

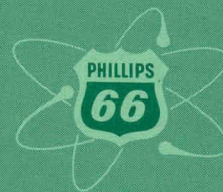
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THE DISSOLUTION OF IRON AND NICKEL
IN DILUTE AQUA REGIA

R. D. Cannon

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ATOMIC ENERGY DIVISION

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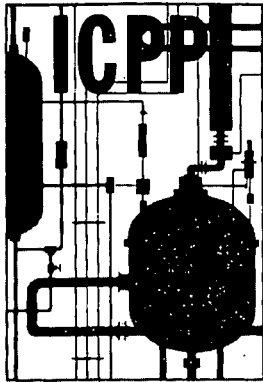
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Chemistry Section

PHILLIPS
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A B S T R A C T

In laboratory studies the dissolution of iron in dilute nitric-hydrochloric acid mixtures shows an apparent reaction order of -0.62 with respect to HCl. No apparent order value for HNO_3 can be determined over the concentration ranges studied. Nickel dissolutions show apparent orders of 1.4 with respect to the HCl and 4.2 for HNO_3 . Activation energies determined from 50 to 80°C are not constant, ranging from 10 to 20 kcal per mole for both metals.

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THE DISSOLUTION OF IRON AND NICKEL
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I. SUMMARY AND CONCLUSIONS

The search for a suitable dissolution process for stainless steel-containing nuclear fuel elements has led to an investigation of the dissolution kinetics of stainless steel components in dilute aqua regia. An attempt was made to determine empirical rate expressions for the dissolution of iron and nickel, since these expressions could be expected to be of value in the selection of a mechanism for dissolution reactions in dilute aqua regia.

The complexity of the reactions involved makes it impossible to write a general empirical rate expression including the effects of both nitric and hydrochloric acids. Simplified expressions were, however, determined describing the effect of the concentration of each acid on the dissolution rate while the other acid concentration was held constant.

Activation energies calculated for the dissolution of each metal showed pronounced temperature dependency, which is believed to be due to other reactions whose activation energies are greater than those for the dissolution reactions of interest. Several reactions known to occur in aqua regia could cause the observed phenomena.

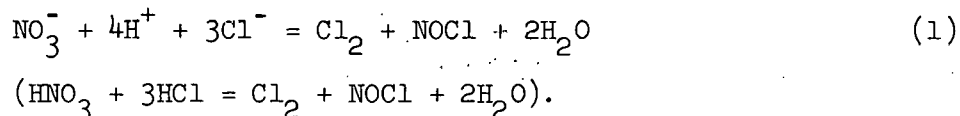
From this work it seems apparent that the elucidation of the mechanism for aqua regia dissolution depends on the identification of the species involved and the determination of their effects on the reaction mechanism.

II. INTRODUCTION

The development of processes for the chemical reprocessing of stainless steel-containing nuclear reactor fuels which are not soluble in nitric acid has led to consideration of dilute aqua regia as a dissolution reagent^(1,2). Since dissolution reaction mechanisms in aqua regia have not been investigated, this study was made in an effort to determine empirical rate expressions for the dissolution of iron and nickel. Complete definition of the mechanism is, of course, beyond the scope of such a study because of the complexity of the reactions involved. It is hoped that the results of this study will provide a basis for further investigation of this reaction system.

Aqua regia, three parts by volume of concentrated hydrochloric acid and one part concentrated nitric acid, will dissolve both gold and platinum, neither of which will dissolve in nitric acid alone.

The mixture of nitric and hydrochloric acids can lead to free chlorine and nitrosyl chloride by the reaction⁽³⁾:



The unusual dissolution characteristics of aqua regia are apparently due not to an increase in the oxidation potential of the nitric acid or to some effect of the nitrosyl chloride, but to an increase in the reduction potential of the metals in the chloride-containing environment. Latimer⁽⁴⁾ gives the oxidation potential for gold, silver, and platinum in chloride solution:

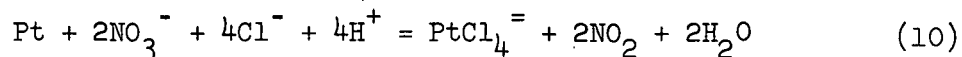
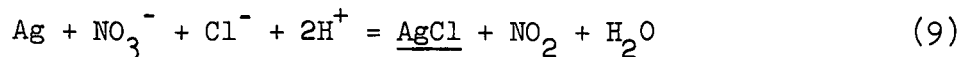
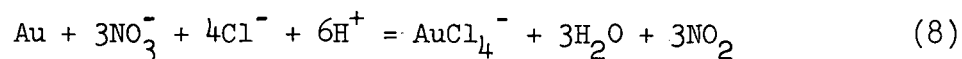


as opposed to:

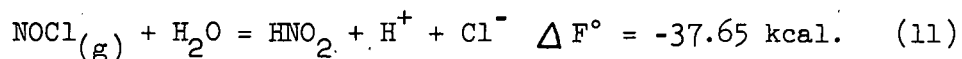


in the absence of chloride.

Using the above data, the following equations can be written⁽³⁾:



It has been suggested by Hedges⁽⁵⁾ and Banerji and Dhar⁽⁶⁾ that the presence of nitrous acid in nitric acid activates passive metals. Latimer⁽⁴⁾ gives an expression for the formation of nitrous acid from the hydrolysis of nitrosyl chloride as:



Therefore, a solution of nitrosyl chloride may be thought of as a source of nitrous acid.

Dissolution kinetics in dilute aqua regia is a relatively untouched field. The dissolution of iron has been studied by Abramson and King⁽⁷⁾, who examined the effect of nitric acid as a depolarizer on the dissolution rate in hydrochloric acid. Figure 1 shows the effect of chloride and bromide on the dissolution rate for iron cylinders rotating in 0.025 and 0.050M HNO_3 , i.e., a small increase in rate followed by a large decrease as the halide concentration increases.

