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John J. Bodner
University of Windsor

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DISSOLUTION OF TITANIUM IN HYDROCHLORIC ACID

BY
JOHN J. BODNER

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ProQuest LLC
789 E. Eisenhower Parkway
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APPROVED BY:

Alex Gnyp

Roger J. Tolbert

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ABSTRACT

A kinetic study of the dissolution of titanium in nitrogen, air, and oxygen saturated hydrochloric (2.4 - 5.8 N) solutions has been made. Cylindrical samples of 0.47 inches in diameter were rotated at speeds up to 25,000 rpm. The dissolution rate, in moles of titanium dissolved per hour per liter of solution, is directly proportional to the three-quarter power of surface area, inversely proportional to the volume of solution, and directly proportional to concentration of acid. Over the range of conditions studied oxygen accelerated the dissolution. An activation energy of 14.6 kcal. per gram mole was evaluated for the temperature range 25°-45° C.

The dissolution rate may be expressed by the empirical rate equation:

$$\frac{d[Ti]}{dt} = \frac{A^{3/4}}{V} \text{ (N HCl) } (1.50 \text{ X } 10^{+4} + 2.00 \text{ X } 10^{+4} (P_{O_2})^{3/4}) \, e^{-14.6 \text{ X} 10^{3}/RT}$$

with a precision of ± 4 percent.

ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to Dr. A.W. Gnyp for his able guidance and constructive criticism, to the Titanium Metal Corporation of America for supplying the research grade titanium, to Mr. Otto Brudy for machining the titanium samples and for constructing the plexiglass-stainless steel shafts, and to my wife for her moral support.

The financial assistance offered by the National Research Council in the form of a Research Grant for 1963-1964 has been appreciated.

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CHAPTER I

INTRODUCTION

In general, comparatively little work has been reported on the corrosion of metals in aqueous solutions by measuring the amount of metal in solution at various time intervals.

Copper[1,2] and tin[3] dissolution rates in hydrochloric acid have already been studied from a rigorous kinetic consideration. Both metals have two valence states and show evidence of autocatalytic dissolution. Titanium with three possible valence states (II, III, IV) provides a more complex extension of the general corrosion problem. Titanium should be similar to tin with respect to dissolution in air-free acid solutions because both can liberate hydrogen by virtue of their positions in the electromotive series as shown below

$$Ti \longrightarrow Ti^{++} + 2e^- \qquad +1.63 \text{ volts}$$

$$Sn \longrightarrow Sn^{++} + 2e^- \qquad +0.14 \text{ volts}$$

$$H_2 \longrightarrow 2H^+ + 2e^- \qquad 0.00 \text{ volts}$$

$$Cu \longrightarrow Cu^{++} + 2e^- \qquad -0.34 \text{ volts}$$

The growing importance of titanium as a material of construction has prompted several investigators in the direction of corrosion studies. Gee and Golden[4] have studied titanium corrosion rates in hydrochloric acid while Straumanis and Chen[5] were concerned with the rate of dissolution in sulfuric, hydrochloric, hydrobromic, hydriodic, and hydrofluoric acid solutions. Hutchinson and Permar[6] have investigated the general corrosion resistance of commercially pure titanium. All of the above investigators used a weight loss method to determine their respective corrosion rates.

The object of this thesis is to study the mechanism of the dissolution of titanium in hydrochloric acid with the hope of providing a more quantitative knowledge of the variables affecting corrosion rates of metals.

CHAPTER II

LITERATURE REVIEW

A. Other Metals Studied by Analyzing the Dissolving Solution

The dissolution rates of copper, by Gnyp[1] and Lu[2], brass, by Kagetsu and Graydon[7] and Bumbulis and Graydon[8], and tin, by Lui[3] have been studied by analyzing the dissolving solution. Kinetic studies were made by rotating cylindrical metal specimens in aerated solutions over a wide range of conditions. All of the above investigators found an autocatalytic effect, with dissolution rate increasing with increasing metal ion concentration in solution.

B. General Corrosion Review of Titanium

Gee and Golden[4] reported the first useful data on the corrosion of titanium. Their method of studying the corrosion was to place 1 inch square samples of 0.040 inch thickness, prepared by sanding with No. 3/0 emery paper and washed with distilled water, into 750 ml of aerated solution maintained at constant temperature. Corrosion rates determined from periodic weighings of the immersed samples were expressed in terms of milligrams of metal lost per square decimeter per hour. They concluded that, with respect to corrosion resistance to nitric, hydrochloric, and sulfuric acids, titanium is similar to Type 316 stainless steel.

Hutchinson and Permar[6] studied the corrosion of titanium in approximately 50 different media using specimens 1 inch long, 1/2 inch wide, and 1/16 inch to 1/32 inch thick. Each of the samples were immersed in 600 ml of the dissolving medium and the top of the container covered with a watch glass. Once again the rates were determined from the weight loss.

C. Corrosion of Titanium in Nitric Acid

Golden, Lane and Acherman[9] report that titanium shows excellent corrosion resistance at 35°, 60° and 100°C. in aerated nitric acid solutions. Tests conducted in 5 and 10% nitric acid at 100°C. showed corrosion rates slightly higher than those at 35°C. for comparable acid concentrations. It has been suggested that the formation of an oxide film in oxidizing media such as nitric acid may produce the high resistance to dissolution in these solutions.

D. Corrosion of Titanium in Hydrofluoric, Hydrobromic, Hydriodic and Sulfuric Acids

Straumanis and Chen[10] studied the dissolution of titanium in various acids. They suggest that in hydrofluoric acid the metal dissolves rapidly according to:

$$2Ti + 6HF \longrightarrow 2TiF_3 + 3H_2 \qquad (1)$$

The formation of the trifluoride was confirmed by titration with potassium permanganate and by measurement of the volume of hydrogen evolved.

The method used for determining the corrosion in hydrofluoric acid consisted of gluing a sample of titanium, sanded with No. 3/0 emery paper and washed with distilled water, to the ebonite foot of a stirrer with plastic cement. The rotational speed of the stirrer was about 250 rpm. The air in the apparatus was replaced by nitrogen before the experimental run began. The removal of oxygen was necessary to eliminate the reaction[5]:

$$4TiF_3 + 4HF + O_2 \longrightarrow TiF_4 + 2H_2O \qquad (2)$$

If Ti^{4+} ions are in solution the following reaction is possible[5]:

$$3Ti^{4+} + Ti \longrightarrow 4Ti^{3+} \qquad (3)$$

The titanium samples reacted with almost all concentrations of hydrofluoric acid. In 52% acid the reaction was very violent and intense heat was evolved. Dark-violet colored solutions were obtained.

No appreciable reaction was observed either in cold or boiling hydrobromic acid of concentrations up to 41%. However, after boiling and standing for a week, violet colored solutions resulted[5].

No reaction was observed either in cold or boiling 10% hydroiodic acid[5].

Gee and Golden[4] and Golden, Lane and Acherman[9] have reported the corrosion of titanium to be a function of temperature, concentration of acid, and the type of aeration supplied. Corrosion rates are less in nitrogen-saturated solutions than in air-saturated solutions.

The following reaction for the dissolution of titanium in sulfuric acid is given by Straumanis and Chen[5]:

$$2Ti + 3H_2SO_4 \longrightarrow Ti_2(SO_4)_3 + 3H_2 \qquad (4)$$

If oxygen is present the following reaction should occur:

$$2Ti_2(SO_4)_3 + 2H_2SO_4 + O_2 \longrightarrow 4Ti(SO_4)_2 + 2H_2 \qquad (5)$$

E. Corrosion of Titanium in Hydrochloric Acid

Straumanis and Chen[5] suggest that titanium dissolves in hydrochloric acid according to:

$$Ti + 3HCl \longrightarrow TiCl_3 + 3/2\ H_2 \qquad (6)$$

If oxygen is present the quadrivalent ion should form by virtue of the reaction:

$$4Ti^{3+} + 4H^{+} + O_2 \longrightarrow 4Ti^{4+} + 2H_2O \qquad (7)$$

Ruff and Neumann[11] suggest the possibility of having Ti^{2+} in solution when titanium dissolves in hydrochloric acid but this is highly improbably because Ti^{2+} is so active that it decomposes water liberating hydrogen.

Strubl[12] and Esin[13] state that titanium dissolves as Ti^{2+} and then quickly is oxidized to Ti^{3+}. If conditions are right, high concentration of Ti^{4+} and a high concentration of acid, the following reaction can occur[5]:

$$3Ti^{4+} + Ti \longrightarrow 4Ti^{3+} \qquad (8)$$

Golden, Lane and Acherman[9] have shown that the dissolution rate of titanium is lower in nitrogen-aerated solutions than in air-aerated solutions.

Cotton and Bradley[14] report that the dissolution of titanium is proportional to both hydrochloric acid concentration and temperature.

Fast[15] reports that when metallic titanium dissolves in hot hydrochloric acid violet colored solutions are obtained.

F. Film Formation on Corroding Samples of Titanium in Non-Oxidizing Acids

During the dissolution process, the formation of titanium hydride film has been reported by many investigators [16-19]. Gibb and Krushwitz[20] report that titanium hydride, formed by the adsorption of gaseous hydrogen on titanium, to be $TiH_{1.73}$ or approximately 75% TiH_2 and the rest TiH. Otsuka[17], using an electron diffraction technique, compared the titanium hydride formed during dissolution of titanium in hydrochloric acid with titanium hydride formed by the adsorption of hydrogen and found them to be identical.

Otsuka[17] reports that if titanium is dissolved in a non-aerated, non-agitated solution, eventually this hydride will reduce the dissolution rate.

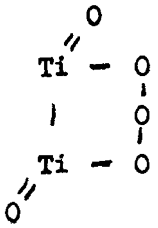
In another publication, Otsuka[16] describes the film as having a gray to black color and to be very adherent. This color is also reported by Straumanis and Chen[5].

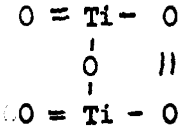
G. Analysis of Titanium Photometrically

There are many methods for determining titanium ions in solution photometrically. Sano[21] used phenylfluorone to determine microquantities of titanium in acidic solutions. The disadvantage of this method is that the acidity of the solution greatly affects the results.

Schwarberg[22] used N-benzoyl-N-phenyl hydroxylamine to detect titanium in solutions, but the pH had to be regulated between 1.6-1.8.

Many authors[23-27] suggest hydrogen peroxide for determining minute quantities of titanium. Titanium and hydrogen peroxide form a yellow titanium peroxy complex. McKenney and Madson[27] postulate that the yellow titanium peroxy complex has one of the following structures:





Other photometric methods based on the formation of titanium complexes are:

1) Azo dye complex with titanium[28]
2) Chromotropic Acid complex with titanium[29]
3) Salicylic acid complex with titanium[30]
4) Hydroxyphenyl benzyl ketone complex with titanium[31]

CHAPTER III

EXPERIMENTAL

A. Materials

1. Titanium

Research grade titanium, supplied by the Titanium Metals Corporation of America, was machined into cylinders of 0.470" in diameter with a concentric hole to fit onto a rotating stainless steel shaft. The lengths of the cylinders varied from 0.400" to 0.700".

The titanium, originally in the form of bars, was made by cold swaging cigar—shaped cast buttons. As a result of this cold work the bars were in a stressed condition. The purity of the metal was better than 99.94% titanium.

2. Hydrochloric Acid

Analar grade hydrochloric acid was obtained from the British Drug House Ltd. Dilute acid solutions were made with distilled water.

3. Hydrogen Peroxide

Analar grade hydrogen peroxide also was obtained from the British Drug House Ltd.

B. Apparatus

The cylindrical titanium samples were rotated on a stainless-steel shaft. Plexiglass sleeves and a cap, screwed tightly at the end of the titanium sample, protected each end of the titanium specimen and stainless-steel shaft from corrosion.

Three shafts were rotated simultaneously by means of a Type 7 HM Hoover vacuum cleaner motor at speeds ranging from 3000 to 25,000 rpm, with 3000 being the primary speed. The three shafts were connected by means of a pulley system designed to maintain each shaft at the same speed. (See Figure 1)

The speed of the motor was regulated by a powerstat and a constant voltage regulator. Shaft speeds were measured by means of a Type 1531-A Strobatac, produced by the General Radio Corporation.

The reaction cells consisted of specially designed jacketed vessels fabricated from two pyrex beakers as shown in Figure 1. Water was forced through the shell, between the beakers, by means of a pump from a constant temperature bath.

A laboratory jack adjusted the reaction vessels to a height which enabled the acid solution level to be one inch above the top of the metal specimen.

On top of each reaction cell there was a 5x5x1/4 inch plexiglass plate from which three baffles extended to within 1/4" of the bottom of the vessel. These baffles prevented vortex formation when the shaft was rotated at high speeds. Three holes, 3/4" diameter were bored in the plexiglass plate. These allowed: (1) the shaft to extend into the reaction vessel, (2) means of aeration, (3) means of removing a sample from the solution.

The acid solutions were saturated with nitrogen, air, or oxygen. Loss of hydrochloric acid over a 15-hour corrosion period was minimized by passing the gases through two wash bottles containing acid of the same concentration as in the reaction vessels. All wash bottles were kept at the same temperature as the corroding specimens.

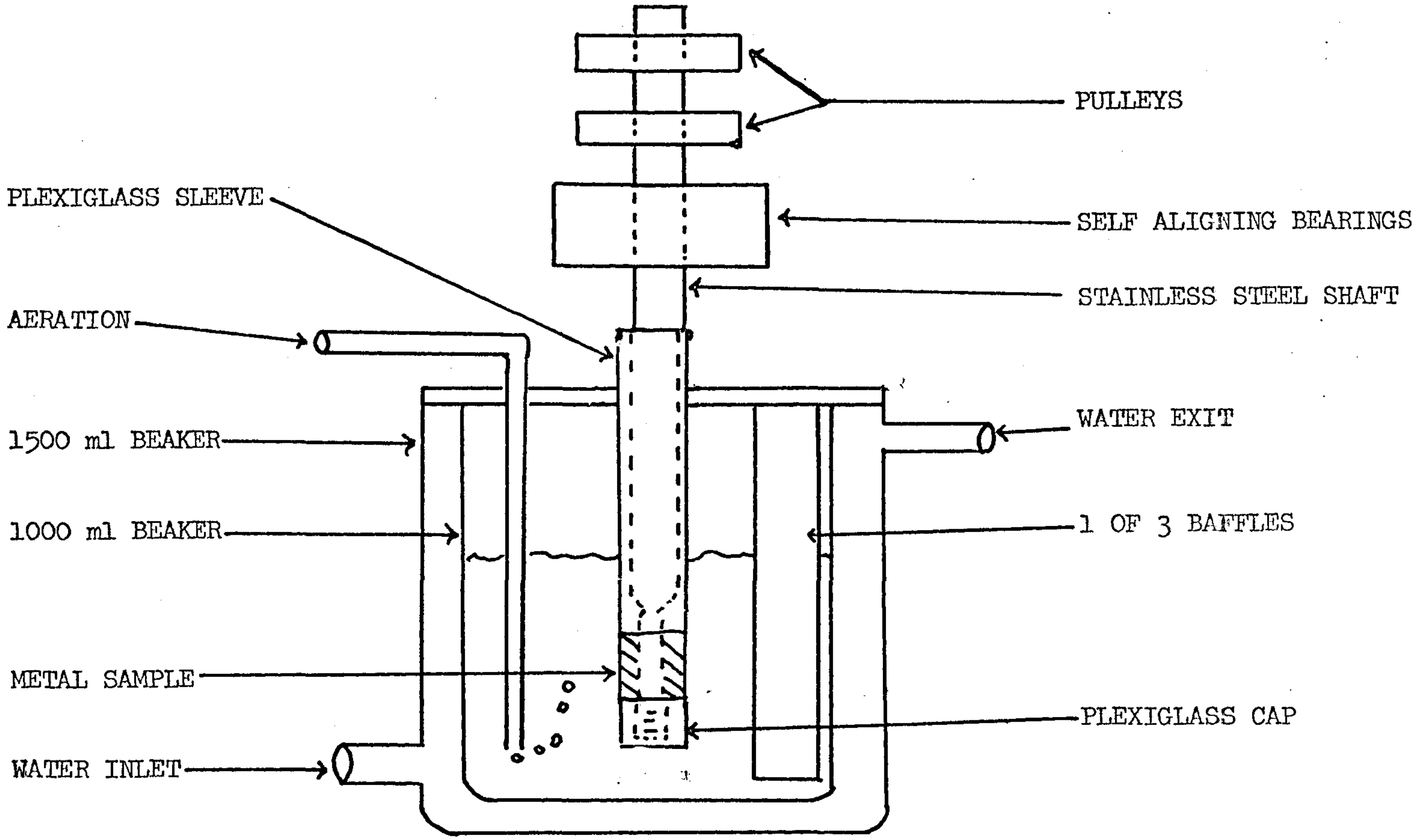


FIGURE 1. APPARATUS ARRANGEMENT

C. Procedure

A measured volume of hydrochloric acid was placed into each reaction vessel and the appropriate gas was flushed through the system for 20 minutes before each run.

Machined samples were manually polished first with No. 320 C and then with No. 3/0 emery papers. The polished samples were washed initially with distilled water, then with acetone for degreasing, and finally rewashed with distilled water. After drying, the samples were individually weighed to 0.0001 grams. After each run, the samples were washed with distilled water, air dried and then weighed. This weighing before and after enabled a material balance comparison to be made with the hydrogen peroxide analytical procedure.

