 2). It was not added until the beryllium had reached its maximum rate of dissolution, which was twenty minutes under these conditions. In each case the reaction rate was measured prior to the addition, at which time the burette was re-zeroed and measurements continued for at least thirty minutes. The salts were added in two milliliter quantities of tenth molar concentration which had been premixed with an equal volume of 0.20 N HF acid. With the exception of the PtCl_4 addition, all the determinations were made with air initially in the reaction vessel. Platinum has the ability to act as a catalyst for the reaction of hydrogen and oxygen so the vessel had to be purged with nitrogen prior to initiating the reaction.

The purpose of this investigation was to assist in determining the mechanism of the attack of hydrofluoric acid on beryllium. Theoretically, if a dissolution process is electrochemical in nature, then the presence of noble metal salts should increase the reaction rate; in that, the noble metal ion should be electrochemically displaced from solution and deposited on the reacting metal to form

a local cathode. The degree of effectiveness the local cathode will have on the reaction rate is dependent upon its hydrogen-overpotential and the ease with which electrons may travel to it.

Before the results of this investigation are discussed in detail, it must be mentioned that they are, at best, semi-quantitative in that the salts were not added in equivalent amounts. This was due to an oversight in measuring the concentration of the additions in terms of molarity instead of normality. Also, only one determination was made for each salt addition.

A comparative indication of the effect of the various noble metal salts may be observed in Figure 9. A numerical tabulation of the results is not included for the reasons mentioned in the previous paragraph, however, the recorded data may be found in Tables XXIX through XXXIV in the Appendix.

Additions of gold and platinum seemed to increase the rate of dissolution for 30 and 20 minutes respectively, at which time their effect diminished. Proof of their displacement from solution was observed by the presence of metallic gold in the bottom of the reaction vessel and the dark color imparted to the acid solution by the platinum. Metallic gold was also observed in scattered areas on the beryllium. The platinum gave an overall dark gray appearance to the specimen which under high magnification revealed a discontinuous film of extremely fine dark particles. The metallic gold particles seemed to adhere much better to the beryllium which probably accounts for its more invigorating effect on the dissolution rate. In both cases the surface of the beryllium was rough

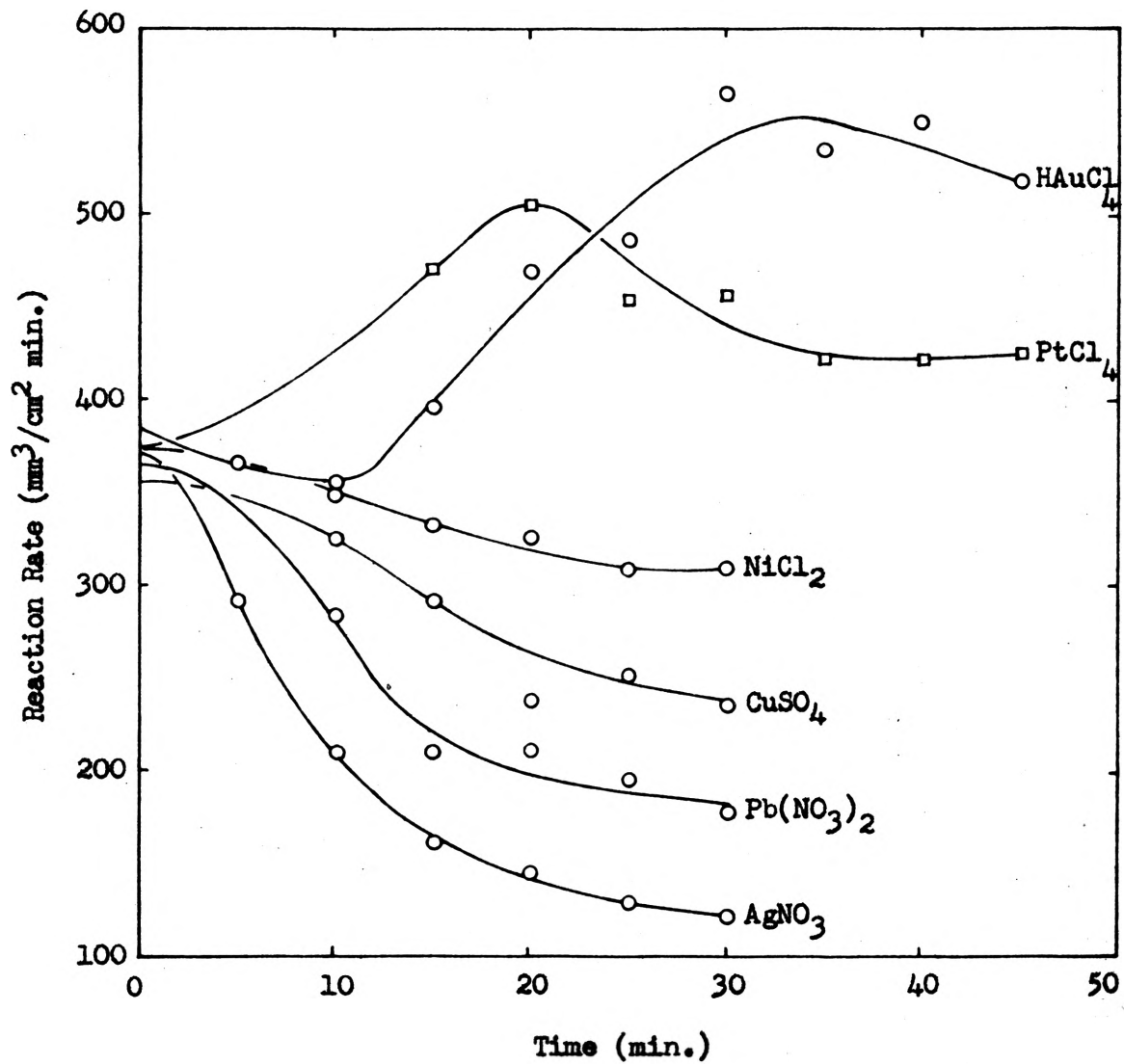


Figure 9

The effect on dissolution rate of adding salts of nobler metals to 0.10 N HF at 30°C

and pitted more than usual, which is what might be expected of an electrochemical type of attack.

The four remaining salts had an attenuating effect upon the reaction rate, with the AgNO_3 addition having the greatest effect. This was probably caused by the greater amount of AgNO_3 added as compared to the $\text{Pb}(\text{NO}_3)_2$. Dark colored loosely adherent films were formed by AgNO_3 , $\text{Pb}(\text{NO}_3)_2$ and NiCl_2 additions, which upon removal revealed a lustrous beryllium sub-surface with pitting visible under high magnification (approximately 450X). The $\text{Pb}(\text{NO}_3)_2$ addition formed a white precipitate, PbF_2 , when it was premixed in two milliliters of 0.2 N HF acid; but apparently sufficient lead ions were made available to form a dense film. The film formed by the CuSO_4 addition was light brown or copper colored and formed a dense continuous layer that adhered to the beryllium better than any of the other films, except the gold particles. Apparently, these latter noble metals were displaced from solution, but, for some reason were rendered ineffective as local cathodes and seemed to form a protective film. This would not be surprising for lead because of its high hydrogen overpotential.

The exact composition of the films formed by the additions is not known since a detailed x-ray analysis was not performed.

VII. THE RATE OF DISSOLUTION OF BERYLLIUM IN HYDROCHLORIC ACID

Qualitative observations of the dissolution of beryllium in dilute hydrochloric acid indicated the reaction had a greater rate and that its mechanism was markedly different from the hydrofluoric acid reaction. The difference was most notably displayed by the accumulation of a black residue as the reaction progressed over a period of hours. Accumulation was greatest in concentrations of less than 0.5 N HCl and it increased with time. Accordingly, the beryllium specimen was observed to acquire a black appearance in a matter of minutes after exposure to all concentrations of HCl. The above observations appeared to apply equally to both vacuum cast (approximately 99.5% Be) and hot pressed powder metallurgy (98.5% Be) material.

Observation of the black residue under high magnification (approximately 450X) revealed needle and prismatic shaped particles, as shown in Figures 10, 11 and 12, which possessed a metallic luster. The needles have a diameter of approximately 0.4 microns and the length of the longest needle is 25 microns. The largest fragments are approximately 10 by 15 microns as compared to an original grain size of 10 to 30 microns in the powder metallurgy material. This prompted a test of the residue in concentrated HCl, whereupon contacting a 3 to 4 N solution the fine particles reacted vigorously; this would be expected with metal powder whose surface area and energy is inherently high. X-ray analysis, with the use of a 0.5 mm diameter capillary specimen, a cylindrical

camera and copper K_{α} radiation, revealed a beryllium metal pattern for the residue from the high purity vacuum cast sample and a metal plus oxide pattern for that from the powder metallurgy material. It originally contained 1.2% max. BeO but during dissolution this proportion would undoubtedly increase.

