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DISSOLUTION OF IRON IN HYDROCHLORIC ACID

A Thesis
Submitted to the Faculty of Graduate Studies Through the
Department of Chemical Engineering in Partial Fulfilment
of the Requirements for the Degree of
Master of Applied Science at the
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by

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177160

ABSTRACT

The kinetics of polycrystalline iron dissolution in nitrogen, air and oxygen saturated hydrochloric acid (2.4 - 5.37 N) solutions have been investigated. Cylindrical samples of 0.47 inches in diameter were rotated at speeds up to 11,000 r.p.m.

The reaction is half-order with respect to the total iron concentration in oxygenated and zero-order in oxygen-free hydrochloric acid solutions. An Arrhenius activation energy of 9.4 kcal per gram mole was evaluated for the temperature range 26° - 45°C.

The dissolution rate in moles of iron dissolved per litre per hour may be expressed by the empirical rate equation:

$$\frac{d(Fe)}{dt} = \frac{(A)^{3/4}}{V}(HCl)\left(\exp\left(-\frac{9400}{RT}\right)\right)\left[13.1 + 1.18 \times 10^{4}(P_{O_2})^{0.5}(Fe)^{0.5}\right]$$

ACKNOWLEDGEMENTS

With great pleasure, I wish to express my sincere gratitude to Dr. A. W. Gnyp for his valuable guidance and constructive criticism, to Armco Steel Corporation, Ohio, U.S.A., for supplying the analysis of iron, to Mr. Halil Parlar for machining the iron samples and to a host of friends for moral support.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

(Fe)	Total iron concentration, moles/litre
$\frac{d(Fe)}{dt}$	Rate of iron dissolution, moles/litre-hour
A	Superficial surface area of specimen, sq.cm.
V	Volume of corroding solution, litres
(HCl)	Normality of hydrochloric acid
T	Temperature, K^o
P_{O_2}	Partial Pressure of oxygen, atm.
k_o	Zero order rate constant
$k_{\frac{1}{2}}$	Half order rate constant
t	Time, hours
s	Surface
b	Bulk
i	Interface
(i-b)	Interface or bulk
R.P.M.	Revolutions per minute
K_1, K_2	Empirical rate constants

CHAPTER I

INTRODUCTION

The wastage of metals by corrosion is still a challenging engineering problem. The fact that millions of dollars are being spent every year to mitigate such losses indicates that corrosion control is hardly a reality. Considerable work still needs to be done on the clarification of the kinetics and mechanisms by which metals are destroyed before any effective measures of control may be developed.

Copper (1,2) and tin (5,6) have been subjected to fundamental investigations. It has been shown that over a wide range of conditions, the dissolution of these metals is an autocatalytic process. Naturally it becomes important and interesting to determine whether other metals capable of existing in two or more oxidation states show similar autocatalytic behaviour.

Iron was chosen for the present investigations because it can exist as Fe^{++} and Fe^{+++}. It was felt that the dissolution of iron by simple hydrogen displacement in air-free solutions would be the same as that of tin and titanium because all the three metals can liberate hydrogen by virtue of their positions in the electromotive series as shown in table 1-1.

TABLE 1-1

PARTIAL ELECTROMOTIVE SERIES

Ti	$\longrightarrow$	$Ti^{++} + 2e^-$	+1.63 Volts
Fe	$\longrightarrow$	$Fe^{++} + 2e^-$	+0.44 Volts
Sn	$\longrightarrow$	$Sn^{++} + 2e^-$	+0.136 Volts
H_2	$\longrightarrow$	$2H^+ + 2e^-$	0.00 Volts

Metals, because of their valuable physical properties of strength and durability, are still the most important materials of construction. Therefore it is important that a thorough knowledge of their corrosion characteristics be obtained. In spite of the considerable contributions made in the past, there is still a need for further investigation.

The object of this thesis is to study the corrosion of iron in hydrochloric acid from the kinetic point of view with the hope of providing a more quantitative knowledge of the variables affecting the corrosion rates of metals in general.

CHAPTER II

LITERATURE REVIEW

Considerable work has been done on the study of the corrosion of copper and tin but comparatively little work has been done on the corrosion study of iron in hydrochloric acid. It will be desirable to review briefly some of the results of the earlier investigators on other metals.

A. Copper Dissolution

Lu and Graydon (1,2) were concerned with the corrosion of copper in aquous ammonium hydroxide and aquous sulphuric acid solutions. Weeks and Hills (3) studied the initial corrosion kinetics in hydrochloric acid solutions and the same work was extended by Gnyp (4).

B. Tin Dissolution

Ammar and Riad (5) investigated the rate of corrosion and corrosion potential of tin in 8 different acid, alkaline and neutral solutions. A kinetic study of tin dissolution has been made by Lui (6) who rotated cylindrical specimens in air saturated hydrochloric acid solutions.

C. Titanium Dissolution

The first useful results on the corrosion of titanium in acids were reported by Gee and Golden (7). Bodner (8) studied the kinetics of titanium dissolution in nitrogen, air and oxygen saturated solutions of hydrochloric acid (2.4 - 5.8 N).

It has been shown that the dissolution of these metals under appropriate conditions is an autocatalytic process, with the dissolution rate increasing with increasing metal ion concentration in the solution.

D. Corrosion Review of Iron

1. Action of Mineral Acids on Iron

The rates of dissolution of iron in hydrochloric acid, sulphuric acid and nitric acid were determined by Schchikow (9) at concentrations ranging from 1 to 10 N. He found that the rate of dissolution in nitric acid was comparatively greater than in hydrochloric and sulphuric acids. Diffusion of cathodically evolved hydrogen was more intense in sulphuric and hydrochloric acids and was not absorbed at all by iron in nitric acid.

Hudson (10) made a study of the relationship between the dissolution rate and hydrogen absorption by steel as a function of acid selected and of acid concentration. The study was made by immersing 2 in. x 3/8 in. coupons for various times in sulphuric, nitric, phosphoric and hydrochloric acids. Results have been reported at 100°, 149° and 194°F in 0.05, 0.5, 2 and 10 N acid concentrations. The weight loss at different time intervals was used as a measure of corrosion and hydrogen content in the steel was determined by the warm extraction method (11) in which steel specimens were placed in specially constructed borosilicate extractors and heated for 16 hours at 160°C under mercury. Hydrogen extracted from the steel by this method was collected over mercury and measured volumetrically.

Hudson concluded that the rates of dissolution of steel in 2 N and 10 N solutions of nitric acid at 100°C were much greater than in other acids of the same concentrations. The rates of dissolution in 0.05 N and 0.5 N sulphuric acid were higher than in hydrochloric acid, but in 10 N solutions the opposite was true. The amount of hydrogen absorbed by steel during dissolution in nitric acid was much lower than for the other acids.

Podesta and Arvia (12) also followed the kinetics of dissolution of polycrystalline iron in acid solutions. Perchloric acid in sodium perchlorate, hydrochloric acid in sodium chloride and nitric acid in sodium nitrate were used for the range of pH between 0 and 6 at temperatures ranging from 40 to 70°C. The rate of corrosion was taken as a measure of hydrogen ion activity keeping the corrosion potential constant during the run. They found that for the same range of pH the corrosion increased in the order ClO_4^-, Cl^-, NO_3^-.

2. Dissolution of Iron In Perchloric Acid

Leko (13) made a study of the dissolution of iron at 100°C in perchloric acid of varying concentrations under a carbon dioxide atmosphere. The amounts of H^+, Fe^{++} and Fe^{+++} were determined. The amount of hydrogen gas decreased with increase of perchloric acid concentration; the decrease being most pronounced between 58% and 60% perchloric acid. In 40% perchloric acid only Fe^{++} was obtained. As the acid concentration was increased Fe^{+++} started appearing and at 58% perchloric acid the ratio of Fe^{++} to Fe^{+++} became equal to 1. Above 60% acid only Fe^{+++} ions were found.

It was suggested that two parallel reactions occur when dilute perchloric acid is used.

$$Fe + 2H^+ \longrightarrow Fe^{++} + H_2$$

$$4Fe + ClO_4^- + 8H^+ \longrightarrow 4Fe^{+++} + Cl^- + 4H_2O$$

In concentrated perchloric acid only

$$8Fe + 3ClO_4^- + 24H^+ \longrightarrow 8Fe^{+++} + 3Cl^- + 12H_2O$$

is possible.

3. Dissolution of Iron in Sulphuric Acid

Demon (14) reported on the dissolution rates of hot rolled and annealed mild steel and carbon steel (containing 0.84 weight percent carbon) in sulphuric acid solutions (1 to 35.5 N) at 25°C. The main theme of his study was to find the effect of carbon content and of the acid concentration on the rate of corrosion of steel in sulphuric acid. The corrosion rate of five different steels was determined for thirteen different concentrations of acid over the range mentioned. In all cases the maximum corrosion rate decreased between 11 N and 14 N sulphuric acid. Higher carbon steels were much more susceptible to corrosion than the lower carbon steels. He found that a steel containing between 0.06 and 0.37 percent carbon had the lowest corrosion rate for all concentrations of acid. The steel specimens became passive in acids more concentrated than 17 N. The passivating film was shown to be ferrous sulphate.

Archer and Howlette (15) studied the corrosion of mild steel by sulphuric acid solution over the concentration range 20.6 to 34.2 N.

The rate of dissolution of unannealed mild steel in sulphuric acid solutions (0.005 to 5 N) was studied by Whitman et al (16) at 23°C. Whitman's main purpose was to find the effect of rotational speed on the corrosion rate. He explains the theory of the corrosion process this way:

The fundamental equation by which the corrosion of iron proceeds is

$$Fe + 2H^{+} \rightleftharpoons Fe^{++} + 2H$$

The rate at which this reaction progresses is dependent on the following factors:

a. Metal: The corrosion tendency of metal is determined by its position in the electromotive series.

b. Acidity: Acidity is a measure of hydrogen ion concentration of the acid. For example the hydrogen-ion concentrations of 5 N and 2 N solutions of different acids is given in table 1-2 (17).

TABLE 1-2

HYDROGEN ION CONCENTRATIONS OF ACIDIC SOLUTIONS

Acid	5N	2N	
HNO_3	2.08	1.48	Equivalents
HCl	2.01	1.39	hydrogen ion
H_2SO_4	1.84	1.01	per litre
H_3PO_4	0.816	0.360	
HAC	0.013	0.006	

c. Ferrous Ion Concentration: According to the law of mass action the increase in ferrous ions should decrease the rate of corrosion but this factor seems to play a minor role.

d. Removal of Hydrogen: This is the most important factor for the progress of corrosion.

Hydrogen can be removed in two ways

i. By evolution of gaseous hydrogen

$$2H \rightleftharpoons H_2$$

ii. By depolarization through oxidation either by dissolved oxygen or by some other oxidizing agent

$$2H + \tfrac{1}{2}O_2 \rightleftharpoons H_2O$$

Gatos (18) reported that the dissolution of iron in sulphuric acid was increased by ferric ions. He found that in 1 N sulphuric acid the dissolution rate increased initially with Fe^{+++} concentration and then decreased beyond 0.47 Fe^{+++} gm ion/litre and at 4.0 Fe^{+++} gm ions/litre, it became approximately equal to the rate in 1 N sulphuric acid containing no Fe^{+++}. The hydrogen evolution rate decreased with time and with Fe^{+++} concentrations.

4. Rate of Dissolution in Hydrofluoric Acid

The rate of dissolution of iron is very high in dilute hydrofluoric acid (19) (up to 48% to 50% HF). In more concentrated solutions (60% to 95% HF) iron is stable.

5. Rate of Dissolution in Nitric Acid

The action of nitric acid on iron is of particular interest. The attack is very severe at low concentrations with the products of corrosion being nitrous peroxide (NO_2), nitric oxide (NO), nitrous oxide (N_2O), nitrogen and ammonia. Whitley and Hallimond (20) showed that the proportion of $N_2 + NH_3$ to $NO + NO_2$ increases if the metal contains internal stresses.

Iron exhibits a periodic surface passivation and activation at concentrations of nitric acid between those responsible for maximum corrosion and complete passivity. This complex phenomenon has been studied by Vetter (21) and Bonhoffer (22). They suggested that this behaviour is due to the formation of nitrous acid during the active period and its diffusion from the surface into the solution during the period of passivity.

The powerful oxidizing action of nitric acid will cause violent attack only if the anodic reaction can keep pace with the cathodic reaction of the nitric acid. An increase in the rate of corrosion has been observed in acids more concentrated than 90%.

In a way the attack of nitric acid on iron differs from that on other metals. Any nitric oxide (NO) formed by reduction of nitrous acid, instead of escaping from the acid, can be retained, by combination with ferrous salts present, to form brown nitroso-compounds such as $Fe(NO_3)_2NO$, which remain available for an autocatalytic cycle. The brown colour generally seen on iron during experiments with nitric acid is due to such compounds.

6. Dissolution of Iron in Organic and Carbonic Acids

Of the organic acids (19), oxallic, formic, citric and acetic attack iron severely but not as readily as the mineral acids do. Carbonic acid attacks iron almost in the same way as any mineral acid by increasing the possibility of corrosion through hydrogen depolarization.

7. Corrosion of Iron in Hydrochloric Acid

The first study on the dissolution of iron in hydrochloric acid was made by Conroy (23) who immersed iron sheets ($2\frac{1}{2}$ inch x $1\frac{1}{2}$ inch) in appropriate solutions. He studied the effects of acid concentration and temperature on the dissolution rates. The loss of weight was determined at one hour intervals, but the rate of corrosion was evaluated from hydrogen gas evolution. He concluded that:

a. The rate of dissolution was doubled for each addition of 30 grams hydrochloric acid per litre of the solution.

b. The rate of dissolution was doubled for each rise of 10^oC in the temperature.

Morris et al (24) made a study of the dissolution rates of pure iron in four concentrations (0.01 N, 0.025 N, 0.04 N and 0.05 N) of hydrochloric acid by rotating iron samples at 2000 rpm at 25°C with increasing amounts of potassium nitrate (Molarity of KNO_3 0 to 0.15) and hydrogen peroxide (Molarity of H_2O_2 0 to 0.16). Cylinders of the purest iron available were rotated in 250 c.c. of corroding solutions. The results were plotted as miligrams of iron dissolved versus molarity of the depolarizer. The initial dissolution rates were nearly linear with peroxide concentration over the molarity range 0 to 0.08 and the maxima were not as high as with nitrate at all four acid concentrations. With further increase in peroxide concentrations, the rate decreased at higher acid concentrations.

The dissolution rate of pure iron in air-free hydrochloric acid was studied by Makrides et al (25). Polished cylindrical coupons (2.5 cm x 1.9 cm) were rotated at 2180 r.p.m. in 400 c.c. of solution. It was shown that the rate of dissolution of iron in air-free hydrochloric acid was a linear function of hydrochloric acid activity for activities between 1 and 10. The potential of dissolving iron was a logarithmic function of hydrochloric acid activity. They found that the dissolution rate in air-free 2 N hydrochloric acid was independent of stirring speed.

A study of mild steel behaviour was also made in air-free hydrochloric acid and it was found that the potential of mild steel in acid solutions containing depolarizers was a linear function of the logarithm of the solution rate.

8. Oxidation of Ferrous Ions

Rigg et al (26) investigated the kinetics of oxidation of ferrous ions by hydrogen peroxide in sulphuric acid. Sobkowski (27) made the same study in perchloric, sulphuric and phosphoric acids.

Rigg and co-workers found the value of the rate constant for the reaction between hydrogen peroxide and ferrous ions by direct spectrometric observations of the ferric salt produced (at $\lambda = 304$ mμ). They confirmed that the rate was independent of acidity (0.05 N - 0.8 N H_2SO_4) and that the reaction was bimolecular over a wide range of reactant concentrations. The concentrations of H_2O_2 and ferrous salts were varied from 1:25 and 1:20 respectively. The rate constant over the temperature range 15° to 40°C could be represented by the equation

$$k = 1.05 \times 10^8 \exp(-\frac{8460}{RT}) \text{ moles}^{-1}\text{sec}^{-1}\text{litre}$$

Sobkowski found the rate constants for the reaction between ferrous ions and hydrogen peroxide in perchloric, sulphuric and phosphoric acids. These constants were measured at different temperatures and he concluded that the rate of reaction between ferrous ions and hydrogen peroxide was highest in the presence of phosphoric acid and lowest in perchloric acid solutions.

A study of the rapid autoxidation of ferrous ions in concentrated hydrochloric acid has been reported by Posner (28). He found that the reaction was first-order with respect to ferrous ion and oxygen but a more complex function of hydrochloric acid concentration. He showed that autoxidation occurs via a complex formed between associated hydrochloric acid and ferrous ions. The mechanism suggested was essentially similar to the modified Haber-Weiss (29) formulation:

$$Fe^{++} + H^{+} + O_2 \longrightarrow Fe^{+++} + HO_2$$

$$HO_2 + Fe^{++} \xrightarrow{K_5} Fe^{+++} + HO_2^{-}$$

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

$$Fe^{++} + H_2O_2 \xrightarrow{K_6} Fe^{+++} + OH + OH^{-}$$

$$Fe^{++} + OH \xrightarrow{K_7} Fe^{+++} + OH^{-}$$

It was suggested by Weiss that the reason for the slow autoxidation of ferrous ions in dilute (<4 N) acid solution is that the primary step is the formation of O_2^{-}

$$Fe^{++} + O_2 \rightleftharpoons O_2^{-} + Fe^{+++} \qquad (2.1)$$

ΔF for this reaction is +30 kcal/mole. This indicates that the equilibrium is well over to the left and the forward reaction is very slow. The next step in the Weiss reaction mechanism is

$$H^{+} + O_2^{-} \rightleftharpoons HO_2$$

$$\Delta F = -10 \text{ kcal/mole.}$$

This shows that the H^{+} ion should constitute an actual part of the active complex formed in the first step, otherwise the reversal of (2.1) is more likely to occur than the forward reaction.

The development of the Haber-Weiss theory leads to an expression

$$\frac{d\ (Fe^{+++})}{dt} = \frac{4k_1\left[Fe^{++}\right]\left[O_2\right]\left[Fe^{++}\right]\left[H^+\right]}{k_2\left[Fe^{++}\right]\left[H^+\right] + k_1 K_{HO_2}\left[Fe^{+++}\right]}$$

It was shown by Posner that Fe^{+++} in hydrochloric acid solution is strongly complexed. It was thought that Fe^{++} ions could also form a complex with hydrochloric acid and attack of oxygen on this complex could be represented as follows:

$$(Fe^{++}.HCl\ \text{complex}) + O_2 \longrightarrow HO_2 + Fe^{+++} + Cl^-$$

If the hydrochloric acid is completely dissociated this complex formation may be expressed by the equilibrium.

$$H^+ + Cl^- + Fe^{++} \rightleftharpoons HFe^{++}Cl,$$

and hence the autoxidation rate should be proportional to $[H^+][Cl^-]$

This would indicate that the reaction should proceed at all acid concentrations but Posner found that the reaction occurred at a measurable rate only at hydrochloric acid concentration above 4 N. As a result Posner concluded that a new reactive species, capable of promoting the autoxidation, is formed in solutions more concentrated than 4 N. It was thought that this species could be associated hydrochloric acid.

The oxygen attack on this complex could be represented by

$$HFe^{++}Cl + O_2 \xrightarrow{K_4} Fe^{+++} + Cl^- + HO_2$$

and the extent of complex formation could be governed by the equilibrium

$$HCl_{ass} + Fe^{++} \rightleftharpoons HFe^{++}Cl$$

with

$$K = \left[HFe^{++}Cl\right] \Big/ \left[HCl_{ass}\right]\left[Fe^{++}\right]$$

George (30) studied the kinetics of the oxidation of ferrous ions by molecular oxygen in perchloric acid solutions as a function of pH over the temperature range 25 - 40°C.

In phosphoric acid solutions Cher and Davidson (31) found that the oxidation of ferrous ions was first order in ferrous ion.

9. Colorimetric Method of Analysis of Iron

There are many methods by which the analysis of iron can be done colorimetrically.

Bipyridine has been used because ferrous iron forms a red complex with 2, 2 - bipyridine at pH 3.4. This can be estimated at 520 $m\mu$ (32,33). The main disadvantage of this reagent is that the minimum concentration of ferrous iron must be of the order of 0.02 - 0.24 miligrams per 100 ml.