Samples of the dissolving solution were withdrawn for analysis by means of a 5-ml. pipet at convenient intervals of time. The concentration of titanium, moles per liter, was determined by a photometric method as described in Appendix 1. For every sample withdrawn an equal volume of fresh acid of the same concentration was added to the reaction vessel to eliminate an excessive volume change during the dissolution run.

Experiments in which material balances differed by more than 5% were discarded.

CHAPTER IV

RESULTS AND DISCUSSION

A. Order of Reaction with Respect to Titanium in Solution

The first point is to determine whether the reaction is autocatalytic in the range of acid concentration studied. Autocatalytic mechanisms have been reported for copper[1,2], brass[7,8], and tin[3] in aerated aqueous solutions. From an examination of Figures 2-8 it appears that for the temperature range 25°-45°C, and acid concentration 2.4-5.8 N HCl, the order is zero with respect to the dissolved titanium in solution.

Thus the dissolution of titanium might be represented by the following equation as suggested by Struble[12] and Esin[13]

$$Ti + 2HCl \longrightarrow Ti^{2+} \qquad (9)$$

or by the reaction suggested by Straumanis and Chen[5]

$$Ti + 3HCl \longrightarrow Ti^{3+} \qquad (10)$$

B. Reproducibility

In order to insure reproducibility most runs were made twice with some being made three times. A typical plot of a duplicate run is shown in Figure 2. In all cases, gas flow rates were approximately 1.5 liters per minute, with the speed being held constant throughout the dissolution run to within ± 8% and the temperature to within ± .1°C.

C. Effect of Rotational Speed on the Dissolution Rate

The effect of rotational speed on the dissolution rate was studied in 4.8 N HCl at 40°C, in air-saturated solutions with rotational speeds of 0, 3000, 8000, 15000 and 25000 rpm. Figure 9 shows that