Evidently, the dissolution reaction in HCl acid is characterized by some form of preferential attack which liberates minute fragments of the parent metal into the acid solution. Evidence of such process is disclosed by the shape of the fragments and the presence of twinning in the larger fragments (Figure 10). They both may be traced to the parent metal as shown in Figures 13 and 14 respectively. This analysis of the dissolution process accounts for the greater accumulation of black residue in the lower concentrations of acid, for in higher concentrations the fragments, if created, would tend to be consumed as part of the reaction. An explanation for their apparent stability and accumulation in very dilute acid could be in the fact that the fragments have a more perfect structure than the unreacted metal.

Previous occurrences of the separation of fragments, or chunks, during anodic dissolution processes have been observed for various metals; more recently this phenomenon has been associated with the term "chunk effect." As mentioned by U.R. Evans,⁽¹⁾ probably the first encounters with the above situation, back to 1928, were in studies on the anodic attack of metals where the corrosion rate was compared to its faradaic equivalent and found to be much greater. Evans cites instances that involve the metals lead, copper, silver,



Figure 10

Loose fragments of beryllium metal produced by the "chunk effect". Note the twinning in the larger fragments which may be traced to the parent metal (Figure 14). Black plastic was used for the background. 450X.



Figure 11

Needle-like fragments produced by the "chunk effect." The diameter of the smallest fragment is approximately 0.4 micron and the longest 25 microns. Black plastic was used for the background. 450X.



Figure 12

A collection of the fragments produced by the "chunk effect." When in large quantities as above, they appear black to the naked eye. Black plastic was used for the background. 450X.



Figure 13

The beryllium metal surface after reacting with HCl acid. This shows the source of the needle shaped fragments. 1300X.



Figure 14

View of the beryllium metal surface after attack by HCl acid, showing a different orientation. Note the evidence of twinning. 1300X.

tin and aluminum as anodes. A more recent observation of non-faradaic conditions with aluminum is reported by M.E. Straumanis,⁽¹⁴⁾ where he accounts for the deviation from Faraday's Law by considering the difference effect theory. The most recent contribution to this subject has been by G. A. Marsh and E. Schaschl.⁽¹⁵⁾ They cite cases that apply to aluminum, iron, magnesium and silver; and they refer to the "chunk effect" as some form of local corrosion and/or undermining process. One similarity noticed in all of the above cases, was the fact that the mode of attack was primarily electrochemical.

A search of the literature revealed no evidence of any previous association of beryllium with the "chunk effect." Mention of the black appearance was found; however, no additional information was available to indicate that further inquiry had been made to explain the appearance. The earliest observation encountered was by J. O'M. Bockris⁽¹⁶⁾ in 1947. He had performed a hydrogen overpotential study on some less common metals when he reported,

"Owing to the ready solubility of Be in N HCl, experiments were carried out in N/10 solution, in which the metal is still slightly soluble at a c.d. of 10^{-3} amp/sq.cm. Further results at a c.d. of 10^{-1} amp/sq.cm. could not be reproduced for Be and the metal surface became darkened so that four values at c.d.'s below 10^{-1} amp/sq.cm. were obtained."

Another reference (17) pertains to an anodic oxidation study on beryllium using an aqueous sodium chloride solution as the electrolyte. In this case it was stated that, "The black substance is formed uniformly throughout the anolyte." They identified the black substance by x-ray analysis as beryllium metal but claimed

that the only way to account for it was by the disproportionation of unipositive beryllium. Undoubtedly, they observed a result of the "chunk effect", since the appropriate conditions for electrochemical attack of the anode were present and the dislodged fragments would be fairly stable in such a neutral solution. Regrettably, a more detailed elucidation of these conflicting mechanisms is not possible because the reference in question did not report pertinent facts about the size, shape, appearance or quantity of their "black substance." It would be interesting to note the outcome of their study if a strict accounting of the observed black substance had been made; very possibly, it would explain the deviation from faradaic conditions that they used to postulate the existence of univalent ions.

After establishing an understanding of the mechanism that caused the difference from dissolution in HF acid, it became apparent why a more vigorous reaction had been observed in approximately 2 N solutions. This led to speculation as to what the activation energy of such a kinetic process would be and could it be of assistance in evaluating the kinetics of the HF acid reaction. Therefore, it was decided to perform a limited investigation; with more detailed attention to follow in a subsequent study.

Dissolution rates were determined for a minimum number of conditions required to calculate a reaction order and activation energy. The results of one test at each condition are tabulated in the Appendix in Tables XXXV through XXXXIV. Purposely, the experimental technique employed was identical to the previous rate study, as outlined in Chapter IV.

At 40 and 50°C, beryllium exhibited a lower dissolution rate in HCl than in HF acid at concentrations less than 0.2 N, however, this condition reversed itself at high acid concentrations. This may be observed in Figure 15, where the rate is plotted with respect to HCl concentration. In contrast to HF acid, a minimum concentration (approximately 0.05 N) of HCl seems to be required before a measurable reaction rate occurs.

A plot of \ln rate versus \ln HCl concentration indicated that the relationship was not linear for this reaction. According to the laws of reaction kinetics, non-linearity would add doubt to any subsequent results obtained by the method used in Chapter IV, and it suggests that the reaction rate is partly dependent upon some other variable, besides the acid concentration. So, this limited amount of work suggests a more complex reaction mechanism than with HF acid.

When the dissolution rate results were treated normally, as described in Chapter IV, section D, an average reaction order of 1.17 and an activation energy of 5.75 K cal/mole were calculated. A more extensive study of this reaction should clarify the doubt associated with this limited investigation.