Walden et al (34) used 0- phenanthroline for analysis of iron. An orange complex of the form $\left[(C_{12}H_8N_2)_3Fe\right]X_2$ is formed when ferrous ion and the reagent react, but the resulting colour takes about 15 minutes to become stable.

A mention of the other colorimetric methods based on iron complex formation is made here.

(1) Koling et al (35) used a, á -Bipyridyl for analysis of ferrous and ferric iron.

(2) Gregory (36) Mehlig (37) and Scott (38) used salicylic acid for the determination of ferric iron.

(3) Ferrous and ferric iron by sulfosalicylic acid (39).

(4) Ferric iron by ferron (40).

(5) Ferrous iron by nitroso R-salt (41).

(6) Ferric iron by 8 hydroxyquinoline (42).

Snell and Snell (43) have made an exhaustive study of colorimetric determinations of metals.

The yellow colour of ferric chloride in hydrochloric acid has been adopted by many authors (44, 45, 46, 47).

CHAPTER III

THEORY

In spite of the vast amount of work that has been devoted to corrosion studies it is not yet possible to predict or control the behaviour of metals in corroding media. Part of the problem is due to the lack of appreciation of the various steps that are involved in the overall corrosion process.

An attempt will be made here to develop a plausible and consistent scheme for the dissolution of metals in general and iron in particular. Future researchers may be stimulated to establish the validity of some of the controversial steps in this proposal. It is felt that a thorough knowledge of the individual processes is necessary before effective corrosion control may be established.

A. Under Anaerobic Conditions

The dissolution of iron in non-oxidizing media, such as hydrochloric acid, can be discussed in terms of

1. An anodic reaction $Fe \longrightarrow Fe^{++} + 2e^-$ (3.1)
2. A cathodic reaction $H^+ + e^- \longrightarrow H$ (3.2)
3. A combination of hydrogen atoms with liberation of hydrogen gas $H + H \longrightarrow H_2$ (3.3)

Equations (3.1), (3.2) and (3.3) represent the net result of several consecutive steps, anyone of which may be very slow and, as a result, rate determining. In order to have some real appreciation of these steps, one should consider the condition of the metal surface exposed to the corroding solution.

Metal specimens in corrosion studies are generally polished to an arithmetic average surface roughness of 20 - 30 microinches. Visual observations suggest a mirror-smoothness of the type, shown in figure 3-1.

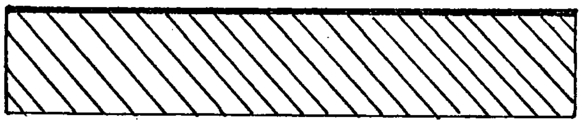

FIGURE 3-1. VISUAL REPRESENTATION OF POLISHED SURFACE

A microscopic study confirms the presence of hills and valleys as shown in figure 3-2.

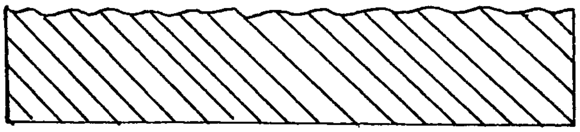

FIGURE 3-2. MICROSCOPIC REPRESENTATION OF POLISHED SURFACE

It will be desirable to say something about the initiation of corrosion when the metal is put into the solution. Figure 3-3 shows a model of the polished surface on an atomic scale assuming a cubic crystal structure for illustrative purposes only.

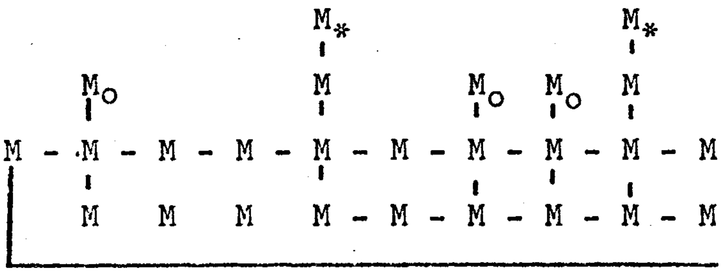

FIGURE 3-3. CUBIC CRYSTAL STRUCTURE ON ATOMIC SCALE

Atoms M_* and M_o are the potentially active sites on the metal surface because they have unsaturated binding energies. If there is any tendency of the matrix to dissolve, these atoms should be the first to leave the structure. Corrosion on iron starts at isolated points (48) and from some of these the attack extends as circles, streaks or arch shaped areas. Not all the points where corrosion is observed to start, however, suffer continued attack.

The dissolution process can now be divided into the following elementary stages:

a. Transfer of hydrogen ions from the bulk of the corroding solution to the iron-solution interface to replace those liberated by reaction (3.2)

$$H_b^+ \xrightarrow{k_1} H_i^+ \qquad (3.4)$$

b. Adsorption of hydrogen ions on the active sites on the iron surface by chemisorption or physical adsorption. Atoms such as M_* shown in figure 3-3 may represent the active sites for this adsorption because they can be easily reached by hydrogen ions

$$\underset{*}{\mathrm{Fe}}_s + \mathrm{H}_i^+ \underset{k_3}{\overset{k_2}{\rightleftharpoons}} \underset{*}{\mathrm{Fe}} - \mathrm{H}_s^+ \qquad (3.5)$$

c. Discharge of adsorbed hydrogen ions by one of the two possible processes

(i)

$$\underset{*}{\mathrm{Fe}} - \mathrm{H}_s^+ + \underset{*}{\mathrm{Fe}} - \mathrm{H}_s^+ \xrightarrow{k_4} \underset{*}{\mathrm{Fe}}^{++} - \mathrm{H}_s + \underset{*}{\mathrm{Fe}} - \mathrm{H}_s \qquad (3.6)$$

(ii)

$$\underset{*}{\mathrm{Fe}} - \mathrm{H}_s^+ + \underset{*}{\mathrm{Fe}} - \mathrm{H}_s^+ + \underset{o}{\mathrm{Fe}} \xrightarrow{k_5} \underset{o}{\mathrm{Fe}}_s^{++} + \underset{*}{\mathrm{Fe}} - \mathrm{H}_s + \underset{*}{\mathrm{Fe}} - \mathrm{H}_s \qquad (3.7)$$

Step (i) represents electron transfer from the original active sites on which adsorption occurs, while step (ii) represents electron transfer from a neighbouring vacant active site.

Step (c) is more likely to occur than the formation of ferric ions because the formation of ions of lower oxidation state requires less energy.

d. Combination of hydrogen atoms to form hydrogen molecules by migration of atoms from site to site

$$\underset{*}{\mathrm{Fe}} - \mathrm{H}_s + \underset{*}{\mathrm{Fe}} - \mathrm{H}_s \xrightarrow{k6} \underset{*}{\mathrm{Fe}} + \underset{*}{\mathrm{Fe}} - \mathrm{H}_{2s} \qquad (3.8)$$

e. Desorption of ferrous ions from the surface

$$\mathrm{Fe} - \underset{*}{\mathrm{Fe}}_s^{++} \xrightarrow{k7} \mathrm{Fe}_s + \underset{*}{\mathrm{Fe}}_i^{++} \qquad (3.9)$$

f. Diffusion of ferrous ions from the interface into the bulk of the corroding solution

$$\underset{*}{Fe}_i^{++} \xrightarrow{k_8} \underset{*}{Fe}_b^{++} \tag{3.10}$$

g. Removal of hydrogen molecules from the surface by one or more of the following possibilities.

(i) Solution of hydrogen gas in the fluid at the metal-solution interface

$$Fe - H_{2s} \xrightarrow{k_9} Fe + H_2 \text{ dissolved} \tag{3.11}$$

(ii) Absorption of hydrogen gas by the metal matrix

$$Fe - H_{2s} \xrightarrow{k_{10}} Fe - H_2 \text{ absorbed} \tag{3.12}$$

(iii) Formation of hydrogen gas bubbles on the surface

$$Fe - H_{2s} + Fe - H_{2s} \xrightarrow{k_{11}} Fe - (H_2)_n + Fe \tag{3.13}$$

(iv) Removal of hydrogen bubbles by separation from the surface

$$Fe - (H_2)_n \xrightarrow{k_{12}} Fe + H_2 \quad \text{gas} \tag{3.14}$$

Small amounts of ferric ion may be found even under anaerobic conditions. Their presence could be result of the following set of reactions:

h. Formation of ferric ions on the surface by disproportionation:

$$Fe_s - Fe^{++} + Fe_s - Fe^{++} + Fe_s - Fe^{++} \rightleftharpoons Fe_s - Fe + Fe_s - Fe^{+++} + Fe_s - Fe^{+++} \tag{3.15}$$

(i) Appearance of these ferric ions at the interface and then in the solution:

$$\mathrm{Fe_s - Fe_s^{+++} \xrightarrow{k_{13}} Fe_s + Fe_i^{+++}} \qquad (3.16)$$

$$\mathrm{Fe_i^{+++} \xrightarrow{k_{14}} Fe_b^{+++}} \qquad (3.17)$$

There is some evidence of autocatalysis even in completely oxygen free corroding solutions at higher acid concentrations (≥ 5 N).

It was suggested by Posner (28) that there is some associated hydrochloric acid at concentrations greater than 5 N. Therefore to provide an explanation for the autocatalysis, it would not be unreasonable to assume that associated hydrochloric acid molecules are also adsorbed on the metal surface.

$$\text{j.} \qquad \underset{*}{\mathrm{Fe}}_s + \mathrm{HCl} \underset{k_{16}}{\overset{k_{15}}{\rightleftharpoons}} \underset{*}{\mathrm{Fe}}_s\mathrm{HCl} \qquad (3.18)$$

Formation of ferric ions can possibly occur by an electron transfer reaction on the surface

$$\underset{o}{\mathrm{Fe}} + \underset{*}{\mathrm{Fe}}\mathrm{HCl_s} + \underset{*}{\mathrm{Fe}}\mathrm{HCl_s} + \underset{*}{\mathrm{Fe}}\mathrm{HCl_s} \xrightarrow{k_{17}} \underset{o}{\mathrm{Fe}}_s^{+++} + \underset{*}{\mathrm{Fe}}\mathrm{H_s} + \underset{*}{\mathrm{Fe}}\mathrm{H_s} + \underset{*}{\mathrm{Fe}}\mathrm{H_s} + 3\mathrm{Cl^-} \qquad (3.19)$$

$$\underset{o}{\mathrm{Fe}}_s^{+++} \xrightarrow{k_{13}} \underset{o}{\mathrm{Fe}}_i^{+++} \qquad (3.16)$$

B. <u>Aerated Solutions</u>

In the case of aerated acids, corrosion of iron takes place by the two processes (16):

1. Corrosion by hydrogen gas evolution as described previously and
2. Corrosion by oxygen depolarization

Oxygen is a very energetic cathodic depolarizer.

It is natural, therefore, that with an increase of oxygen concentration in the electrolyte there should be an increase in the rate of corrosion of metals, particularly iron. Iron is an easily passivated metal, but in the presence of chloride ions, the passivity of iron is not observed (19). Therefore higher oxygen concentration in solution should correspond to increasing rates of corrosion.

When oxygen is introduced into the solution, the increase in corrosion can be considered in terms of the following elementary steps:

a. Transport of oxygen from the bulk of the solution to the iron-solution interface

$$O_{2_b} \xrightarrow{k18} O_{2_i} \qquad (3.20)$$

b. Adsorption of oxygen on the metal surface by one of the two possible processes

$$Fe_s + O_{2_i} \underset{k20}{\overset{k19}{\rightleftharpoons}} Fe - O_{2s} \qquad (3.21)$$

$$Fe_s + Fe_s + O_{2_i} \underset{k22}{\overset{k21}{\rightleftharpoons}} Fe - O_s + Fe - O_s \qquad (3.22)$$

c. Surface reaction between adsorbed species

$$Fe - H_s^+ + Fe - O_s \xrightarrow{k23} Fe_s^{++} + Fe - OH_s^- \qquad (3.23)$$

d. Removal of OH^- by one of the two possible ways

$$Fe - OH_s^- \xrightarrow{k24} Fe_s + OH_i^- \qquad (3.24)$$

$$Fe - OH_s^- + H^+ + \xrightarrow{k25} Fe_s + H_2O \qquad (3.25)$$

e. Formation of ferric ions either at the interface or in the bulk.

$$Fe^{++}_{(i-b)} + H^{+}_{(i-b)} + O_{2(i-b)} \xrightarrow{k_{26}} Fe^{+++}_{(i-b)} + HO_2 \tag{3.26}$$

$$Fe^{+++}_{i} + H_s \xrightarrow{k_{27}} Fe^{++}_{i} + H_s^{+} \tag{3.27}$$

$$Fe^{+++}_{(i-b)} + HO_{2(i-b)} \xrightarrow{k_{28}} Fe^{++}_{(i-b)} + HO^{-}_{2(i-b)} \tag{3.28}$$

$$HO^{-}_{2(i-b)} + H^{+}_{(i-b)} \underset{k_{30}}{\overset{k_{29}}{\rightleftharpoons}} H_2O_{2(i-b)} \tag{3.29}$$

$$Fe^{++}_{(i-b)} + H_2O_{2(i-b)} \xrightarrow{k_{31}} Fe^{+++}_{(i-b)} + OH_{(i-b)} + OH^{-}_{(i-b)} \tag{3.30}$$

$$OH_{(i-b)} + H_2O_{2(i-b)} \xrightarrow{k_{32}} H_2O_{(i-b)} + HO_{2(i-b)} \tag{3.31}$$

$$HO_{2(i-b)} + H_2O_{2(i-b)} \xrightarrow{k_{33}} O_{2(i-b)} + H_2O_{(i-b)} + OH_{(i-b)} \tag{3.32}$$

$$2Fe^{+++}_{s} + Fe \underset{k_{36}}{\overset{k_{35}}{\rightleftharpoons}} 3Fe^{++}_{s} \tag{3.33}$$

where

s is surface

b is bulk

i is interface

(i-b) is interface or bulk

CHAPTER IV

EXPERIMENTAL

A. Materials

1. Iron

Iron rod, supplied by Armco Steel Corporation, Ohio, U.S.A., was machined into cylinders of 0.47" in diameter. Different lengths of cylinders varying from 0.148" to 0.592" were used. The purity of the metal was 99.715%. The analysis as given by the manufacturer is found in Appendix I.

2. Hydrochloric Acid

Analar grade hydrochloric acid supplied by the British Drug House Ltd. was diluted with distilled water.

3. Hydrogen Peroxide

Analar grade hydrogen peroxide was also supplied by the British Drug House Ltd.

B. Apparatus

The cylindrical iron samples were rotated on a stainless steel shaft. Plexiglass sleeves and a cap screwed tightly at the end protected the ends of the iron sample and steel shaft from corrosion.

The samples were rotated at speeds ranging from 2000 to 12000 r.p.m. by means of a type 7HM Hoover Vacuum cleaner motor. Figure 4-1 is schematic representation of the experimental apparatus.

The speed of the motor was regulated by a powerstat and a constant voltage power supply. Shaft speeds were measured by means of a type 1531-A strobotac, produced by the General Radio Corporation.

The reaction cells consisted of specially designed jacketted vessels fabricated from two pyrex beakers. Water was forced through the space between the beakers by means of a pump from a thermostated bath. A laboratory jack was used to adjust the reaction vessels to the required height.

The reaction vessel was fitted with a 5 x 5 x $\frac{1}{4}$ inch plexiglass plate holding three radially mounted baffles. These baffles were designed to prevent vortex formation when the shaft was rotated at high speeds. Three holes of 3/4" diameter were bored in the plexiglass plate to provide means of aeration, means of removing a sample from the solution and entry of the shaft into the corroding solution.

The acid solutions were saturated with air, nitrogen or oxygen as required. In order to minimize the loss of hydrochloric acid over the normal period of corrosion, these gases were passed through three wash bottles containing acid of the same concentration as in the reaction vessel. All wash bottles were kept at the same temperature as the corroding samples.

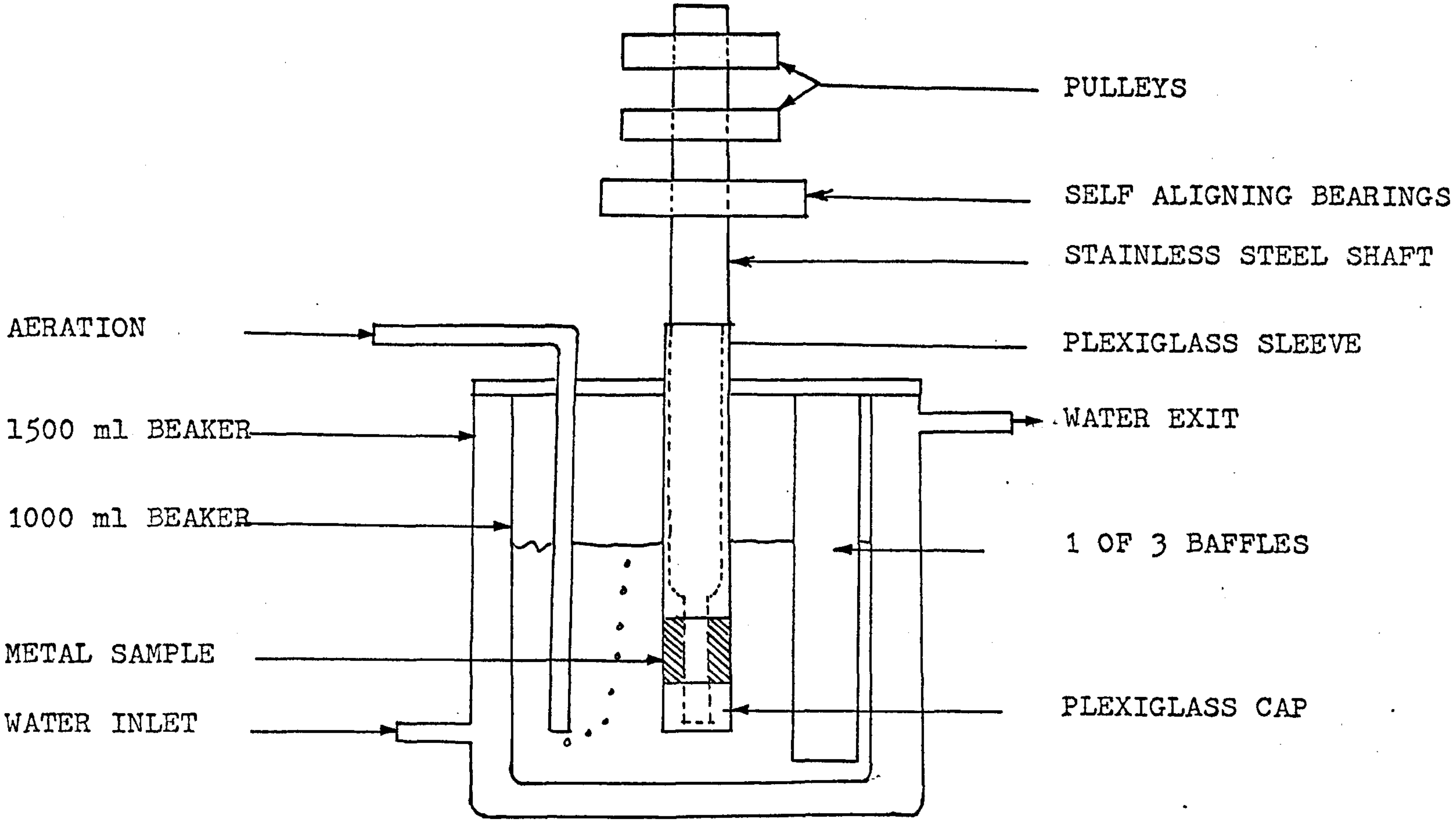

FIGURE 4-1 APPARATUS ARRANGEMENT

C. Procedure

A measured volume of hydrochloric acid solution in the reaction vessel was flushed with the appropriate gas for about 20 - 30 minutes before each corrosion run.

The machined specimens were manually polished with 180, 240, 320, 400 and 500 emery papers. The polished samples were washed initially with distilled water, then with acetone for degreasing and finally rewashed with distilled water.

When dry, the samples were individually weighed. After each run the samples were washed with distilled water, dried and then re-weighed. This weighing before and after enabled a material balance comparison to be made with the hydrogen peroxide analytical procedure. Experiments in which material balances differed by more than 6% were rejected.