The dissolution of several metals in nitric acid has been studied by T. G. Owe Berg⁽⁸⁾⁽⁹⁾, who has found the dissolution rate of iron to be a linear function of acid concentration in agitated solutions. He presents⁽⁹⁾ a series of mechanisms covering the several regions of acid concentration up to 8.8M HNO_3 which are in satisfactory agreement with the experimental work he has described⁽¹⁰⁾.

The dissolution of nickel in nitric acid has also been studied⁽¹¹⁾⁽¹²⁾, and the rate found to be proportional to the square root of the acid concentration over the concentration region in which the acid is completely dissociated, $c < 3.35\text{N}$.

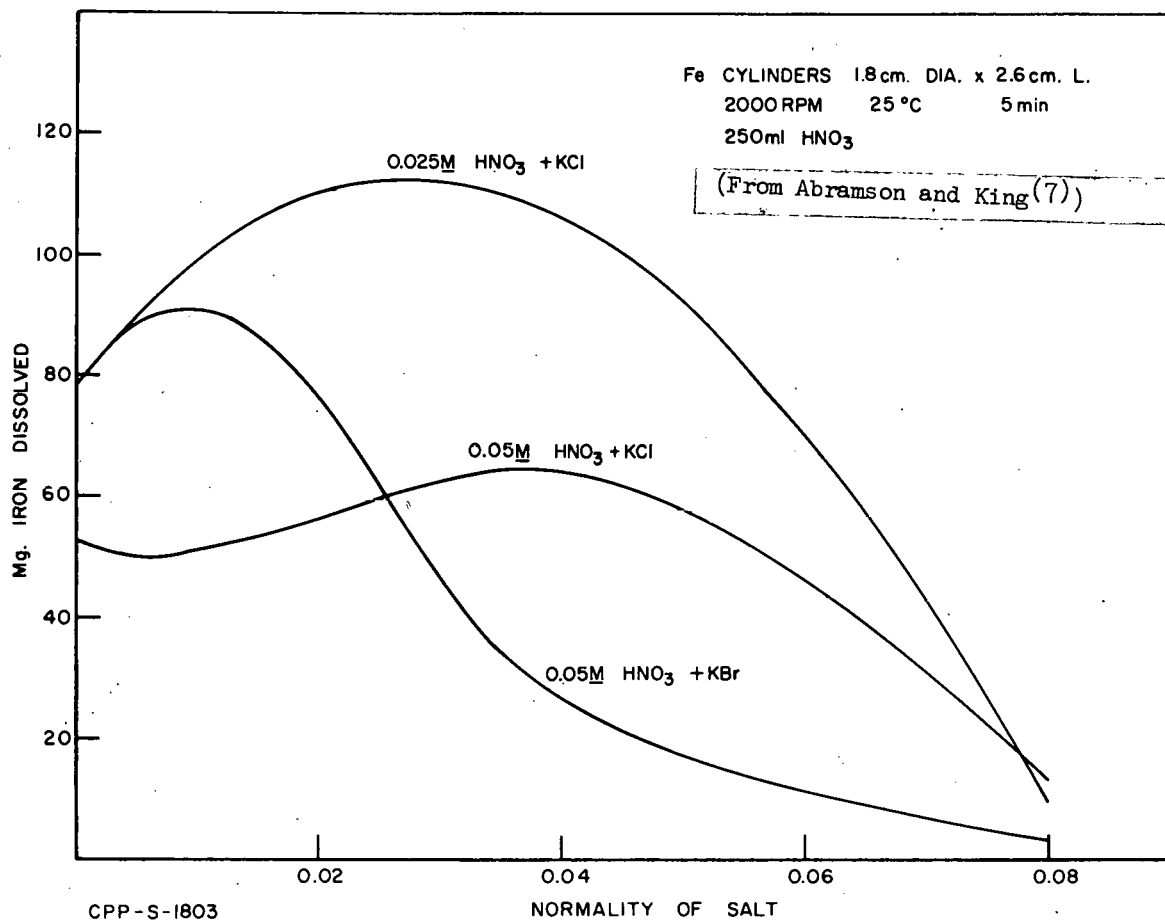


Figure 1
 Effect of Halide Salts on the
 Dissolution Rate of Iron

III. EXPERIMENTAL WORK

A. Reaction Equipment

Figure 2 is a photograph of the laboratory equipment which included:

1. A two-liter resin reaction flask with four standard taper openings in the lid. The flask was equipped with an Allihn condenser through which a three-bladed polyethylene stirrer was run.

2. The reaction vessel temperature control system. A thermostat in the reaction vessel controlled the intermittent flow of cooling water through the internal cooling coil shown in the figure. Heat was supplied continuously by the hot plate beneath the reaction vessel. Temperature response of the system was $\pm 0.2^{\circ}\text{C}$ at 80°C .

B. Reagents

All solutions were prepared from reagent grade chemicals and distilled water. Coupons were one by one-half by one-quarter inch pieces cut from sheets of metal purchased from A. D. Mackay, Inc., New York. Analyses of the metals are given in the Analytical section.

C. Experimental Procedures

Coupons were measured, washed with water and acetone, accurately weighed, and placed in the reaction vessel for timed intervals after which they were removed, washed, and weighed. Sample aliquots were taken prior to addition of another coupon. Samples were immediately refrigerated to prevent the breakdown of the mixed acid solvent due to high temperature reactions.