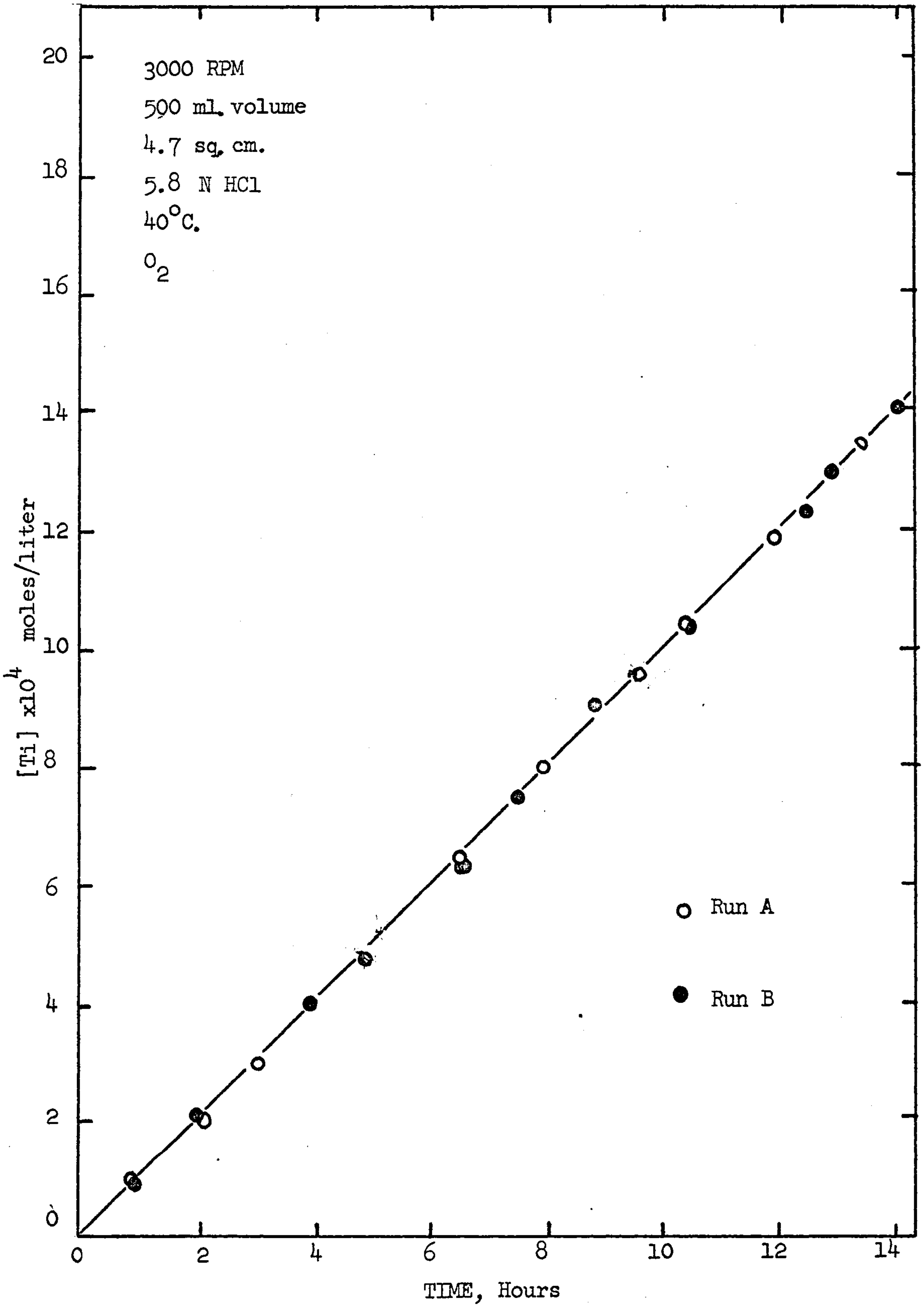


FIGURE 2. REPRODUCIBILITY

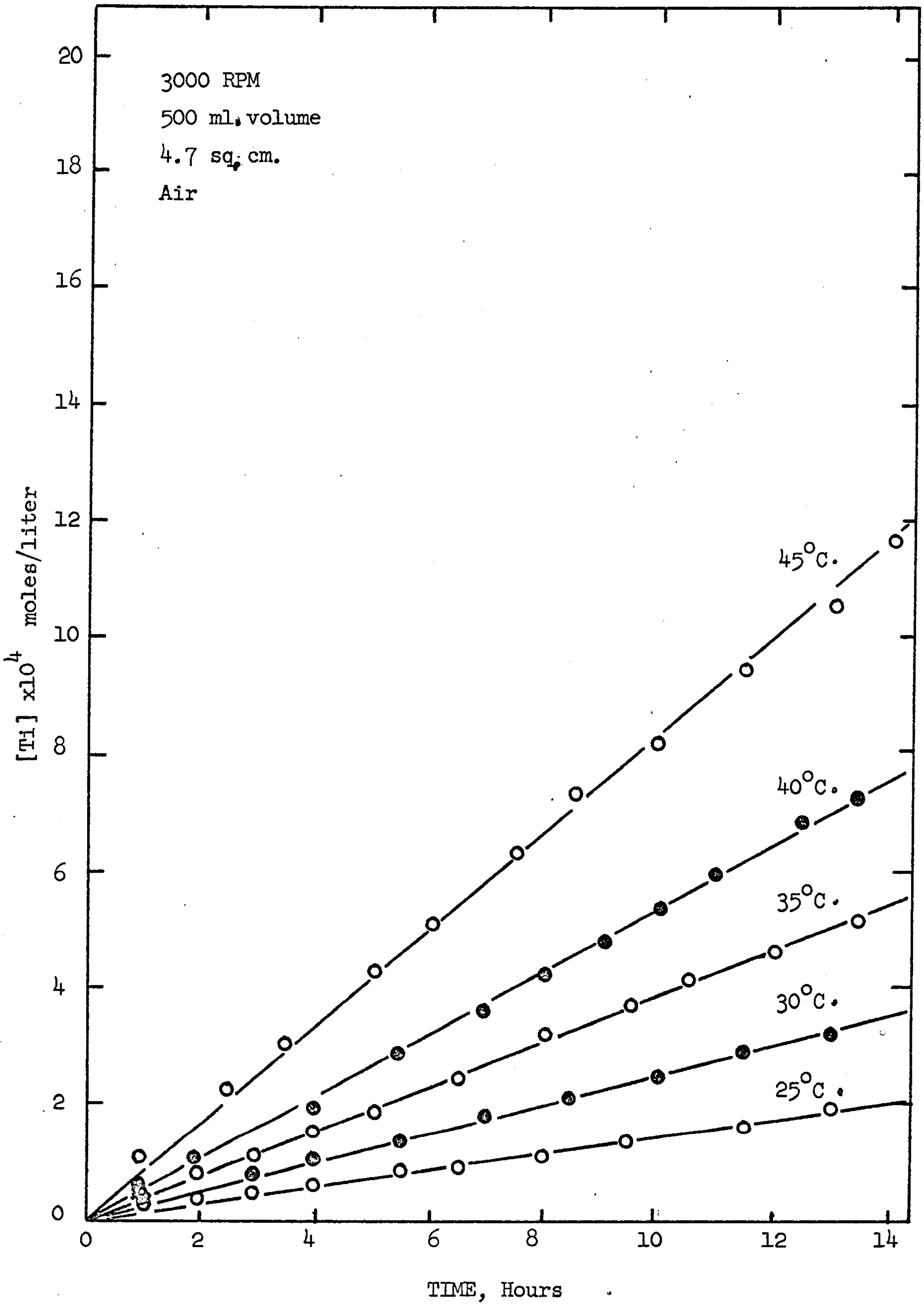


FIGURE 3. RATE OF DISSOLUTION OF TITANIUM IN 5.8 N HCl

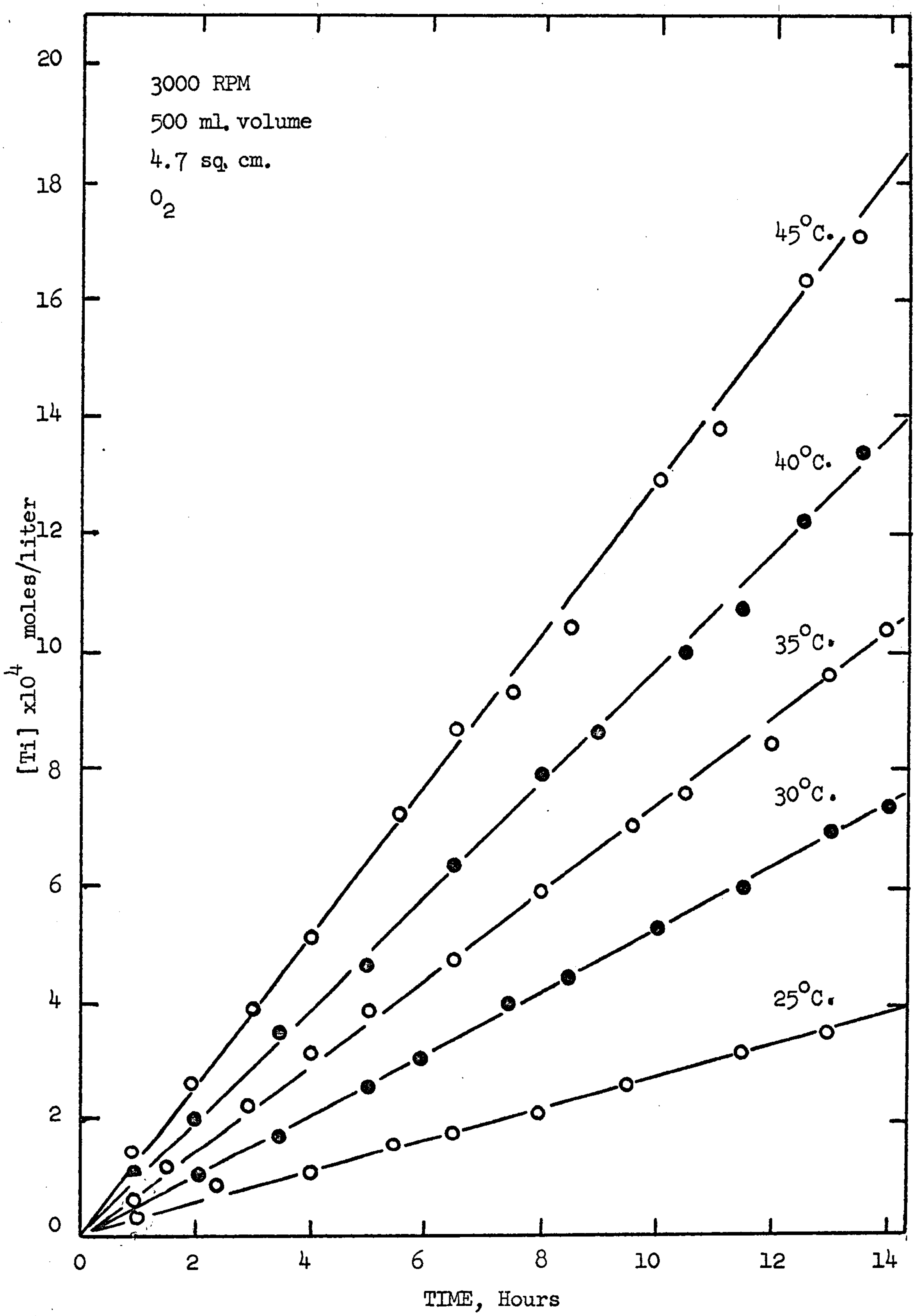


FIGURE 4. RATE OF DISSOLUTION OF TITANIUM IN 5.8 N HCl

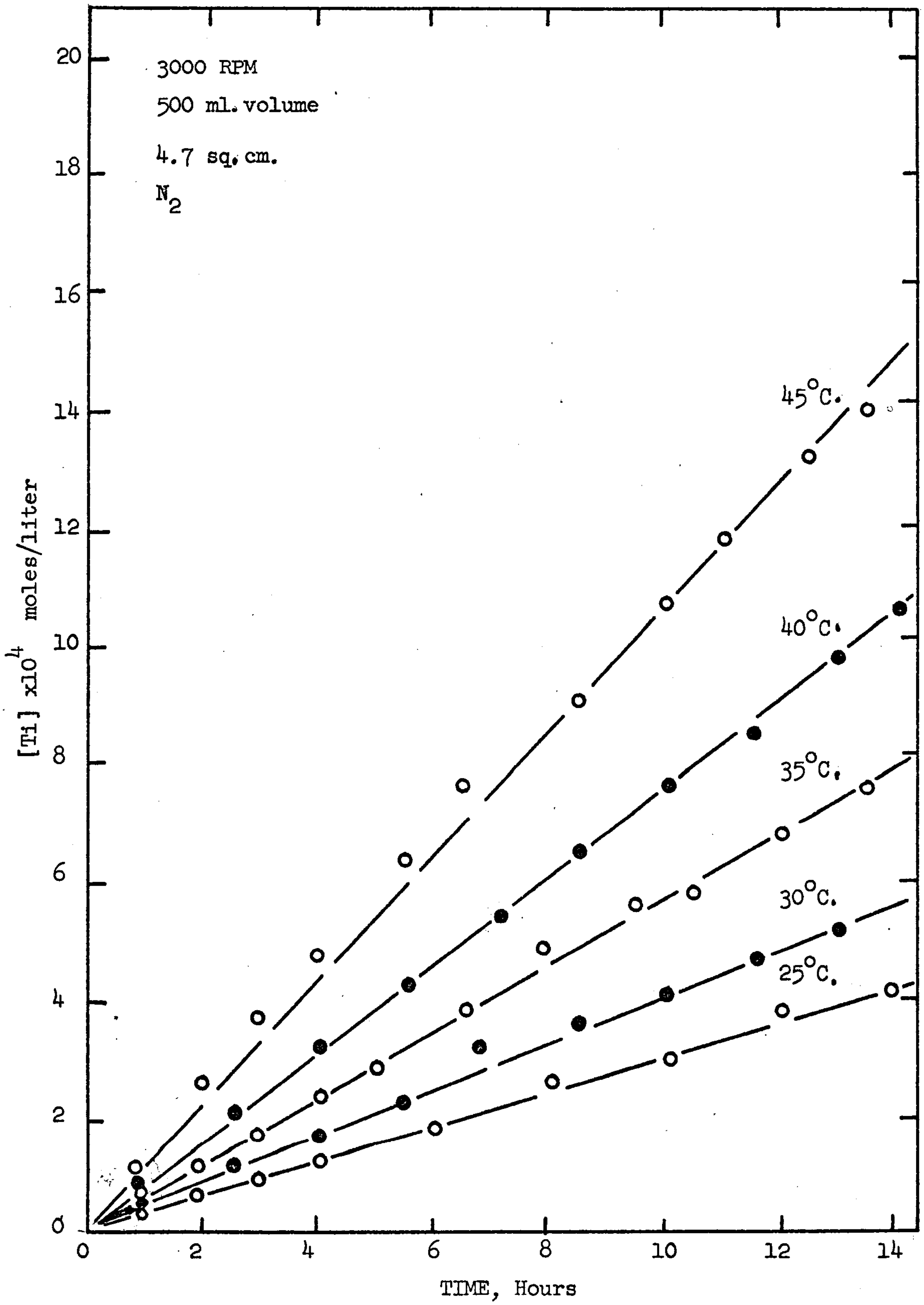


FIGURE 5. RATE OF DISSOLUTION OF TITANIUM IN 5.8 N HCl

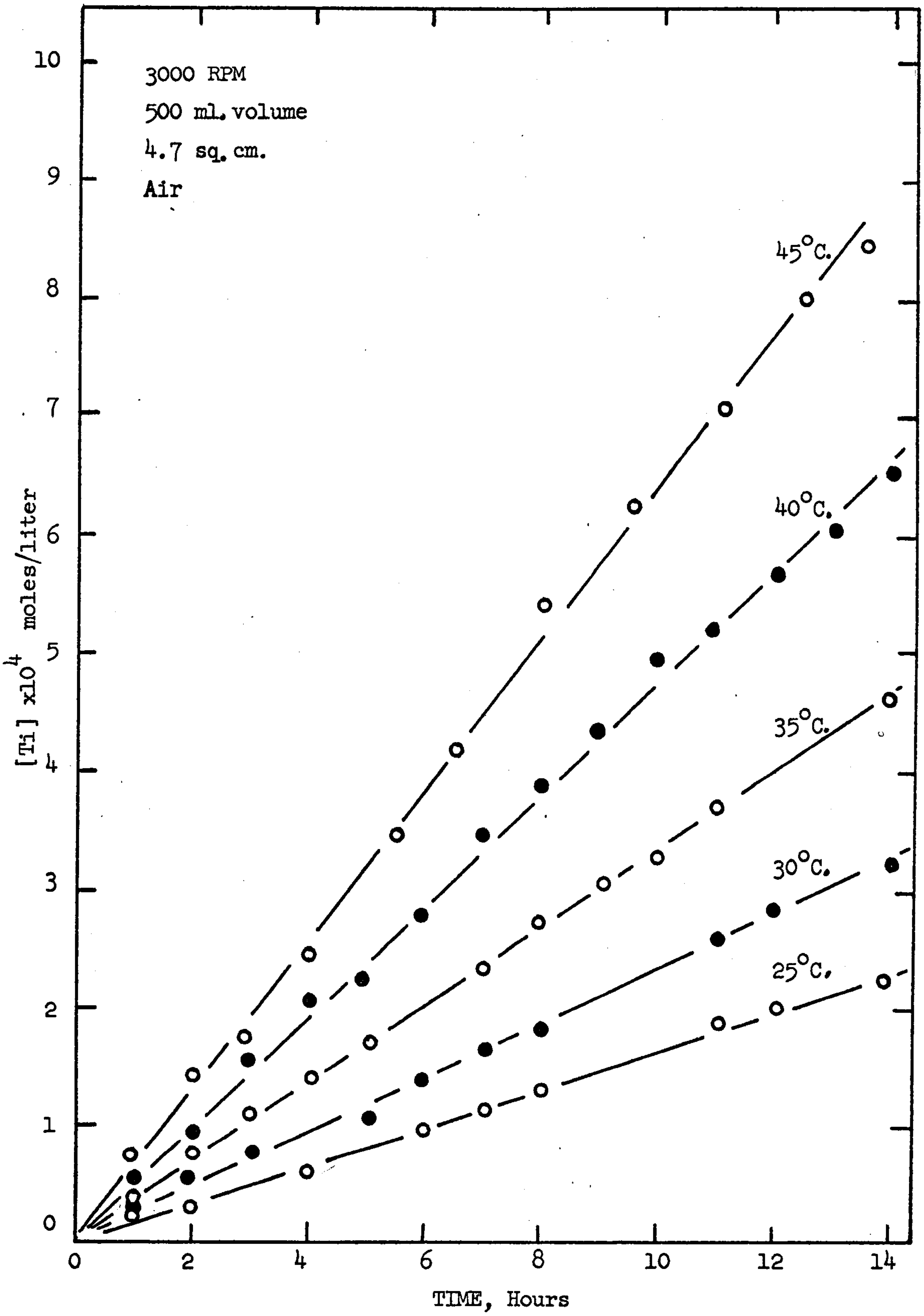


FIGURE 6. RATE OF DISSOLUTION OF TITANIUM IN 4.8 N HCl

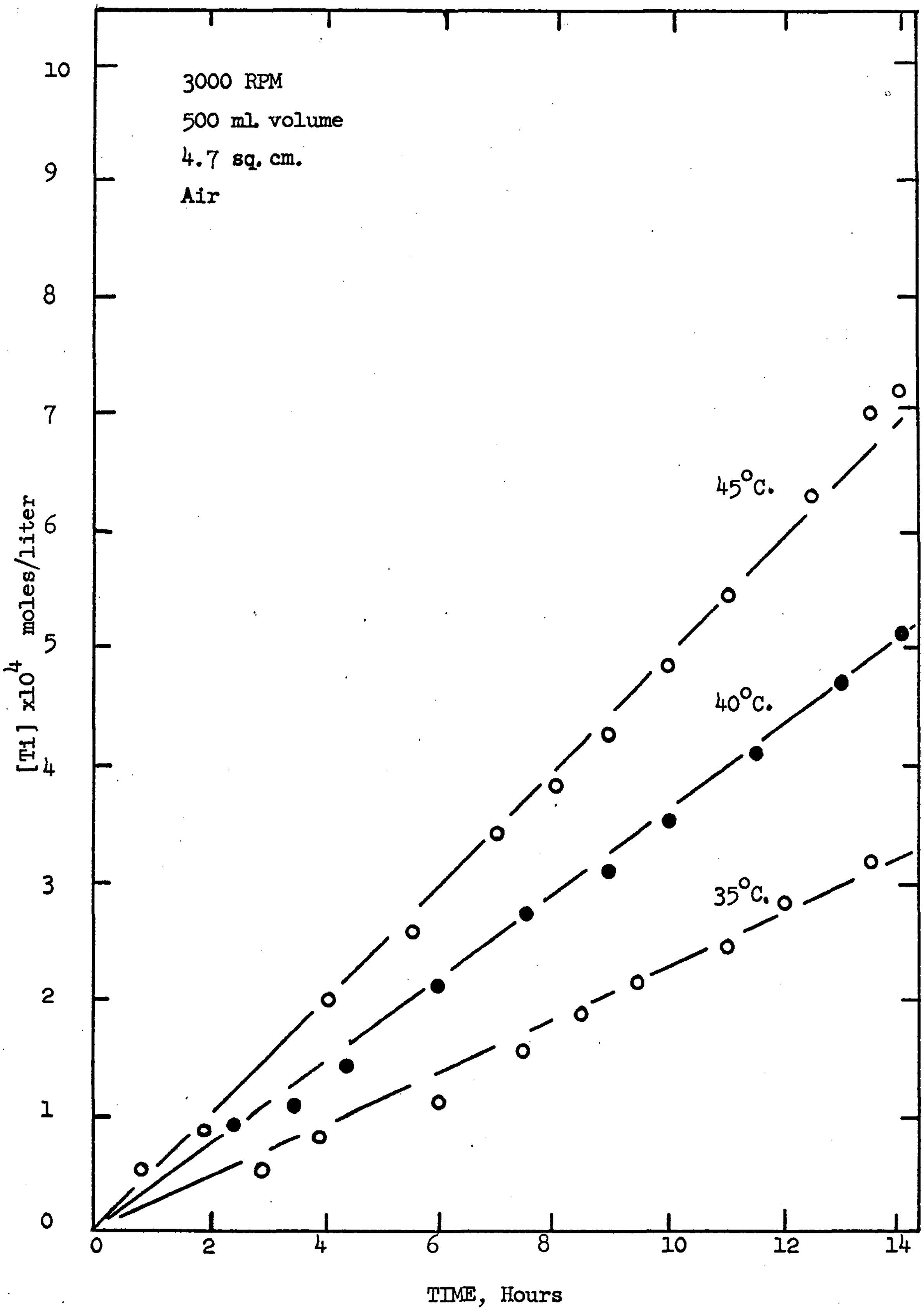


FIGURE 7. RATE OF DISSOLUTION OF TITANIUM IN 3.6 N HCl

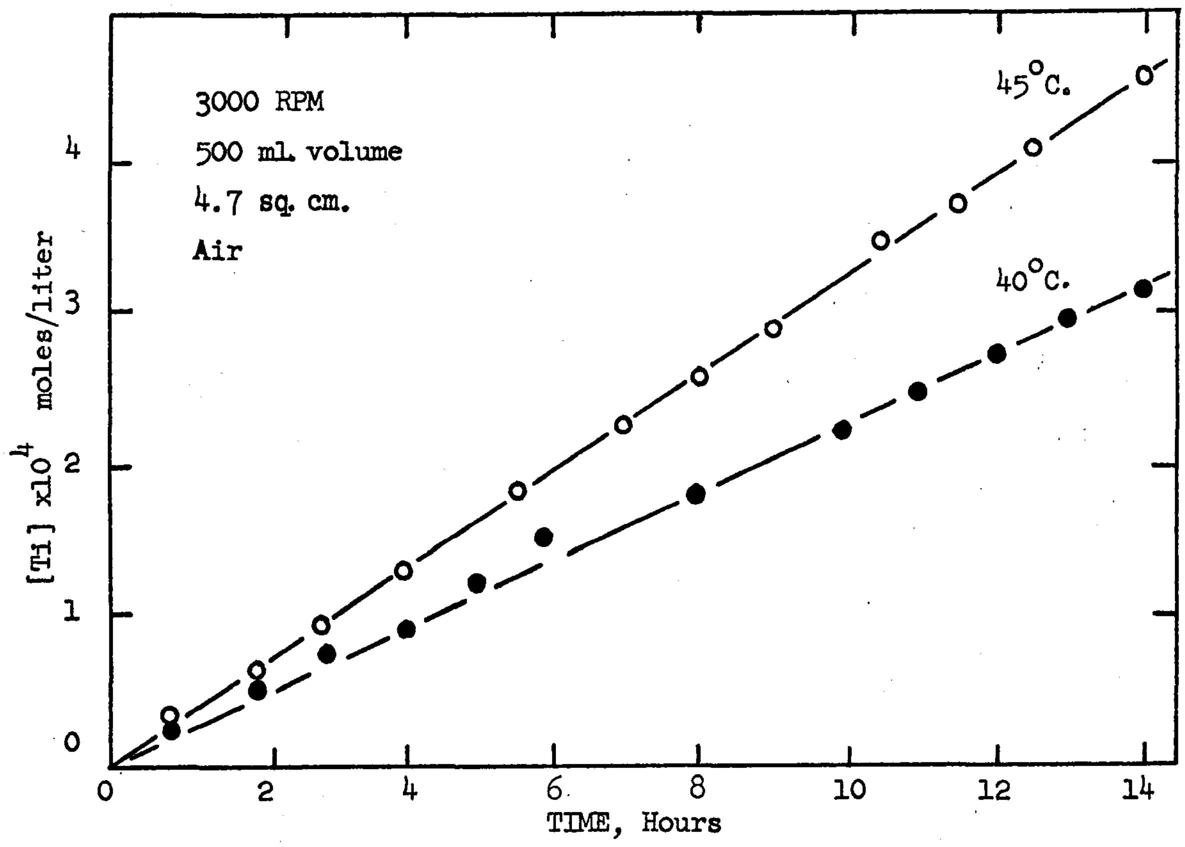


FIGURE 8. RATE OF DISSOLUTION OF TITANIUM IN 2.4 N HCl

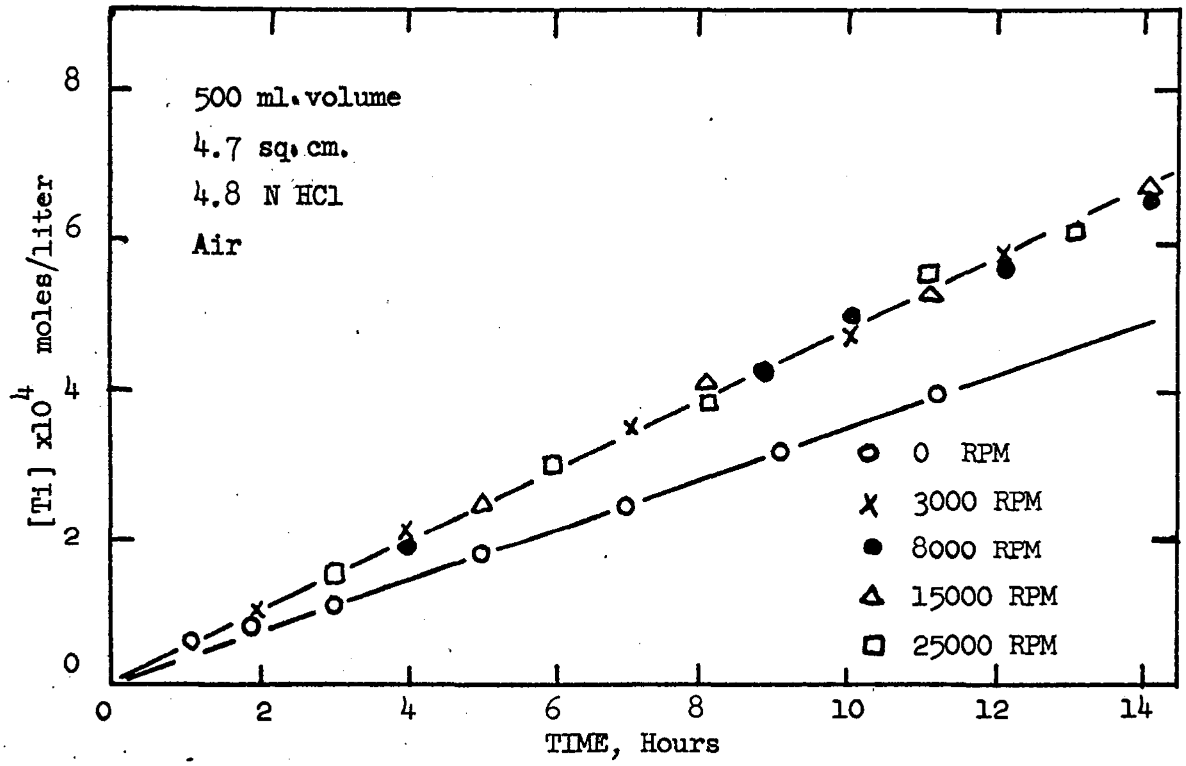


FIGURE 9. ROTATIONAL SPEED EFFECT ON DISSOLUTION OF TITANIUM

diffusion plays some part in the dissolution process during a stagnant run (0 rpm) but rotational speeds in the range 3000-25000 rpm show a different dissolution rate. This behavior suggests that at rotational speeds above 3000 rpm chemical control of the dissolution process has been established. To minimize damage to the experimental equipment a rotational speed of 3000 rpm was chosen for most investigations.

D. Effect of Temperature on the Dissolution Rate

The zero-order rate constant dependence on temperature was studied over the range 25°C-45°C under nitrogen, air, and oxygen saturation.

From Figure 10, the Arrhenius activation energy was found to be of the order of 14.6 kcal. per gram mole. This plot shows only the data for 5.8 N HCl but similar results were obtained for the other acid concentrations.

The high activation energy and negligible effect of increasing rotational speeds up to 25000 rpm are fairly conclusive evidence that the rate controlling step in the dissolution of titanium is chemical and not diffusional.

E. Effect of Hydrochloric Acid Concentration on the Dissolution Rate

The effect of acid concentration in air-saturated solutions was studied over the range 2.4-5.8 N HCl A plot of the zero-order rate constant from Figures 3-8 versus the concentration of acid, as in Figure 11, produces a linear relationship suggesting that the rate constant is a linear function of acid concentration.