Periodically a sample of solution was withdrawn by means of a pipete for analysis. The concentration of iron as (Fe^{+++}) and total iron was determined by a photometric method described in Appendix II.

To eliminate excessive volume change during the corrosion period, an equal volume of fresh acid was added to the reaction vessel for every sample of solution withdrawn for analysis.

Throughout the corrosion period, the flow of gas, rotational speed and temperature were kept constant.

The surface roughness of the samples was measured before and after each run by means of a Profilometer supplied by

Micrometrical Manufacturing Company of Ann Arbor, Michigan, U.S.A.

CHAPTER V

RESULTS AND DISCUSSION

A. General Corrosion Behaviour of Iron

Both oxidation states of iron are found in corroding solutions of hydrochloric acid over the concentration range (3 to 5.37 N). The proportion of ferrous ion is much greater at the lower acid concentrations. The relative proportions of ferrous and ferric ion depend upon the acid concentration and on the gas with which the acid is saturated. The relative amount of ferric ion increases while that of ferrous decreases with increasing oxygen and acid concentrations. The effect of acid concentration is so pronounced that even in oxygen free solutions, there appears to be some ferric ion present if the concentration is greater than 5 N.

The relative ferric ion concentrations under different conditions are shown in figure 5-1.

B. Dissolution of Iron In Oxygen-free Solutions

1. Order of Reaction

The first point is to establish the order of dissolution of iron under anaerobic conditions. Corrosion of iron in nitrogen saturated solutions is due, simply, to the evolution of hydrogen gas, therefore it will be easiest to consider the dissolution in oxygen-free solutions. Most

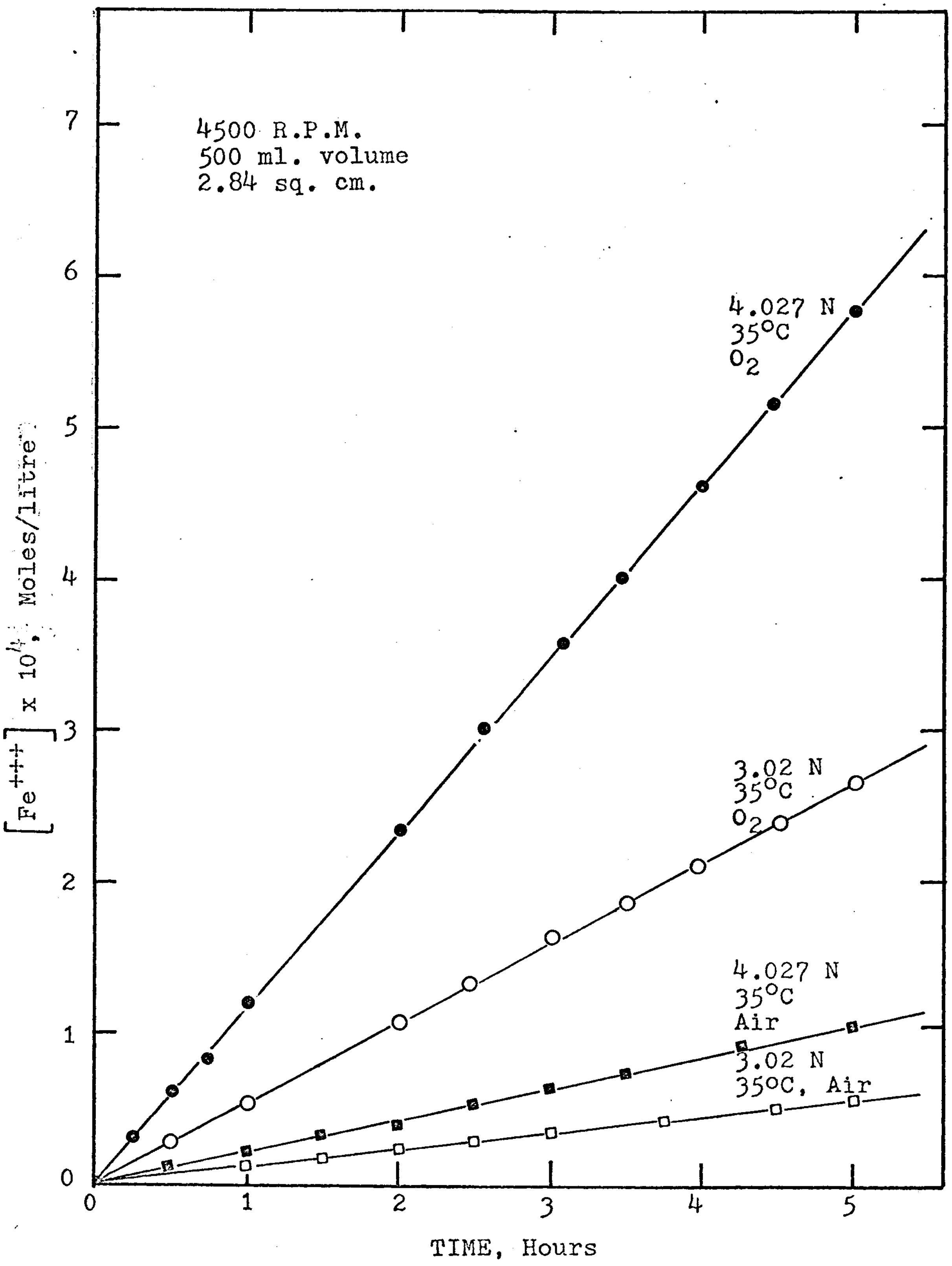

FIGURE 5-1 COMPARISON OF FERRIC IRON CONCENTRATIONS UNDER DIFFERENT CONDITIONS

of the present work has been carried out at 4500 r.p.m. in 4.027 N hydrochloric acid with exploratory experiments having been done in 3.027 N and 5.37 N hydrochloric acid solutions.

Analytical studies during corrosion show that most of the iron in solution is in the ferrous state but substantial quantities of ferric ions have been found also. The presence of ferric ions could be due to the disproportionation.

$$3Fe^{++} \rightleftharpoons 2Fe^{+++} + Fe \qquad (5.1)$$

which has been considered to be a surface phenomenon according to equation (3.15). It must be emphasized that there is never an equilibrium relationship between the ferric and ferrous ion concentrations in solution.

The rate of formation of ferric ions in solution is about 3 - 5% of the ferrous ion rate. The slight variation of ferric ion concentration with temperature and surface area shows that their presence cannot be related to experimental conditions very readily. It is not unreasonable to suspect that a small amount of oxygen from the atmosphere could leak into the solution and be responsible for the presence of ferric ions.

Figure 5-2 shows some typical data for the dissolution of iron in oxygen-free solutions of hydrochloric acid over a fairly wide range of temperatures. Plots of total iron concentrations versus time are always linear,

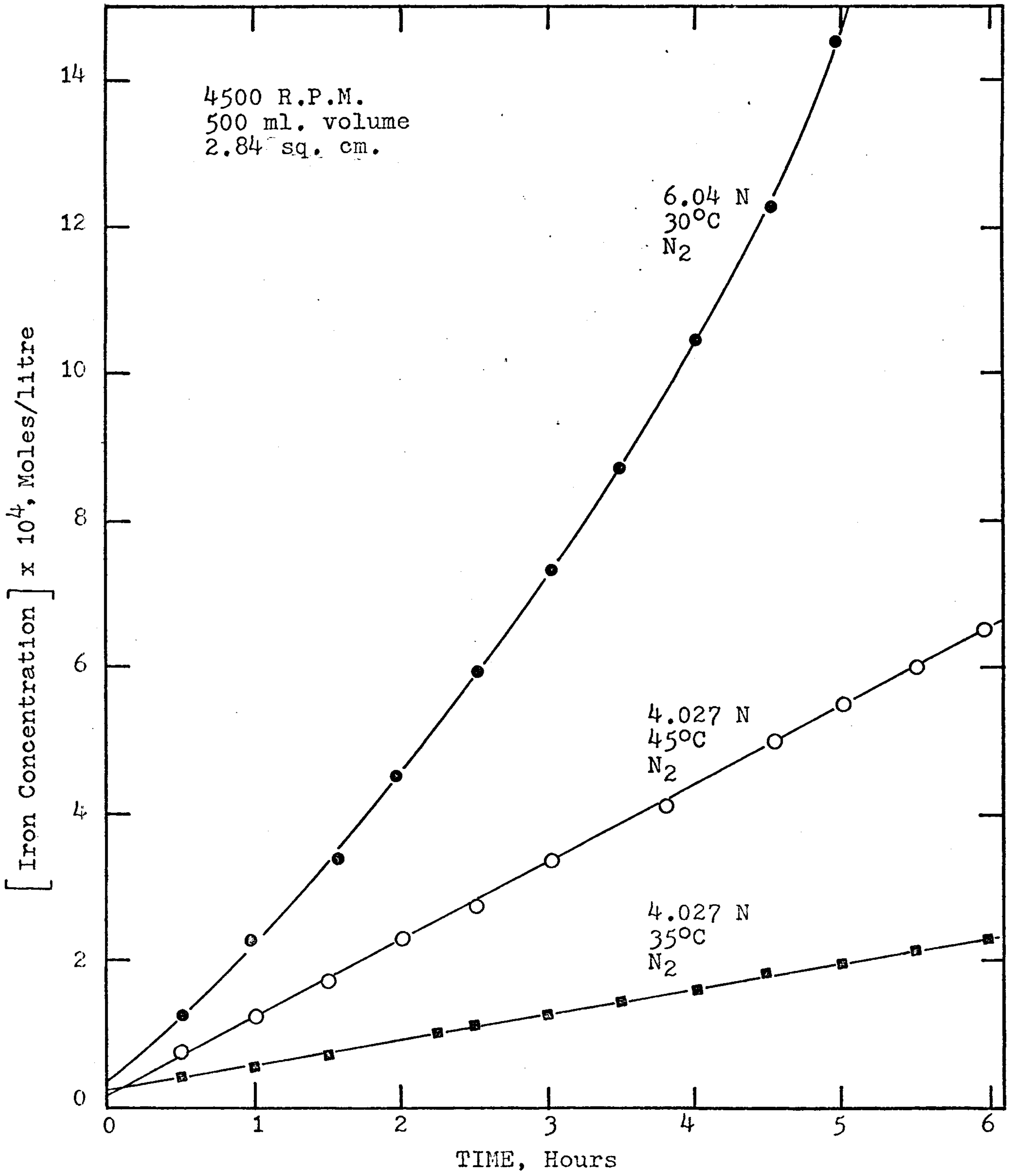

FIGURE 5-2 RATE OF DISSOLUTION OF IRON IN AIR-FREE HCl

for acid concentrations below 6 N. At low acid concentrations the rate of dissolution of iron can be written as

$$\frac{d}{dt}\,(Fe) = k_o$$

where k_o, the rate constant, is a function of temperature, area and possibly of rotational speed.

When this study was extended to higher acid concentrations (>5.37 N), it was found that the dissolution rate was a function of time. Plots of total iron concentration versus time become curved as shown in figure 5-2. This curvature implies autocatalytic dissolution under oxygen-free conditions.

A possible explanation for this autocatalytic phenomenon could be considered in terms of the work of Posner (28) who suggested that associated hydrochloric acid molecules could play a significant role at higher acid concentrations. It would be reasonable to assume that some associated hydrochloric acid molecules are adsorbed on the metal surface with subsequent formation of ferric ions by an electron transfer reaction on the surface according to

$$\begin{aligned} Fe + FeHCl_s + FeHCl_s + FeHCL_s \rightarrow Fe_s^{+++} + FeH_s + FeH_s \\ + FeH_s + 3Cl^- \qquad (3.19) \end{aligned}$$

Ferric ions formed by (3.19) could then take part in reaction (5.1) to produce ferrous ions to give an indication of autocatalysis during corrosion at higher acid concentrations with nitrogen as the saturating gas. In the present study it is not possible to justify fully the above explanations. Further work must be done before dissolution at higher acid concentrations can be completely appreciated.

2. Effect of Temperature and Rotational Speed on the Dissolution Rate

The effect of temperature on the dissolution rate of iron under anaerobic conditions was studied over the temperature range 26° - 45°C. Figure 5-3 shows the data from runs made in 4.027 N hydrochloric acid. The Arhenius activation energy is of the order of 9.4 kcals per gram mole.

The high value of the activation energy suggests that the controlling step in the dissolution of iron under anaerobic conditions may be a chemical process rather than a physical one at lower acid concentrations.

A few exploratory runs were made in 3.04 N hydrochloric acid to determine whether variation of rotational speed would have any effect on the corrosion rate. Table 5-1 shows that for the range 3300 - 6500 r.p.m. the dissolution rate is essentially constant. This behaviour confirms the suspicion that the controlling step in the dissolution of iron in oxygen free hydrochloric acid solutions of low concentration is a chemical process.

TABLE 5-1

EFFECT OF ROTATIONAL SPEED ON THE DISSOLUTION RATE

R.P.M.	RATE CONSTANT X 10^4
3300	0.35
6500	0.34

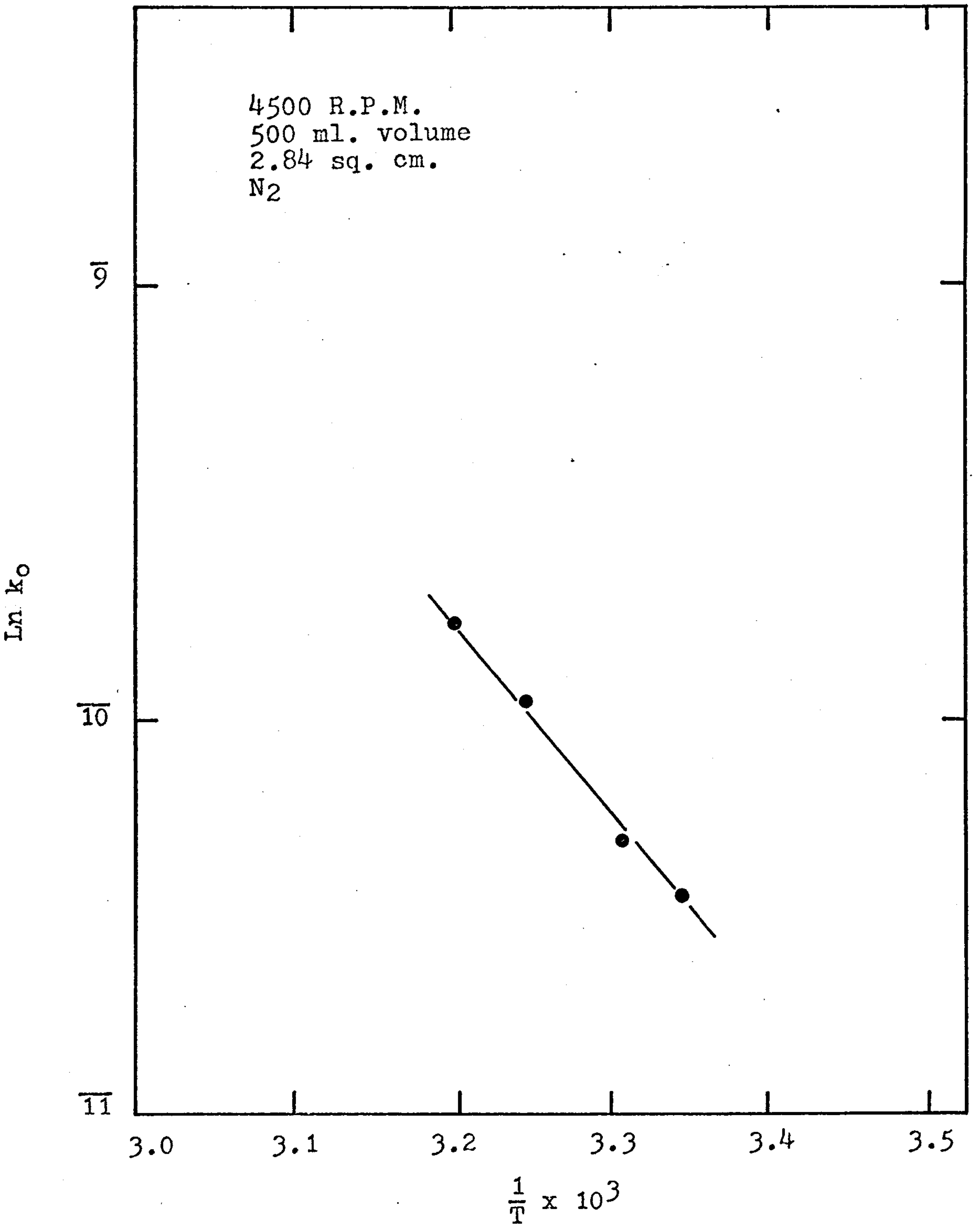

FIGURE 5-3 ARRHENIUS PLOT FOR 4.027 N HCl

3. Effect of Superficial Surface Area on the Dissolution Rate

The effect of superficial surface area was studied in 4.027 N hydrochloric acid at 35°C in nitrogen saturated solutions. Figure 5-4A suggests that there must be some relationship between the zero order rate constant and the apparent surface area of the specimen.

Figure 5-4B shows that the zero order rate constant is proportional to three quarter power of area. This dependance on area may be characteristic of metals which can displace hydrogen gas from acid solutions. This behaviour has been confirmed by Bodner (8) who found the rate of dissolution of titanium to be proportional to the three quarter power of area.

The three quarter power-area dependance could be explained possibly in terms of the molecular hydrogen formation on the surface of the corroding sample. Atomic hydrogen in forming a molecule would require a surface on which to unite and this could cause blocking of the surface available for corrosion. The mechanism of hydrogen formation is clear from the equations:

Anodic reaction $Fe \longrightarrow Fe^{++} + 2e^-$

Cathodic reaction $2H^+ + 2e^- \longrightarrow \underset{\text{Nascent}}{2(H)} \longrightarrow H_2$

4. Empirical Equation

The results indicate that corrosion under anaerobic conditions occurs only by the evolution of hydrogen gas. The dissolution of iron under anaerobic conditions could

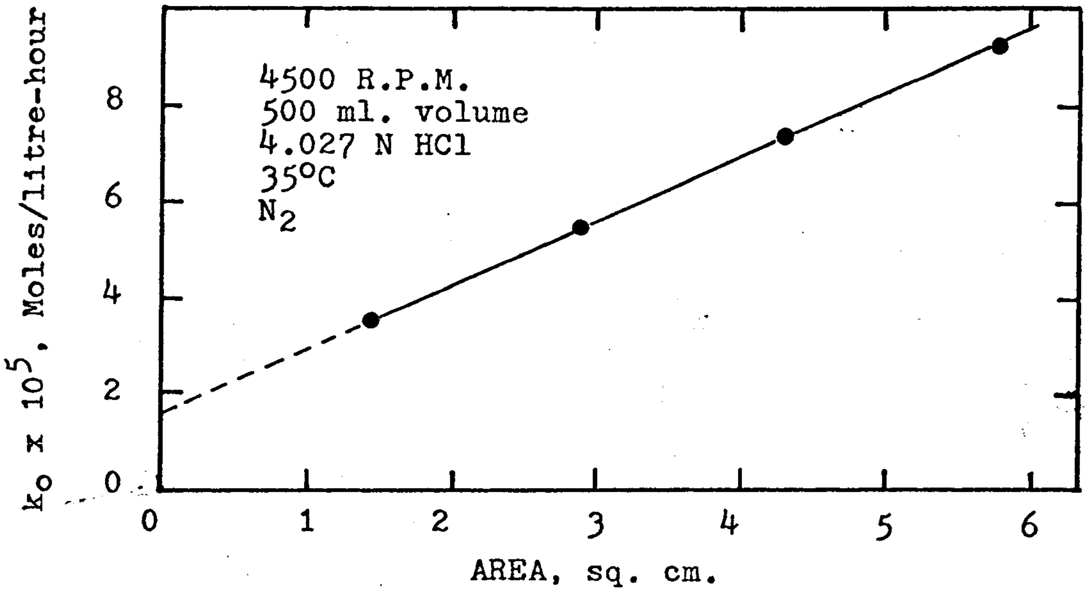

FIGURE 5-4A EFFECT OF SUPERFICIAL AREA UNDER ANAEROBIC CONDITIONS

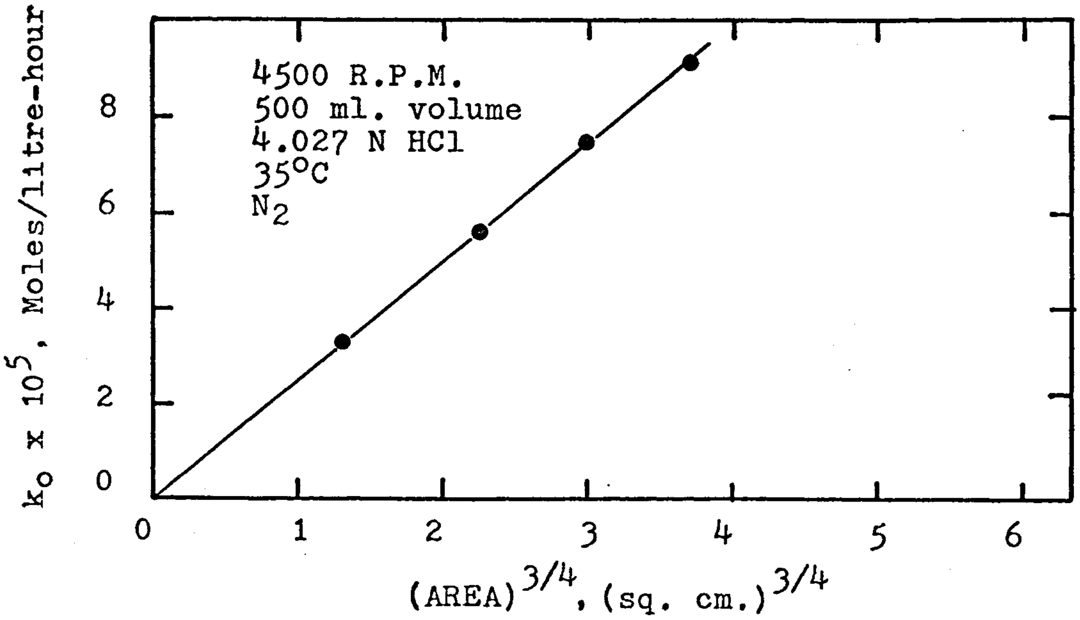

FIGURE 5-4B EFFECT OF SUPERFICIAL AREA UNDER ANAEROBIC CONDITIONS be discussed in terms of the following basic processes:

$$Fe_* - H_s^+ + Fe_* - H_s^+ \xrightarrow{k_4} Fe_*^{++}H_s + Fe_* - H_s \qquad (3.6)$$

or $$Fe_* - H_s^+ + Fe_* - H_s^+ + Fe_o \xrightarrow{k_5} Fe_o^{++} + Fe_* - H_s + Fe_* - H_s \qquad (3.7)$$

$$3Fe^{++} \rightleftharpoons 2Fe^{+++} + Fe \qquad (3.15)$$

In essence, the dissolution of iron in hydrochloric acid is in the form of ferrous iron with only a small quantity of ferric ions being generated..