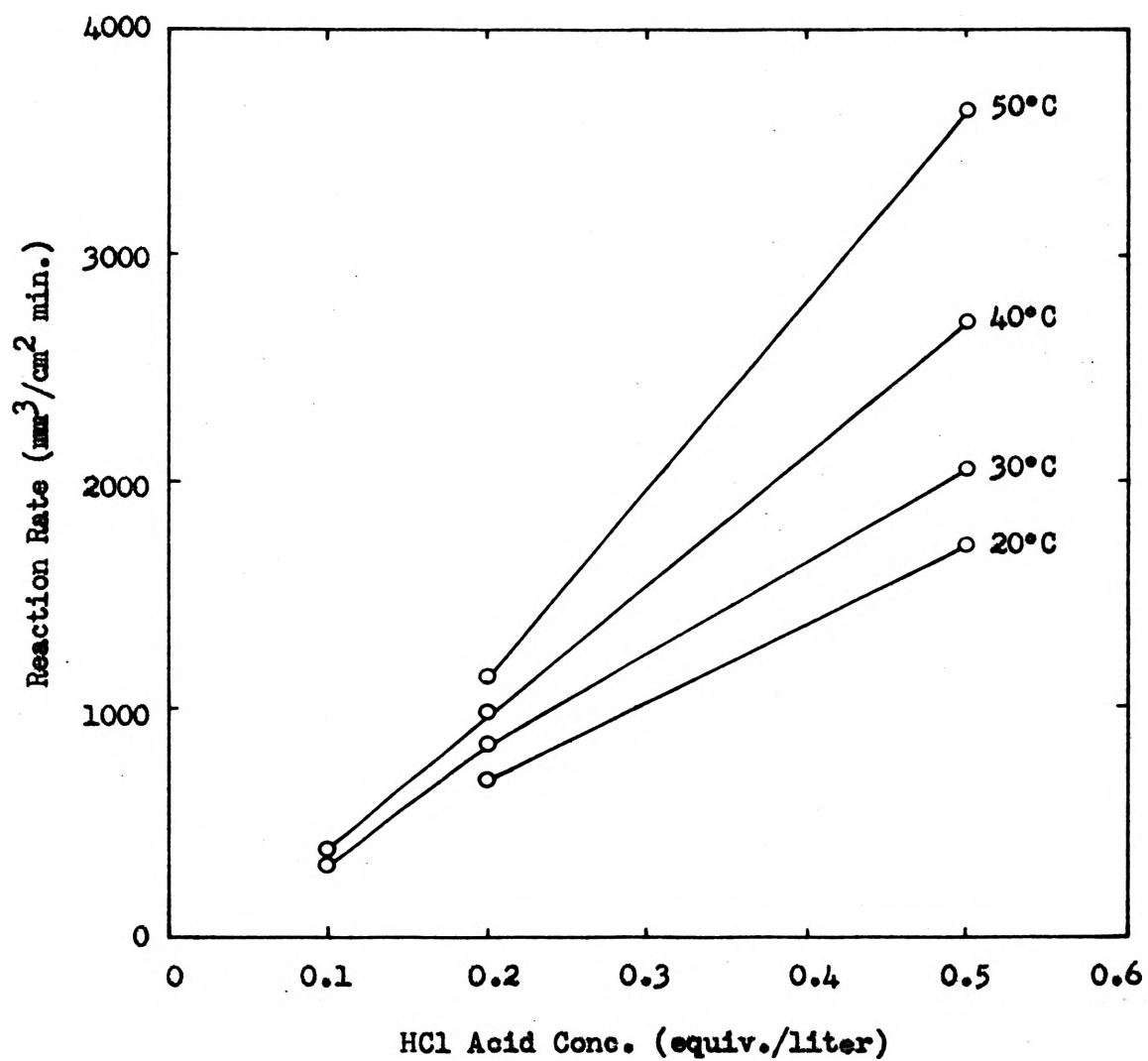


Figure 15

The effect of HCl conc. on the rate of dissolution of Be

VIII. DISCUSSION

Results from the dissolution rate study in HF acid conformed with the kinetic treatment chosen but resulted in a reaction order of less than one (0.88), suggesting the assumption of first order dependency on the HF concentration to be questionable. Further evidence of another influencing factor was revealed in the experimental activation energy of 6.8 K cal/mole. Compared to an ideally diffusion controlled process (4.5 K cal/mole), this value is rather high, but not uncommon since previous observations of high activation energies are reported and attributed to an oxide film acting as an energy barrier. If an electrochemical process is considered, 6.8 K cal/mole would normally be considered low, but this outlook is complicated by the 5.8 K cal/mole observed for the HCl reaction.

One dominant factor is the 98.5% purity of the beryllium, whereas 99.9+% purity is common for metals in such studies. For example, the largest impurity, BeO, was observed to accumulate during dissolution as a light gray film. This film, identified by x-ray analysis, undoubtedly complicated the reaction kinetics. This oxide being a non-conductor could act as a barrier to the diffusion of reaction product away from the metal surface. Potential measurements might reveal the effect of this film.

In addition to BeO as an impurity, beryllium is known to possess an ever-present oxide film much like aluminum. This characteristic has been studied rather thoroughly by electron diffraction.⁽¹⁸⁾ The oxide film, plus beryllium's chemical and normal potential similarities, suggested a comparison with previous work on aluminum

in HF solutions.⁽¹⁹⁾ It showed that the effect of nobler salts on dissolution rate is similar but a comparison of activation energies was not possible because dissolution rates were reported only for 25°C. From the rate data at 25°C a reaction order of 0.95 was calculated. Potential and difference effect measurements would be of great value in completing this analogy. A possible deterrent is the characteristically higher dissolution rate of beryllium, since the oxide film on aluminum appears to be more resistant to HF acid. Beryllia is reported to be attacked by HF acid rapidly.⁽²⁾ This was also observed in the laboratory, along with HCl which reacted much slower.

A slowly soluble product (BeF_2) is another factor which could have affected the dissolution rate. According to Hoar⁽²⁰⁾ this is unlikely. However, in this particular case the BeO film, present or accumulated, could hinder diffusion of ionized products away from the reaction interface. Also, the formation of products which do not diffuse quickly from the metal surface and deposit in the metal pores may lead to the formation of oxides (possibly hydrated). However, such oxides are usually formed under anodic polarization and it is unlikely that internal currents would be of sufficient magnitude to promote this mechanism or make it thermodynamically possible.⁽²⁰⁾ Reference to Seidell⁽²¹⁾ revealed the solubility of solid BeF_2 in water at 25°C as follows:

Beryllium fluoride is extremely soluble but dissolves very slowly in water, and did not reach the saturation value within two to three months of constant agitation.

<u>Days Stirred</u>	<u>Mole BeF₂/liter</u>
21	9.72
38	13.74
66	16.73
82	17.08

Darwin and Buddery⁽²⁾ report the solubility of BeF₂ in water at room temperature to be 50 gm/100 gm water. An evaluation of this factor was not possible from x-ray analysis of the BeO film, which may have contained some of the reaction product, because BeF₂ is amorphous and only produced a faint halo when the hydrated material itself was x-rayed.

The steady decrease in reaction rate, after the maximum, is not wholly attributable to a depletion of the HF solution. Calculations of this effect showed it could only account for approximately 10% of the decrease. Since the decrease in rate was uniform, it could be related to the uniformly accumulated oxide film which originated from the BeO present in the metal as an impurity.

In HCl solutions qualitative observations indicated an electrochemical type of attack. These observations were based on the effect of adding salts of nobler metals, of touching the reacting metal with a platinum wire and the observance of the "chunk effect." For this reaction the light gray BeO film was not observed; probably it was dislodged with the chunks. The induction period noticed with HCl is attributed to its slow attack of the ever-present oxide film, to the accumulation of admixtures, and to the development of the rough surface associated with the "chunk effect." Actually, this acid would be expected to be favorable to an electrochemical process,

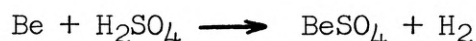
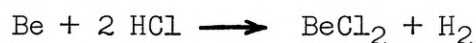
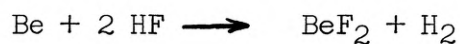
plus, Be has a favorable hydrogen overpotential, slightly less than copper. Most outstanding of the above criteria is the "chunk effect" which has always been observed during primarily electrochemical conditions.

Conversely, since the "chunk effect" was not observed during reaction with HF or H_2SO_4 solutions, it indicates an absence or minor amount of electrochemical attack. If the "chunk effect" had been present, beryllium metal lines should have appeared in the x-ray pattern of the associated accumulated BeO film. Also, the surface after attack had a different appearance, as described in the results of Chapter IV.

Beryllium appeared to become passivated in pure HNO_3 solutions but when small amounts of H_2SO_4 were added reaction soon commenced. The addition of H_2SO_4 to HNO_3 solutions is reported in the literature. If the concentration of HNO_3 was about 8 N the added H_2SO_4 appeared not to affect the passivity.

IX. SUMMARY AND CONCLUSIONS

Beryllium was shown to react stoichiometrically, with the three acid solutions studied, in accordance with a plus two valence, as follows:



Subsequent dissolution rate determinations in 0.05 N to 0.75 N HF solutions indicated the rate at 30°C could be expressed by

$$R = 3200 C^{0.88}$$

where R is in mm³/cm² min. and C in moles/liter or when R is in mg.Be/cm²min., it may be expressed by

$$R = 1.285 C^{0.88}$$

Actually, this is a high rate of dissolution and compared to other metals studied at 30°C in 0.5 N HF acid with a stirring speed of 200 rpm the rate approximates the following: 10 times Al, 4 times Ti and 1.5 times Zr. This high dissolution rate is attributable to the very negative free energy of formation of BeF₂ and the ability of HF acid to readily attack BeO. Other metals with a spontaneous oxide film (that occupies a greater volume than the original metal) are usually afforded more protection.

A kinetic evaluation of the dissolution results produced a reaction order of 0.88 and an activation energy of 6.8 K cal/mole. The magnitude of these properties is difficult to interpret by ordinary means since it was caused by complex surface conditions.

The influence of stirring speed was determined as a reference

for future studies of this reaction.

By adding noble metal salts during dissolution rate determinations, beryllium was shown to be prone to electrochemical attack only under extreme conditions, where hydrogen overvoltage was at a minimum.

A preliminary investigation of the dissolution process in HCl solutions revealed a very different mode of attack. The process appeared to be electrochemical and it exhibited the phenomenon known as the "chunk effect", which is a property certain corrosive media possess to dislodge fragments of the parent metal during anodic attack. Undoubtedly, the "chunk effect" will be revealed in later studies by causing a very negative difference effect.

Throughout this study invariably BeO arose in some form as a controlling factor, which emphasizes the rate determining influence it must have. Consequently, any corrosion studies performed on beryllium will be dependent on the BeO content of the metal. Unfortunately, the present state of knowledge does not permit a decisive statement of this deduction.