Any one of five steps can be rate determining for reaction on a surface⁽¹³⁾:

1. Diffusion of reagent to the surface
2. Adsorption of reagent molecules on the surface
3. Reaction of adsorbed molecules
4. Desorption of product molecules from surface
5. Diffusion of products away from surface

Since steps one and five involve ordinary diffusion of materials through the solution, these processes are characteristic not of the reactions

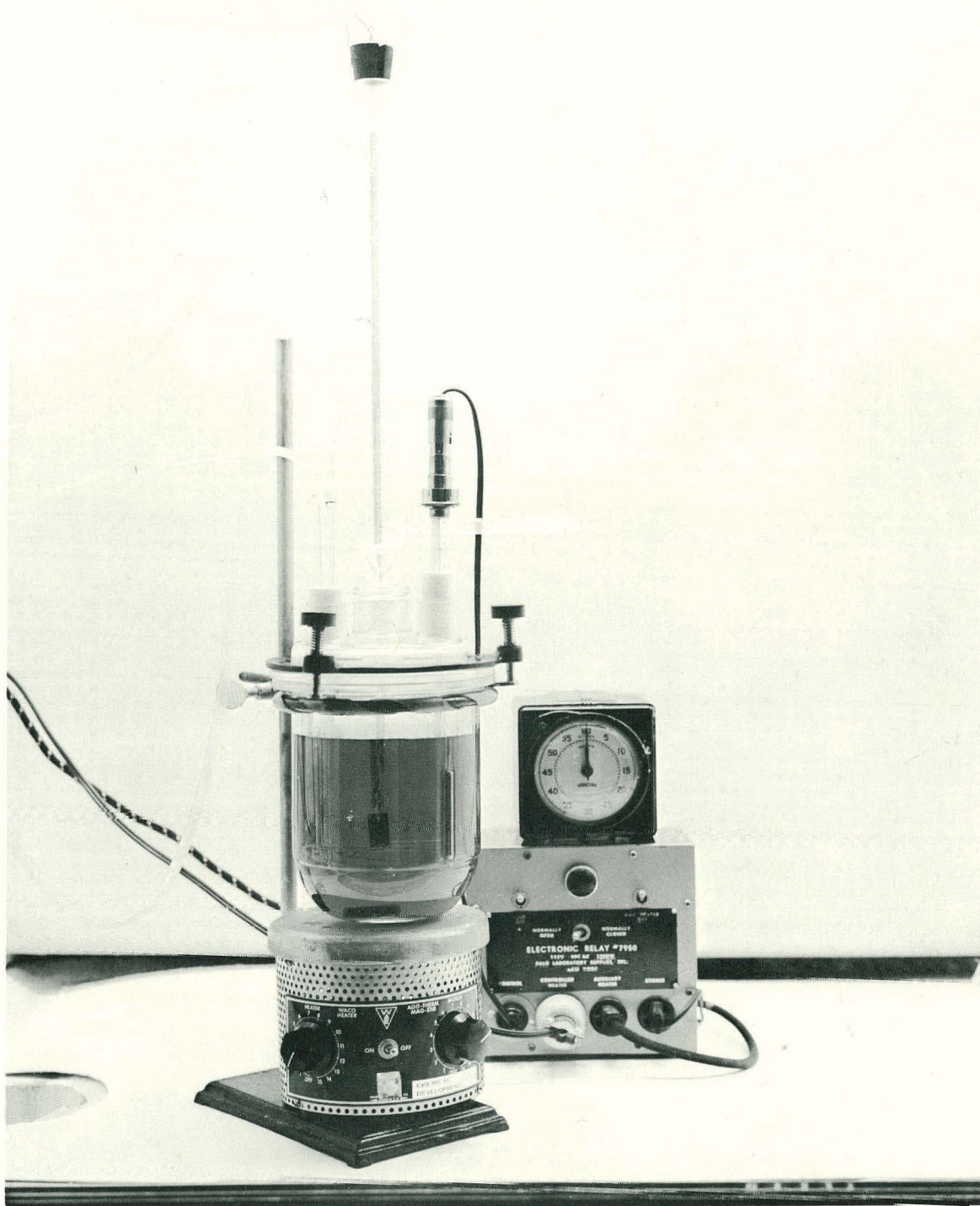


Figure 2
Dissolver and Temperature Control System
Used in Experiments

involved but of the solution properties, stirring rate, surface geometry, etc. In order to measure the limiting chemical reaction rate rather than gross transport through the solution, vigorous stirring was employed in the experimental work. Preliminary runs were made at constant temperature and reagent concentrations, and the stirring rate was varied from approximately 200 to 620 revolutions per minute of the three-bladed stirrer. Figure 3 shows the dissolution rate (arbitrary units) plotted as a function of stirring speed for both metals. The subsequent experimental work was done at 620 RPM except for check runs periodically made to make certain that changes in reagent concentrations had not raised the stirring requirements of the system.

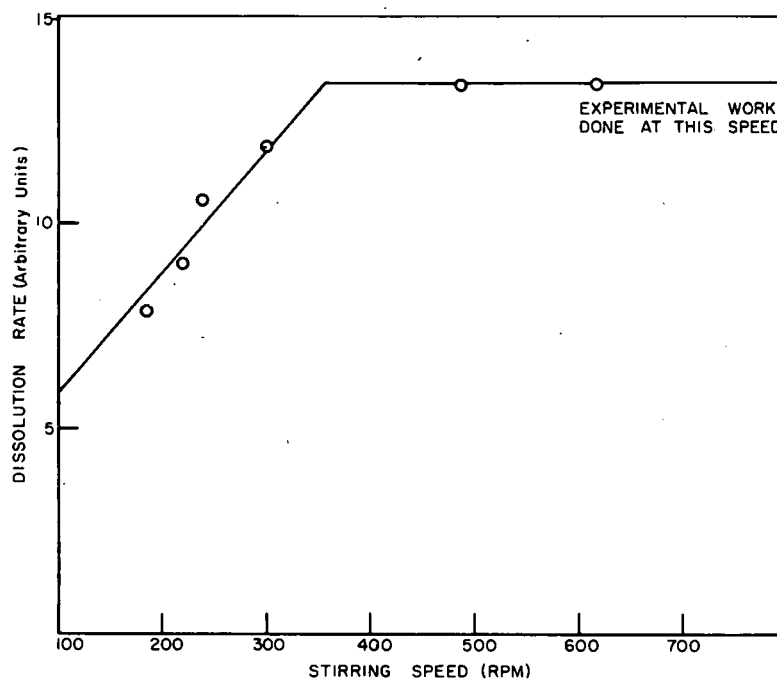


Figure 3

Effect of Stirring Speed on Dissolution Rate

The effect of coupon pre-treatment on the dissolution rate was determined by several experiments in which etched, polished, and as-received coupons were dissolved. Etched and polished coupons showed essentially identical rates, while the rates for as-received coupons were as much as 20 per cent lower for the first half-minute of contact. When the rectangular faces of the dissolving coupons began to lose their

shape, making accurate surface area measurements impossible, the coupons were ground to shape on a silicon carbide 120-C belt sander and smoothed with 180-C silicon carbide paper.