The results of these experiments can be summarised by the following empirical equation

$$\frac{d(Fe)}{dt} = K_1 \frac{(A)^{3/4}}{V} \left(\exp\left(- \frac{9400}{RT}\right)\right)(R.P.M.)^o(HCl) \qquad (5.2)$$

where $\frac{d(Fe)}{dt}$ = rate of formation of total iron species in solution expressed in moles/litre-hour

A = superficial surface area, cm^2

V = volume of corroding solution, litres

The average value of K_1 has been found to be 13.1. Therefore equation (5.2) can be written tentatively as

$$\frac{d(Fe)}{dt} = 13.1 \frac{(A)^{3/4}}{V} \left(\exp\left(- \frac{9400}{RT}\right)\right)(R.P.M.)^o(HCl) \qquad (5.3)$$

Equation (5.3) is a valid correlation of experimental data over the range of conditions

1) Temperature : 26-45°C

2) Volume : 400-600 ml.

3) Area : 1.43 - 5.72 cm^2

4) Hydrochloric Acid Concentration: 3.04 - 4.027 N HCl

5) Time upto : 6 hours

6) Rotational Speeds : 3300 - 6500 R.P.M.

On the basis of the work of Makrides (25) and figure 5-5, this equation may not be too unreasonable for the concentration range $0 < (HCl) < 4$ N. It must be emphasized that this is a good approximation for the present. More work is needed to establish the complete validity of this relationship.

C. Dissolution of Iron in Air and Oxygen Saturated Solutions

1. Colour of the Iron Solutions During Dissolution

All corroding solutions were colourless before any corrosion occured. After the iron specimen was immersed in the solution, yellow colour started appearing under air and oxygen saturation. This yellow colour is an indication of ferric ions.

In the case of nitrogen saturation, the solutions were almost colourless indicating that there was hardly any ferric ion present.

The colour intensity of ferric chloride increased with the concentration of the acid as well as with the amount of iron in the solution.

2. Order of Reaction

To find the order of reaction corrosion studies were made both in air and oxygen saturated solutions. Most of

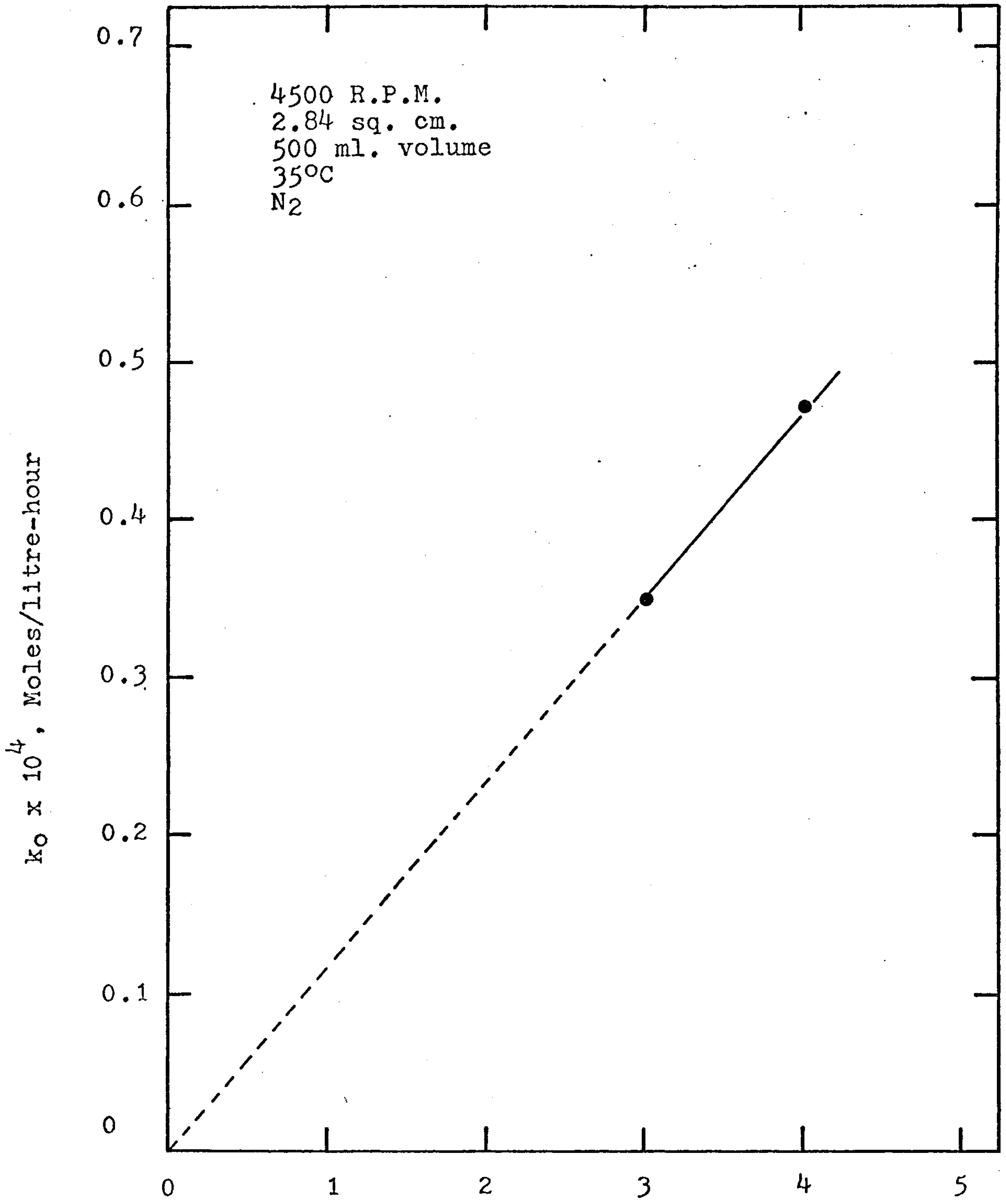

FIGURE 5-5 EFFECT OF ACID CONCENTRATION UNDER ANAEROBIC CONDITIONS

the present work has been carried out at 4500 r.p.m. in 3.04 N and 4.027 N hydrochloric acid with exploratory experiments having been done in 6.04 N hydrochloric acid solutions.

Analytical studies show the presence of both ferrous and ferric ions in the corroding solutions. The relative proportions of ferrous and ferric ions depend upon the acid concentration and on the gas with which the acid is saturated.

As shown in figure 5-6, plots of total iron concentration versus time are always curved. This curvature is essentially an evidence of autocatalytic behaviour. The increase in surface area produced by increasing surface roughness during the course of corrosion is not responsible for this curvature. Substitution of four freshly polished iron specimens during the course of a normal 5 - 6 hour corrosion period had no effect on the curvature as shown in figure 5-7.

The rate of dissolution of iron in solutions containing oxygen can be written as

$$\frac{d(Fe)}{dt} = k_n (Fe)^n$$

where Fe is total iron concentration in the corroding solution. Taking logs on both sides yields

$$\log \frac{d}{dt} (Fe) = \log k_n + n \log (Fe)$$

where k_n, the rate constant, is a function of temperature, surface area, acid concentration and possibly of rotational

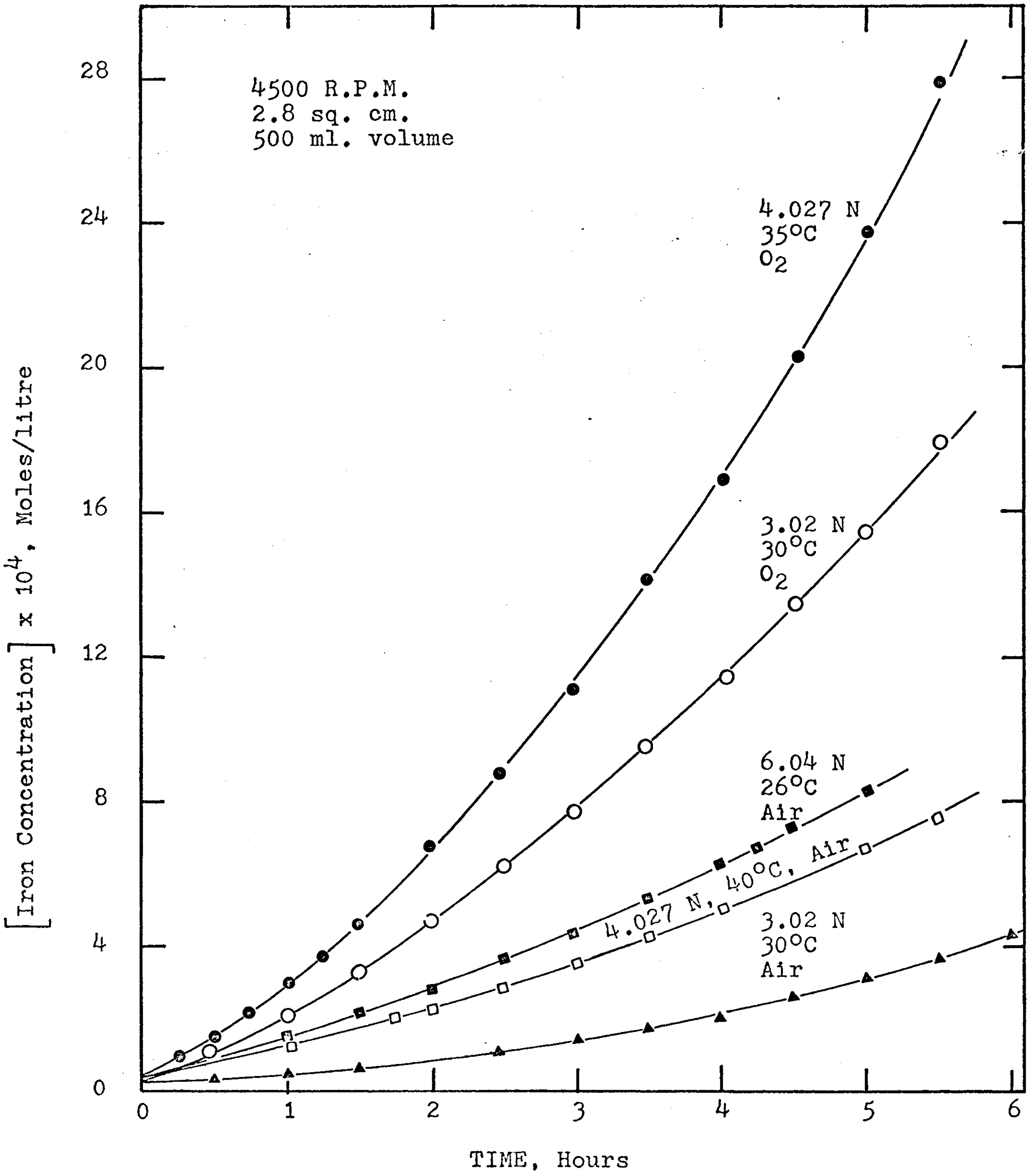

FIGURE 5-6 RATE OF DISSOLUTION OF IRON UNDER AERATED CONDITIONS

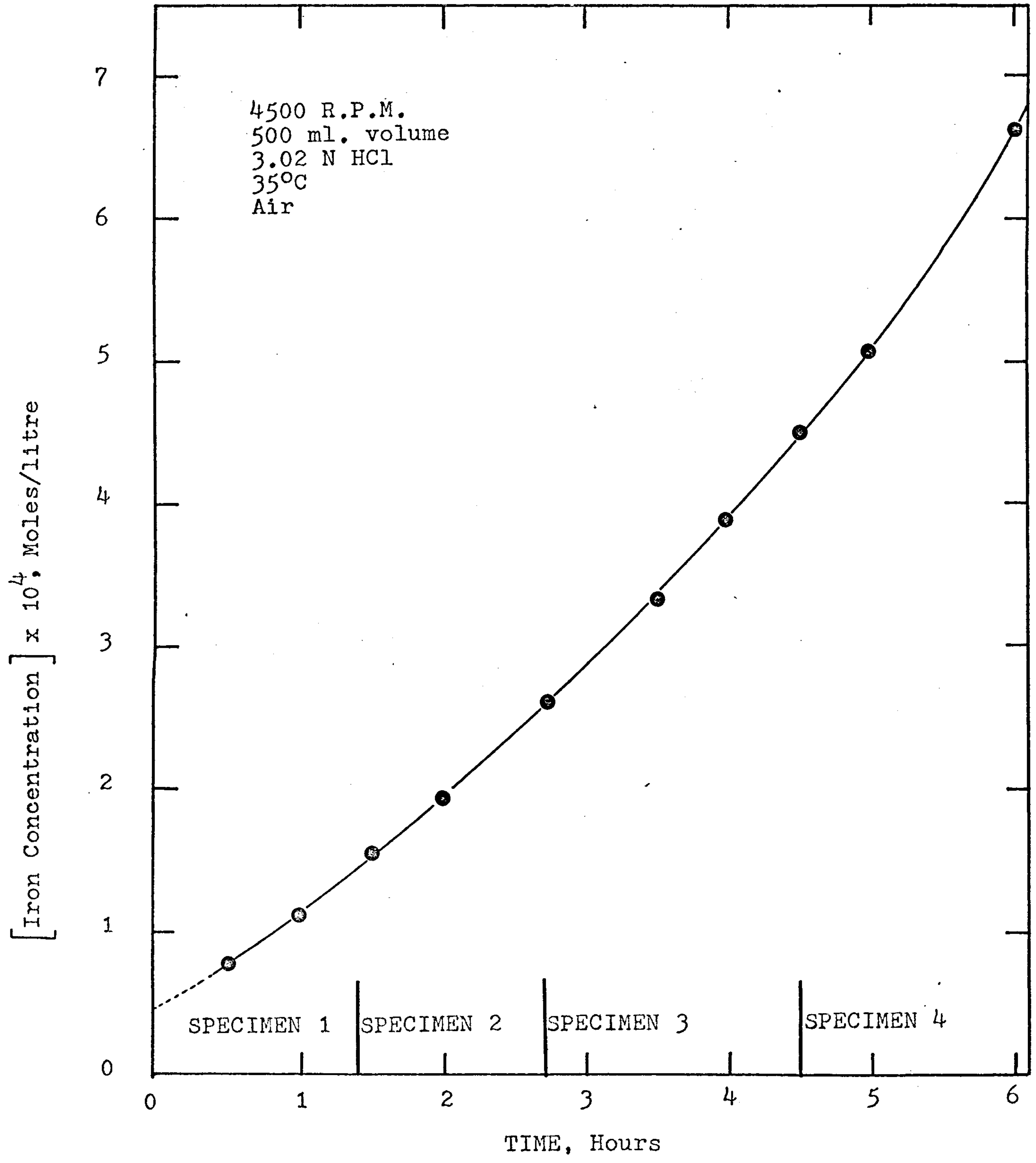

FIGURE 5-7 EFFECT OF FRESH SURFACE SUBSTITUTION

speed and n is the order of reaction.

A plot of log $\frac{d}{dt}$ (Fe) versus log (Fe) showed the value of n to be in the range $0.4<n<0.6$. By the method of trial and error the most appropriate value of n seems to be 0.5 because this value gives the best linear relationship for the total iron versus time plots.

A plot of $(Fe)^{\frac{1}{2}}$ versus time for a wide range of conditions gives a linear relationship as shown in figure 5-8. This indicates that there must be half order dependance on total iron concentration during the corrosion.

All of the plots in figure 5-8 show an ordinate which is somewhat variable, implying some iron concentration at zero time. All of the data given have been determined in apparatus which was cleaned and rinsed in the normal way. Previous researchers (50) have shown that considerable metal may be adsorbed on the glass surface. Part of the iron concentration at zero time can be explained in terms of the attack of acid vapors on the specimen surface over a 5 minute period during which the shaft was brought to constant rotational speed with the specimen just above the corroding solution.

3. Reproducibility

In order to check the reproducibility, duplicate runs were made and some were made three times. A typical plot of a duplicate run is shown in figure 5-9. Gas flow rate, temperature and speed were kept constant in all the cases.