Equation (9) suggests that the rate should increase linearly

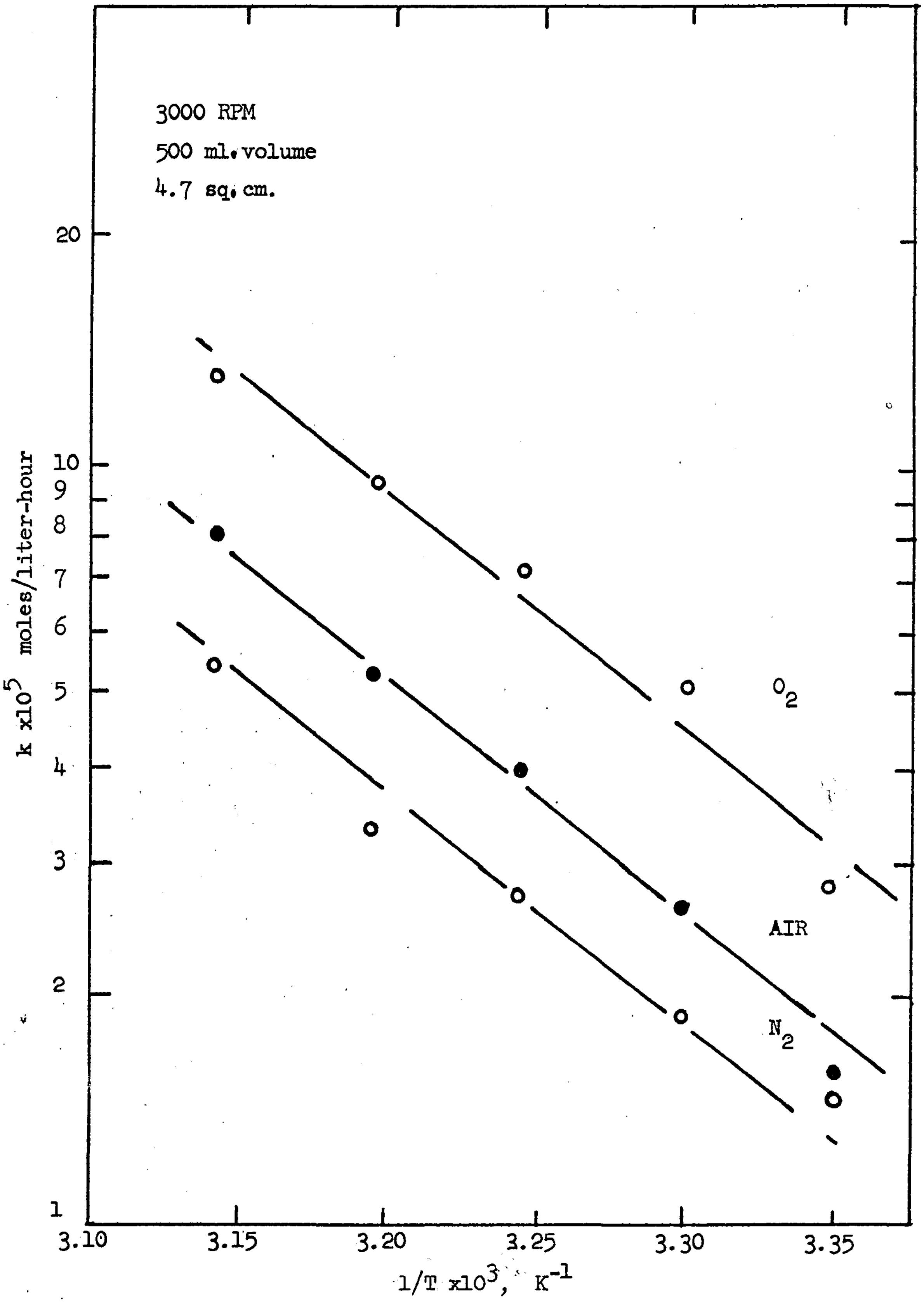


FIGURE 10. ARRHENIUS PLOT FOR 5.8 N HCl

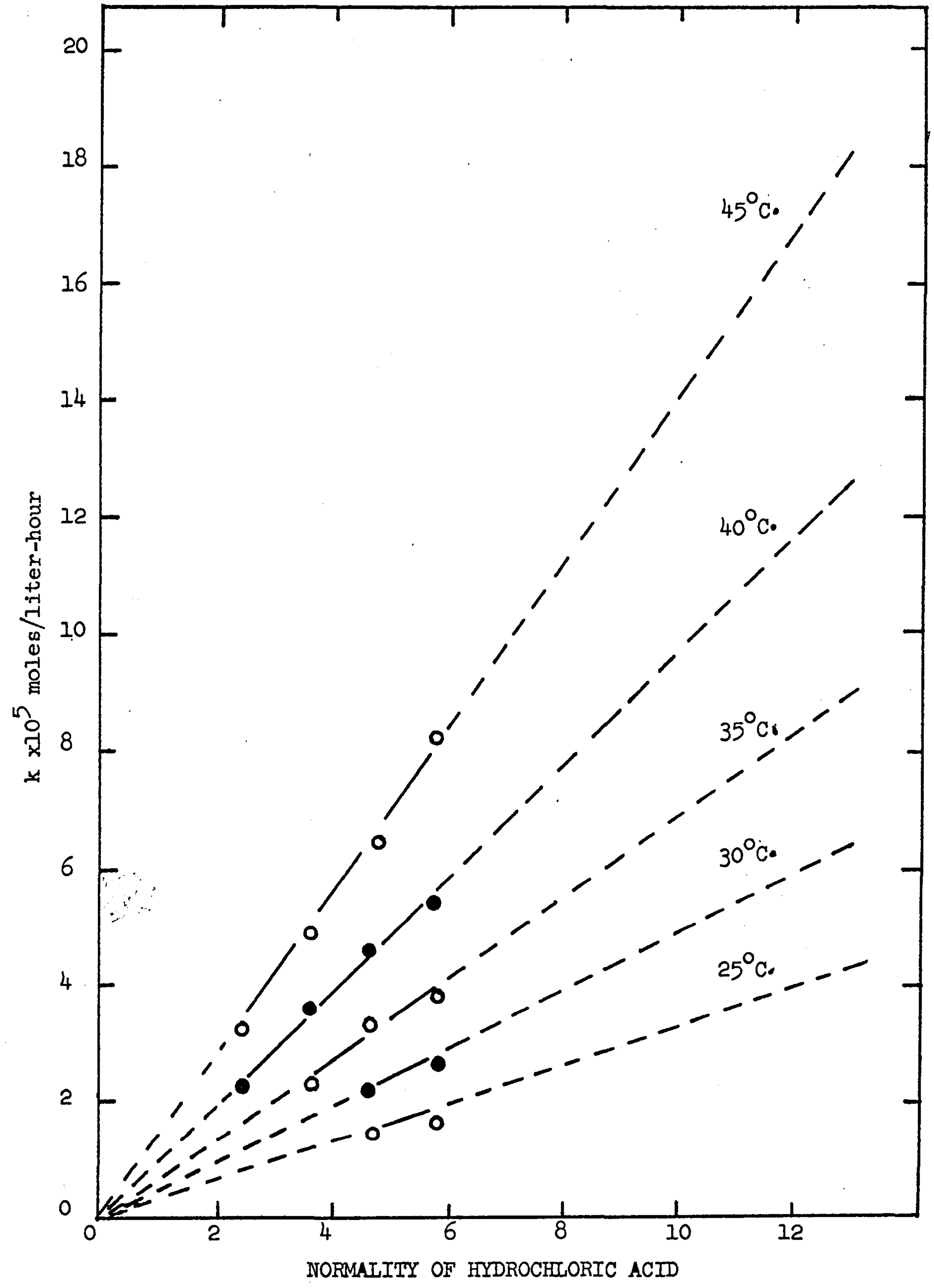


FIGURE 11. EFFECT OF ACID CONCENTRATION ON THE RATE CONSTANT

as the square of the concentration of acid and equation (10) suggests that the rate should increase linearly as the cube of the acid concentration if either of these two equations represents the elementary process.

F. Film Formation Effect on the Dissolution Rate

In all cases a gray to blackish film formed on the surface of the dissolving titanium specimens. It was adherent, did not come off with water, and could be removed only with emery paper or other abrasive means. This film, forming within one-half hour after the sample was immersed in hydrochloric acid, has the characteristics of titanium hydride films described by Otsuka[16,17] and Straumanis and Chen[5].

Berg[32] suggests a mechanism for the adsorption of hydrogen ions and water on metal surfaces in dilute acidic solutions. His ideas when extrapolated to higher acid concentration could lead to predominantly hydrogen-ion adsorption. A titanium surface in concentrated hydrochloric acid solutions may adsorb hydrogen ions according to :

$$Ti + H^+ \overset{fast}{\rightleftarrows} TiH^+ \qquad (11)$$

$$TiH^+ + H^+ \rightleftarrows TiH_2^{2+} \qquad (12)$$

with the equilibria set up to maintain about 75% surface coverage as TiH_2^{2+} and 25% TiH^+.

If the hydride film is formed according to equations (11) and (12) it could be removed by a process such as ;

$$TiH_2^{2+} + H^+ \xrightarrow{slow} Ti^{3+} + 3/2\ H_2 \qquad (13)$$

G. Effect of Area on the Dissolution Rate

The effect of surface area was studied in 5.8 N HCl at 45°C. in both air- and nitrogen-saturated solutions. (See Appendix 10) Figure 12-A shows the zero-order rate constant as a function of area. Because extrapolation to zero area shows a finite rate constant it appears that the corrosion rate is not directly proportional to area.

Both Figures 12-B and 12-C show evidence that the zero-order rate constant is proportional to the three quarter power of the area. Dissolution rates not directly proportional to the area may be characteristic of the corrosion of metals capable of displacing hydrogen from acid media. Lui[3], studying the dissolution of tin, found the dissolution rate to be proportional to the square root of the area. The rate of dissolution of copper has been found to be directly proportional to the surface area in aqueous solutions[1,2].

A possible explanation for this three quarter power dependence on area could be given in terms of molecular hydrogen formation on the surface of the corroding specimen. Equation (13) suggests a possible mechanism for the dissolution of the film and formation of hydrogen molecules. Atomic hydrogen in forming a molecule would require a surface on which to unite. Mobility of atomic hydrogen could cause effective screening of the surface available for corrosion.

H. Effect of Volume on the Dissolution Rate

To study the effect of solution volume on the dissolution rate, samples were rotated in 400, 500, and 600 ml. of 5.8 N air-saturated solutions of hydrochloric acid at 45°C. Figure 13-A shows the concentration, moles of titanium dissolved per liter of solution, as a function