D. Analytical Work

Spectrochemical estimates of the impurities present in the dissolution coupons are given in Table 1. Values for carbon and sulfur are not available using this technique.

Sample aliquots taken as indicated under Experimental Procedures were analyzed by the Idaho Chemical Processing Plant Shift Control Laboratory, using standard methods⁽¹⁴⁾ for iron (or nickel), hydrogen ion and chloride ion. Nitrate concentrations were determined by difference.

Iron was determined (Fe-3)⁽¹⁴⁾ by measuring the optical adsorbance of the 1,10-phenanthroline-iron complex in buffered solution and calculating the iron concentration by use of the known molar extinction coefficient of the complex.

Table 1

Spectrochemical Estimation of Impurities
in Metal Coupons

<u>In Ni</u>		<u>In Fe</u>	
Cr	.001%	Cr	.020%
Cu	.010	Cu	.010
Fe	.010	Mg	.001
Mg	.030	Mn	.010
Mn	.100	Mo	.001
Mo	.003	Ni	.020
Si	.003	Si	.003
Co	.010	Co	.001
	<u>.167</u>		<u>.066</u>

Nickel was determined by one of two methods, depending on the concentration of the metal in solution. The volumetric procedure (Ni-2)⁽¹⁴⁾

involved precipitation of nickel with dimethylglyoxime, nitric-perchloric acid digestion to destroy the organic matter, followed by addition of excess ethylenediaminetetraacetic acid and titration with standard zinc solution to the "Zincon" end point. Colorimetric determinations were run on solutions below the limits of the volumetric procedure. The color of the nickel dimethylglyoxime complex in an alkaline medium was measured and the concentration determined using the molar extinction coefficient for the complex.

Chloride determinations (Cl-3)⁽¹⁴⁾ were made by adding excess silver ion which was titrated with ammonium thiocyanate.

Hydrogen ion (H-Pot-4-Mod-5)⁽¹⁴⁾ was determined by titration after complexing the hydrolyzable ions present with oxalate ion. The pH of the complexing solution is set at a predetermined level and the sample aliquot is added after which the solution pH is returned to its original value by titration with standard base (or acid).

IV. PRESENTATION OF DATA

The experiments were designed to investigate the effects of nitric acid, hydrochloric acid, dissolved metal, and temperature on the dissolution rate of each of the pure metals.

A. Iron Dissolution Data

The experimental data can be divided into two groups by plotting the logarithm of the dissolved iron concentration as a function of log time. The first group as shown in Figure 4 is characterized by a relatively constant slope which is approximately 1. The second group as shown in Figure 5 is characterized by non-linear, non-reproducible dissolutions.

The data presented in Figure 4 were taken in dissolution runs in which the HNO_3 concentration was held constant at 2M , the temperature was 50°C , and the stirring speed was held constant while the HCl concentration was varied from 0 to 3M . When the HCl concentration was held constant at 2M and the HNO_3 concentration varied (other conditions held constant), the data in Figure 5 were obtained. Interpretation of these data is reserved for the next section.

B. Nickel Dissolution Data

The dissolution of nickel in the mixed acid system was plotted as in the iron case. Figure 6 is a plot of log nickel in solution as a function of the log time in 7M HNO_3 with HCl varied from 0 to 2.5M with constant stirring at 80°C . Figure 7 shows log nickel concentration in solution as a function of log time, as above, in 1.5M HCl as HNO_3 varies from 5 to 7M .

These data show log dissolved nickel as a linear function of log time except in the case of 2.5M HCl - 7M HNO_3 where the function begins to deviate markedly above 5 grams per liter dissolved metal.