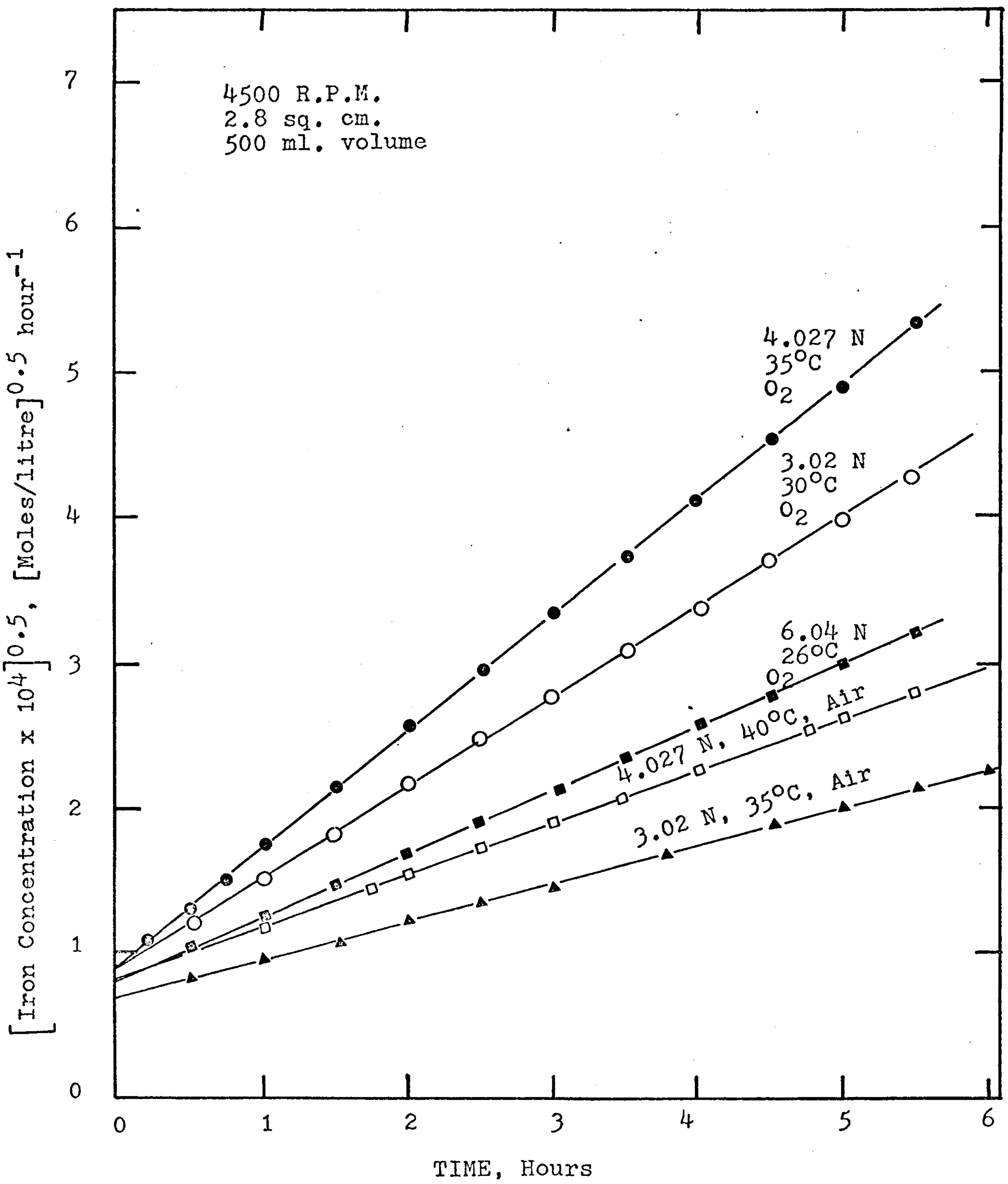

FIGURE 5-8 HALF ORDER PLOTS UNDER AERATED CONDITIONS

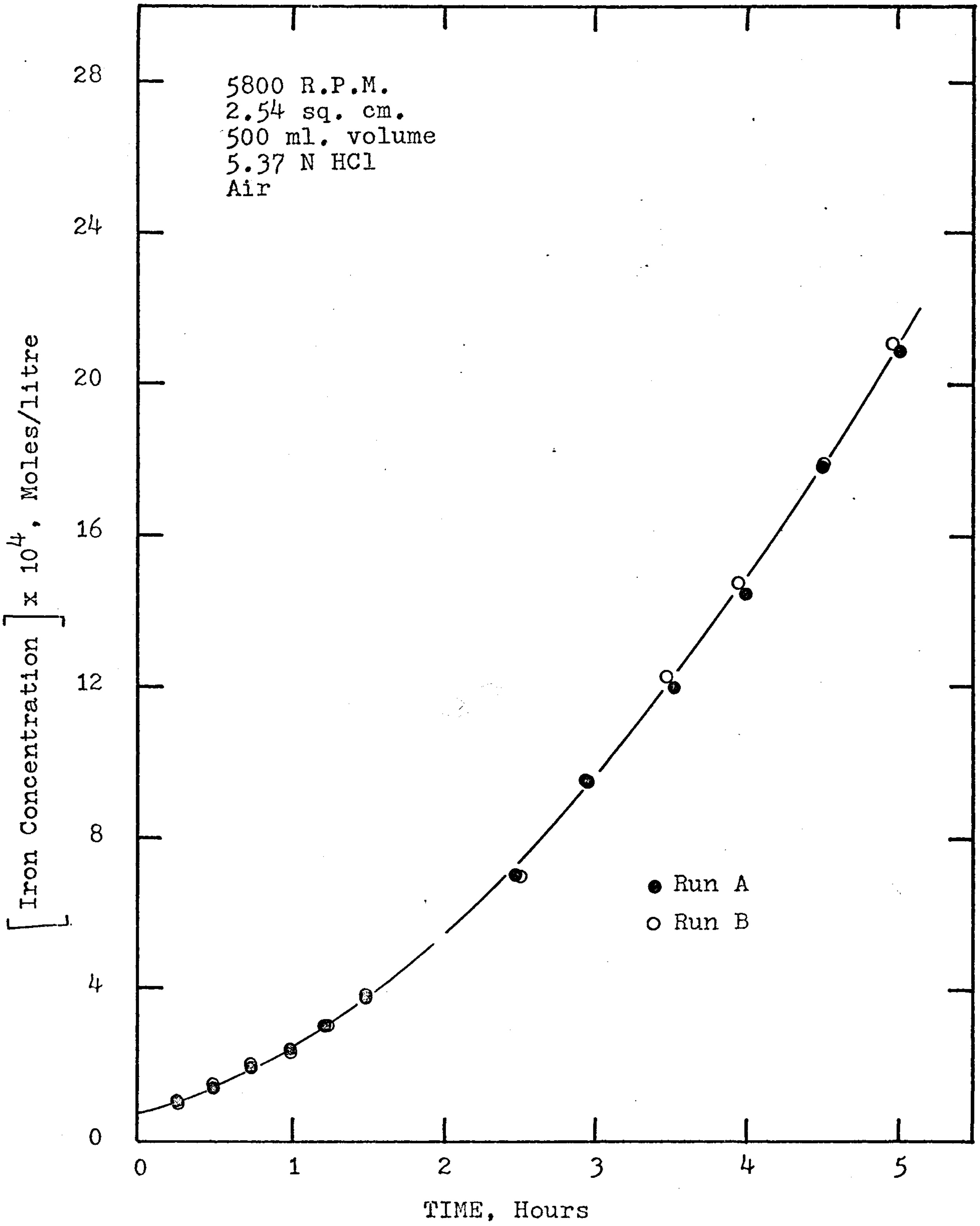

FIGURE 5-9 REPRODUCIBILITY

4. Effect of Rotational Speed on the Dissolution Rate

The effect of rotational speed on the dissolution rate was studied in 4.027 N and 6.04 N hydrochloric acid at 35°C in air saturated solutions at speeds ranging from 0 to 11000 r.p.m. Figure 5-10 illustrates the dependance of velocity constant on rotational speed. It will be noted that at the higher acid concentration the corrosion rate decreases with increasing velocity initially, passes through a minimum and then increases. A similar phenomenon was observed by Whitman and Russel (17) who studied the corrosion of iron cylinders in sulphuric acid. They found that the corrosion of stationary samples depended on the acidity, but it is significant that the corrosion rate was independent of acid concentration at 4000 r.p.m.

Their results could be explained on the basis that corrosion in air saturated solutions proceeds by two processes. The first is "corrosion by hydrogen gas evolution" and the second is "corrosion by oxygen depolarization".

The decrease of corrosion with increase of speed has been explained by MacInnes' work (49) in terms of overvoltage variation. Corrosion of stationary samples is primarily determined by the rate of hydrogen gas evolution, particularly with the concentrated acids. The effect of sample velocity is to decrease the size of hydrogen bubbles thus increasing the work required to form smaller gas bubbles. Velocity increases corrosion by oxygen depolarization, since it thins down the effective film through which

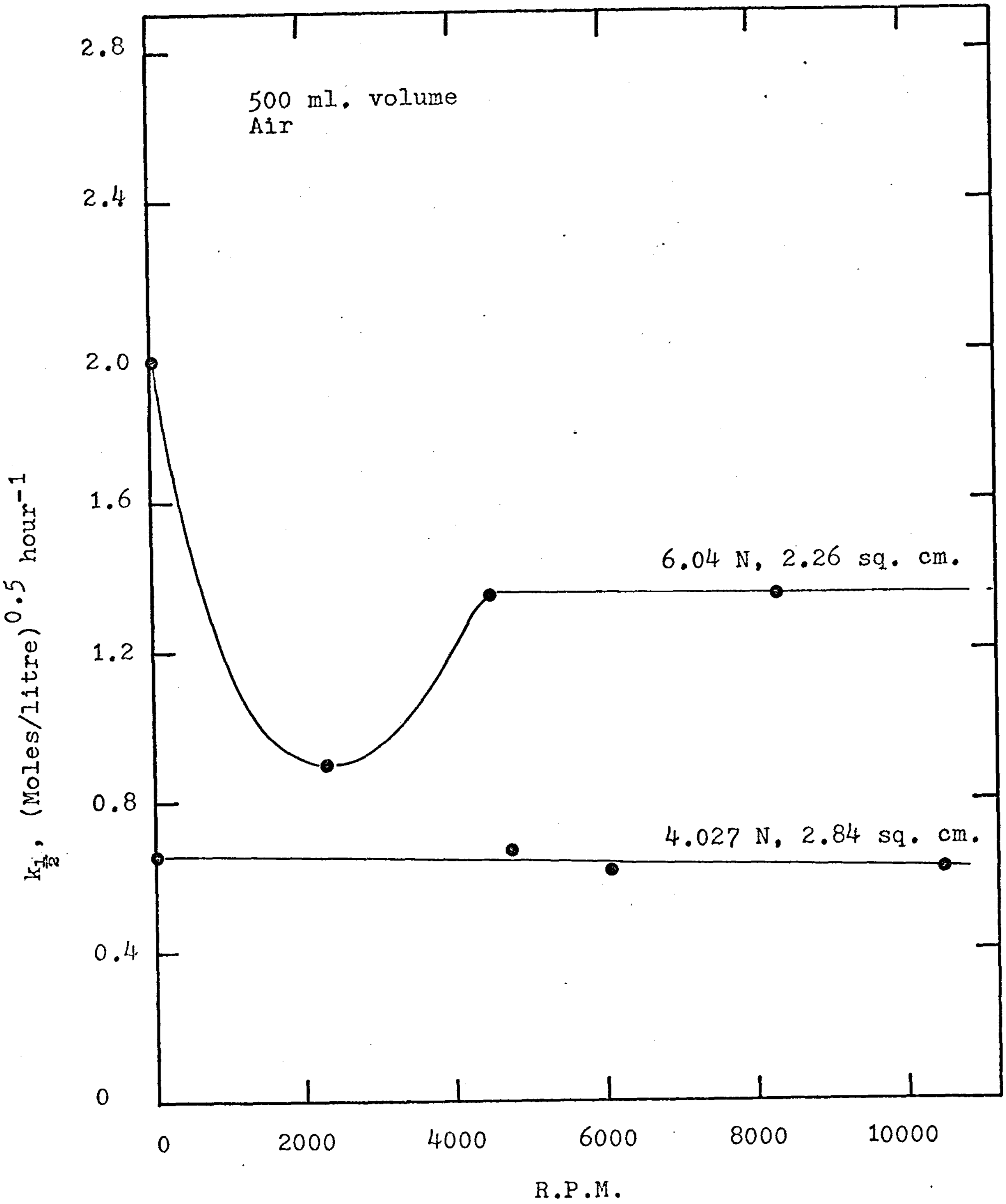

FIGURE 5-10 EFFECT OF ROTATIONAL SPEED ON DISSOLUTION RATE

oxygen must diffuse.

The corrosion, being the sum of two effects, will be determined mainly by the hydrogen gas evolution at low velocities and by oxygen depolarization at high velocities and should consequently pass through the minimum point in the intermediate range.

In the present study it has been shown that the rate of corrosion decreases with increase of speed in the initial stages and then increases to a constant value for speeds higher than 4500 r.p.m. To avoid damage to the experimental equipment a rotational speed of 4500 r.p.m. was chosen for most of the research work.

At lower acid concentrations the corrosion rate is independent of rotational speed. This suggests that oxygen depolarization plays a predominant role.

5. Effect of Temperature on Dissolution Rate

The effect of temperature on the dissolution rate of iron was studied over the range 26° - 45°C under oxygen and air saturation. Figure 5-11 shows the data from runs made in 4.027 N hydrochloric acid. The Arhenius activation energy is of the order of 9.4 kcals per gram mole. Similar results were obtained for other acid concentrations.

The high value of activation energy and negligible effect of rotational speed after 4500 r.p.m. indicates that the controlling step in the dissolution of iron is a

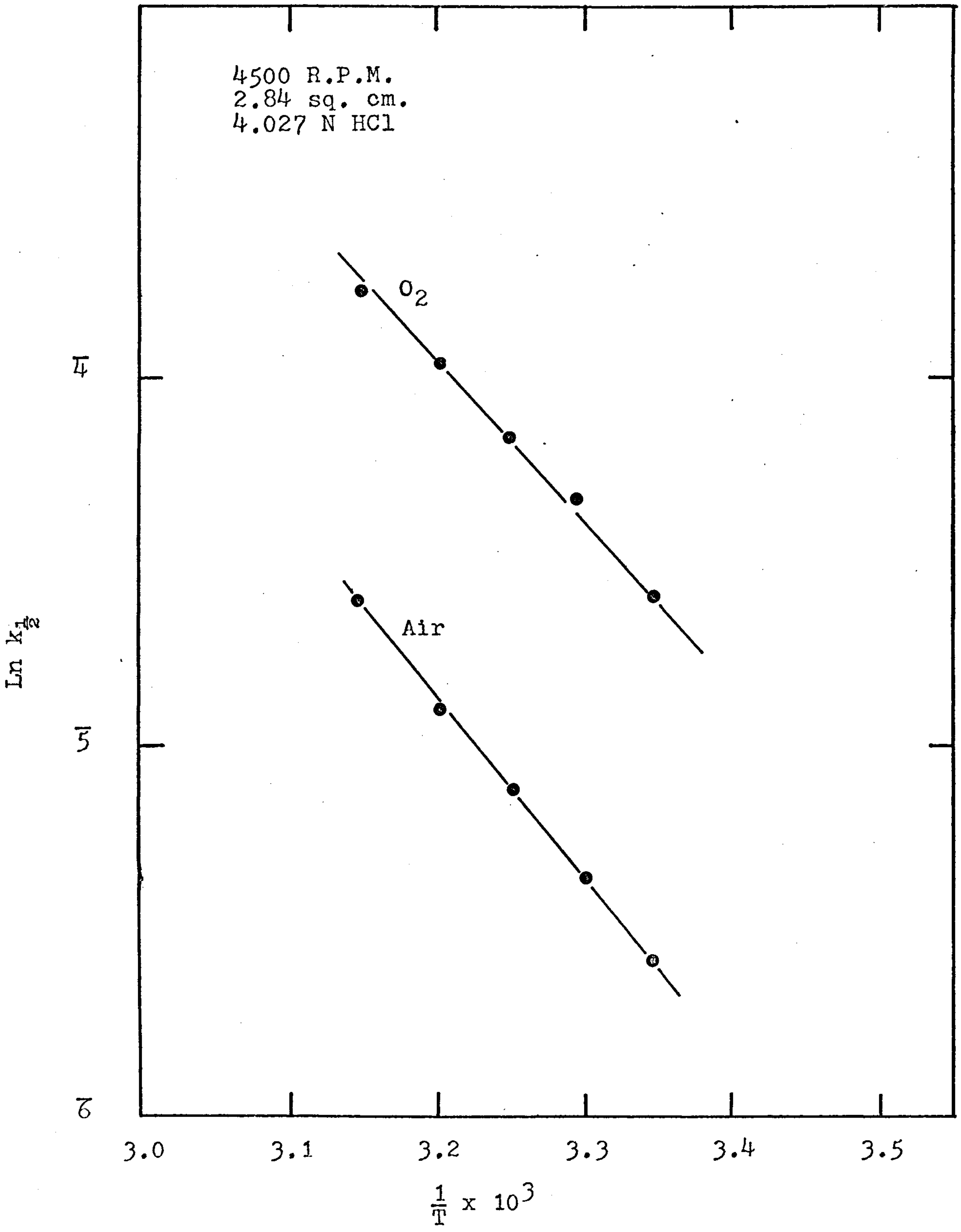

FIGURE 5-11 EFFECT OF TEMPERATURE ON DISSOLUTION RATE

chemical process rather than a physical one.

6. Effect of Hydrochloric Acid Concentration on the Dissolution Rate

The effect of acid concentration under air-saturation was studied over the range 3.04 - 6.04 N hydrochloric acid. A plot of the half order rate constant versus acid concentration as shown in figure 5-12 gives a linear relationship for moderately concentrated acids (up to 5 N) but at higher concentrations the rate becomes a more complex function of acid concentration.

This behaviour is explained by Posner (28) by assuming that there is a complex formed between ferrous ion and hydrochloric acid as described previously in the Literature Review.

In the present study it is not possible to write the rate expression for higher acid concentrations. Further work must be done before it can be completely appreciated.

7. Effect of Superficial Surface Area on the Dissolution Rate

The effect of area was studied in 4.027 N hydrochloric acid at 35°C in air saturated solutions. Figure 5-13A shows the half order rate to be a linear function of the apparent surface area. This plot implies that there is a finite half order rate with zero surface. From this apparent contradiction it appears that the corrosion rate cannot be directly proportional to superficial surface area.