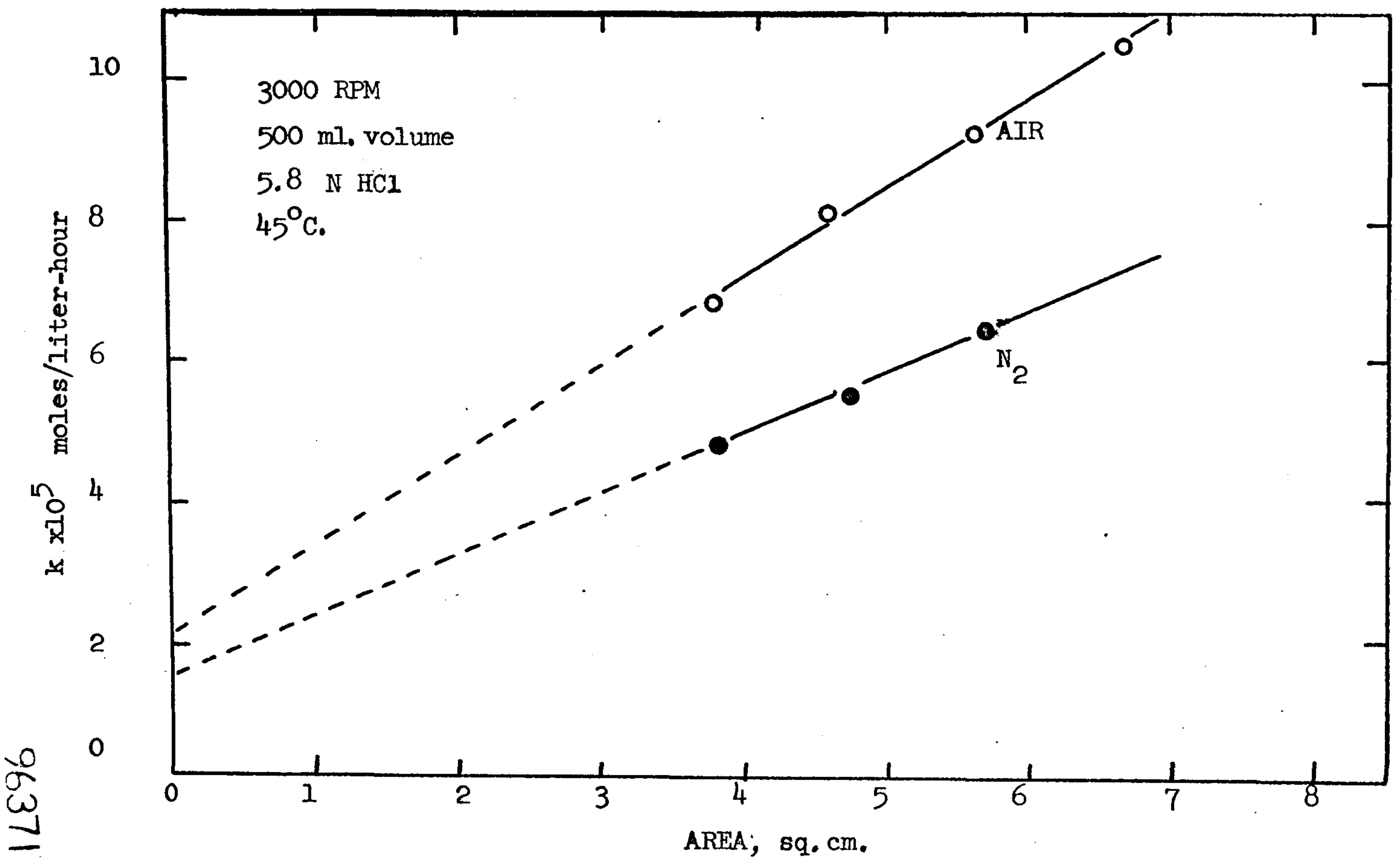


FIGURE 12-A. EFFECT OF AREA

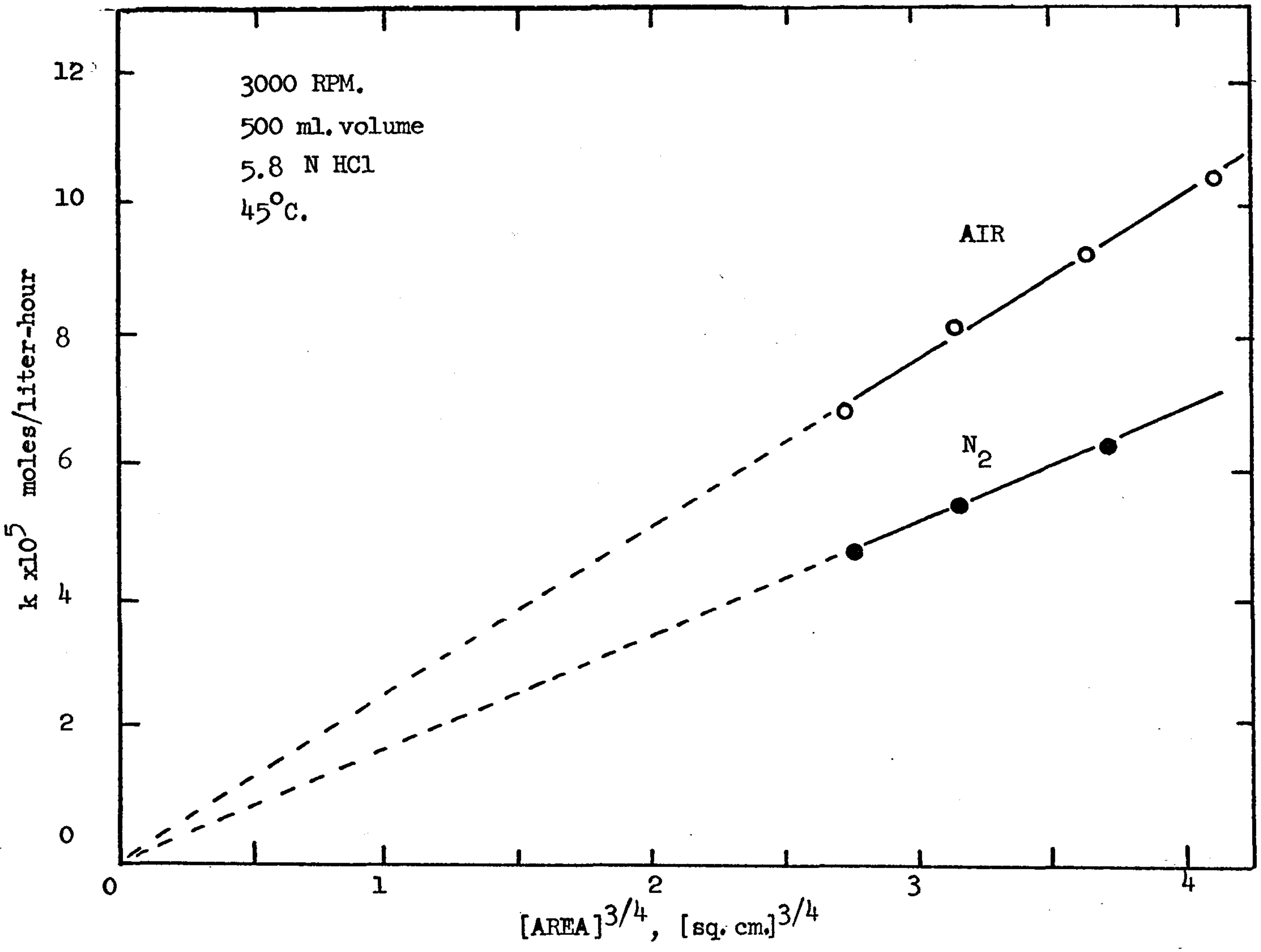


FIGURE 12-B. EFFECT OF AREA

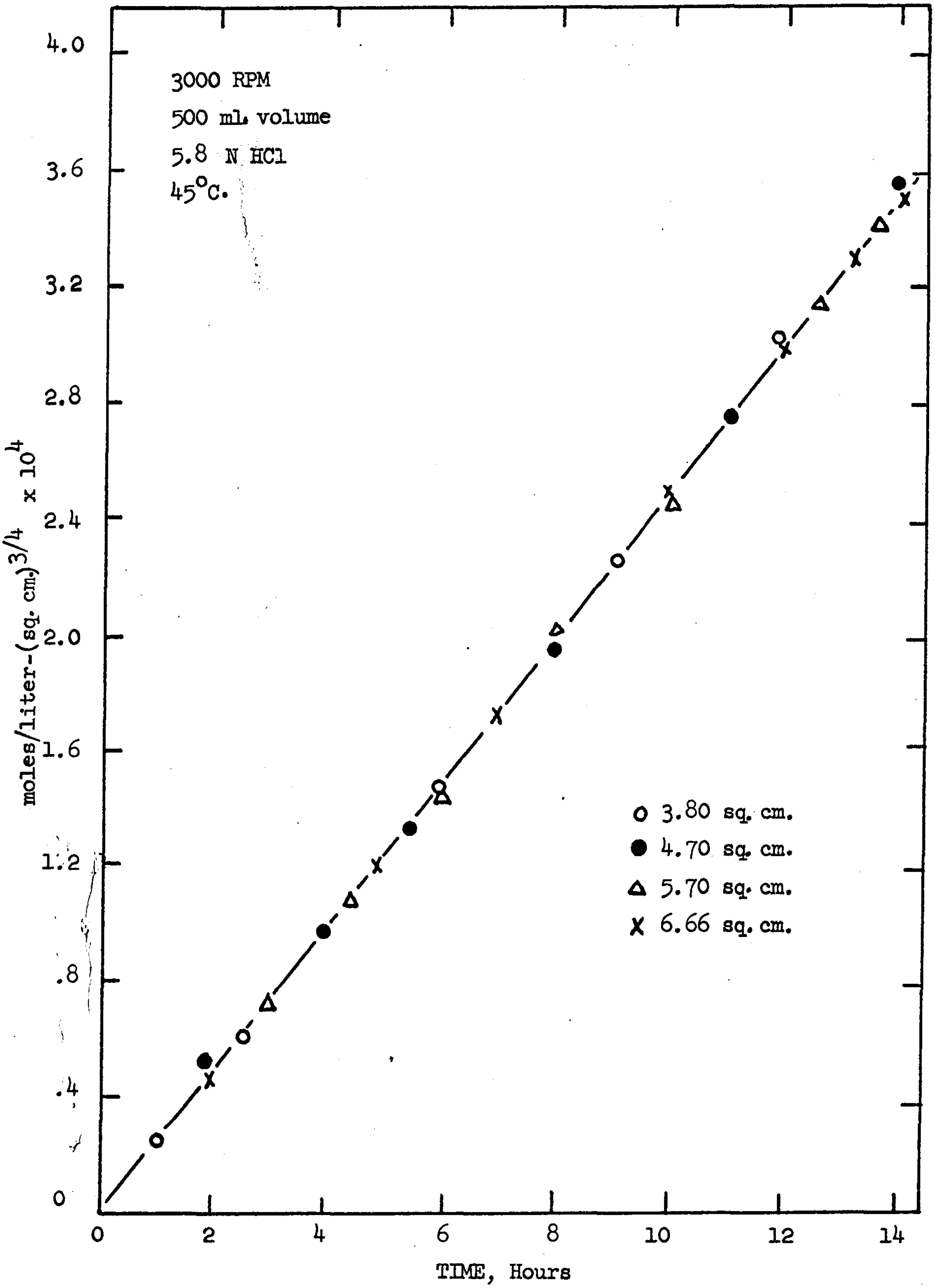


FIGURE 12-C. EFFECT OF AREA

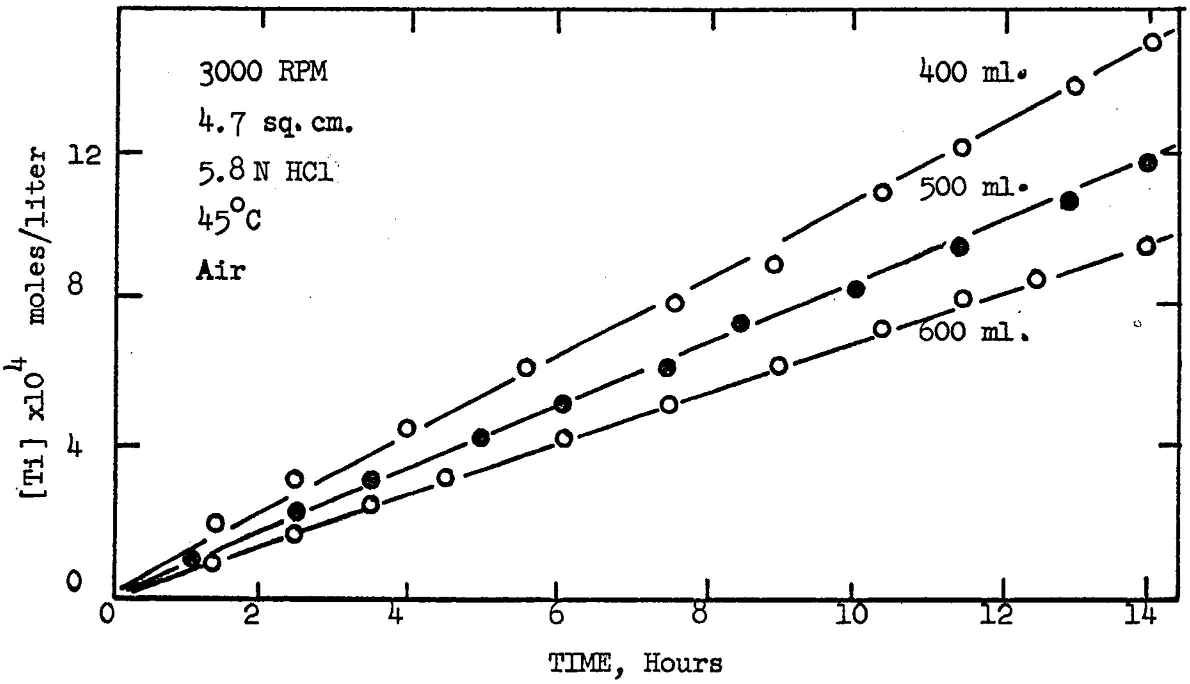


FIGURE 13-A. EFFECT OF VOLUME

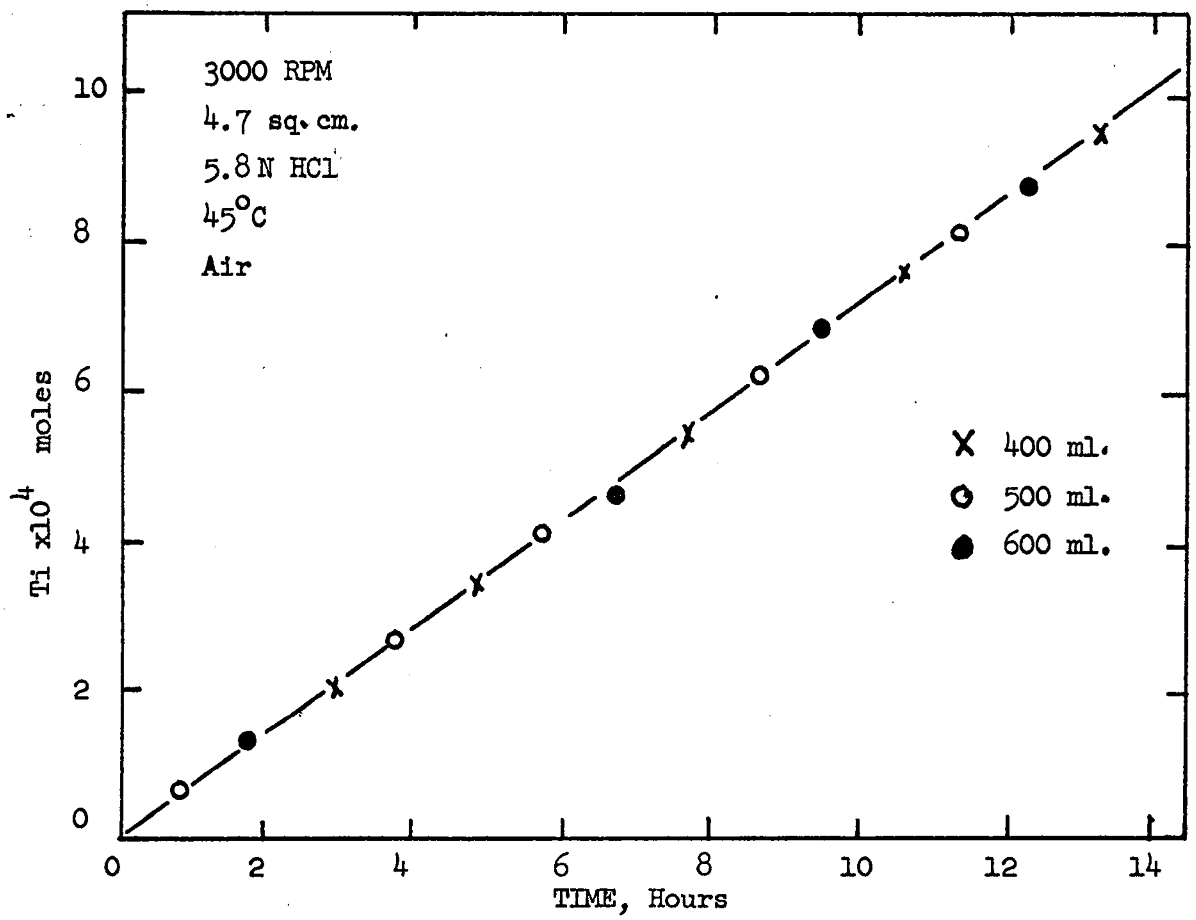


FIGURE 13-B. EFFECT OF VOLUME

of time for the three different volumes, and Figure 13-B shows the moles of titanium dissolved as a function of time. It is evident that the corrosion rate in moles per liter per hour is inversely proportional to the solution volume.

I. Effect of Oxygen on the Dissolution Rate

The influence of oxygen on the dissolution rate was determined by bubbling nitrogen, air or oxygen through the solution at a rate of 1.5 liters per minute. A detailed study of oxygen dependence was made over the temperature range of 25°-45°C. (See Table 1). Figure 14 shows the effect of oxygen at 45°C. Typical results were obtained at other acid concentrations over a more limited temperature range.

TABLE 1

Effect of Oxygen
3,000 rpm
4.7 sq. cm.
5.8 N HCl

Temperature °C.	Type of Aeration	Rate Constant X 10^4, moles/liter-hr.
45	O_2	13.0
45	Air	8.2
45	N_2	5.4
40	O_2	9.6
40	Air	5.4
40	N_2	3.3
35	O_2	7.3
35	Air	4.0
35	N_2	2.8
30	O_2	5.2
30	Air	2.6
30	N_2	1.9
25	O_2	2.8
25	Air	1.6
25	N_2	1.4

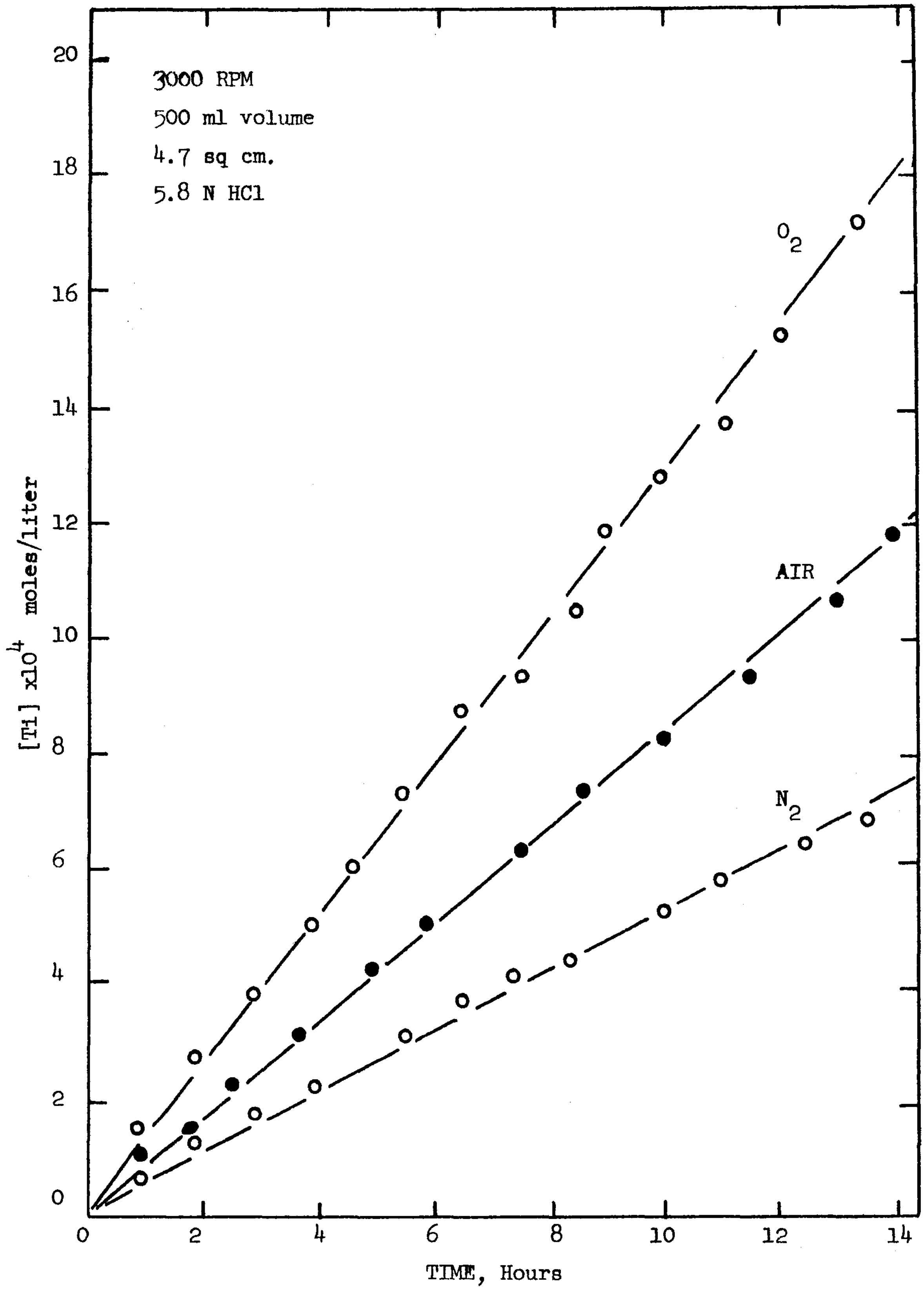


FIGURE 14 EFFECT OF OXYGEN

The dependence of dissolution rate on oxygen in 5.8 N HCl is depicted in Figure 15-A and Figure 15-B. Figure 15-A shows the zero-order rate constant as a function of partial pressure of oxygen and Figure 15-B shows the zero-order rate constant as a function of the partial pressure of oxygen raised to the three-quarter power. This three-quarter power should be considered in terms of the processes that can occur in the reacting system.

In the absence of oxygen the dissolution is by hydrogen evolution according to the equation

$$TiH_2^{2+} + H^+ \rightleftharpoons Ti^{3+} + 3/2\ H_2 \qquad (13)$$

When oxygen is introduced into the corroding solution the Ti^{+++} ions should be oxidized to the quadrivalent state by virtue of a homogeneous reaction of the type :

$$Ti^{3+} + H^+ + O_2 \longrightarrow Ti^{4+} + HO_2 \qquad (14)$$

and

$$Ti^{3+} + HO_2 \longrightarrow Ti^{4+} + HO_2^- \qquad (15)$$

This set of reactions does not explain an increase of dissolution with increasing oxygen concentrations.

A possible process which involves oxygen in the dissolution is :

$$TiH_2^{2+} + H^+ + O_2 \text{ ——— } Ti^{4+} + HO_2^- + H_2 \qquad (16)$$

This reaction would imply first order dependence on oxygen. Since titanium surfaces have an affinity for oxygen[33,34] it is not unreasonable to assume that increasing oxygen concentrations in solution could produce irregular protective oxide films. These films could form in such a way as to decrease the effective area available for corrosion.