Based upon the outcome of this study the following hypothesis is offered for the dissolution reaction in HF acid. The dissolution of beryllium in dilute concentrations of hydrofluoric acid is primarily a diffusionally controlled process. As the un-ionized HF molecule proceeds over the concentration gradient, which terminates at the metal surface, it encounters a BeO layer. This layer offers more resistance to diffusion than would concentration polarization and therefore more of an energy barrier, which would contribute to

the high activation energy observed in this study.

Besides being an energy barrier, some of the HF molecules react with the BeO before reaching the metal surface, as follows:



This reaction does not liberate hydrogen so it is not reflected in the results. Therefore, it is not possible to estimate the magnitude of this reaction, or its effect on the mechanism, from the results of this study. Also, the present state of knowledge does not allow an explanation of the fractional reaction order. Ultimately, the reaction at the metal surface would be rapid and not rate controlling.

Evaluation of this mechanism might be accomplished if more were known of the HF acid-BeO reaction or if stoichiometric studies were performed with the impure powder metallurgy beryllium. However, potential and difference effect measurements should prove more effectual. Also radioactive tracer techniques would prove useful.

Dissolution rates indicative of pure Be might be realized if high purity cast material were used, but the inherent large grain size would unavoidably complicate the study because of crystallographic influence on the rates.

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XI APPENDIX

The appendix contains tables of all of the hydrogen evolution data recorded during the course of this investigation. It is assembled in the same order as the table of contents.

Tables I through XXIV contain the data for:

The Rate of Dissolution of Beryllium in Dilute Concentrations of Hydrofluoric Acid at Various Temperatures

Tables XXV through XXVIII contain the data for:

The Effect of Stirring Speed on the Dissolution Rate

Tables XXIX through XXXIV contain the data for:

The Influence of Salts of Nobler Metals on the Rate of Dissolution

Tables XXXV through XXXIV contain the data for:

The Rate of Dissolution of Beryllium in Dilute Concentrations of Hydrochloric Acid at Various Temperatures

Table I

Dissolution of Be in 0.01 N HF at 10.0°C

Run No. 1 (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume</u> <u>(ml.)</u>
0	0.00
5	0.00
10	0.00
15	0.00
20	0.00
25	0.00

Apparent rate: 0

Dissolution of Be in 0.05 N HF at 10.0°C

Run No. 1 (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume</u> <u>(ml.)</u>
0	0.00
5	0.00
10	0.00
15	0.00
20	0.00
25	0.00

Apparent rate: 0

Table II

Dissolution of Be in 0.10 N HF at 10.0°C

Run No. 1 (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.00	0.00
5	0.00	0.00
10	0.00	0.00
15	0.34	0.34
20	0.67	0.33
25	1.30	0.63
30	2.06	0.76*
35	2.73	0.67*
40	3.48	0.75*
45	4.11	0.63

* Average maximum rate for first run: 145

Run No. 2

0	0.00	0.00
5	0.00	0.00
10	0.00	0.00
15	0.42	0.42
20	0.84	0.42
25	1.35	0.51
30	2.32	0.97*
35	3.12	0.80*
40	3.92	0.80*
45	4.55	0.63

* Average maximum rate for second run: 171

Average maximum rate for both runs: 158

Table III

Dissolution of Be in 0.50 N HF at 10.0°C

Run No. 1 (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.00	0.00
5	1.57	1.57
10	5.46	3.89
15	9.51	4.05*
20	13.66	4.15*
25	17.68	4.02*
30	21.52	3.84
35	25.49	3.97
40	29.24	3.75

* Average maximum rate for first run: 815

Run No. 2 (specimen #1)

0	0.00	0.00
5	1.48	1.48
10	5.24	3.76
15	9.16	3.92*
20	13.09	3.93*
25	16.76	3.67
30	20.42	3.66
35	24.18	3.76
40	27.76	3.58

* Average maximum rate for second run: 785

Average maximum rate for both runs: 800 mm³/cm² min.

Table IV

Dissolution of Be in 0.75 N HF at 10.0°C

Run No. 1 (specimen #1)

Time (minutes)	Volume at STP (ml.)	Δ Vol (cm ³)
0	0.00	0.00
1	0.27	0.27
2	0.62	0.35
3	1.42	0.80
4	2.48	1.06
5	3.54	1.06
6	4.65	1.11*
7	5.75	1.10*
8	6.82	1.07*
9	7.92	1.10*
10	9.03	1.11*
11	10.14	1.11*
12	11.29	1.15*
13	12.39	1.10*
14	13.55	1.16*
15	14.65	1.10*
20	20.01	5.36
25	25.23	5.22
30	30.45	5.22
35	35.59	5.14
40	40.72	5.13

* Average maximum rate for first run: 1111 mm³/cm² min.

Table V

Dissolution of Be in 0.75 N HF at 10.0°C

Run No. 2 (specimen #1)

Time (minutes)	Volume at STP (ml.)	Δ Vol. (cm ³)
0	0.00	0.00
1	0.18	0.18
2	0.53	0.35
3	1.14	0.61
4	2.16	1.02
5	3.17	1.01
6	4.22	1.05
7	5.28	1.06
8	6.43	1.15*
9	7.53	1.10*
10	8.63	1.10*
11	9.77	1.14*
12	10.91	1.14*
13	12.01	1.10*
14	13.11	1.10*
15	14.22	1.11*
16	15.32	1.10*
17	16.37	1.05
18	17.34	0.97
19	18.40	1.06
20	19.54	1.14
25	24.82	5.28
30	30.10	5.28
35	35.21	5.11

* Average maximum rate for second run: 1116 mm³/cm² min.Average maximum rate for both runs: 1114 mm³/cm² min.

Table VI

Dissolution of Be in 0.01 N HF at 20.0°C

Run No. 1 (specimen # 1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.00	0.00
5	0.00	0.00
10	0.17	0.17
15	0.26	0.09
20	0.35	0.09
25	0.35	0.00
30	0.39	0.04
35	0.52	0.13
40	0.73	0.21*
45	0.90	0.17
50	1.07	0.17

* Maximum rate for first run: 42

Run No. 2 (specimen #1)

0	0.00	0.00
5	0.00	0.00
10	0.00	0.00
15	0.00	0.00
20	0.17	0.17
25	0.00	0.00
30	0.21	0.21*
35	0.34	0.13
40	0.43	0.09

* Maximum rate for second run: 42

Maximum rate for both runs: 42 mm³/cm² min.

Table VII

Dissolution of Be in 0.05 N HF at 20.0°C

Run No. 1 (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.00	0.00
5	0.00	0.00
10	0.30	0.30
15	0.86	0.56
20	1.59	0.73*
25	2.27	0.68*
30	3.00	0.73*
35	3.60	0.60*
40	4.20	0.60*
45	4.84	0.64*
50	5.66	0.82*
55	6.43	0.77*
60	7.20	0.77*
65	7.76	0.56

* Average maximum rate for first run: 141

Run No. 2 (specimen #1)

0	0.00	0.00
5	0.17	0.17
10	0.56	0.39
15	1.29	0.73*
20	1.97	0.68*
25	2.70	0.73*
30	3.43	0.73*
35	4.16	0.73*
40	4.85	0.69*
45	5.58	0.73*
50	6.31	0.73*
55	7.04	0.73*
60	7.55	0.51

* Average maximum rate for second run: 144

Average maximum rate for both runs: 143 mm³/cm² min.

Table VIII

Dissolution of Be in 0.10 N HF at 20.0°C

Run No. 1 (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.00	0.00
1	0.17	0.17
2	0.26	0.09
3	0.30	0.04
4	0.43	0.13
5	0.56	0.13
10	1.72	1.16
15	3.18	1.46*
20	4.60	1.42*
25	5.98	1.38*
30	7.40	1.42*
35	8.52	1.12
40	9.81	1.29
45	11.02	1.21

* Average maximum rate for first run: 284

Run No. 2 (specimen #1)

0	0.00	0.00
5	0.60	0.60
10	1.91	1.31
15	3.27	1.36*
20	4.68	1.41*
25	6.08	1.40*
30	7.44	1.36*
35	8.72	1.28
40	10.03	1.31
45	11.31	1.28

* Average maximum rate for second run: 277

Average maximum rate for both runs: 281 mm³/cm² min.