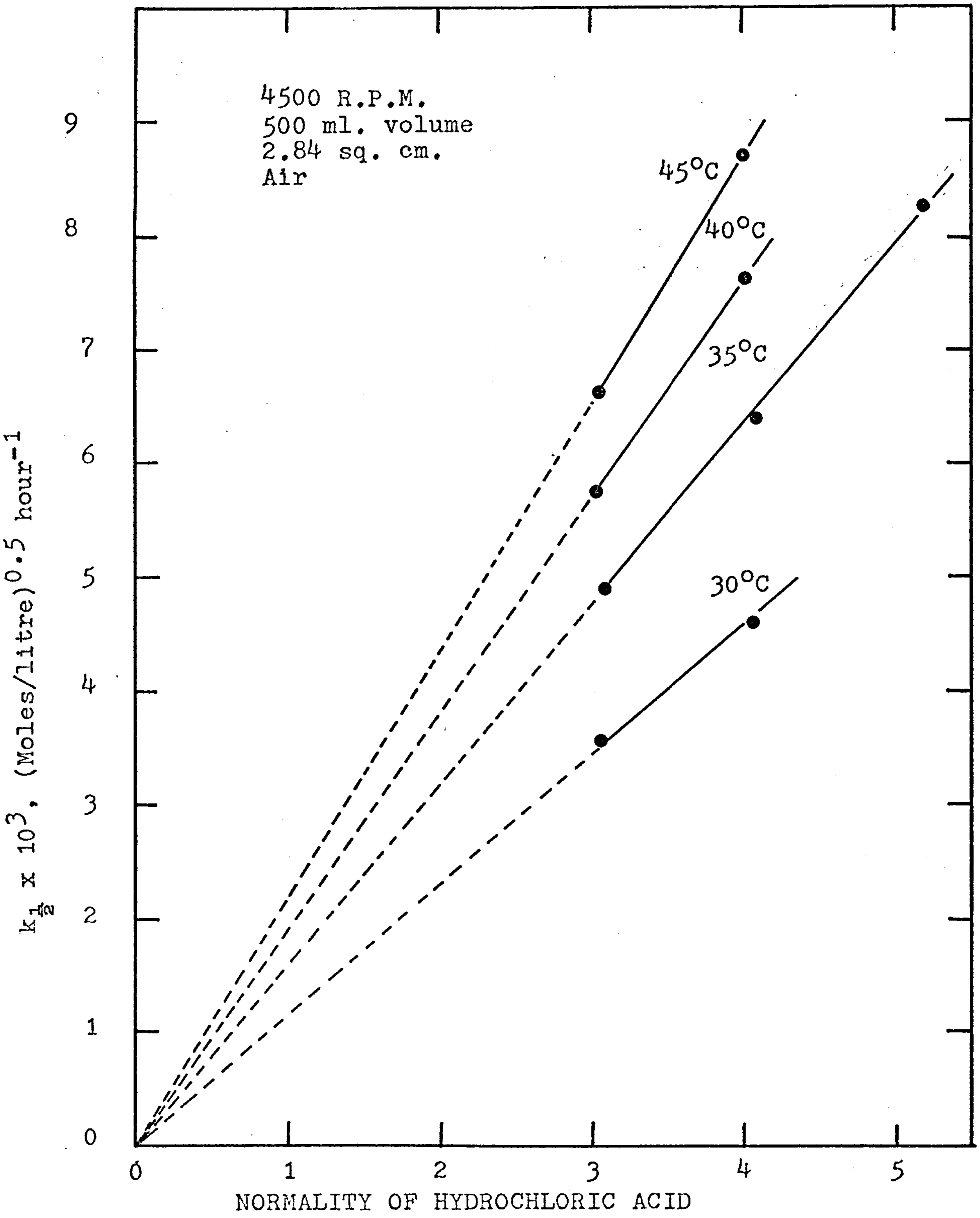

FIGURE 5-12 EFFECT OF ACID CONCENTRATION UNDER AERATED CONDITIONS

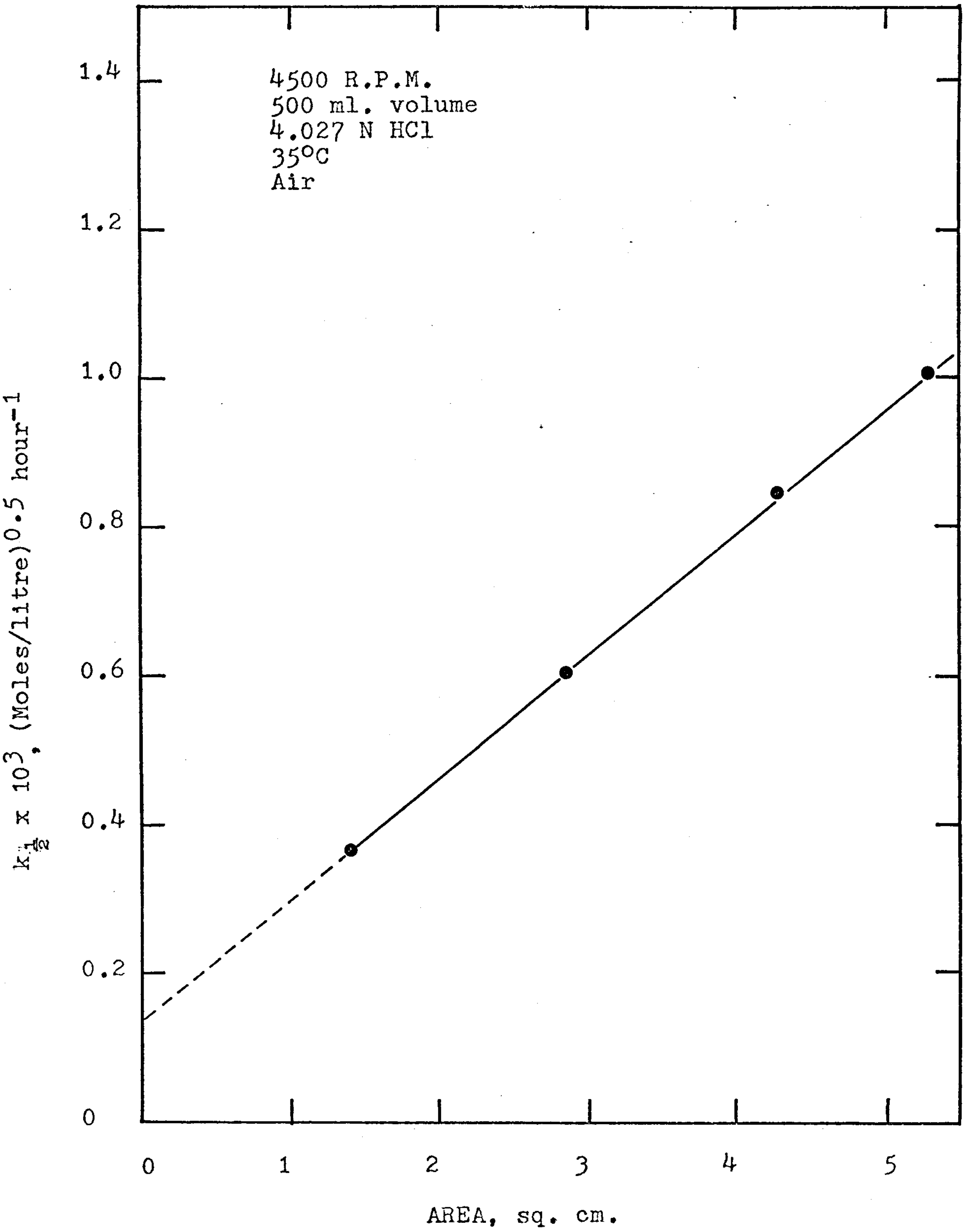

FIGURE 5-13A EFFECT OF AREA UNDER AERATED CONDITIONS

Figure 5-13B shows that the half order rate is proportional to the three quarter power of the area. This may be the characteristic of metals which can displace hydrogen gas from acid solutions. This has been confirmed by Lui (6) and Bodner (8), who found the rates of dissolution of tin and titanium to be proportional to the sqare root and three quarter power of areas respectively. The rate of dissolution of copper (1,4) has been found to be directly proportional to the surface area in acid solutions. Copper does not displace hydrogen from acid solutions.

8. Effect of Volume on Dissolution Rate

The effect of solution volume was studied in 6.04 N hydrochloric acid at 40°C in air-saturated solutions by rotating the iron samples in 400, 500 and 600 ml. of corroding fluid. Plots of iron concentration in moles per litre versus time have been shown in figure 5-14 for the three volumes. Figure 5-15 shows the moles of iron dissolved as a function of time. It becomes clear that the rate of corrosion in moles per litre per hour is inversely proportional to the volume of corroding solution.

9. Effect of Oxygen on Dissolution Rate

The effect of oxygen on the dissolution rate was determined by bubbling nitrogen, air and oxygen through the solution keeping the rate of the gas constant (about 1.5 litres/min.). Figure 5-16 indicates that the rates of dissolution are most effectively correlated in terms of the

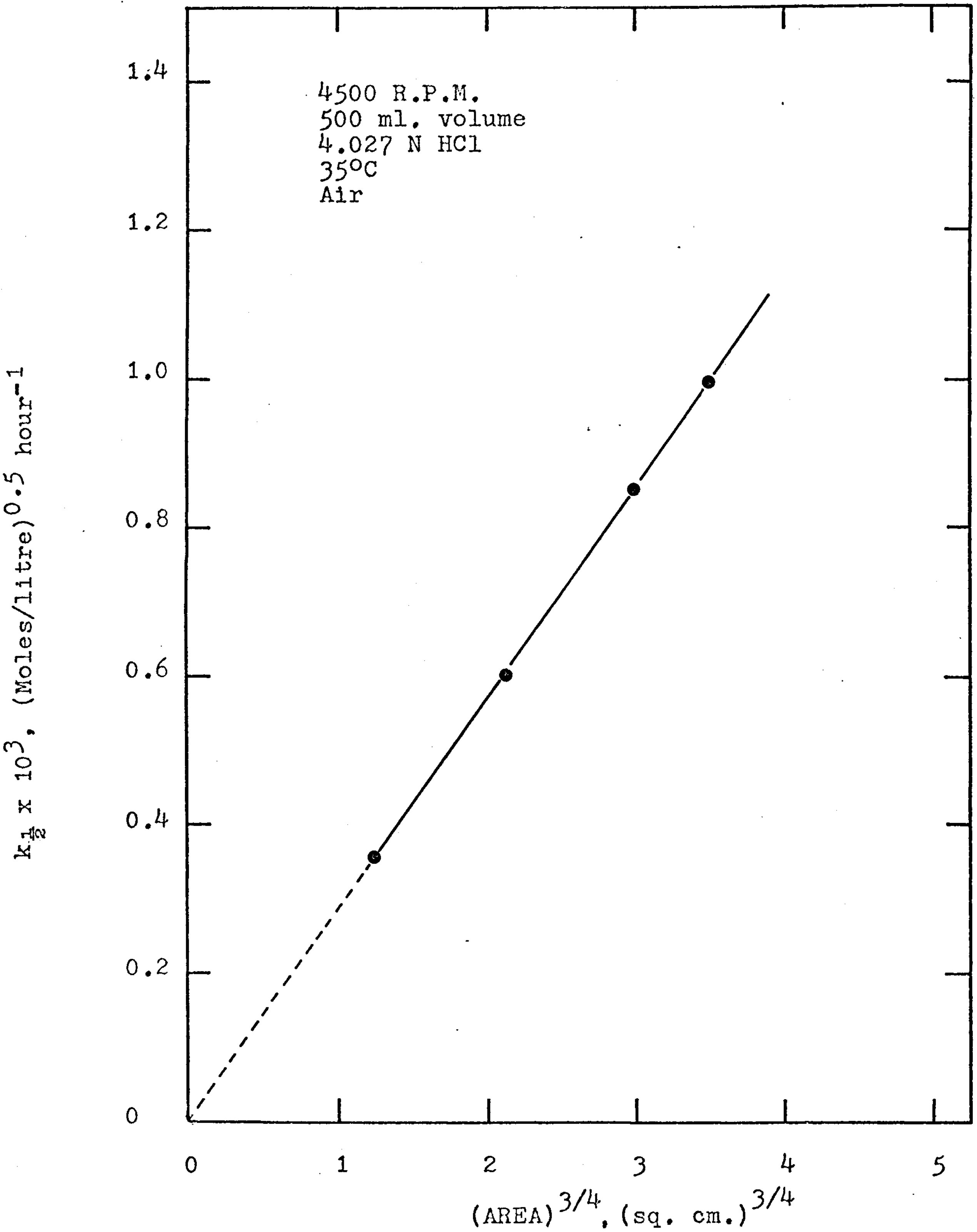

FIGURE 5-13B EFFECT OF AREA UNDER AERATED CONDITIONS

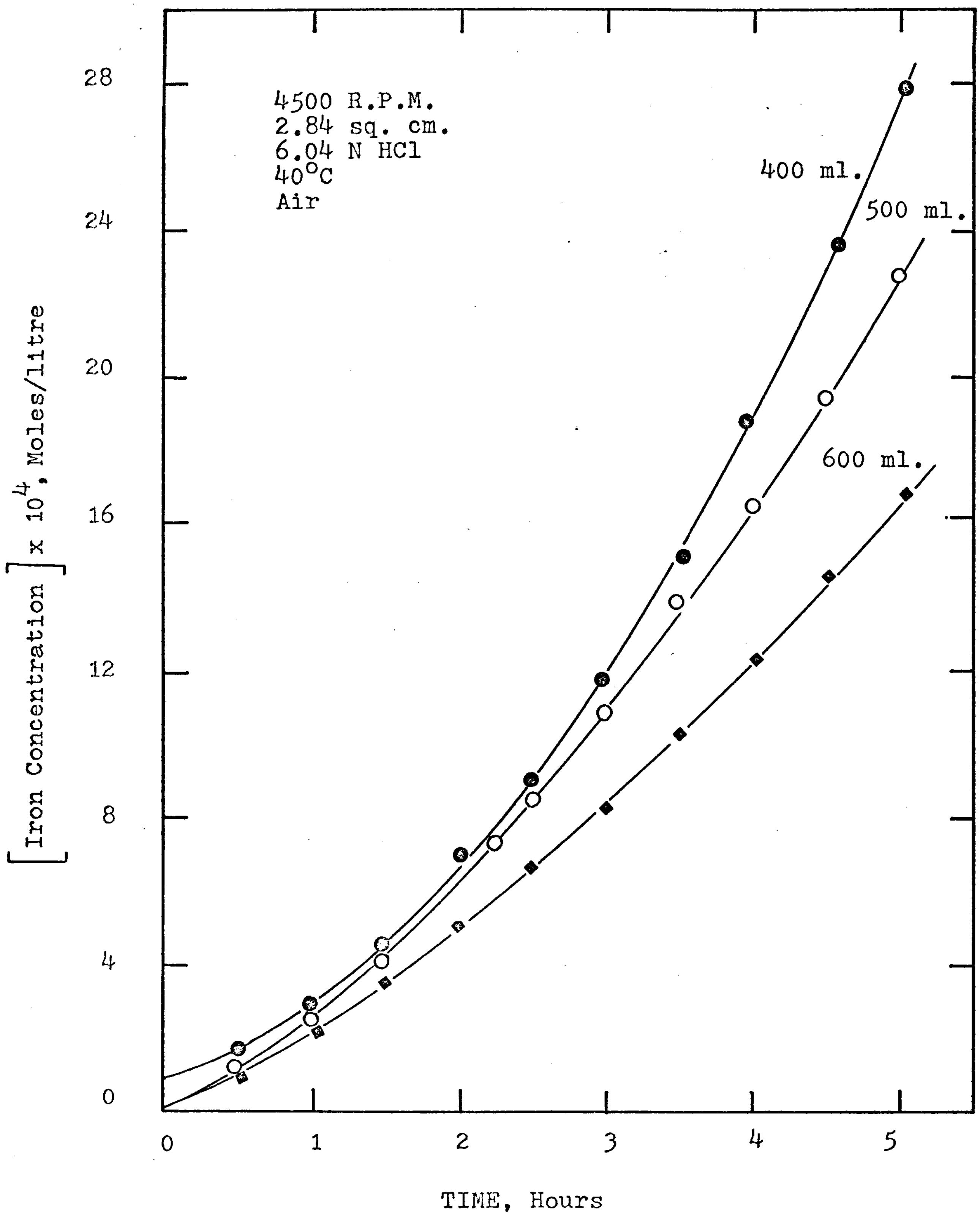

FIGURE 5-14 EFFECT OF VOLUME ON DISSOLUTION RATE

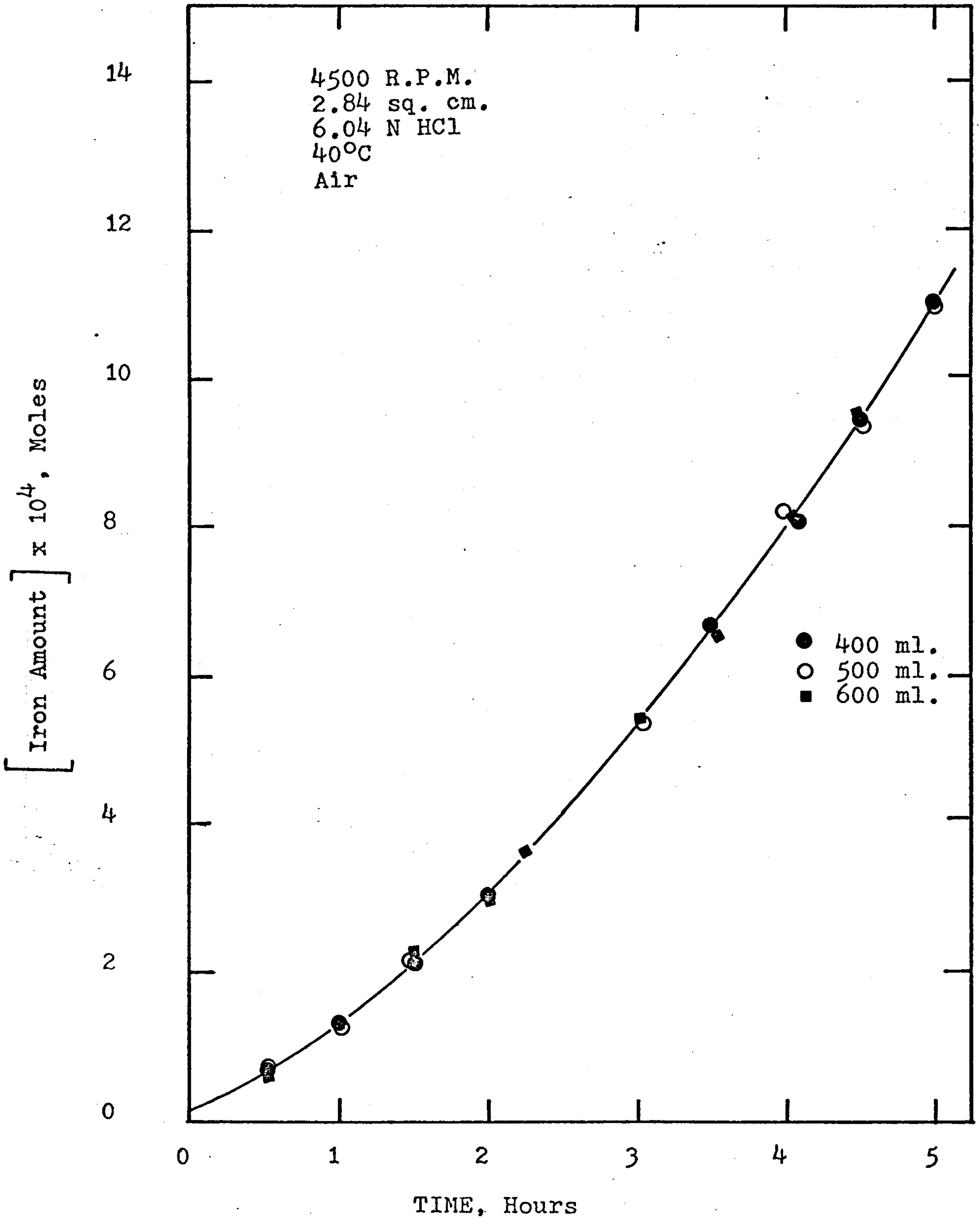

FIGURE 5-15 EFFECT OF VOLUME ON DISSOLUTION RATE

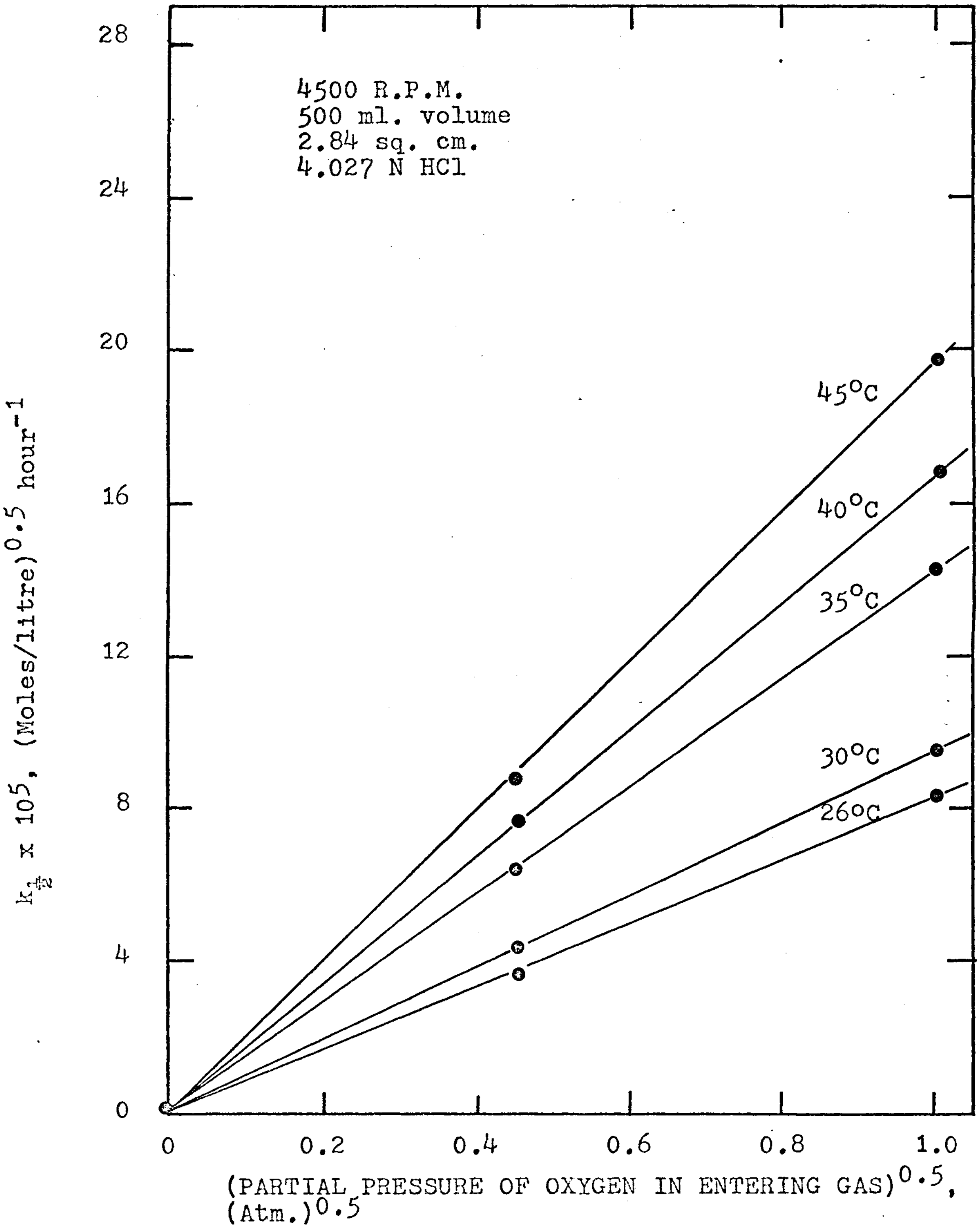

FIGURE 5-16 EFFECT OF OXYGEN ON DISSOLUTION RATE

square root of the oxygen partial pressure in the gas phase with which the solution is equilibrated.