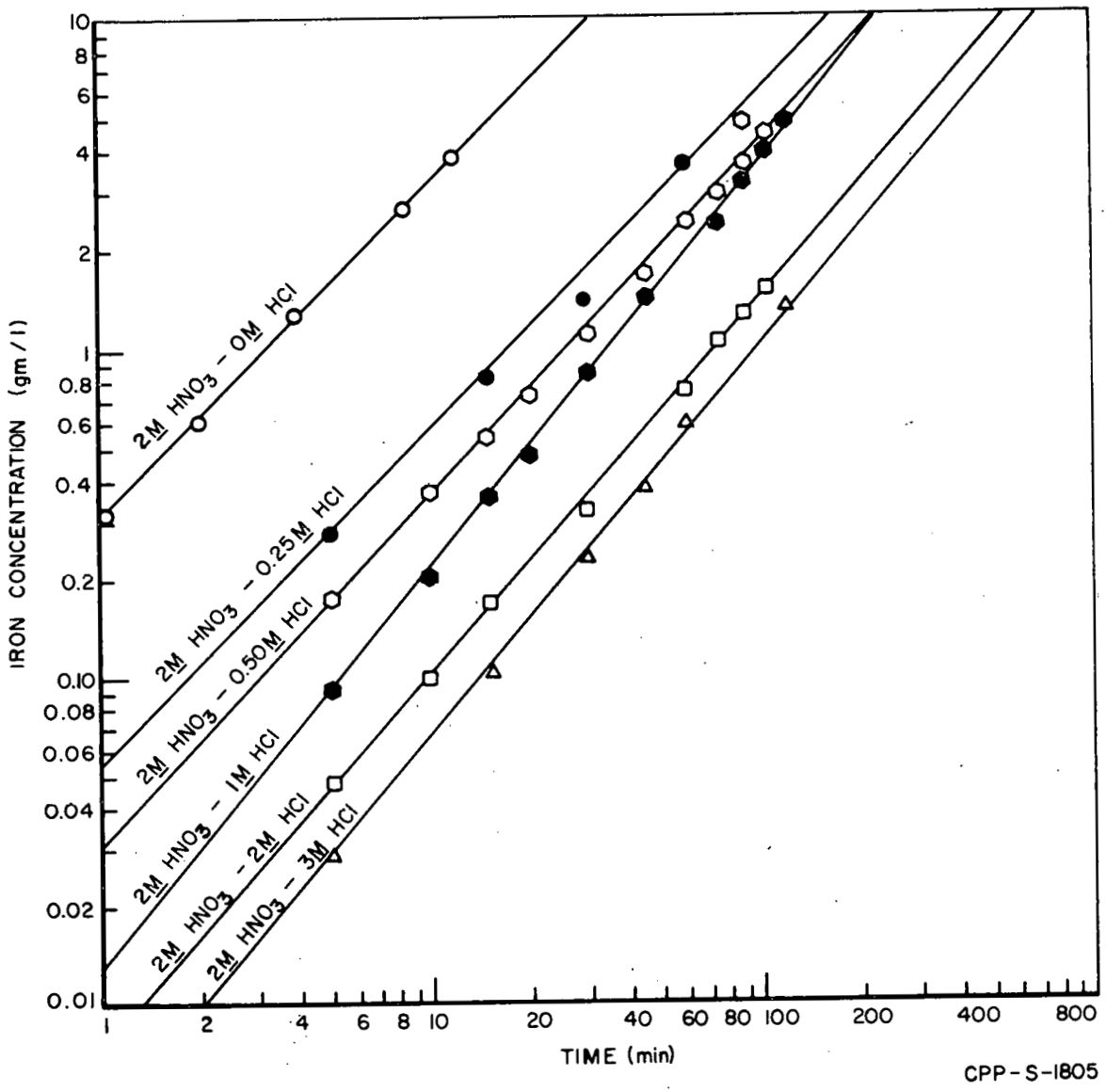


Figure 4
 Dissolution of Iron in 2M HNO₃-0 to 3M HCl at 50°C