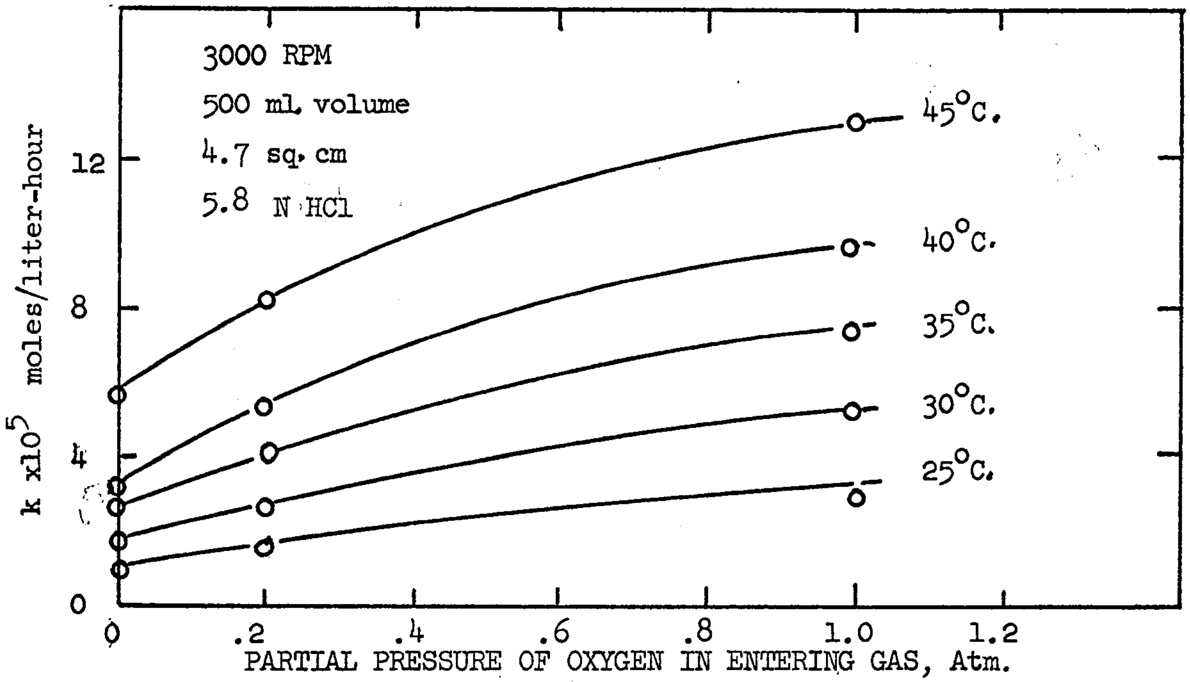


FIGURE 15-A. EFFECT OF OXYGEN ON DISSOLUTION RATE

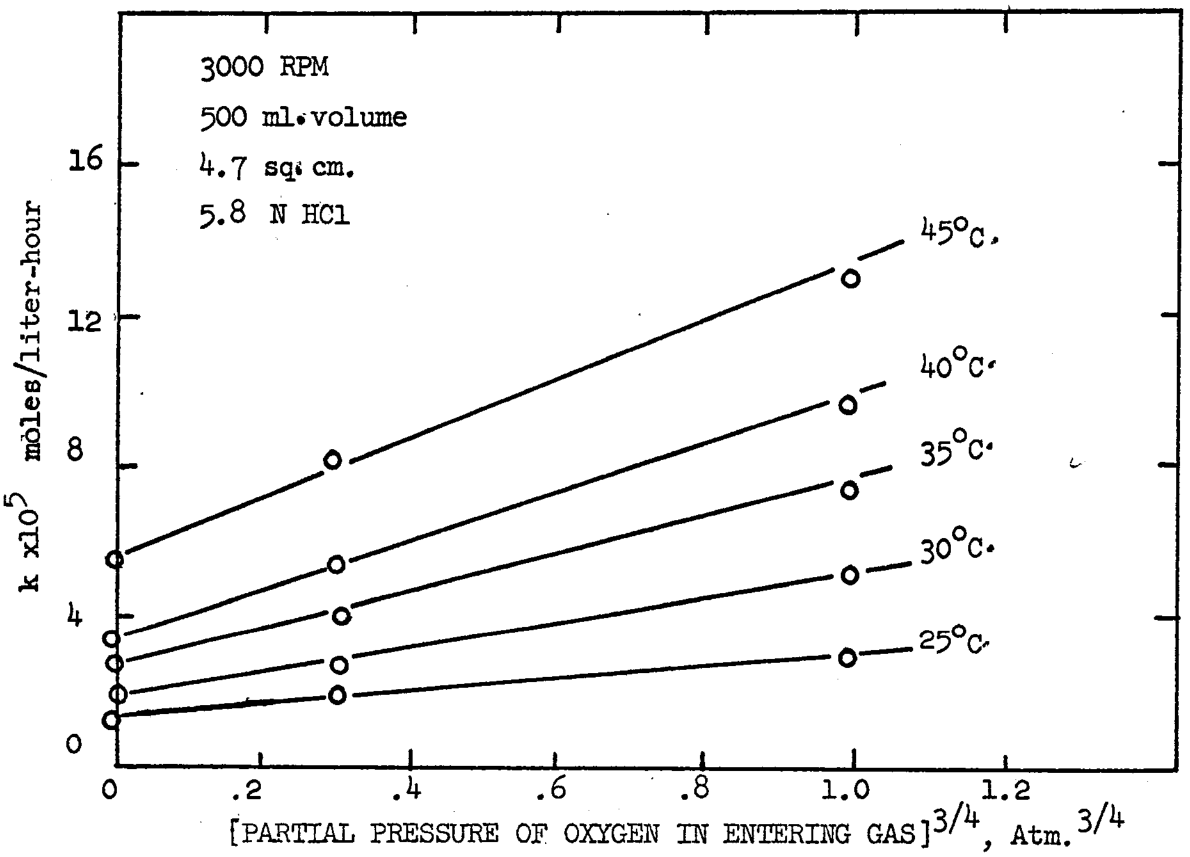


FIGURE 15-B. EFFECT OF OXYGEN ON DISSOLUTION RATE

An increase in rate according to equation (16) coupled with a simultaneous decrease in area could lead to a three quarter power dependence on oxygen.

J. Color of the Titanium Solutions During Dissolution

Initially all corroding solutions were colorless. Under nitrogen saturation only violet colored solutions were obtained thus indicating the presence of trivalent titanium as suggested by Straumanis and Chen[5]. According to equation (13):

$$TiH_2^{2+} + H^+ \longrightarrow Ti^{3+} + 3/2\ H_2 \tag{13}$$

When oxygen was introduced, with air or oxygen saturation, yellow colored solutions were produced. The intensity of this color increased with increasing titanium in solution. Straumanis and Chen[5] suggest that this yellow color is due to quadrivalent titanium ions produced by the oxidation of the trivalent titanium by virtue of the reaction:

$$4Ti^{3+} + 4H^+ + O_2 \longrightarrow 4Ti^{4+} + 2H_2O \tag{7}$$

The yellow color could be the result of complex formation between quadrivalent titanium ions and hydrogen peroxide. The peroxide could form in solution by a process such as:

$$TiH_2^{2+} + H^+ + O_2 \longrightarrow Ti^{4+} + H_2 + HO_2^- \tag{16}$$

$$H^+ + HO_2^- \rightleftharpoons H_2O_2 \tag{17}$$

$$H_2O_2 + Ti^{4+} \longrightarrow \text{titanium peroxy complex} \tag{18}$$

K. Effect of Longer Timed Runs on the Dissolution Rate

There was essentially no difference in the dissolution rate for 15 hours or for 56 hours as shown in Appendix 1X. Various concentrations (2.4, 4.8 and 5.8 N HCl) were used for this study.

L. Empirical Equation

The formation of a hydride film on a titanium surface immersed in hydrochloric acid solutions may be discussed in terms of

$$\mathrm{Ti} + \mathrm{H}^+ \overset{k_1}{\rightleftharpoons} \mathrm{TiH}^+ \qquad (11)$$

and

$$\mathrm{TiH}^+ + \mathrm{H}^+ \underset{k_3}{\overset{k_2}{\rightleftharpoons}} \mathrm{TiH}_2^{2+} \qquad (12)$$

If reactions (11) and (12) are fast, film formation should be completed well before any significant corrosion occurs. In practice a clean titanium surface is covered by the black film within one-half hour after immersion in an acid solution. The equilibria are probably set up in such a manner that 75 percent of the surface exists as TiH_2^{2+}. This woul correspond to the data of Gibb and Krushwitz[20] and Otsuka[17] who found that the hydride was essentially $\mathrm{TiH}_{1.73}$.

The removal of this film may occur in two ways, one involving oxygen and the other in the absence of oxygen according to the following steps:

$$\mathrm{TiH}_2^{2+} + \mathrm{H}^+ \xrightarrow{k_4} \mathrm{Ti}^{3+} + 3/2\,\mathrm{H}_2 \qquad (13)$$

$$\mathrm{TiH}_2^{2+} + \mathrm{H}^+ + \mathrm{O}_2 \xrightarrow{k_5} \mathrm{Ti}^{4+} + \mathrm{H}_2 + \mathrm{HO}_2^- \qquad (14)$$

In essence, the dissolution of titanium in hydrochloric acid is the dissolution of the film. First order dependency in hydrochloric acid is shown in Figure 9. The effect of area and oxygen are both to the 3/4 power, respectively, as shown in Figures 10-13. The reaction rate was inversely proportional to the volume of corroding solution as shown by Figure 11. The activation energy from the Arrhenius plot of Figure 14, was found to be 14.6 kcal. per gram mole for nitrogen, air, and oxygen saturation.

Since the dissolution rate of titanium is the dissolution of the film, the empirical rate equation can be written as:

$$\frac{d[Ti]}{dt} = \frac{A^{3/4}(N\ HCl)\ e^{-14.6x10^3/RT}}{V} \ (k_4 + k_5) \qquad (19)$$

where k_4 and k_5 have been determined from Figures 2-9 and found to be 1.50 $x10^4$ and 2.00 $x10^4$ (P_{O_2}) respectively, thus equation (19) can be written as

$$\frac{d[Ti]}{dt} = \frac{A^{3/4}(N\ HCl)\ e^{-14.6x10^3/RT}}{V} \ (1.50\ x10^4 + 2.00\ x10^4\ (P_{O_2}) \qquad (20)$$

This equation (20) is a valid correlation of experimental data over the range of conditions

1) Temperature : 25-45°C.
2) Hydrochloric acid concentrations: 2.4-5.8 N HCl
3) Volume: 400-600 ml.
4) Area: 3.86-6.66 cm^2.
5) Time: up to 56 hours
6) Partial Pressure of Oxygen: 0-1 atm.
7) Rotational Speeds: 3000-2500 r.p.m.

Table 2 procides a comparison of the experimental dissolution rates with those predicted by equation (20).

TABLE 2

Comparison of Experimental and Empirical Dissolution Rates

Temp. °C.	Gas	Acid Con.	Vol. ml.	Area cm^2	Exp. Rate $X10^5$	Emp. Rate $X10^5$	Deviation from Exp. Results
45	Air	5.8	500	4.7	8.2	8.1	- 1.2%
45	O	5.8	500	4.7	13.0	13.3	+ 2.3
45	N	5.8	500	4.7	5.5	5.7	+ 3.6
45	Air	5.8	600	4.7	7.1	6.8	- 5.6
45	Air	5.8	400	4.7	10.6	10.3	- 2.6
45	Air	5.8	500	3.86	6.9	6.9	0.0
45	Air	5.8	500	6.66	10.5	10.5	0.0
45	Air	5.8	500	5.70	9.3	9.4	+ 1.1
40	O	5.8	500	4.7	9.6	9.4	- 2.1
40	Air	5.8	500	4.7	5.4	5.6	+ 3.7
40	N	5.8	500	4.7	3.8	4.0	+ 5.3
35	O	5.8	500	4.7	6.7	6.6	- 1.5
35	N	5.8	500	4.7	3.3	2.8	-15.1
35	Air	5.8	500	4.7	3.8	4.0	+ 5.0
30	O	5.8	500	4.7	5.4	4.4	-18.5
30	N	5.8	500	4.7	1.9	1.9	0.0
30	Air	5.8	500	4.7	2.6	2.6	0.0
25	O	5.8	500	4.7	2.7	2.9	+ 7.4
25	Air	5.8	500	4.7	1.6	1.8	+12.5
25	N	5.8	500	4.7	1.3	1.3	0.0
45	O	4.8	500	4.7	11.0	11.0	0.0
45	N	4.8	500	4.7	4.6	4.7	+ 2.2
45	Air	4.8	500	4.7	6.5	6.6	+ 1.5
40	O	4.8	500	4.7	6.9	7.7	+11.5
40	N	4.8	500	4.7	3.4	3.3	- 2.9
40	Air	4.8	500	4.7	4.7	4.7	0.0
35	O	4.8	500	4.7	5.2	5.4	+ 3.8
35	Air	4.8	500	4.7	3.3	3.3	0.0
30	Air	4.8	500	4.7	2.3	2.2	- 4.3
25	Air	4.8	500	4.7	1.5	1.5	0.0
45	Air	3.6	500	4.7	4.9	5.0	+ 2.0
40	Air	3.6	500	4.7	3.6	3.6	0.0
35	Air	3.6	500	4.7	2.3	2.5	+ 8.6
45	Air	2.4	500	4.7	3.3	3.4	+ 3.0
40	Air	2.4	500	4.7	2.2	2.3	+ 4.5
					Average Deviation		± 4.0%

M. Effect of Higher Acid Concentration on the Dissolution Rate

At higher acid concentrations, (6.3 and 8.4N HCl), there seems to be some evidence of an autocatalytic mechanism as shown in Figure 16 and in Appendix 10. It was found during the analysis of titanium solutions with peroxide that with 6.3 and 8.4N HCl solutions the yellow titanium peroxy complex was not stable. This instability of the titanium peroxy complex in high acid may provide free quadrivalent titanium ions in solution. The quadrivalent titanium ions could initiate an autocatalytic mechanism such as:

$$TiH_2^{2+} + 3Ti^{4+} \rightleftarrows 4Ti^{+++} + 2H^+ \qquad (21)$$

This equation is a slight modification of the reaction suggested by Straumanis and Chen[5]:

$$3Ti^{4+} + Ti \rightleftarrows 4Ti^{3+} \qquad (8)$$

Their reaction is highly improbable if the titanium surface is covered with hydride film.

At higher acid concentrations two dissolution mechanisms are possible:

1) simple hydrogen evolution according to these equations (13) and (14)

$$TiH_2^{2+} + H^+ \longrightarrow Ti^{3+} + 3/2\ H_2 \qquad (13)$$

$$TiH_2^{2+} + H^+ + O_2 \rightleftarrows Ti^{4+} + H_2 + HO_2^- \qquad (14)$$

2) an autocatalytic mechanims involving free quadrivalent titanium ions

$$TiH_2^{2+} + 3Ti^{4+} \rightleftarrows 4Ti^{3+} + 2H^+ \qquad (21)$$

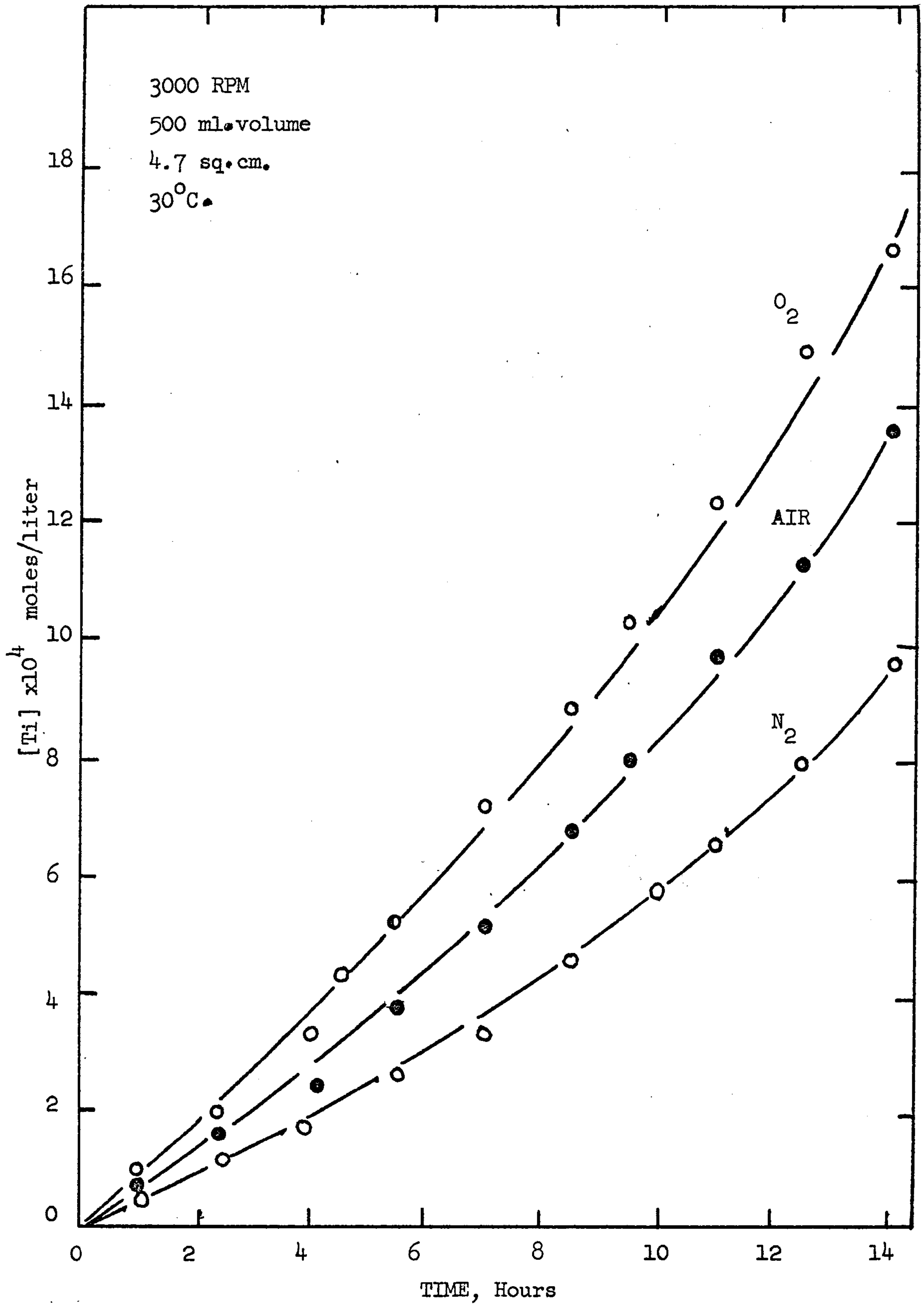


FIGURE 16. DISSOLUTION OF TITANIUM IN 8.4 N HCl

The rate equation in higher acids might be represented as

$$\frac{d[Ti]}{dt} = a' + b(Ti)^{3/4} \tag{22}$$

where

$$a = \frac{A^{3/4}}{V}[NHCl]\, e^{-\frac{14.65 \times 10^{-3}}{RT}} \left(1.50 \times 10^{-4} + 2.00 \times 10^{-4}(P_{O_2})^{.75}\right)$$

and b is some function of area, volume, oxygen concentration, concentration of acid, and temperature.