A detailed study of the oxygen-effect was made in 4.027 N hydrochloric acid over the temperature range of 26° - 45°C. Table 5-2 shows the typical values of rate constants.

TABLE 5-2

EFFECT OF OXYGEN

4500 r.p.m.
2.84 sq. cm.
4.027 NHCl

Temperature °C	Type of Aeration	Rate Constant x 10^4 $(\text{moles/litre})^{0.5}\text{hr}^{-1}$
45	O_2	198
45	Air	87.0
45	N_2	1.03*
40	O_2	168
40	Air	76
40	N_2	0.56*
35	O_2	144.0
35	Air	62.0
35	N_2	0.47*
30	O_2	96
30	Air	43
30	N_2	0.316*
26	O_2	85
26	Air	35
26	N_2	0.29*

* These are zero order rates with units moles/litre-hr.

This half order dependance on the concentration of oxygen implies dissociation of oxygen. This may be the result of some process similar to that suggested by equation 3.21.

10. Empirical Equation

The results indicate that three processes of corrosion may be proceeding simultaneously in aerated acids. The first process, corrosion with the evolution of hydrogen gas, occurs alone in the runs under nitrogen and is termed corrosion by hydrogen gas evolution. The second occurs together with the first, in runs under air or oxygen and is known as corrosion by oxygen depolarization. The third is an autocatalytic contribution.

These three processes of corrosion can be represented as follows:

$$Fe + 2H^{+} \longrightarrow Fe^{++} + 2H \qquad (5.5)$$

$$Fe + H^{+} + O_2 \longrightarrow Fe^{++} + HO_2^{-} \qquad (5.6a)$$

$$Fe^{++} + H^{+} + O_2 \longrightarrow Fe^{+++} + HO_2 \qquad (5.6b)$$

$$2Fe^{+++} + Fe \rightleftharpoons 3\ Fe^{++} \qquad (5.7)$$

Reactions (5.6) and (5.7) would be responsible for the increase in corrosion when oxygen is introduced into the hydrochloric acid solution.

In the present work it is not possible to separate corrosion due to oxygen depolarization from that due to autocatalysis. Therefore the results of these experiments can be summarized by the following empirical rate equation.

$$\frac{d(Fe)}{dt} = \frac{(A)^{3/4}}{V} (HCl) \exp\left(-\frac{9400}{RT}\right) \left[K_1 + K_2 (P_{O_2})^{0.5} (Fe)^{0.5}\right] \quad (5.8)$$

where (Fe) is the total iron concentration in the corroding solution expressed in moles/litre

t is the time in hours

A is the superficial area in cm^2

V is the volume in litres

(HCl) is the normality of hydrochloric acid

P_{O_2} is the partial pressure of oxygen in atmospheres

T is the temperature in K^o

The values of K_1 and K_2 have been found to be 13.1 and 1.18×10^4 with the detailed calculations shown in Appendix III.

Thus equation (5.8) can be written as

$$\frac{d(Fe)}{dt} = \frac{(A)^{3/4}}{V} (HCl) \exp\left(-\frac{9400}{RT}\right) \left[13.1 + 1.18 \times 10^4 (P_{O_2})^{0.5} (Fe)^{0.5}\right] \quad (5.9)$$

This equation (5.8) is a valid correlation of experimantal data over the range of conditions.

1) Temperature 26^o - 45^oC

2) Partial Pressure of oxygen: 0 - 1 atm.

3) Time up to 6 hours $(0 < Fe < 23.1 \times 10^{-4})$

4) Hydrochloric acid concentration 2.4 - 5.37 NHCl

5) Volume 400 - 600 ml.

6) Area 1.43 - 5.72 cm^2

7) Rotational speeds 4500 - 11000 R.P.M.

CHAPTER VI

CONCLUSIONS

The corrosion of iron proceeds by three processes:

A. Corrosion due to hydrogen gas evolution

B. Corrosion due to depolarization by oxygen

C. Corrosion due to autocatalysis

Corrosion by hydrogen gas evolution is responsible for the appearance of ferrous ions in solution. The presence of oxygen will accelerate the dissolution. By virtue of slow autoxidation of ferrous species, oxygenated solutions contain both ferrous and ferric ions. The simultaneous existence of the two oxidation states in solution makes it difficult to separate the effect of oxygen depolarization from that of autocatalysis.

Because the corrosion rate was independent of rotational speed for peripheral velocities above 6700 cm/min and the Arhenenius activation energy was quite high, of the order of 9.4 K cal per gram mole, it is reasonable to suggest that the controlling step in the dissolution of iron is chemical rather than physical for the range of conditions studied.

The surfaces of corroded iron samples are distinctly different from those of copper, tin and titanium (1,4,6,8).

The deep furrows suggest that the corrosion process is not completely uniform over the cylindrical surface. Absorption of evolved hydrogen by the metal matrix may lead to formation of high pressure gas pockets which may stress the corroding surface.

As expected, the corrosion of iron shows an autocatalytic behaviour. The metals copper, titanium, tin and iron have been subjected to fundamental studies and all show an evidence of autocatalysis. It is possible to generalize that any metal capable of existing in two or more oxidation states should show an autocatalytic behaviour.

CHAPTER VII

SCOPE OF WORK IN FUTURE

As a result of the present investigation, the following recommendations can be made for the future:

A. Work should be done at lower acid concentrations where the dissolution rates would be quite low. Under these conditions it may be possible to separate the effects of oxygen depolarization from that of autocatalysis.

B. Work is needed under nitrogen saturation before the complete validity of the present empirical equation can be accepted.

C. Attempts should be made to measure the amount of hydrogen gas evolved during corrosion to confirm the suspicion that some hydrogen is absorbed by the metal matrix when the specimens are rotating.

D. Development of techniques to measure the concentrations of species adsorbed on the metal surface may help in interpreting the experimental data theoretically. It would be useful to test for the presence of hydrogen peroxide in the corroding solution.

E. The corrosion study should also be extended to specimens of different shapes and cylindrical samples of different diameters keeping the area constant.

F. The real proof of validity of a rate equation is its prediction of corrosion rates for other configurations of sample and corroding fluid. It would be worthwhile to determine how well the presently derived rate equation will correlate the results of studies made on a system involving a fluid flowing through an iron pipe. Another approach would be to flow the liquid over the walls of a horizontal cylinder, with streamlined protective plastic end-caps, at rates comparable to the peripheral velocities of the present experiments.

REFERENCES

1. Lu, B.C.Y. and Graydon, W.F., J. Am. Chem. Soc., 77, 6136 (1955).
2. Lu, B.C.Y. and Graydon, W.F., Can. J. Chem., 32, 153 (1954).
3. Weeks, J.R. and Hills, G.R., J. Electrochem. Soc., 103, 203 (1956)
4. Gnyp, A.W., Ph. D. Thesis, Toronto, (1958).
5. Ammar, I. A. and Riad, S., J. Electrochem. Soc., 106, 926 (1959).
6. Lui, Alex W.K., Ph. D. Thesis, Windsor, (1964).
7. Gee, E.A. and Golden, L.B., Ind. Eng. Chem., 41, 1668 (1949).
8. Bodner, J.J., M. A. Sc. Thesis, University of Windsor, (1964).
9. Schchikow, Krasil, J., J.Chem., (U.S.S.R.), 14, 261, (1944).
10. Hudson, R.M., Corrosion, 20, 245t (1964).
11. Hudson, R.M., Magor, J.K. and Stragand, G.L., J. Amer. Ceram. Soc., 41, 23 (1958).
12. Podesta, J.J. and Arvia, J.J., Electrochimica Acta, 10, 159 (1965).
13. Leko, A.M., Bull. Soc. Chim., Belgrade, 14, 249 (1944).
14. Demon, G.H., Ind. and Eng. Chem., 33, 67 (1941).
15. Archer, H.R. and Howlett, J., Chemistry and Industry, 35, 605 (1949).
16. Whitman, W., Russell, R., Welling, C. and Cochrane, J., Ind. and Eng. Chem., 15, 672 (1923).

17. Landolt - Bernstein, 5th ed., 1104.

18. Gatos, Harry, C., J. Electrochem. Soc., 5, 286 (1956)

19. Tomashov, N.D.,"Theory of Corrosion and Protection of Metals", The Macmillan Company, New York 1st edition (1966).

20. Whitley and Hallimond, Carnegie Schol. Mem., 9, 1 (1918).

21. Vetter, K.J., Z. Electrochem., 56, 106 (1952).

22. Bonhoffer, K.F., Brauer, E. and Langhammer, Z. Electrochem., 29, 52 (1948).

23. Conroy, Games, T., J. Soc. Chem. Ind., 20, 316 (1901).

24. Morris, B., Abramson and Cecil V. King., J. Am. Chem. Soc., 61, 2290 (1939).

25. Makrides, A.C., Komodromos, N.M. and Hackerman, J. Electrochem. Soc., 102, 363 (1955).

26. Rigg Tyson, Taylor Willium and Weiss Joseph, J. Chem. Phys., 22, 575 (1954).

27. Sobkowski, Jerzy, Roczniki Chemi.Ann Soc. Chim., Polonorum, 36, 1503 (1962).

28. Posner, A.M., Trans. Faraday Soc., 49, 382, 389 (1953).

29. Haber and Weiss, Proc. Roy. Soc. A., 147, 332 (1934).

30. George, P.J., Chem. Soc., (London), 4349 (1954).

31. Cher, M. and Davidson, N.J., Am. Chem. Soc., 77, 793 (1955).

32. "Book of A.S.T.M. methods of Chemical Analysis of Metals", 325 (1946).

33. "American Soc. for Testing Materials" (1946).

34. Walden, G.H., Jr., Hammett, Louis, P. and Chapman, Ray, P., J. Am. Chem. Soc., 53, 3908 (1931).

35. Koenig, Ruth, A. and Johnson, C.R., J. Biol. Chem., 143, 159 (1942).

36. Gregory, A.W., J. Chem. Soc. Trans. 93, 93 (1908).

37. Mehlig, J.P., Ind. Eng. Chem. Anal. Ed., 10, 136 (1938).

38. Scott, R.O., Analyst, 66, 142 (1941).

39. Kennard Martha and Johnson, C.R., Proc. Trans. Texas Acad. Sci., 27, 45 (1944).

40. John, H. Yoe., J. Am. Chem. Soc., 54, 4139 (1932).

41. Van Klooster, H.S., J. Am. Chem. Soc., 43, 746 (1921).

42. Moeller Therald, Ind. Eng. Chem., Anal. Ed., 15, 346 (1943).

43. Snell, F.D. and Snell, C.T., "Colorimetric Methods of Analysis", D. Van. Nostrand Co. Inc., New York 3rd ed. 2, (1954).

44. Huttner, C., Z Anorg. Chem., 86, 341 (1914).

45. Hostetter, J.C., J. Am. Chem. Soc., 41, 1531 (1919).

46. "Book of A.S.T.M. Methods of Chemical Analysis of Metals" (1946).

47. "American Soc. for Testing Materials", Philadelphia, Pa (1946).

48. Evans, Ulick, R., "An Introduction to Metallic Corrosion", Edward Arnold (Publishers) Ltd., 2nd ed. (1963).

49. MacInnes and Contieri, J. Am. Chem. Soc., 41, 2013 (1919).

50. Lu, B.C.Y. and Graydon, W.F., Can. J. Chem., 32, 153 (1954).

APPENDIX I

Typical Analysis of High Purity Research Iron
Supplied by Armco Steel Corporation, Ohio, U.S.A.

Hardness

75 RB (Rockwell Hardness Tester)

Analytical Results

Element	Percent	Method
C	0.013	Combustion (Leco)
S	0.020	Leco
Mn	0.051	Direct reading spect.
P	0.007	Direct reading spect.
Al	0.004	Spectrograph
Si	0.0004	Spectrograph
Sn	0.007	Spectrograph
Cr	0.008	Spectrograph
Co	0.006	Spectrograph
Pb	0.001	Spectrograph
Ni	0.046	Spectrograph
Mo	0.005	Spectrograph
Cu	0.10	Direct reading spect.
Va Sb As Cb	Less than 0.010	Direct reading spect.
Cd	Less than 0.010	Direct reading spect.

Metallographic examination disclosed equiaxed grains of ASTM size number 4 to 5. The general appearance of the grain structure is typical of ingot iron in the angular or somewhat rugged grains.

Light cold working was done on the iron rod.

APPENDIX II

Colorimetric Determination of Ferric Chloride Concentration

A Bausch and Lamb Spectronic 20 colorimeter has been used for the analysis of iron in the corroding solution. The following procedure was used:

Iron wire of purity 99.86% was used for this calibration. A small piece of wire weighing 0.100 grams was dissolved in 10 ml of 1:1 hydrochloric acid by heating the acid gently. One millilitre of 30 percent hydrogen peroxide was added and the solution was boiled till there was no evidence of further evolution of chlorine gas. After cooling, the solution was diluted with acid of the desired normality to 100 ml. Thus an iron solution of 1.79 x 10^{-2} molar concentration was obtained. A solution of 1.79 x 10^{-3} molar concentration was prepared by diluting 10 ml. of 1.79 x 10^{-2} molar solution to 100 ml. with the acid of the desired normality. Finally by various proportions of these solutions and pure acid, eight solutions of different concentrations of iron were prepared.

The colorimeter was set at a wavelenth of 370 mμ because at this wavelength maximum absorbance was obtained as reported by many investigators (44,45,47) and also found by this author. With the colorimeter set at this wavelength, transmittances of standard solutions were read with a blank solution of hydrochloric acid being taken as 100 percent transmission and a graph of percent transmittance versus concentration was plotted as shown in figure II-1. This plot can be used for both ferric and ferrous ion determination in the following manner: An initial reading of the unknown sample yields (Fe^{+++}). Subsequent oxidation with a drop of 30% hydrogen peroxide and rereading yields the total ion concentration. The latter figure minus the former gives (Fe^{++}).

The effect of temperature on the intensity of ferric chloride was also studied. A plot of transmittance versus temperature as depicted in figure II-2, shows that transmittance decreases as the temperature is increased.

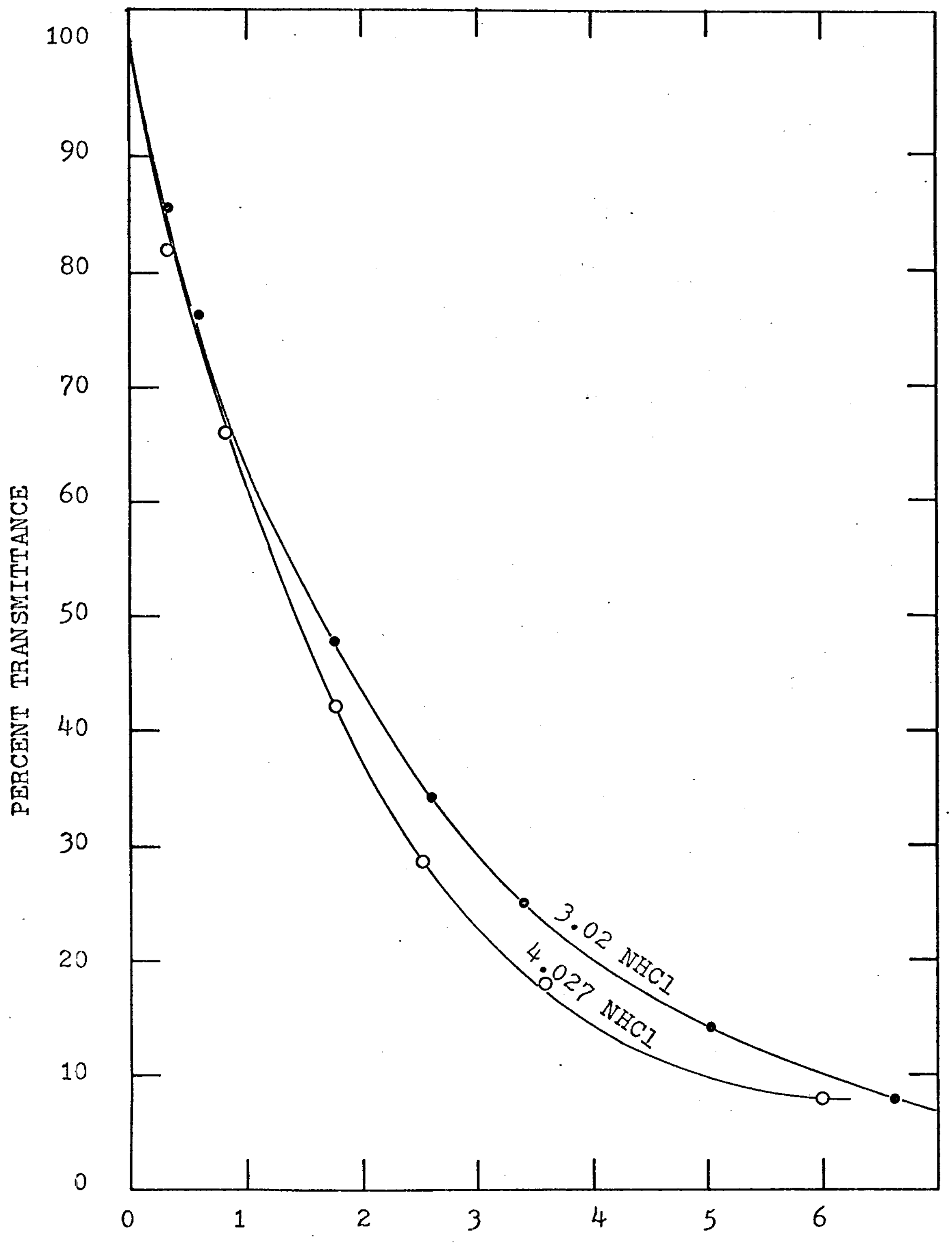

FIGURE II-1 CALIBRATION CURVE FOR IRON ANALYSIS

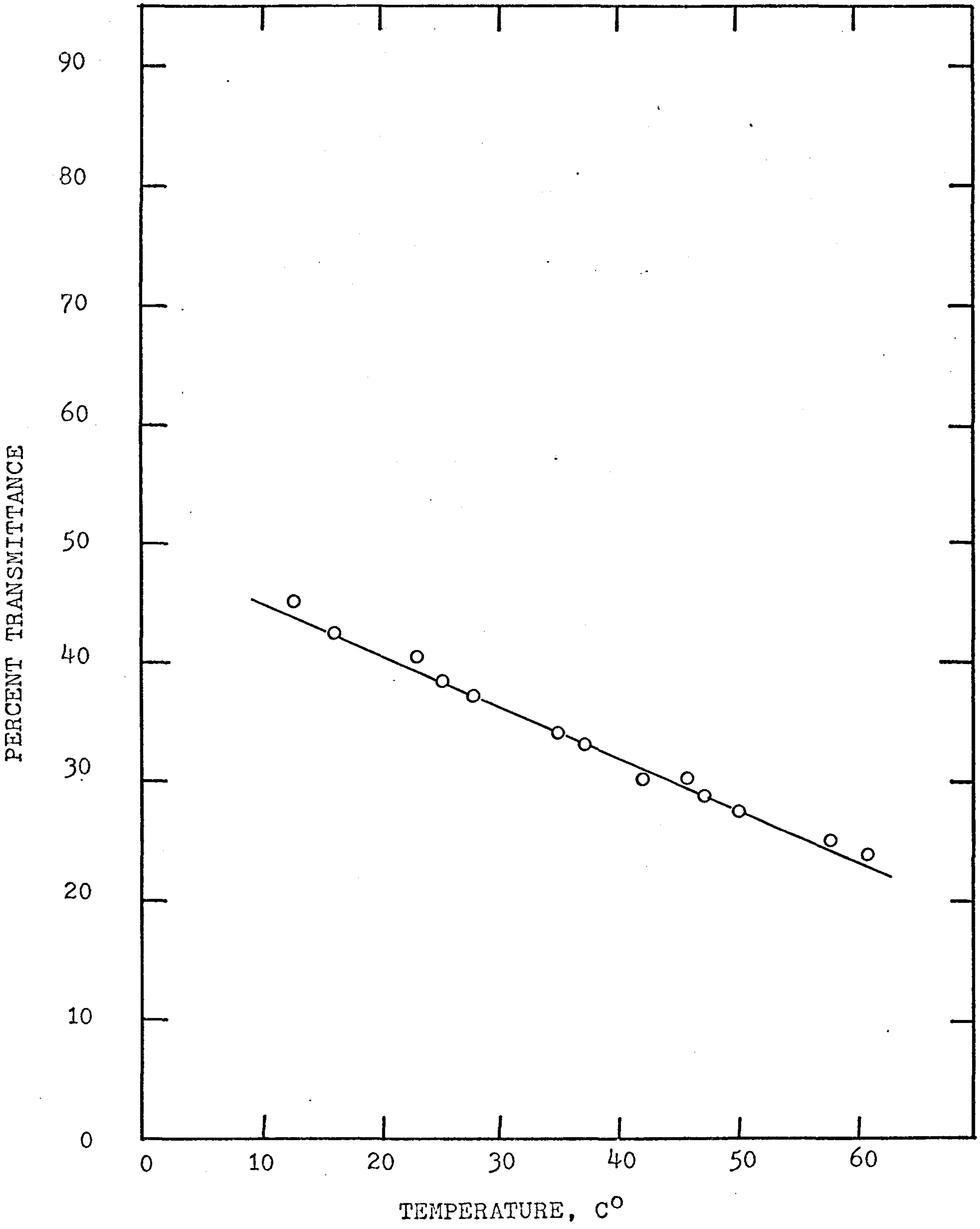

FIGURE II-2 EFFECT OF TEMPERATURE ON TRANSMITTANCE OF IRON SOLUTIONS

APPENDIX III

Detailed Calculations of Constants K_1 and K_2 in Equation (5.8)