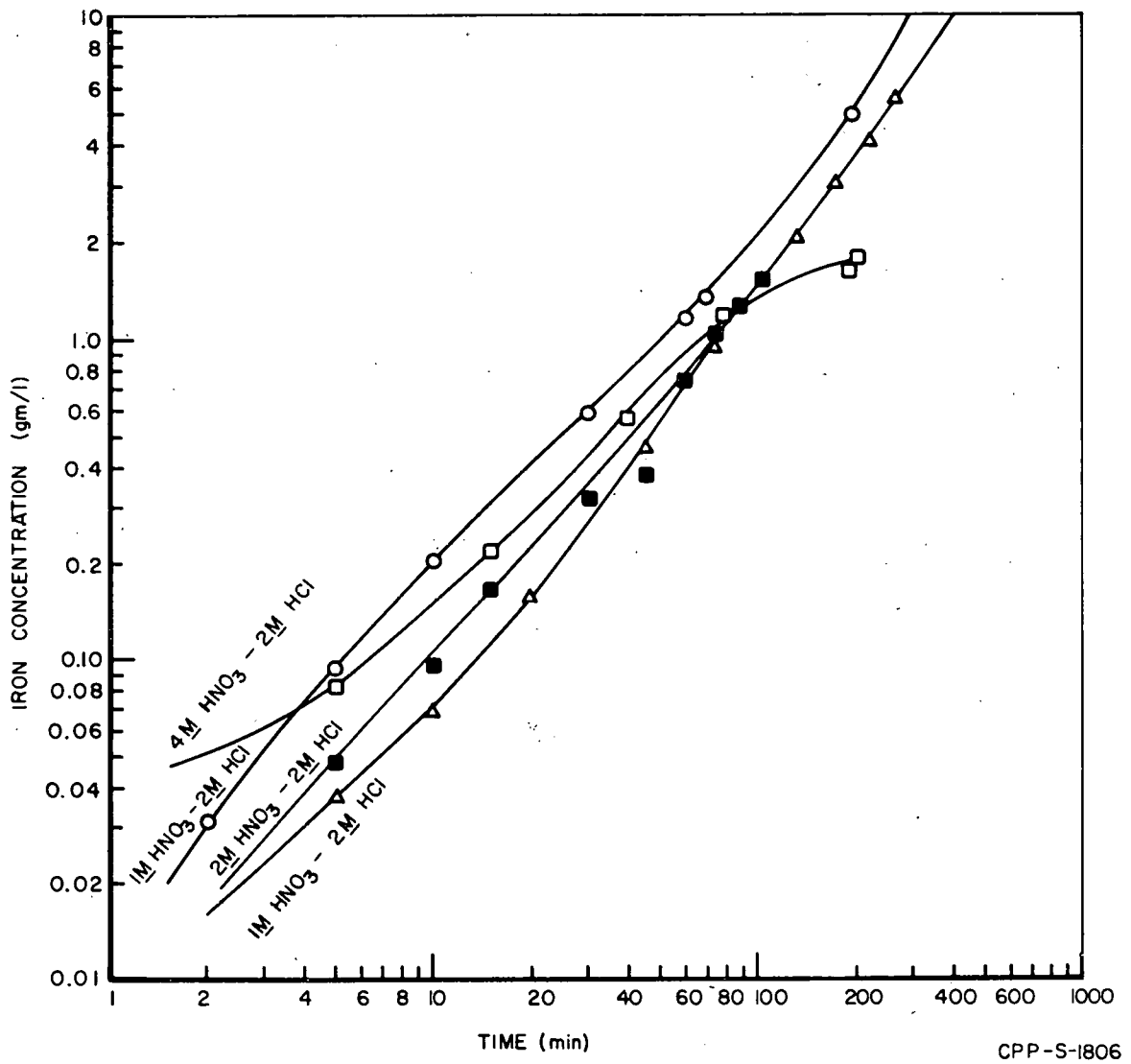
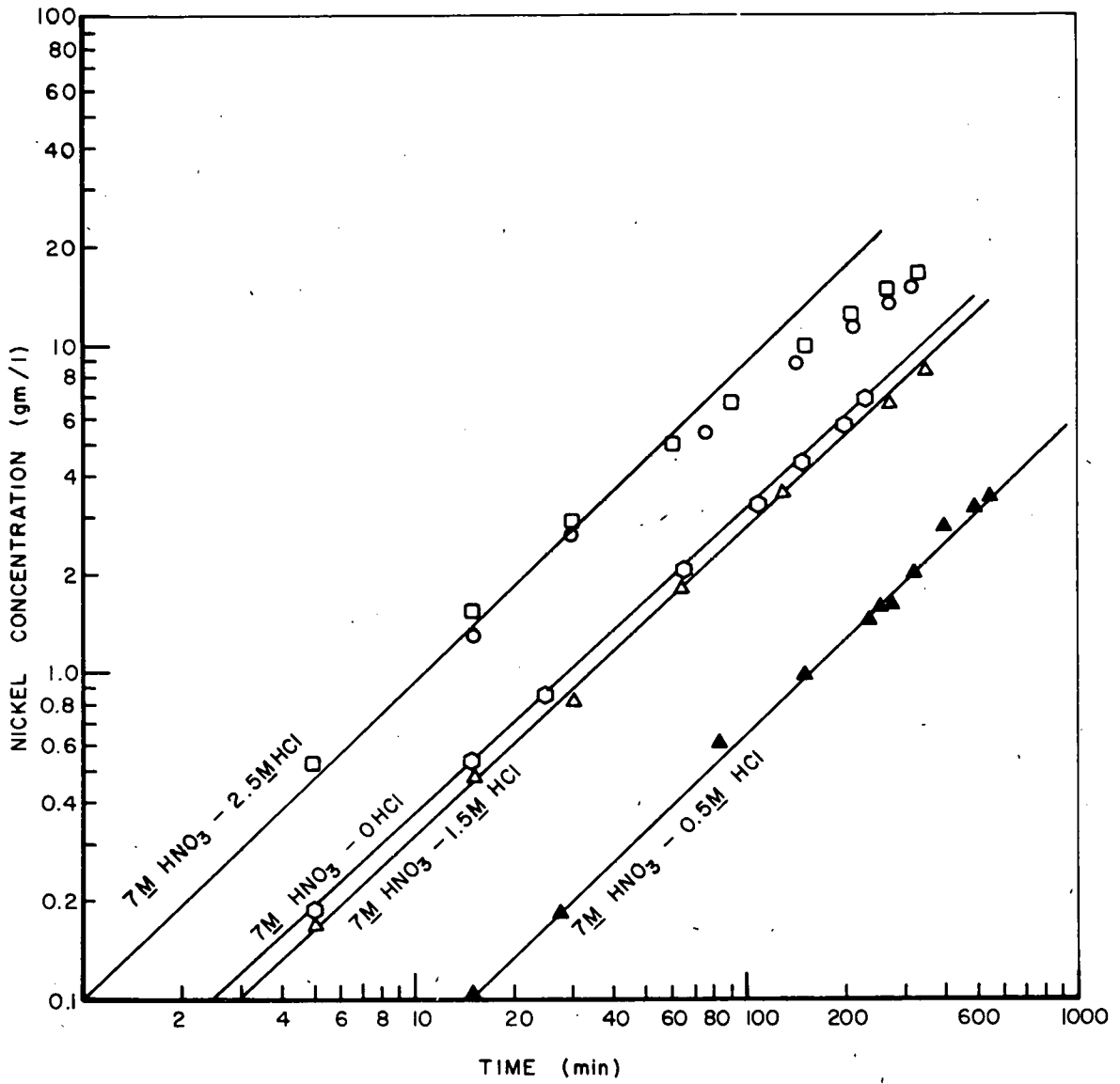
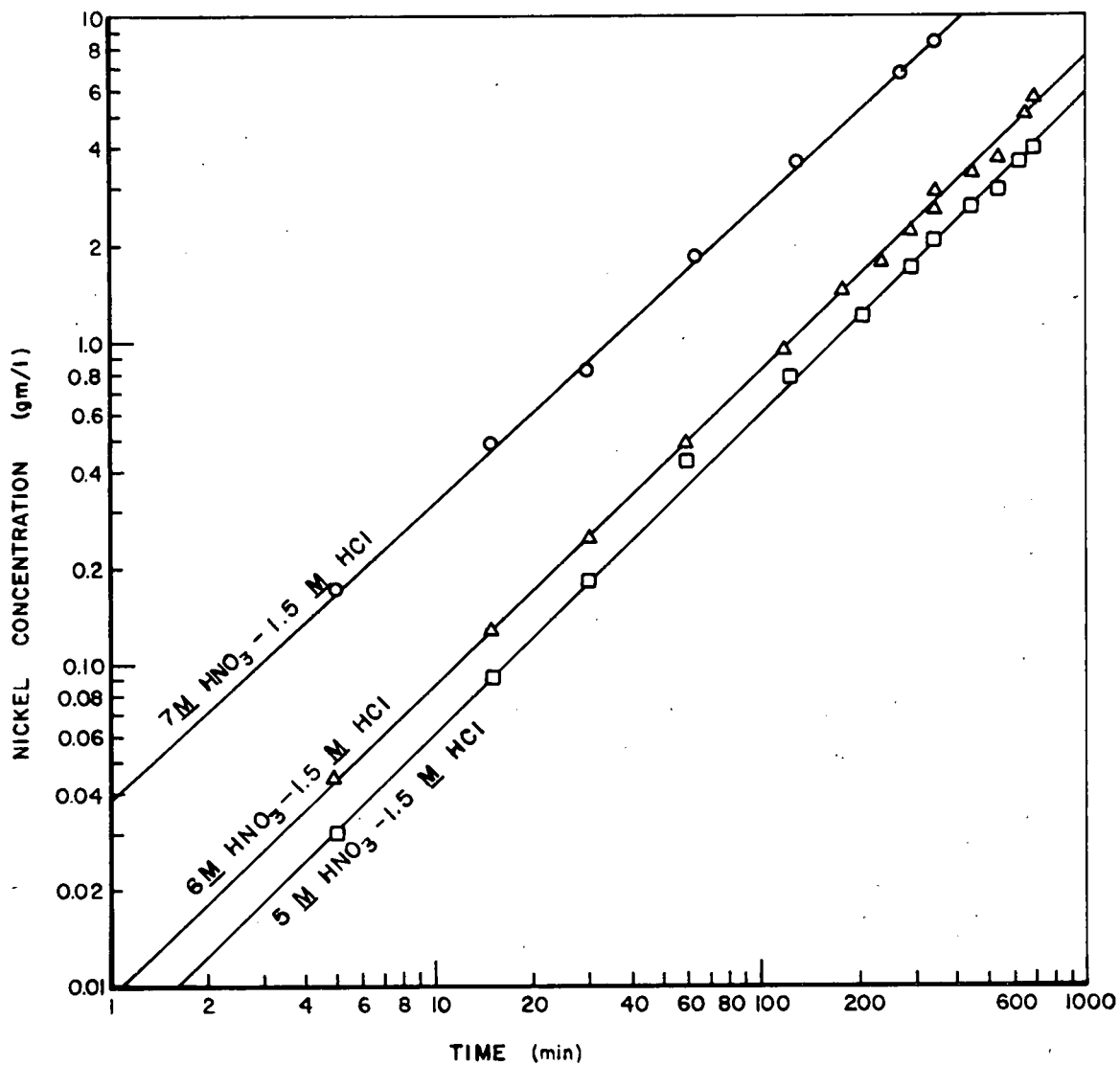