The three quarter power was chosen because a plot of log d[Ti]/dt versus [Ti] yields a linear relationship with a slope of 0.75. The three quarter power is also suggested by equation (21).

The constant a, in air saturation solutions, can be determined from Figure 11 by extrapolation to the higher acid concentrations and b can be evaluated from slopes on the experimental curves. Table 3 shows a limited investigation of the values of a and b in higher acids.

TABLE 3

Constants for Equation (22)

Concn. of Acid	a	b	Temperature
6.3	4.3×10^{-5}	1×10^{-3}	35°C.
6.3	8.9×10^{-5}	1.2×10^{-3}	45
8.4	4.2×10^{-5}	1.3×10^{-3}	30
8.4	8.0×10^{-5}	1.5×10^{-3}	35

Figures 17 show a plot of the experimental data and that predicted by using the constants provided in Table 3 in the integrated form of equation (22).

Further work must be done on this autocatalytic process before it can be completely appreciated.

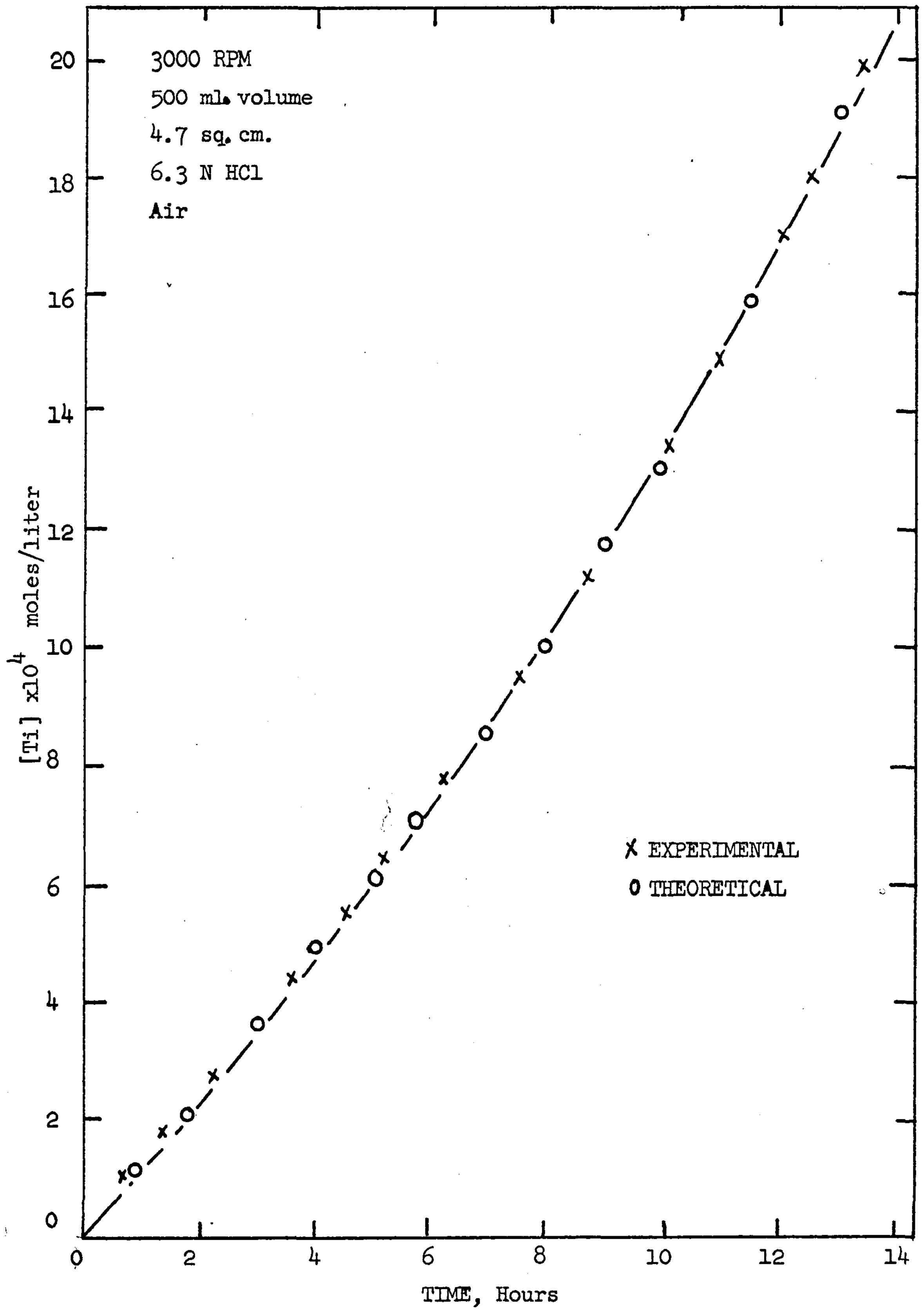


FIGURE 17. EMPIRICAL AND EXPERIMENTAL COMPARISION

CHAPTER V

Conclusion

There seems little doubt that the dissolution rate of any metal will depend upon experimental conditions. Simple immersion of a sample in the dissolving medium will, in general, result in a diffusion controlled mechanism. To eliminate physical control and to remove any boundary layer the sample or solution must be moved. For titanium, rotation of the sample at 3000 rpm seems to remove all traces of diffusional control. The high activation energy, 14.6 kcal. per gram mole, suggests that the dissolution is truly a chemically controlled process.

For dissolution periods up to 56 hours and hydrochloric acid concentrations up to 5.8N (19%) the dissolution rate is zero order with respect to titanium dissolved in solution, first order in acid concentration, 3/4 order with respect to surface area, and inversely proportional to the volume of solution. Oxygen in the solution accelerates the corrosion over the range of conditions studied.

A film formation was noted, and this film was believed to be a mixture of TiH and TiH_2 with approximately 75% TiH_2.

The mechanism presented agrees with observations of Straumanis and Chen[5,10] but also takes into consideration the film formation which many investigators report[16-19]. Since the dissolution of the film is, in essence, the dissolution of titanium, the mechanism presented seems to be a much clearer approach than that of Straumanis and Chen.

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APPENDIX I

Analysis of Titanium Photometrically

A Bausch and Lomb Spectronic 20 Colorimeter was used for the analysis of titanium in the corroding solution. A modification of the hydrogen peroxide method as presecibed by Neal[23] was developed for this study.

A stock solution of 3×10^{-3} M titanium was prepared by dissolving titanium shavings in 5 N hydrochloric acid. Standard solutions were prepared by diluting the stock with hydrochloric acid.

The calibration curve is based on the addition of 1 ml. of (10-15 percent) hydrogen peroxide to 5 ml. of standard titanium solution in a 1/2 inch Spectronic 20 test tube. (see Figure 18) The concentration of the hydrogen peroxide was not critical as long as there was an excess of peroxide with respect to titanium in solution. The intensity of the color was measured by means of the Spectronic 20 at a wavelength of 410 mμ with a blank solution of hydrochloric acid being chosen as 100 percent transmission. At this wavelength, 410 mμ. the maximum absorbance occurs as reported by other investigators[23-25], and also found by the author.

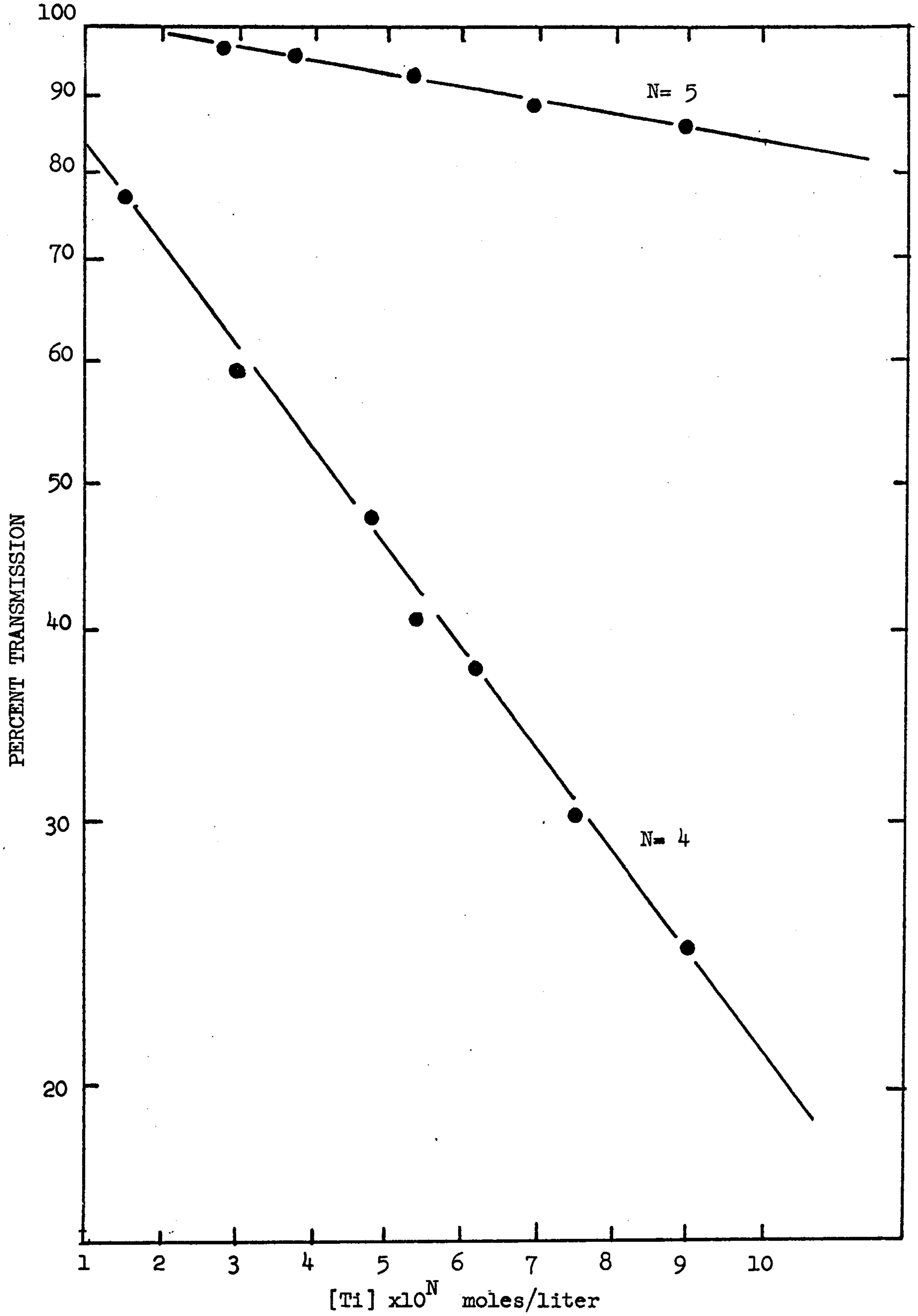

FIGURE 18. CALIBRATION CURVE

APPENDIX II

5.8 N HCl Dissolution Runs
3,000 rpm
4.7 sq. cm.
500 ml. volume

Run 1 - 45°C, Air		Run 2 - 45°C, Air		Run 3 - 45°C, O_2		Run 4 - 45°C, O_2	
Time (hour)	Concn mol/1.	Time (hour)	Concn mol/1.	Time (hour)	Concn mol/1.	Time (hour)	Concn mol/1.
0	0.00×10^{-4}	0	0.00×10^{-4}	0	0.00×10^{-4}	0	0.00×10^{-4}
1.0	1.05	1.0	1.30	1.0	1.45	1.0	1.05
2.5	2.35	2.5	2.30	2.0	2.70	2.5	2.70
3.5	3.00	3.5	2.90	3.0	3.95	4.0	4.30
5.0	4.25	5.0	4.00	4.0	5.15	5.5	6.00
6.0	5.10	6.0	4.80	5.5	7.20	7.0	8.15
7.5	6.35	7.5	5.90	6.5	8.65	8.5	10.25
8.5	7.40	8.5	6.60	7.5	9.40	9.5	11.62
10.0	8.30	10.0	7.40	8.5	10.50	11.0	14.45
11.5	9.30	11.5	8.10	10.0	12.90	12.0	15.50
13.0	10.60	13.0	10.05	11.0	13.80	13.0	17.40
14.0	11.90	14.0	11.40	13.5	17.10	14.0	19.40
				14.5	19.20		

Time (hour)	Concn. mol/l.	Time (hour)	Concn. mol/l.	Time (hour)	Concn. mol/l.	Time (hour)	Concn. mol/l.
Run 5 - 45°C, N_2		Run 6 - 40°C, Air		Run 7 - 40°C, O_2		Run 8 - 40°C, O_2	
2.0	1.30×10^{-4}	1.0	0.56×10^{-4}	1.0	1.10×10^{-4}	1.0	1.00×10^{-4}
3.0	1.85	2.0	0.88	2.0	2.10	2.0	1.90
4.0	2.40	3.0	1.34	3.5	3.50	3.0	2.80
5.5	3.20	4.0	1.75	5.0	4.60	4.0	3.70
6.5	3.80	5.5	2.10	6.5	6.40	5.5	5.10
7.5	4.25	7.0	3.60	8.0	8.00	6.5	6.10
8.5	4.50	8.0	4.20	9.0	8.70	7.5	7.30
10.00	5.40	9.0	4.80	10.5	10.00	8.5	8.00
11.0	5.90	10.0	5.40	11.5	10.80	9.0	9.40
12.5	6.60	11.0	6.00	12.5	12.20	11.0	10.80
13.5	7.00	12.5	7.00	13.5	13.50	12.5	12.40
14.5	7.50	13.5	7.30	14.5	14.20	14.0	14.00
		14.5	8.30				
Run 9 - 40°C, N_2		Run 10 - 35°C, Air		Run 11 - 35°C, O_2		Run 12 - 35°C, N_2	
1.0	0.41×10^{-4}	1.5	0.55×10^{-4}	1.5	1.40×10^{-4}	1.5	0.40×10^{-4}
2.5	1.00	3.0	1.10	3.0	2.35	3.0	0.85
4.0	1.60	4.0	1.55	4.0	3.20	4.0	1.20
5.5	2.10	5.0	1.90	5.0	3.90	5.0	1.40
7.0	2.70	6.5	2.40	6.5	4.80	6.5	1.90
8.5	3.30	8.0	3.10	8.0	6.00	8.0	2.40
10.0	3.80	9.5	3.60	9.5	7.10	9.5	2.80
11.5	4.30	10.5	4.10	10.5	7.60	10.5	2.90
13.0	4.90	12.0	4.60	12.0	8.50	12.0	3.40
14.0	5.30	13.5	5.20	13.5	9.85	13.5	3.80
		14.5	5.70	14.5	10.40	14.5	4.20

Time (hour)	Concn. mol/1.	Time (hour)	Concn. mol/1.	Time (hour)	Concn. mol/1.	Time (hour)	Concn. mol/1.
Run 13 - 30^{o}C, Air		Run 14 - 30^{o}C, O_2		Run 15 - 30^{o}C, N_2		Run 16 - 25^{o}C, Air	
1.0	0.38 X 10^{-4}	1.0	0.38 X 10^{-4}	1.0	0.32 X 10^{-4}	1.0	0.28 X 10^{-4}
2.5	0.80	2.0	0.96	2.5	0.62	2.5	0.40
4.0	1.00	3.5	1.65	4.0	0.80	4.0	0.65
5.5	1.35	5.0	2.50	5.5	1.20	5.5	0.88
7.0	1.80	6.0	3.10	7.0	1.60	6.5	0.96
8.5	2.15	7.5	4.10	8.5	1.80	8.0	1.10
10.0	2.55	8.5	4.45	10.0	2.00	9.5	1.30
11.5	2.85	10.0	5.40	11.5	2.40	11.5	1.65
13.0	3.30	11.5	6.00	13.0	2.55	13.0	2.05
14.5	3.85	13.0	7.00	14.5	2.90	14.5	2.35
		14.0	7.40			16.0	2.55
Run 17 - 25^{o}C, O_2		Run 18 - 25^{o}C, N_2					
1.0	0.25 X 10^{-4}	2.0	0.30 X 10^{-4}				
2.5	0.88	4.0	0.60				
4.0	1.10	6.0	0.90				
5.5	1.60	8.0	1.30				
6.5	1.80	10.0	1.50				
8.0	2.20	12.0	1.90				
9.5	2.70	14.0	2.10				
11.5	3.30	16.0	2.45				
13.0	3.60						
14.5	4.10						
16.0	4.45						