Table IX

Dissolution of Be in 0.50 N HF at 20.0°C

Run No. 1 (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	Δ <u>Vol.</u> <u>(cm³)</u>
0	0.00	0.00
1	0.53	0.53
2	1.41	0.88
3	2.51	1.10*
4	3.69	1.18*
5	4.79	1.10*
6	5.89	1.10*
7	6.99	1.10*
8	8.13	1.14*
9	9.41	1.28*
10	10.42	1.01*
11	11.51	1.09*
12	12.61	1.10*
13	13.71	1.10*
14	14.77	1.06
15	15.82	1.05

* Average maximum rate for first run: 1118

Run No. 2 (specimen #1)

0	0.00	0.00
1	0.61	0.61
2	1.41	0.80
3	2.50	1.09*
4	3.65	1.15*
5	4.79	1.14*
6	5.97	1.18*
7	7.07	1.10*
8	8.21	1.14*
9	9.35	1.14*
10	10.45	1.10*
11	11.64	1.19*
12	12.74	1.10
13	13.79	1.05

* Average maximum rate for second run: 1133

Average maximum rate for both runs: 1126 mm³/cm² min.

Table X

Dissolution of Be in 0.75 N HF at 20.0°C

Run No. 1 (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.00	0.00
1	0.97	0.97
2	2.20	1.23
3	3.70	1.50
4	5.33	1.63*
5	7.05	1.72*
6	8.72	1.67*
7	10.40	1.68*
8	11.89	1.49*
9	13.48	1.59*
10	15.15	1.67*
11	16.65	1.50*
12	18.32	1.67*
13	19.82	1.50
14	21.41	1.59
15	22.99	1.58

* Average maximum rate for first run: 1624

Run No. 2 (specimen #1)

0	0.00	0.00
1	0.97	0.97
2	2.29	1.32
3	3.88	1.59*
4	5.55	1.67*
5	7.14	1.59*
6	8.81	1.67*
7	10.49	1.68*
8	12.16	1.67*
9	13.79	1.63*
10	15.33	1.54*

* Average maximum rate for second run: 1630

Average maximum rate for both runs: 1627 mm³/cm² min.

Table XI

Dissolution of Be in 0.05 N HF at 30.0°C

Run No. 1 (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.00	0.00
5	0.72	0.72
10	1.70	0.98*
15	2.59	0.89*
20	3.48	0.89*
25	4.46	0.98*
30	5.43	0.97*
35	6.24	0.81
40	7.13	0.89
45	8.06	0.93
50	9.00	0.94

* Average maximum rate for first run: 188

Run No. 2 (specimen #1)

0	0.00	0.00
5	0.94	0.94
10	2.05	1.11*
15	3.08	1.03*
20	4.06	0.98*
25	5.05	0.99*
30	6.03	0.98*
35	6.84	0.81
40	7.70	0.86
45	8.60	0.90
50	9.41	0.81

* Average maximum rate for second run: 192

Average maximum rate for both runs: 190 mm³/cm² min.

Table XII

Dissolution of Be in 0.10 N HF at 30.0°C

Run No. 1 (specimen #2)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	Δ <u>Vol.</u> <u>(cm³)</u>
0	0.00	0.00
5	2.22	2.22
10	4.28	2.06*
15	6.33	2.05*
20	8.38	2.05*
25	10.43	2.05*
30	12.49	2.06*
35	14.45	1.96*
40	16.25	1.80
45	18.13	1.88
50	20.01	1.88

* Average maximum rate for first run: 385

Run No. 2 (specimen #2)

0	0.00	0.00
5	2.05	2.05*
10	4.11	2.06*
15	6.12	2.01*
20	8.13	2.01*
25	10.10	1.97*
30	12.11	2.01*
35	13.95	1.84
40	15.79	1.84
45	17.63	1.84
50	19.39	1.76

* Average maximum rate for second run: 381

Average maximum rate for both runs: 383 mm³/cm² min.

Table XIII

Dissolution of Be in 0.50 N HF at 30.0°C

Run No. 1 (specimen #2)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.00	0.00
1	1.88	1.88
2	3.85	1.97
3	5.65	1.80*
4	7.37	1.72*
5	9.17	1.80*
6	10.96	1.79*
7	12.76	1.80*
8	14.61	1.85*
9	16.36	1.75*
10	18.16	1.80*
15	27.07	8.91*
20	34.69	7.62
25	42.32	7.63
30	49.94	7.62

* Average maximum rate for first run: 1685

Run No. 2 (specimen #2)

0	0.00	0.00
1	1.97	1.97
2	3.94	1.97
3	5.75	1.81*
4	7.55	1.80*
5	9.52	1.97*
6	11.32	1.80*
7	13.21	1.89*
8	15.01	1.80*
9	16.81	1.80*
10	18.61	1.80*
15	27.36	8.75*
20	35.50	8.14
25	43.48	7.98
30	51.11	7.63

* Average maximum rate for second run: 1700

Average maximum rate for both runs: 1693 mm³/cm² min.

Table XIV

Dissolution of Be in 0.75 N HF at 30.0°C

Run No. 1 (specimen #2)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.00	0.00
1	2.31	2.31
2	4.79	2.48*
3	7.35	2.56*
4	9.83	2.48*
5	12.40	2.57*
6	14.88	2.48*
7	17.36	2.48*
8	19.84	2.48*
9	22.24	2.40
10	24.63	2.39
15	36.52	11.89
20	47.89	11.37
25	58.58	10.69

* Average maximum rate for first run: 2363

Run No. 2 (specimen #2)

0	0.00	0.00
1	2.27	2.27
2	4.71	2.44*
3	7.36	2.65*
4	10.02	2.66*
5	12.67	2.65*
6	15.24	2.57*
7	17.81	2.57*
8	20.38	2.47*
9	22.91	2.53*
10	25.35	2.44*
15	37.33	11.98
20	48.98	11.65

* Average maximum rate for second run: 2419

Average maximum rate for both runs: 2391 mm³/cm² min.

Table XV

Dissolution of Be in 0.01 N HF at 40.0°C

Run No. 1 (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	Δ Vol. <u>(cm³)</u>
0	0.21	0.00
1	0.51	0.30
2	0.77	0.26*
3	0.94	0.17*
4	1.07	0.13*
5	1.20	0.13*
10	1.80	0.60
15	2.23	0.43
20	2.53	0.30
25	2.79	0.26

* Average maximum rate for first run: 173

Run No. 2 (specimen #1)

Average barometric pressure: 734.4 mmHg
Average room temperature: 24.33°C

0	0.17	0.00
1	0.34	0.17*
2	0.51	0.17*
3	0.68	0.17*
4	0.86	0.18*
5	0.94	0.08
10	1.28	0.34
15	1.54	0.26

* Average maximum rate for second run: 173

Average maximum rate for both runs: 173 mm³/cm² min.

Table XVI

Dissolution of Be in 0.05 N HF at 40.0°C

Run No. 1 (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.21	0.00
1	0.94	0.73
2	1.24	0.30*
3	1.49	0.25*
4	1.66	0.17*
5	1.92	0.26*
10	2.98	1.06
15	3.88	0.90
20	4.82	0.94
25	5.88	1.06
30	6.91	1.03

* Average maximum rate for first run: 245

Run No. 2 (specimen #1)

0.0	0.21	0.00
0.5	0.68	0.47
1.0	0.94	0.26
1.5	1.07	0.13*
2.0	1.36	0.29*
2.5	1.53	0.17*
3.0	1.70	0.17*
3.5	1.83	0.13*
4.0	2.09	0.26*
4.5	2.26	0.17*
5.0	2.43	0.17*
6.0	2.64	0.21
7.0	2.90	0.26
8.0	3.07	0.17
9.0	3.32	0.25
10.0	3.41	0.09

* Average maximum rate for second run: 373

Average maximum rate for both runs: 309 mm³/cm² min.

Table XVII

Dissolution of Be in 0.10 N HF at 40.0°C

Run No. 1 (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	Δ <u>Vol.</u> <u>(cm³)</u>
0.0	0.21	0.00
0.5	0.85	0.64
1.0	1.23	0.38
1.5	1.53	0.30*
2.0	1.79	0.26*
2.5	2.09	0.30*
3.0	2.38	0.29*
3.5	2.60	0.22
4.0	2.81	0.21
4.5	3.07	0.26
5.0	3.28	0.21

* Average maximum rate for first run: 575

Run No. 2 (specimen #1)

0.00	0.21	0.00
0.25	0.51	0.30
0.50	0.76	0.25
0.75	0.93	0.17
1.00	1.06	0.13
1.25	1.19	0.13*
1.50	1.31	0.12*
1.75	1.48	0.17*
2.00	1.69	0.21*
2.25	1.86	0.17*
2.50	1.95	0.09*
2.75	2.12	0.17*
3.00	2.20	0.08*
3.50	2.46	0.26*
4.00	2.71	0.25*
4.50	3.05	0.34*
5.00	3.26	0.21

* Average maximum rate for second run: 569

Average maximum rate for both runs: 572 mm³/cm² min.