Figure 5
 Dissolution of Iron in 1 to 4M HNO₃-2M HCl at 50°C



CPP-S-1807

Figure 6
 Dissolution of Nickel in 7M HNO₃- 0 to 2.5M HCl at 70°C



CPP-S-1808

Figure 7

Dissolution of Nickel in 5 to 7M HNO₃-1.5M HCl at 70°C

V. ANALYSIS OF DATA

The plots of the data given in the preceding section lead to consideration of an expression of the form:

$$\log C = n \log t + \log k \quad (12)$$

where:

C = concentration of dissolved metal
t = time
k = constant characteristic of the dissolution reaction
n = slope of the plotted data.

If n can be considered 1 (one):

$$C = kt. \quad (13)$$

The dissolution rate (R) can be evaluated since:

$$R = \frac{dC}{dt} = k. \quad (14)$$

At $t = 1$, $n \log t$ drops out of equation (12) and k for the reaction is equal to C. Therefore, k is equal to the value of C at $t = 1$ on the $\log C$ vs $\log t$ plot. In this study, n was assumed to be constant and 1 except in the non-linear, non-reproducible iron dissolutions shown in Figure 5. The non-linear data obtained for iron dissolutions where the HNO_3 concentration was not $2M$ were not considered, since no correlation with the observed data was found. Given the assumptions indicated above, it should be possible to write an expression describing the slow step of the reaction in terms of the ionic or molecular species involved in that part of the complete reaction mechanism. It might be expected that the expression would be of the form:

$$R = a[X]^b[Y]^c \quad (15)$$

where:

[X] = concentration of species x
[Y] = concentration of species y
a, b, c = constants characteristic of the reaction mechanism
if x and y are the species of interest mentioned above. The reaction

order is defined⁽¹⁵⁾ as the sum of the exponents (i.e., b, c, etc.) appearing in the rate expression which describes the reaction of interest. This value can be thought of as the number of chemical entities participating in the rate-determining portion of the reaction and therefore can be expected to be a small integral number.

Several expressions of the general form indicated in equation (15) were considered using calculated values for the concentrations of species for which no direct analytical procedure was available. Evaluation of the constants in these equations using the experimental data leads to unreasonably high values for the reaction order, in some cases as high as 31. This indicates a complex reaction mechanism for the dissolution which cannot be explained in terms of the gross constituents of the system whose concentrations can be measured or calculated.

This degree of complexity is not totally unexpected in view of the several reactions which occur in mixtures of nitric and hydrochloric acids, i.e., the production of nitrosyl chloride, equation (1); nitrous acid, equation (11); oxides of nitrogen, equations (8-10); elemental chlorine, equation (1); and other, as yet unidentified, species.

An attempt to determine empirical equations applicable over limited concentration regions was made by grouping runs with constant hydrochloric acid concentrations and then with constant nitric acid concentrations. Using the following relationships:

$$R = a [\text{HCl}]^b \quad \text{at constant HNO}_3 \text{ concentration} \quad (16)$$

$$R = c [\text{HNO}_3]^d \quad \text{at constant HCl concentration} \quad (17)$$

dissolution rates can be related to the concentration of one acid at a given concentration of the other.

Solving for the constants in equation (16) using the experimental data for the dissolution of iron gives:

$$R = 1.34 \times 10^{-4} \text{ HCl}^{-0.62} \quad \text{in } \underline{2\text{M}} \text{ HNO}_3 \text{ at } 50^\circ\text{C.} \quad (18)$$

Since no consistent effect on the dissolution rate of iron in constant hydrochloric acid concentration as a function of nitric acid concentration was observed, no solution for the constants in equation (17) is possible.

In the case of nickel dissolutions, evaluation of equations (16) and (17) leads to:

$$R = 4.67 \times 10^{-5} \text{ HCl}^{1.38} \quad \text{in } 7\text{M HNO}_3 \text{ at } 80^\circ\text{C} \quad (19)$$

and

$$R = 1.76 \times 10^{-8} \text{ HNO}_3^{4.18} \quad \text{in } 1.5\text{M HCl} \text{ at } 80^\circ\text{C} \quad (20)$$

It must be noted that equations (18) and (19) do not hold in the absence of HCl, and (20) does not hold in the absence of HNO₃.