APPENDIX III

4.8 N HCl Dissolution Runs
3,000 rpm
4.7 sq cm
500 ml volume

Run 19 - 45°C., Air		Run 20 - 45°C., O_2		Run 21 - 45°C., N_2		Run 22 - 40°C.; Air	
Time (hour)	Concn. mol/l.	Time (hour)	Concn. mol/l.	Time (hour)	Concn. mol/l.	Time (hour)	Concn. mol/l.
0	0.00×10^{-4}	0	0.00×10^{-4}	0	0.00×10^{-4}	0	0.00×10^{-4}
1.0	0.72	1.0	1.05	1.0	0.59	1.0	0.62
2.0	1.40	2.0	2.10	2.0	1.00	2.0	0.96
3.0	1.70	3.0	3.15	3.0	1.50	3.0	1.70
4.0	2.40	4.0	4.20	4.0	2.00	4.0	2.10
5.5	3.50	5.5	6.20	5.0	2.50	5.0	2.45
6.5	4.15	6.5	7.20	7.0	3.50	6.0	2.80
8.0	5.40	7.5	8.30	8.0	3.85	7.0	3.50
9.5	6.25	8.5	8.90	9.0	4.30	8.0	3.90
11.0	7.00	10.0	11.00	10.0	4.90	10.0	5.00
12.5	8.00	11.0	12.20	13.0	5.80	11.0	5.25
13.5	8.50	12.5	13.90	14.0	6.40	12.0	5.70
14.5	8.90	13.5	15.60	15.0	6.80	13.0	6.05
		14.5	16.70			14.0	6.50
						15.0	6.89

Time (hour	Concn. mol/1.	Time (hour)	Concn. mol/1.	Time (hour)	Concn. mol/1.	Time (hour)	Concn. mol/1.
Run 23 - 40°C, Air		Run 24 - 40°C, O_2		Run 25 - 40°C, O_2		Run 26 - 40°C, N_2	
1.0	0.66 X 10^{-4}	1.0	0.86 X 10^{-4}	1.0	0.48 X 10^{-4}	1.0	0.48 X 10^{-4}
2.0	1.00	2.0	1.40	2.0	1.10	2.0	0.88
3.0	1.50	3.5	2.40	3.0	1.85	3.0	1.20
4.0	2.18	5.0	3.50	5.0	3.30	5.0	1.85
5.0	2.50	6.5	4.60	7.0	4.70	6.0	2.15
6.0	3.18	8.0	5.60	8.0	5.40	7.0	2.50
7.0	3.60	9.0	6.25	9.0	6.20	8.0	2.65
8.0	4.10	10.5	7.00	11.0	7.40	9.0	3.00
10.0	5.40	11.5	8.00	12.0	8.25	11.0	3.60
11.0	5.90	12.5	8.60	13.0	8.85	12.0	3.75
12.0	6.35	13.5	9.20	14.0	9.30	13.0	4.00
13.0	6.70	14.5	9.80	15.0	9.85	14.0	4.25
14.0	7.10						
15.0	7.65						
Run 27 - 35°C, Air		Run 28 - 35°C, O_2		Run 29 - 30°C, Air		Run 30 - 30°C, Air	
2.0	0.80 X 10^{-4}	1.0	0.93 X 10^{-4}	2.0	0.58 X 10^{-4}	2.0	0.59 X 10^{-4}
3.0	1.10	2.0	0.98	5.0	1.20	3.0	0.75
5.0	1.75	3.0	1.50	6.0	1.45	5.0	1.10
7.0	2.40	4.0	2.10	7.0	1.60	6.0	1.40
8.0	2.75	6.0	3.20	8.0	1.85	7.0	1.60
10.0	3.30	7.0	3.75	11.0	2.50	8.0	1.85
11.0	3.70	8.0	4.30	12.0	2.90	11.0	2.62
14.0	4.60	9.0	4.80	14.0	3.20	12.0	2.90
15.0	4.90	10.0	5.15	15.0	3.50	14.0	3.20
		12.0	6.40			15.0	3.45
		13.0	6.80				

Time (hour)	Concn. mol/1.	Time (hour)	Concn. mol/1.
Run 31 - 25°C, Air		Run 32 - 25°C, Air	
2.0	0.20×10^{-4}	2.0	0.32×10^{-4}
4.0	0.58	3.0	0.56
6.0	0.96	5.0	0.96
7.0	1.10	6.0	1.05
8.0	1.20	7.0	1.15
10.0	1.50	8.0	1.30
11.0	1.65	11.0	1.90
14.0	2.15	12.0	2.00
15.0	2.60	14.0	2.30
		15.0	2.45

APPENDIX IV

3.6 N HCl Dissolution Rates
3,000 rpm
4.7 sq. cm.
500 ml. volume

Run 33 - 45°C, Air		Run 34 - 40°C; Air		Run 35 - 35°C; Air	
Time (hour)	Concn. mol/1.	Time (hour)	Concn. mol/1.	Time (hour)	Concn. mol/1.
0	0.00×10^{-4}	0	0.00×10^{-4}	0	0.00×10^{-4}
1.0	0.44	1.0	0.32	1.5	0.30
2.0	0.84	2.5	0.92	3.0	0.50
3.0	1.05	3.5	1.10	4.0	0.80
4.0	1.75	4.5	1.50	6.0	1.10
5.5	2.55	6.0	2.10	7.5	1.50
7.0	3.40	7.5	2.65	8.5	1.80
8.0	3.80	9.0	3.10	9.5	2.10
9.0	4.30	10.0	3.50	11.0	2.45
10.0	4.85	11.5	4.10	12.0	2.85
11.0	5.40	13.0	4.75	13.5	3.20
12.5	6.30	14.0	5.15	15.0	3.50
13.5	7.00				
14.0	7.20				

APPENDIX V

2.4N HCl Dissolution Runs
3,000 rpm
4.7 sq.cm.
500 ml. volume

Run 36 - 45°C., Air		Run 37 - 40°C., Air	
Time (hour)	Concn. mol/l.	Time (hour)	Concn. mol/l.
0	0.00×10^{-4}	0	0.00×10^{-4}
1.0	0.30	1.0	0.27
2.0	0.60	2.0	0.55
3.0	0.90	3.0	0.77
4.0	1.30	4.0	0.85
5.5	1.80	5.0	1.20
7.0	2.30	6.0	1.50
8.0	2.60	8.0	1.80
9.0	2.90	10.0	2.25
10.5	3.50	11.0	2.45
11.5	3.70	12.0	2.75
12.5	4.10	13.0	2.95
14.0	4.50	14.0	3.15
		15.0	3.40

APPENDIX VI

Effect of Area on Dissolution Rate

3,000 rpm
5.8 N HCl
500 ml. volume
45°C.

Run 38 - 3.86 cm^2. Air		Run 39 - 4.7 cm^2. Air		Run 40 - 5.7 cm^2. Air		Run 41 - 6.66 cm^2. Air	
Time (hour)	Concn mol/1.	Time (hour)	Concn. mol/1.	Time (hour)	Concn. mol/1.	Time (hour)	Concn. mol/1.
0	0.00×10^{-4}	0	0.00×10^{-4}	0	0.00×10^{-4}	0	0.00×10^{-4}
1.0	0.80	1.0	1.05	1.0	1.00	1.0	1.10
2.5	1.80	2.5	2.35	2.0	2.00	2.0	2.10
4.0	2.80	3.5	3.00	3.5	3.20	3.5	3.60
6.0	4.40	5.0	4.25	5.0	4.60	5.0	5.20
7.0	5.20	6.0	5.10	6.5	5.80	6.5	6.60
8.0	5.60	7.5	6.35	8.0	7.60	7.5	7.50
9.5	6.50	8.5	7.40	9.0	8.20	9.0	9.20
11.0	7.60	10.0	8.30	10.0	9.20	10.0	10.30
13.0	9.00	11.5	9.30	11.5	10.60	11.5	11.80
14.0	9.60	13.0	10.60	13.0	12.00	13.0	13.20
		14.0	11.90	14.0	12.85	14.0	14.20

Run 38N - 3.86 cm^2 N_2		Run 39N - 4.7 cm^2 N_2		Run 40N - 5.7 cm^2 N_2	
1.0	0.58×10^{-4}	2.0	1.30×10^{-4}	1.0	1.00×10^{-4}
3.0	1.50	3.0	1.85	3.0	1.90
4.0	1.96	4.0	2.40	4.0	2.80
8.0	3.90	5.5	3.20	8.0	5.20
9.0	4.35	6.5	3.80	9.0	5.35
10.0	4.85	7.5	4.25	10.0	6.40
11.0	5.30	8.5	4.50	11.0	7.10
12.0	5.75	10.0	5.40	12.0	7.65
		11.0	5.90		
		12.5	6.60		
		13.5	7.00		
		14.5	7.50		

APPENDIX VII

Effect of Volume on Dissolution Rate

3000 rpm
4.7 sq.cm.
5.8 N HCl
Air

Run 42 - 400 ml.vol.		Run 43 - 500 ml.vol		Run 44 - 600 ml.vol.		Run 45 - 400 ml.vol	
Time (hour)	Concn. mol/l.	Time (hour)	Concn. mol/l.	Time (hour)	Concn. mol/l.	Time (hour)	Concn. mol/l.
0	0.00×10^{-4}	0	0.00×10^{-4}	0	0.00×10^{-4}	0	0.00×10^{-4}
1.5	2.10	1.0	1.05	1.0	0.88	1.5	2.20
2.5	3.20	2.5	2.35	2.5	2.00	2.5	3.00
4.0	4.50	3.5	3.00	3.5	2.70	4.0	4.50
5.5	6.05	5.0	4.25	4.5	3.33	5.5	5.90
6.5	7.00	6.0	5.10	6.0	4.30	6.5	6.70
7.5	7.90	7.5	6.35	7.5	5.20	7.5	7.60
9.0	9.00	8.5	7.40	9.0	6.33	9.0	8.40
10.5	10.90	10.0	8.30	10.5	7.25	10.5	10.35
11.5	12.20	11.5	9.30	11.5	8.33	11.5	11.40
13.0	13.90	13.0	10.60	14.0	9.66	13.0	13.35
14.0	14.90	14.0	11.90			14.0	14.75

APPENDIX VIII

Effect of Rotational Speed on Dissolution Rate

500 ml·volume
4.8 N HCl
4.7 sq.·cm.
40°C.
Air

Run 46 - 3000 rpm Time (hour)	 Concn. mol/l.	Run 47 - 8000 rpm Time (hour)	 Concn. mol/l.	Run 48 - 0 rpm Time (hour)	 Concn. mol/l.	Run 49 - 15000 rpm Time (hour)	 Concn. mol/l.
0	0.00 X 10^{-4}	0	0.00 X 10^{-4}	0	0.00 X 10^{-4}	0	0.00 X 10^{-4}
1.0	0.62	1.0	0.62	2.0	0.865	1.0	0.50
2.0	0.96	2.0	1.00	3.0	1.24	4.0	1.70
3.0	1.70	3.0	1.40	5.0	1.85	5.0	2.25
4.0	2.10	4.0	2.00	7.0	2.50	6.0	2.50
5.0	2.45	5.0	2.40	9.0	3.10	7.0	3.00
6.0	2.80	6.0	2.75	20.0	6.90	10.0	4.70
7.0	3.50	7.0	3.55	21.0	7.20		
8.0	3.90			22.0	7.40		
10.0	5.00			24.0	7.80		
11.0	5.25			26.0	8.70		
12.0	5.70			29.0	9.60		
13.0	6.05			31.0	10.50		
14.0	6.50			33.0	10.80		
15.0	6.89			44.0	16.00		
				45.0	16.70		
				48.0	18.00		

Run 50 - 25000 rpm	
1.0	0.50 X 10^{-4}
2.0	1.00
4.0	2.00
6.0	3.00
8.0	4.1
10.0	5.0
11.0	5.6
13.0	6.4
15.0	7.4

APPENDIX IX

Longer Timed Runs
3,000 rpm
4.7 sq. cm.
500 ml. volume
40°C.

Run 51 - 2.4 *N* HCl		Run 52 - 4.8 *N* HCl		Run 53 - 5.8 *N* HCl	
Time (hour)	Concn. mol/1.	Time (hour)	Concn. mol/1.	Time (hour)	Concn. mol/1.
0	0.00×10^{-4}	0	0.00×10^{-4}	0	0.00×10^{-4}
1.0	0.27	1.0	0.48	2.0	1.10
2.0	0.55	2.0	1.00	4.0	2.30
3.0	0.77	3.0	1.50	6.0	3.40
4.0	0.85	5.0	2.45	8.0	4.50
5.0	1.20	7.0	3.45	10.0	5.55
6.0	1.50	9.0	4.45	11.0	6.20
8.0	1.80	10.0	4.85	13.0	7.30
10.0	2.25	11.0	5.30	15.0	8.40
11.0	2.45	13.0	6.30	25.0	13.75
12.0	2.75	20.0	9.60	27.0	14.90
13.0	2.95	22.0	10.60	29.0	16.00
14.0	3.15	24.0	11.50	32.0	17.55
15.0	3.40	29.0	13.00	35.0	19.20
24.0	6.10	32.0	15.80	37.0	20.75
26.0	6.25	40.0	19.50	47.0	36.25
29.0	7.20	42.0	20.50	49.0	37.80
32.0	7.90	50.0	24.50	50.0	39.40
35.0	8.80	52.0	25.90		
37.0	9.30	55.0	27.20		
		56.0	27.80		

APPENDIX X

Effect of 6.3N and 8.4N HCl
3,000 rpm
500 ml. volume

Run 54 45°C, 6.3N HCl, Air		Run 55 45°C, 6.3N HCl, O_2		Run 56 45°C, 6.3N HCl, N_2		Run 57 45°C, 8.4N HCl, Air	
Time (hour)	Concn. mol/1.	Time (hour)	Concn. mol/1.	Time (hour)	Concn. mol/1.	Time (hour)	Concn. mol/1.
0	0.00 X 10^{-4}	0	0.00 X 10^{-4}	0	0.00 X 10^{-4}	0	0.00 X 10^{-4}
1.0	1.30	1.0	1.60	1.0	1.24	1.0	0.88
2.0	2.00	2.0	2.20	2.0	2.00	2.5	1.68
3.0	3.50	3.0	4.20	3.0	2.80	4.0	2.20
4.0	4.70	4.0	5.80	4.0	3.50	5.5	3.80
5.0	5.70	5.5	8.60	5.5	4.70	7.0	5.20
7.0	8.60	6.0	9.00	7.0	6.60	8.5	6.80
8.0	10.00	7.0	11.40	8.0	6.80	9.5	8.00
9.0	11.80	8.0	13.20	9.0	8.00	11.0	9.80
10.0	13.20	9.0	15.30	10.5	9.80	12.5	11.40
11.5	15.85	10.0	17.70	11.5	10.00	14.0	13.60
13.0	19.10	11.0	20.10	12.5	12.30		
14.0	22.20	12.5	24.00	13.5	14.40		
15.0	24.50	13.5	26.40	14.0	14.80		
		14.0	27.40				

Run 58		Run 59		Run 60		Run 61	
30°C, 8.4 N HCl, O_2		30°C, 8.4 N HCl, N_2		35°C, 6.3 N HCl, Air		35°C, 8.4 N HCl, Air	
Time (hour)	Concn. mol/l.	Time (hour)	Concn. mol/l.	Time (hour)	Concn. mol/l.	Time (hour)	Concn. mol/l.
1.0	0.86×10^{-4}	1.0	0.68×10^{-4}	1.0	0.64×10^{-4}	1.0	1.38×10^{-4}
2.5	1.98	2.5	1.48	2.0	1.12	2.0	2.00
4.0	3.30	4.0	1.92	3.0	1.50	3.0	3.40
5.5	5.30	5.5	2.60	4.0	1.80	4.0	4.50
7.0	7.20	7.0	3.40	5.0	2.00	5.0	5.80
8.5	8.90	8.5	4.60	6.0	2.50	6.0	7.30
9.5	10.30	9.5	5.10	7.5	3.00	7.5	9.60
11.0	12.40	11.0	6.55	8.5	3.60	8.5	11.40
12.5	15.00	12.5	8.00	9.5	4.00	9.5	13.0
14.0	16.65	14.0	9.65	11.0	4.60	11.0	15.6
				12.0	5.00	12.0	17.8
				13.5	5.80	13.5	20.1
				15.0	7.10	15.0	22.5

APPENDIX XI

Typical Analyses of High Purity Research Titanium Supplied by Titanium Metal Corps. of America

Hardness

63-68 Bhn

Chemical Analyses

Element	Percent
O	0.005 to 0.020
Fe	0.003 to 0.007
N	< 0.001
H	0.003
C	0.01 to 0.02

Spectrographic Analyses

Element	Percent
Cr	0.019
Mo	0.004
Al	0.01
V	0.014
Mn	0.008
Mg	0.002
Ni	0.005
Cu	0.004
Zn	< 0.001
B	< 0.001

VITA AUCTORIS

1941	Born in Sandusky, Ohio, U.S.A.
1955	Completed grade school in St. Mary School, Sandusky, Ohio.
1959	Completed high school in St. Mary School, Sandusky, Ohio.
1963	Received the Degree of Bachelor of Science in Chemical Engineering from the University of Dayton, Dayton, Ohio.
1964	Currently, a candidate for the Degree of Master of Applied Science in Chemical Engineering at the University of Windsor, Windsor, Ontario, Canada.