Table XVIII

Dissolution of Be in 0.50 N HF at 40.0°C

Run No. 1 (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	Δ <u>Vol.</u> <u>(cm³)</u>
0.00	0.21	0.00
0.25	1.18	0.97
0.50	1.60	0.42
0.75	2.40	0.80*
1.00	3.08	0.68*
1.25	3.79	0.71*
1.50	4.30	0.51*
1.75	4.89	0.59*
2.00	5.39	0.50*
2.25	5.98	0.59*
2.50	6.49	0.51*
2.75	7.08	0.59*
3.00	7.75	0.67*
3.50	8.85	1.10*
4.00	9.99	1.14*
4.50	11.04	1.05
5.00	12.14	1.10

* Average maximum rate for first run: 2397

Run NO. 2 (specimen #1)

0.00	0.21	0.00
0.25	0.85	0.64
0.50	1.44	0.59
0.75	2.11	0.67*
1.00	2.71	0.60*
1.25	3.30	0.59*
1.50	3.89	0.59*
1.75	4.57	0.68*
2.00	5.24	0.67*
2.25	5.83	0.59*
2.50	6.34	0.51*
2.75	6.93	0.59*
3.00	7.52	0.59*
3.50	8.66	1.14*
4.00	9.81	1.15*
4.50	10.91	1.10
5.00	12.05	1.14

* Average maximum rate for second run: 2391

Average maximum rate for both runs: 2394 mm³/cm² min.

Table XIX

Dissolution of Be in 0.75 N HF at 40.0°C

Run No. 1 (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0.00	0.21	0.00
0.25	1.18	0.97
0.50	2.06	0.88*
0.75	3.08	1.02*
1.00	3.88	0.80*
1.25	4.76	0.88*
1.50	5.60	0.84*
1.75	6.57	0.97*
2.00	7.41	0.84*
2.25	8.26	0.85*
2.50	9.18	0.92*
2.75	10.07	0.89*
3.00	10.91	0.84*
3.50	12.55	1.64*
4.00	14.32	1.77*
4.50	16.01	1.69
5.00	17.69	1.68

* Average maximum rate for first run: 3504

Run No. 2 (specimen #1)

0.00	0.21	0.00
0.25	1.19	0.98
0.50	1.95	0.76*
0.75	2.88	0.93*
1.00	3.73	0.85*
1.25	4.49	0.76*
1.50	5.43	0.94*
1.75	6.28	0.85*
2.00	7.12	0.84*
2.25	7.97	0.85*
2.50	8.73	0.76*
2.75	9.67	0.94*
3.00	10.52	0.85*
3.50	12.21	1.69*
4.00	13.91	1.70*
4.50	15.44	1.53
5.00	17.13	1.60

* Average maximum rate for second run: 3392

Average maximum rate for both runs: 3448 mm³/cm² min.

Table XX

Dissolution of Be in 0.01 N HF at 50.0°C

Run No. 1 (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0.00	0.51	0.00
0.25	1.20	0.69
0.50	1.88	0.68
0.75	2.26	0.38
1.00	2.48	0.22
2.00	2.86	0.38*
3.00	3.07	0.21*
4.00	2.16	0.09
5.00	3.24	0.08
10.00	3.54	0.30
15.00	3.76	0.22
20.00	3.97	0.21

* Average maximum rate for first run: 300

Run No. 2 (specimen #1)

0.00	0.51	0.00
0.25	1.11	0.60
0.50	1.71	0.60
0.75	1.97	0.26
1.00	2.18	0.21
2.00	2.69	0.51*
3.00	3.16	0.47*
4.00	3.42	0.26*
5.00	3.55	0.13
10.00	4.27	0.72
15.00	4.70	0.43

* Average maximum rate for second run: 413

Average maximum rate for both runs: 357 mm³/cm² min.

Table XXI

Dissolution of Be in 0.05 N HF at 50.0°C

Run No. 1 (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0.00	0.51	0.00
0.25	1.11	0.60
0.50	1.80	0.69
0.75	2.14	0.34
1.00	2.40	0.26
1.50	2.70	0.30*
2.00	2.96	0.26*
2.50	3.22	0.26*
3.00	3.39	0.17*
3.50	3.60	0.21*
4.00	3.77	0.17
4.50	3.94	0.17
5.00	4.16	0.22

* Average maximum rate for first run: 480

Run No. 2 (specimen #1)

0.00	0.51	0.00
0.25	1.97	1.46
0.50	2.66	0.69
0.75	2.96	0.30
1.00	3.17	0.21
1.50	3.52	0.35*
2.00	3.73	0.21*
2.50	3.86	0.13*
3.00	4.12	0.26*
3.50	4.25	0.13
4.00	4.38	0.13
4.50	4.50	0.12
5.00	4.68	0.18

* Average maximum rate for second run: 475

Average maximum rate for both runs: 478 mm³/cm² min.

Table XXII

Dissolution of Be in 0.10 N HF at 50.0°C

Run No. 1 (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0.00	0.50	0.00
0.25	1.51	1.01
0.50	2.09	0.58
0.75	2.43	0.34
1.00	2.68	0.25*
1.25	2.93	0.25*
1.50	3.22	0.29*
1.75	3.51	0.29*
2.00	3.68	0.17*
2.25	3.85	0.17*
2.50	4.02	0.17*
2.75	4.27	0.25*
3.00	4.39	0.12
3.50	4.73	0.34
4.00	5.02	0.29
4.50	5.31	0.29
5.00	5.57	0.26

* Average maximum rate for first run: 920

Run No. 2 (specimen #1)

0.00	0.50	0.00
0.25	1.34	0.84
0.50	1.93	0.59
0.75	2.22	0.29
1.00	2.56	0.34*
1.25	2.85	0.29*
1.50	3.06	0.21*
1.75	3.31	0.25*
2.00	3.52	0.21*
2.25	3.69	0.17*
2.50	3.85	0.16*
2.75	4.06	0.21*
3.00	4.23	0.17
3.50	4.48	0.25
4.00	4.82	0.34
4.50	5.07	0.25
5.00	5.36	0.29

* Average maximum rate for second run: 920

Average maximum rate for both runs: 920 mm³/cm² min.

Table XXIII

Dissolution of Be in 0.50 N HF at 50.0°C

Run No. 1 (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0.00	0.51	0.00
0.25	1.62	1.11
0.50	2.89	1.27
0.75	3.91	1.02*
1.00	4.80	0.89*
1.25	5.65	0.85*
1.50	6.55	0.90*
1.75	7.40	0.85*
2.00	8.16	0.76
2.25	8.93	0.77
2.50	9.56	0.63
2.75	10.37	0.81
3.00	11.14	0.77
3.50	12.58	1.44
4.00	14.11	1.53
4.50	15.47	1.36
5.00	17.00	1.53

* Average maximum rate for first run: 3608

Run No. 2 (specimen #1)

0.00	0.51	0.00
0.25	1.70	1.19
0.50	2.81	1.11
0.75	3.75	0.94*
1.00	4.60	0.85*
1.25	5.49	0.89*
1.50	6.39	0.90*
1.75	7.24	0.85*
2.00	8.18	0.94*
2.25	9.11	0.93*
2.50	9.96	0.85*
2.75	10.90	0.94*
3.00	11.75	0.85*
3.50	13.37	1.62
4.00	15.08	1.71
4.50	16.74	1.66
5.00	18.40	1.66

* Average maximum rate for second run: 3576

Average maximum rate for both runs: 3592 mm³/cm² min.