Although a reaction mechanism cannot be determined from the data available, an apparent activation energy (E_a) for the reactions can be determined by use of the expression⁽⁸⁾:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_2 T_1} \right] \quad (21)$$

where:

$$\begin{array}{ll} R = \text{gas constant} & T_1 = \text{temperature 1} \\ k_1 = \text{rate constant at } T_1 & T_2 = \text{temperature 2} \\ k_2 = \text{rate constant at } T_2. & \end{array}$$

The rate constant for iron dissolution, a in equation (16), was evaluated at 50, 60, and 70°C in 2M HNO₃ - 1M HCl, as described above. Figure 8 shows the variation of the iron rate constant as a function of 1/T. The activation energies, ranging from 10.5 to 19.3 kcal per mole, were calculated from equation (21). The data for nickel dissolution at 60, 70, and 80°C in 7M HNO₃ - 1.5M HCl are plotted in Figure 9, as well as the calculated activation energies which range from 9.9 to 17.2 kcal per mole. Activation energies from 10 to 100 kcal per mole have been observed for chemisorption⁽⁸⁾. Diffusion-controlled reactions, due to processes one and five listed on page 8 of this report, have activation energies not greater than 5 kcal per mole⁽⁸⁾, and therefore need not be considered rate determining.

The apparent decrease in activation energy with increasing temperature found in the dissolution of both metals could be due to a competing reaction whose activation energy is higher than that for the dissolution reaction under study. Any one of the several reactions referred to on page 19 could compete more successfully with the dissolution at higher temperatures if its activation energy were high enough.

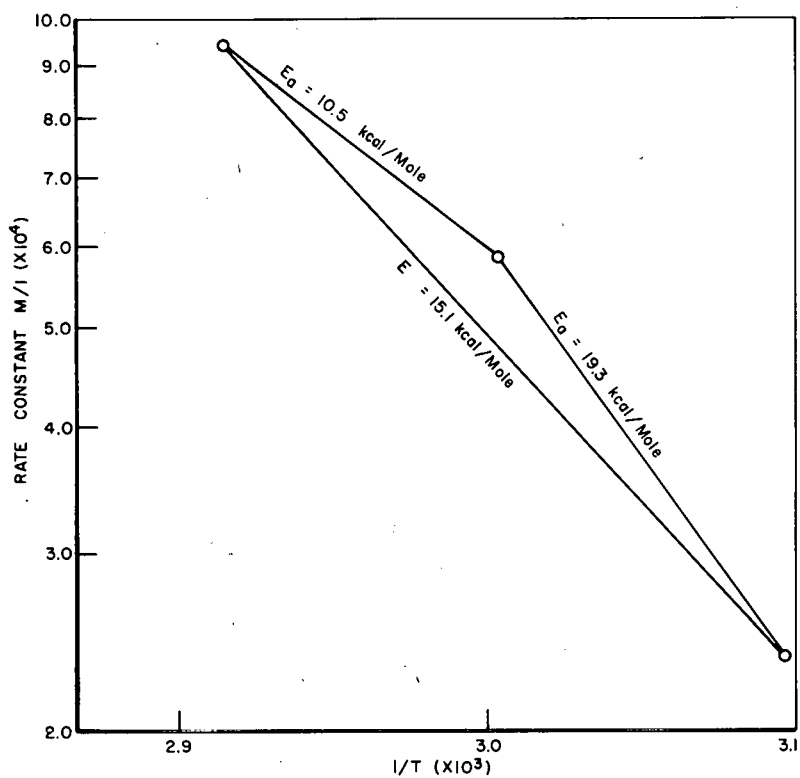


Figure 8

Effect of Temperature on the Dissolution Rate of Iron in 2M HNO₃ - 1M HCl

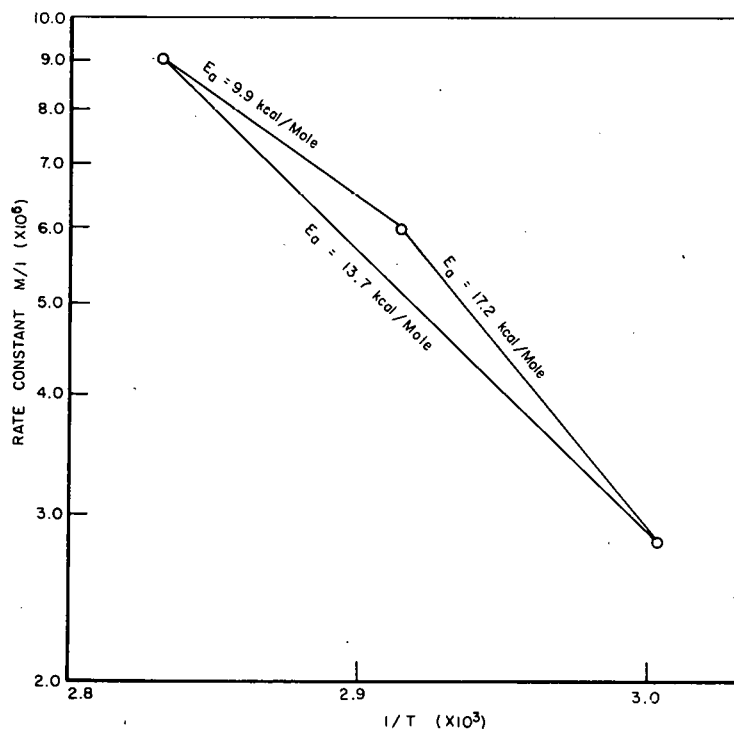


Figure 9

Effect of Temperature on the Dissolution Rate of Nickel in 7M HNO₃ - 1.5M HCl

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