Table XXIV

Dissolution of Be in 0.75 N HF at 50.0°C

Run No. 1 (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0.00	0.51	0.00
0.25	2.21	1.70
0.50	3.74	1.53
0.75	5.27	1.53
1.00	6.55	1.28*
1.25	7.83	1.28*
1.50	9.06	1.23*
1.75	10.38	1.32*
2.00	11.49	1.11
2.25	12.68	1.19
2.50	13.83	1.15
2.75	15.02	1.19
3.00	16.34	1.32
3.50	18.55	2.21
4.00	20.93	2.38
4.50	23.14	2.21
5.00	25.27	2.13

Run No. 2 (specimen #1)

0.00	0.51	0.00
0.25	2.27	1.76
0.50	3.85	1.58
0.75	5.44	1.59
1.00	6.85	1.41*
1.25	8.09	1.24*
1.50	9.42	1.33*
1.75	10.71	1.29*
2.00	11.95	1.24*
2.25	13.15	1.20
2.50	14.39	1.24
2.75	15.63	1.24
3.00	16.87	1.24
3.50	19.10	2.23
4.00	21.58	2.48
4.50	23.81	2.23
5.00	26.12	2.31

* Average maximum rate for second run: 5208

Average maximum rate for both runs: 5159 mm³/cm² min.

Table XXV

Effect of Stirring Speed on Dissolution Rate
(0.10 N HF-30°C)

75 RPM (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.00	0.00
5	1.02	1.02
10	2.13	1.11
15	3.33	1.20*
20	4.52	1.19*
25	5.72	1.20*
30	6.91	1.19*
35	8.11	1.20*
40	9.31	1.20*

* Average maximum rate: 239 mm³/cm² min.

150 RPM (specimen #1)

0	0.00	0.00
5	1.54	1.54
10	3.13	1.59*
15	4.72	1.59*
20	6.26	1.54*
25	7.85	1.59*
30	9.43	1.58*
35	10.97	1.54
40	12.48	1.51

* Average maximum rate: 316 mm³/cm² min.

Table XXVI

Effect of Stirring Speed on Dissolution Rate
(0.10 N HF-30°C)

200 RPM (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.00	0.00
1	0.34	0.34*
2	0.68	0.34*
3	1.06	0.38*
4	1.44	0.38*
5	1.87	0.43*
10	3.73	1.86*
15	5.43	1.70
20	7.30	1.87*
25	9.16	1.86*
30	10.82	1.66
35	12.56	1.74
40	14.17	1.61

* Average maximum rate: 373 mm³/cm² min.

250 RPM (specimen #1)

0	0.00	0.00
5	2.09	2.09*
10	4.18	2.09*
15	6.26	2.08*
20	8.31	2.05*
25	10.40	2.09*
30	12.31	1.91
35	14.19	1.88

* Average maximum rate: 416 mm³/cm² min.

Table XXVII

Effect of Stirring Speed on Dissolution Rate
(0.10 N HF-30°C)

300 RPM (specimen #1)

<u>Time</u> (minutes)	<u>Volume at STP</u> (ml.)	<u>Δ Vol.</u> (cm ³)
0	0.00	0.00
1	0.43	0.43
2	0.95	0.52
3	1.55	0.60
4	2.11	0.65
5	2.58	0.47
10	4.82	2.24*
15	7.05	2.23*
20	9.29	2.24*
25	11.53	2.24*
30	13.59	2.06
35	15.48	1.89

* Average maximum rate: $448 \text{ mm}^3/\text{cm}^2 \text{ min.}$

400 RPM (specimen #1)

0	0.00	0.00
1	0.34	0.34
2	0.69	0.35
3	1.38	0.69
4	1.89	0.51
5	2.32	0.43
10	4.86	2.54*
15	7.40	2.54*
20	9.55	2.15
25	11.96	2.41
30	14.28	2.32
35	16.52	2.24
40	18.50	1.98

* Average maximum rate: $508 \text{ mm}^3/\text{cm}^2 \text{ min.}$

Table XXVIII

Effect of Stirring Speed on Dissolution Rate
(0.10 N HF-30°C)

525 RPM (specimen #1)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.00	0.00
1	0.51	0.51*
2	1.20	0.69*
3	1.80	0.60*
4	2.44	0.64*
5	3.00	0.56*
10	6.00	3.00*
15	8.92	2.92*
20	11.53	2.61
25	14.15	2.62
30	16.63	2.48
35	19.12	2.49

* Average maximum rate: 595 mm³/cm² min.

Table XXIX

The Effect on Dissolution Rate of Adding 2 drops of
concentrated HAuCl_4 to 0.10 N HF at 30.0°C

(specimen #2)

<u>Time</u> <u>(min.)</u>	<u>Volume at STP</u> <u>(ml.)</u>	Δ <u>Vol.</u> <u>(cm^3)</u>	<u>Rate</u> <u>($\text{mm}^3/\text{cm}^2 \text{ min.}$)</u>
0	0.00	0.00	
5	1.63	1.63	
10	3.60	1.97*	
15	5.65	2.05*	
20	7.70	2.05*	Avg. 382
0	0.00	0.00	
5	1.93	1.93	364
10	3.81	1.88	355
15	5.91	2.10	396
20	8.39	2.48	468
25	10.96	2.57	485
30	13.95	2.99	564
35	16.78	2.83	534
40	19.69	2.91	549
45	22.43	2.74	517

Table XXX

The Effect on Dissolution Rate of Adding 2 drops of
concentrated PtCl_4 to 0.10 N HF at 30.0°C

(specimen #2)

<u>Time</u> <u>(min.)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm^3)</u>	<u>Rate</u> <u>($\text{mm}^3/\text{cm}^2 \text{ min.}$)</u>
0	0.00	0.00	
5	1.55	1.55	
10	3.35	1.80	
15	5.24	1.89*	Avg. 360
20	7.17	1.93*	
0	0.26	0.00	
5	0.69	0.43	
10	2.23	1.54	
15	4.72	2.49	470
20	7.29	2.67	504
25	9.79	2.40	453
30	12.20	2.41	455
35	14.43	2.23	421
40	16.66	2.23	421
45	18.90	2.24	423

Table XXXI

The Effect on Dissolution Rate of Adding 2 ml. of
0.1 Molar $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ to 0.10 N HF at 30.0°C

<u>Time</u> <u>(min.)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm^3)</u>	<u>Rate</u> <u>($\text{mm}^3/\text{cm}^2 \text{ min.}$)</u>
0	0.00	0.00	
5	1.85	1.85	
10	3.86	2.01*	
15	5.79	1.93*	Avg. 375
20	7.81	2.02	
0	0.00	0.00	
5	2.15	2.15	406
10	3.99	1.84	347
15	5.75	1.76	332
20	7.47	1.72	325
25	9.10	1.63	308
30	10.73	1.63	308

Table XXXII

The Effect on Dissolution Rate of Adding 2 ml. of
 0.1 Molar $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to 0.10 N HF at 30.0°C

(specimen #2)

<u>Time</u> <u>(min.)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm^3)</u>	<u>Rate</u> <u>($\text{mm}^3/\text{cm}^2 \text{ min.}$)</u>
0	0.00	0.00	
5	1.71	1.71	
10	3.51	1.80	
15	5.40	1.89*	Avg. 356
20	7.28	1.88*	
0	0.00	0.00	
5	1.71	1.71	323
10	3.43	1.72	325
15	4.97	1.54	291
20	6.21	1.24	234
25	7.54	1.33	251
30	8.78	1.24	234

Table XXXIII

The Effect on Dissolution Rate of Adding 2 ml. of
0.1 Molar $\text{Pb}(\text{NO}_3)_2$ to 0.10 N HF at 30.0°C

(specimen #2)

<u>Time</u> <u>(min.)</u>	<u>Volume at STP</u> <u>(ml.)</u>	Δ <u>Vol.</u> <u>(cm^3)</u>	<u>Rate</u> <u>($\text{mm}^3/\text{cm}^2 \text{ min.}$)</u>
0	0.00	0.00	
5	1.54	1.54	
10	3.47	1.93*	
15	5.40	1.93*	Avg. 364
20	7.19	1.79	
0	0.00	0.00	
5	1.93	1.93	364
10	3.43	1.50	283
15	4.54	1.11	209
20	5.65	1.11	209
25	6.68	1.03	194
30	7.62	0.94	177

Table XXXIV

The Effect on Dissolution Rate of Adding 2 ml. of
0.1 Molar AgNO_3 to 0.10 N HF at 30.0°C

(specimen #2)

<u>Time</u> <u>(min.)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm^3)</u>	<u>Rate</u> <u>($\text{mm}^3/\text{cm}^2 \text{ min.}$)</u>
0	0.00	0.00	
5	1.71	1.71	
10	3.67	1.96*	370 Avg.
15	5.63	1.96*	
20	7.51	1.88	
0	0.00	0.00	
5	1.54	1.54	291
10	2.65	1.11	209
15	3.50	0.85	160
20	4.27	0.77	145
25	4.95	0.68	128
30	5.59	0.64	121

Table XXXV

Dissolution of Be in 0.20 N HCl at 10.0°C

(specimen #2)

<u>Time</u> <u>(minutes)</u>	<u>Volume</u> <u>(ml.)</u>
0	0.00
5	0.00
10	0.00
15	0.00
20	0.00
25	0.00
30	0.00

Dissolution of Be in 0.50 N HCl at 10.0°C

(specimen #2)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.00	0.00
5	0.00	0.00
10	2.44	2.44
15	7.41	4.97
20	14.02	6.61
25	21.39	7.37*
30	28.89	7.50*
35	36.22	7.33*
40	43.38	7.16

* Average maximum rate: 1396 mm³/cm² min.

Table XXXVI

Dissolution of Be in 0.20 N HCl at 20.0°C

(specimen #2)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.00	0.00
5	0.08	0.08
10	0.08	0.00
15	0.68	0.60
20	1.95	1.27
25	4.07	2.12
30	7.04	2.97
35	10.09	3.05
40	13.48	3.39
45	17.38	3.90*
50	20.86	3.48*
55	24.42	3.56*
60	27.94	3.52*
65	31.46	3.52*
70	34.76	3.30
75	38.07	3.31

* Average maximum rate: 678 mm³/cm² min.Dissolution of Be in 0.50 N HCl at 20.0°C

(specimen #2)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.00	0.00
5	2.93	2.93
10	10.69	7.76
11	12.39	1.70
12	14.29	1.90*
13	16.20	1.91*
14	17.98	1.78*
15	19.85	1.87*
16	21.63	1.78*
17	23.41	1.78*
18	25.24	1.83*
19	27.02	1.78*
20	28.80	1.78*

* Average maximum rate: 1720 mm³/cm² min.

Table XXXVII

Dissolution of Be in 0.05 N HCl at 30.0°C

(specimen #2)

<u>Time</u> <u>(Minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.00	0.00
5	0.17	0.17
10	0.17	0.00
15	0.17	0.00
20	0.17	0.00
25	0.17	0.00
30	0.33	0.16*
35	0.50	0.17*
40	0.50	0.00
45	0.59	0.09

* Average maximum rate: 31 mm³/cm² min.

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.00	0.00
5	0.29	0.29
10	0.50	0.21
15	0.58	0.08
20	0.92	0.34
25	1.67	0.75
30	2.50	0.83
35	3.71	1.21
40	5.41	1.70*
45	7.00	1.59*
50	8.66	1.66*
55	10.20	1.54

* Average maximum rate: 311 mm³/cm² min.

Table XXXVIII

Dissolution of Be in 0.20 N HCl at 30.0°C

(specimen #2)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	Δ <u>Vol.</u> <u>(cm³)</u>
0	0.00	0.00
1	0.17	0.17
2	0.17	0.00
3	0.17	0.00
4	0.21	0.04
5	0.38	0.17
6	0.67	0.29
7	0.88	0.21
8	1.22	0.34
9	1.59	0.37
10	2.05	0.46
11	2.51	0.46
12	3.02	0.51
13	3.69	0.67
14	4.27	0.58
15	5.03	0.76
16	5.78	0.75
17	6.54	0.76
18	7.29	0.75
19	8.04	0.75
20	8.80	0.76
21	9.64	0.84
22	10.39	0.75
23	11.23	0.84*
24	12.15	0.92*
25	13.03	0.88*
26	13.97	0.94*
27	14.90	0.93*
28	15.80	0.90*
29	16.69	0.89*
30	17.54	0.85*
31	18.35	0.81
32	19.20	0.85
33	20.01	0.81

* Average maximum rate: $843 \text{ mm}^3/\text{cm}^2 \text{ min.}$

Table XXXIX

Dissolution of Be in 0.50 N HCl at 30.0°C

(specimen #2)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.00	0.00
1	0.25	0.25
2	1.09	0.84
3	2.59	1.50
4	4.51	1.92
5	6.69	2.18
6	9.19	2.50
7	11.62	2.43
8	13.79	2.17*
9	16.05	2.26*
10	18.22	2.17*
11	20.39	2.17*
12	22.57	2.18*
13	24.66	2.09*
14	26.83	2.17*
15	29.00	2.17*
16	31.18	2.18*

* Average maximum rate: 2050 mm³/cm² min.

Table XXXX

Dissolution of Be in 0.10 N HCl at 40.0°C

(specimen #2)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.21	0.00
5	1.40	1.19
10	2.68	1.28
15	3.95	1.27
20	5.78	1.83
25	7.73	1.95*
30	9.72	1.99*
35	11.72	2.00*
40	13.76	2.04*
45	15.67	1.91

* Average maximum rate: 376 mm³/cm² min.

Table XXXXI

Dissolution of Be in 0.20 N HCl at 40.0°C

(specimen #2)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.21	0.00
1	0.34	0.13
2	0.59	0.25
3	0.98	0.39
4	1.27	0.29
5	1.66	0.39
6	2.21	0.55
7	2.89	0.68
8	3.65	0.76
9	4.37	0.72
10	5.26	0.89
11	6.11	0.85
12	7.00	0.89
13	7.94	0.94
14	8.91	0.97
15	10.02	1.11*
16	11.04	1.02*
17	11.97	0.93*
18	12.99	1.02*
19	14.01	1.02*
20	15.11	1.10*
21	16.13	1.02*
22	17.23	1.10*
23	18.21	0.98*
24	19.19	0.98*
25	20.29	1.10*
26	21.27	0.98*
27	22.41	1.14*
28	23.39	0.98*
29	24.45	1.06*
30	25.39	0.94

* Average maximum rate: 977 mm³/cm² min.

Table XXXXII

Dissolution of Be in 0.50 N HCl at 40.0°C

(specimen #2)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.21	0.00
1	0.68	0.47
2	3.40	2.72
3	6.30	2.90
4	9.19	2.89
5	12.34	3.15
6	15.15	2.81*
7	17.96	2.81*
8	20.85	2.89*
9	23.66	2.81*
10	26.55	2.89*
11	29.45	2.90*
12	32.17	2.72
13	34.98	2.81
14	37.79	2.81
15	40.68	2.89*
16	43.58	2.90*
17	46.47	2.89*
18	49.28	2.81
19	52.09	2.81
20	54.90	2.81
21	57.70	2.80

* Average maximum rate: 2703 mm³/cm² min.

Table XXXXIII

Dissolution of Be in 0.20 N HCl at 50.0°C

(specimen #2)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.85	0.00
1	1.88	1.03
2	2.82	0.94
3	3.58	0.76
4	4.35	0.77
5	5.29	0.94
6	6.32	1.03
7	7.34	1.02
8	8.45	1.11
9	9.64	1.19*
10	10.84	1.20*
11	12.03	1.19*
12	13.23	1.20*
13	14.51	1.28*
14	15.62	1.11*
15	16.90	1.28*
16	18.13	1.23*
17	19.33	1.20*
18	20.40	1.07*
19	21.68	1.28*
20	22.91	1.23*
21	24.07	1.16
22	25.26	1.19
23	26.54	1.28
24	27.74	1.20
25	28.93	1.19

* Average maximum rate: $1137 \text{ mm}^3/\text{cm}^2 \text{ min.}$

Table XXXIV

Dissolution of Be in 0.50 N HCl at 50.0°C

(specimen #2)

<u>Time</u> <u>(minutes)</u>	<u>Volume at STP</u> <u>(ml.)</u>	<u>Δ Vol.</u> <u>(cm³)</u>
0	0.85	0.00
1	3.32	2.47
2	6.81	3.49
3	10.55	3.74
4	14.38	3.83*
5	18.21	3.83*
6	22.13	3.92*
7	25.87	3.74*
8	29.79	3.92*
9	34.02	4.25
10	37.95	3.91*
11	42.29	4.34
12	46.63	4.34

* Average maximum rate: 3640 mm³/cm² min.

VITA

The author was born on January 13, 1933 in St. Louis, Missouri. He received his Bachelor of Science Degree in Metallurgical Engineering from the Missouri School of Mines and Metallurgy in September, 1956. After serving in the Army and completing two and one half years employment as a Test Engineer with the McDonnell Aircraft Corporation in St. Louis, Missouri; he enrolled in the Graduate School of the Missouri School of Mines and Metallurgy in September, 1959. During the course of this research the author has held the position of Research Assistant as provided for under Contract AEC AT(11-1)-73, Project 5, "Corrosion of Nuclear Metals."