A. Under Anaerobic Conditions:

Equation (5.8) reduces to

$$\frac{d(Fe)}{dt} = K_1 \frac{(A)^{3/4}}{V} (HCl) \exp\left(-\frac{9400}{RT}\right)$$

$$K_1 = \frac{d(Fe)}{dt} \frac{V}{(A)^{3/4}(HCl)} \exp\left(+\frac{9400}{RT}\right)$$

Substitution of the values for $\frac{d(Fe)}{dt}$, V, A and (HCl), shows the average value of K_1 to be 13.1

B. Under Aerated Conditions:

Equation (5.8) becomes

$$\frac{d(Fe)}{dt} = \frac{(A)^{3/4}}{V} (HCl) \exp\left(-\frac{9400}{RT}\right) \left[13.1 + K_2 (P_{O_2})^{0.5} (Fe)^{0.5}\right]$$

$$dt = \frac{d(Fe)}{\frac{(A)^{3/4}}{V} (HCl) \exp\left(-\frac{9400}{RT}\right) \left[13.1 + K_2 (P_{O_2})^{0.5} (Fe)^{0.5}\right]}$$

This equation can be written in the form

$$dt = \frac{dX}{C + BX^{\frac{1}{2}}}$$

where C and B are constants

X is (Fe)

Now putting $X^{\frac{1}{2}} = Y$

$$\text{then } \tfrac{1}{2}X^{-\frac{1}{2}}\,dX = dY$$

$$dX = 2dYX^{\frac{1}{2}}$$

$$= 2YdY$$

$$dt = \frac{2YdY}{C + BY}$$

Intergration of both sides gives

$$\int dt = \int \frac{2YdY}{C + BY}$$

$$= \frac{2}{B} \int \frac{dYBY}{C + BY}$$

$$= \frac{2}{B} \int \frac{dy(C + BY - C}{C + BY}$$

$$= \frac{2}{B}\left[\int dY - \int \frac{C}{C + BY}\, dY\right]$$

$$t = \frac{2Y}{B} - \frac{2C}{B^2} \ln(C + BY)$$

$$t = \frac{2(Fe)^{0.5}}{K_2 \frac{(A)^{3/4}}{V} (HCl) \exp\left(-\frac{9400}{RT}\right) (P_{O_2})^{0.5}} - \frac{\left[2 \times 13.1 \frac{(A)^{3/4}}{V} (HCl) \exp\left(-\frac{9400}{RT}\right)\right]}{\left[K_2 \frac{(A)^{3/4}}{V} (HCl) \exp\left(-\frac{9400}{RT}\right) (P_{O_2})^{0.5}\right]^2}$$

$$\left\{ \ln\left[13.1 \frac{(A)^{3/4}}{V} (HCl) \exp\left(-\frac{9400}{RT}\right) + K_2 \frac{(A)^{3/4}}{V} (HCl) \exp\left(-\frac{9400}{RT}\right) (P_{O_2})^{0.5} (Fe)^{0.5}\right]\right\}$$

The average value of K_2 was found to be 1.18×10^4.

APPENDIX IV

4.027 N HCl Dissolution Runs

4500 rpm
2.84 sq. cm.
500 ml. volume

All Concentrations are in (Moles/litre) x 10^4

Run 1 - 45°C, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.2	0.8	0.6
1.0	0.45	1.56	1.11
1.5	0.60	2.15	1.55
2.0	0.77	2.90	2.13
2.5	1.06	3.95	2.89
3.25	1.39	5.5	4.11
3.5	1.6	6.0	4.4
4.0	2.2	7.08	5.48
4.5	2.28	8.6	6.32
5.0	2.48	10.2	7.72
5.5	2.84	11.9	9.06

Run 2 - 40°C, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.17	0.96	0.79
1.75	0.38	2.03	1.65
2.0	0.49	2.35	1.86
2.5	0.6	2.8	2.2
3.0	0.75	3.55	2.8
3.5	0.86	4.2	3.34
4.0	1.0	4.6	3.6
4.75	1.4	6.26	4.86
5.0	1.6	6.52	4.92
5.5	1.84	7.48	5.64

Run 3 - 35°C, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
1.0	0.2	1.19	0.99
1.5	0.27	1.65	1.38
2.0	0.36	2.15	1.79
2.5	0.49	2.72	2.23
3.0	0.55	3.16	2.61
3.5	0.67	3.75	3.08
4.25	0.82	4.8	3.98
5.0	1.12	5.96	4.84
5.5	1.24	6.6	5.36

Run 4 - 30°C, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.16	0.81	0.65
1.0	0.23	1.0	0.77
1.5	0.30	1.52	1.22
2.0	0.40	1.82	1.42
2.5	0.45	2.06	1.61
3.0	0.5	2.41	1.91
3.5	0.65	2.73	2.08
4.5	0.79	3.5	2.71
5.0	0.85	4.25	3.05
5.5	0.96	4.85	3.89

All Concentrations are in (Moles/litre) x 10^{-4}

Run 5 - 26°C, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.1	0.5	0.4
1.0	0.14	0.83	0.69
1.5	0.19	1.01	0.82
2.0	0.22	1.26	1.04
2.5	0.27	1.45	1.18
3.0	0.28	1.7	1.42
3.5	0.35	1.93	1.58
4.0	0.40	2.2	1.8
4.5	0.45	2.39	1.94
5.0	0.45	2.57	2.12
5.5	0.46	2.8	2.34

Run 6 - 45°C, N_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.0	0.77	0.77
1.0	0.0	1.38	1.38
1.5	0.09	1.69	1.6
2.0	0.12	2.3	2.18
2.5	0.14	2.69	2.55
3.0	0.14	3.35	3.21
3.75	0.14	3.95	3.81
4.5	0.18	5.0	4.82
5.0	0.20	5.5	5.3
5.5	0.20	6.0	5.8
6.0	0.36	6.68	6.32

Run 7 - 40°C, N_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.02	0.75	0.73
1.0	0.02	1.06	1.04
1.5	0.04	1.35	1.31
2.0	0.04	1.64	1.6
2.5	0.05	2.0	1.95
3.0	0.05	2.25	2.20
3.5	0.05	2.5	2.45
4.0	0.10	2.8	2.7
4.5	0.12	3.06	2.94
5.0	0.14	3.39	3.25
5.5	0.15	3.55	3.40

Run 8 - 35°C, N_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.04	0.75	0.71
1.0	0.04	0.93	0.89
1.5	0.05	1.25	1.20
2.0	0.05	1.45	1.40
2.5	0.06	1.67	1.61
3.25	0.06	2.10	2.04
3.5	0.07	2.12	2.05
4.0	0.09	2.45	2.36
5.0	0.37	2.95	2.58
5.25	0.54	3.12	2.58

All Concentrations are in(Moles/litre) x 10^{-4}

Run 9 - $30^{o}C$, N_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.01	0.4	0.39
1.0	0.04	0.6	0.56
1.5	0.04	0.81	0.77
2.25	0.04	1.02	0.98
2.5	0.04	1.11	1.07
3.0	0.04	1.29	1.25
3.5	0.04	1.45	1.41
4.0	0.04	1.55	1.51
4.5	0.04	1.72	1.68
5.0	0.04	1.9	1.86
5.5	0.04	2.06	2.02
6.0	0.06	2.2	2.14

Run 10 - $26^{o}C$, N_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.0	0.3	0.3
1.0	0.0	0.5	0.5
1.5	0.01	0.67	0.66
2.0	0.01	0.86	0.85
2.5	0.01	0.97	0.96
3.0	0.01	1.11	1.1
3.5	0.01	1.26	1.25
4.0	0.04	1.46	1.42
5.0	0.04	1.67	1.63
5.5	0.04	1.77	1.73
6.0	0.04	2.0	1.96

Run 11 - $45^{o}C$, O_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	1.1	2.57	1.47
0.75	1.52	3.81	2.29
1.0	2.0	5.25	3.25
1.5	3.52	9.0	5.48
2.0	4.52	11.76	7.24
2.5	6.0	15.8	9.8
3.0	7.2	22.0	14.8
3.5	8.76	25.5	16.74
4.0	10.22	28.7	18.48
4.5	11.9	33.95	22.05
5.0	13.86	44.44	30.58
5.5	16.06	53.35	37.29

Run 12 - $40^{o}C$, O_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.66	1.74	1.08
1.0	1.52	3.75	2.23
1.5	2.55	6.4	3.85
2.0	3.40	9.2	5.8
2.5	4.24	11.6	7.36
3.0	5.6	15.0	9.4
3.5	6.4	18.4	12.0
4.0	7.42	24.08	16.66
4.5	8.75	27.65	18.9
5.0	9.8	33.95	24.15

All Concentrations are in (Moles/litre) x 10^{-4}

Run 13 - 35°C, O_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.25	0.28	0.93	0.65
0.5	0.52	1.59	1.07
0.75	0.78	2.18	1.40
1.0	1.17	3.06	1.89
1.25	1.46	3.75	2.29
1.5	1.71	4.5	2.79
2.0	2.3	6.4	4.1
2.5	3.12	8.8	5.68
3.0	3.68	11.0	7.32
3.5	4.08	13.76	9.68
4.0	4.64	15.8	11.16
4.5	5.2	20.4	15.2
5.0	5.8	24.0	18.2
5.5	6.3	28.00	21.70

Run 14 - 30°C, O_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.57	1.46	0.89
1.0	1.0	2.45	1.45
1.5	1.45	3.6	2.15
2.0	1.87	4.86	2.99
2.5	2.68	6.1	3.42
3.0	2.92	7.8	4.88
3.5	3.4	9.0	5.6
4.0	3.8	10.88	7.08
4.5	4.24	12.64	8.40
5.0	4.6	14.44	9.84

Run 15 - 26°C, O_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.4	1.0	0.6
1.0	0.8	1.8	1.0
1.5	1.2	2.5	1.3
2.0	1.6	4.0	2.4
2.5	2.1	4.7	2.6
3.0	2.4	6.0	3.6
3.5	2.85	7.2	4.35
4.0	3.2	8.5	5.3
4.5	3.65	10.0	6.35
5.0	4.05	11.6	7.55
5.5	4.4	13.2	8.8

APPENDIX V

3.02 N HCl Dissolution Runs

4500 r.p.m.
2.84 sq. cm.
500 ml. volume

All Concentrations are in (Moles/litre) x 10^{-4}

Run 16 - 45°C, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.08	0.7	0.62
1.0	0.15	1.25	1.1
1.5	0.25	1.8	1.55
2.0	0.34	2.3	1.96
2.75	0.43	3.1	2.67
3.0	0.52	3.35	2.83
3.5	0.61	3.9	3.29
4.0	0.66	4.6	3.94
4.5	0.8	5.5	4.7
5.0	0.87	6.05	5.18

Run 17 - 40°C, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.06	0.45	0.39
1.0	0.11	0.88	0.77
1.5	0.20	1.35	1.15
2.0	0.30	1.73	1.43
2.5	0.36	2.14	1.78
3.0	0.41	2.58	2.17
3.5	0.48	3.1	2.62
4.0	0.55	3.6	3.05
4.5	0.63	4.25	3.62
5.0	0.70	4.8	4.1
5.5	0.76	5.35	4.59
6.0	0.83	6.05	5.22

Run 18 - 35°C, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.05	0.45	0.4
1.0	0.10	0.70	0.6
1.5	0.16	1.03	0.87
2.0	0.21	1.40	1.19
2.5	0.27	1.75	1.48
3.0	0.30	2.37	2.07
3.75	0.40	2.84	2.44
4.0	0.42	3.1	2.68
4.5	0.48	3.4	2.92
5.0	0.53	3.73	3.20
5.5	0.60	4.53	3.93
6.0	0.63	5.15	4.52

Run 19 - 30°C, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.05	0.32	0.27
1.0	0.09	0.56	0.47
1.5	0.12	0.80	0.68
2.25	0.16	1.12	0.96
2.5	0.22	1.2	0.98
3.0	0.25	1.48	1.23
3.5	0.27	1.70	1.43
4.0	0.32	1.96	1.64
4.5	0.35	2.6	2.25
5.0	0.38	3.0	2.62
5.5	0.45	3.7	3.25
6.0	0.50	4.3	3.80

All Concentrations are in (Moles/litre) x 10^{-4}

Run 20 - 26°C, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.02	0.25	0.23
1.0	0.08	0.45	0.37
1.5	0.1	0.63	0.53
2.0	0.13	0.8	0.67
2.5	0.17	1.08	0.91
3.0	0.20	1.25	1.05
3.5	0.25	1.49	1.24
4.0	0.28	1.77	1.49
5.0	0.35	2.14	1.79
5.5	0.38	2.37	1.99
6.0	0.41	2.7	2.29

Run 21 - 45°C, O_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.83	2.8	1.97
1.0	1.92	5.5	3.58
1.5	2.52	9.04	6.52
2.0	3.24	11.84	8.6
2.5	4.44	15.2	10.76
3.0	4.8	18.8	14.0
3.5	5.52	23.6	18.08
4.0	5.7	28.2	22.5
4.5	7.0	33.9	26.9
5.0	8.0	38.70	30.7

Run 22 - 40°C, O_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.71	2.3	1.59
1.0	1.73	4.7	2.97
1.5	2.3	6.75	4.45
2.0	3.0	9.9	6.9
2.5	3.65	13.0	9.35
3.0	4.28	16.72	12.44
3.5	5.02	19.8	14.78
4.0	5.7	24.0	18.3
4.5	6.3	28.0	21.7
5.0	6.9	32.0	25.1

Run 23 - 30°C, O_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.7	0.97	0.27
1.0	1.15	2.1	0.95
1.5	1.65	3.3	1.65
2.0	2.1	4.8	2.7
2.5	2.62	6.3	3.68
3.0	2.92	7.68	4.76
3.5	3.6	9.36	5.76
4.0	3.88	11.68	7.8
4.5	4.4	13.4	9.0
5.0	4.64	15.4	10.76
5.5	5.4	18.0	12.6

All Concentrations are in (Moles/litre) x 10^{-4}

Run 24 - 26°C, O_2				Run 25 - 35°C, N_2			
Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})	Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.27	0.76	0.49	1.0	0.03	0.82	0.79
1.0	0.73	1.88	1.15	1.5	0.03	1.04	1.01
1.5	1.28	2.96	1.68	2.0	0.03	1.38	1.35
2.0	1.78	4.18	2.40	2.75	0.05	1.70	1.65
2.5	2.37	5.5	3.13	3.5	0.20	1.92	1.72
3.0	2.64	7.2	4.56	4.0	0.12	2.16	2.04
3.5	3.04	8.56	5.52	4.75	0.020	2.34	3.23
4.0	3.52	10.2	6.68	6.0	0.050	2.72	2.67
4.5	3.96	11.68	7.72	6.5	0.120	2.92	2.80
5.0	4.28	13.4	9.12	7.5	0.160	3.3	3.14
5.5	4.72	15.4	10.68				

APPENDIX VI

5.37 N HCl Dissolution Runs

4500 r.p.m.
2.635 sq. cm.
500 ml. volume

All Concentrations are in (Moles/litre) x 10^{-4}

Run 26 - 45°C, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.25	0.3	1.0	0.7
0.5	0.37	1.25	0.88
0.75	0.57	1.85	1.28
1.0	0.78	2.35	1.57
1.25	1.11	3.0	2.89
1.50	1.24	3.64	2.90
2.0	2.22	5.1	2.98
2.5	2.68	6.6	3.92
3.0	3.2	8.28	5.08
3.5	4.68	12.0	7.32
4.0	5.8	14.56	8.76
4.5	8.0	18.0	10.0
5.0	8.82	23.1	14.28

Run 27 - 45°C, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.25	0.28	1.0	0.76
0.5	0.35	1.45	1.1
0.75	0.54	2.04	1.50
1.0	0.73	2.5	1.57
1.25	0.91	3.11	2.20
1.50	1.15	3.77	2.62
2.0	1.82	5.25	3.43
2.5	2.4	6.92	4.52
3.0	3.0	9.6	6.3
3.5	3.72	12.0	8.28
4.0	4.12	14.56	10.46
4.5	6.29	18.0	11.76
5.0	6.72	23.1	16.38

Run 28 - 35°C, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.25	0.05	0.75	0.7
0.50	0.26	1.11	0.85
0.75	0.38	1.40	1.02
1.0	0.42	1.88	1.46
1.25	0.51	2.22	1.71
1.5	0.71	2.74	2.03
2.0	0.96	3.77	2.81
2.5	1.24	4.6	3.36
3.0	1.8	5.76	3.96
4.5	2.68	9.84	7.16
5.0	3.32	11.80	8.48
5.5	4.52	14.28	9.76
6.0	4.96	16.60	11.64

Run 29 - 40°C, N_2 2.95 sq.cm.

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.1	1.05	0.95
1.25	0.16	2.4	2.24
3.0	0.4	6.8	6.4
3.5	0.48	8.6	8.12
4.0	0.72	9.72	9.0
4.5	1.12	10.80	9.68
5.0	1.20	12.96	11.76
5.5	1.40	15.08	13.68
6.0	1.6	15.72	14.12

APPENDIX VII

6.04 N HCl Dissolution Runs

4500 r.p.m.
2.84 sq. cm.
500 ml. volume

All Concentrations are in (Moles/litre) x 10^{-4}

Run 30 - 45°C, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.47	1.71	1.24
1.0	1.2	3.0	1.8
1.5	2.13	4.25	2.12
2.0	3.88	6.84	2.96
2.5	4.2	8.8	4.6
3.0	5.6	12.0	6.4
3.5	7.8	15.48	7.68
4.0	10.84	18.6	7.76
4.5	12.0	22.2	10.2
5.0	14.5	26.0	11.5

Run 31 - 40°C, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.36	1.48	1.12
1.0	0.72	2.53	1.81
1.5	1.47	3.95	2.48
2.0	2.1	5.56	3.46
2.5	3.2	7.24	4.04
3.0	4.36	9.12	4.76
3.5	5.5	11.8	6.3
4.0	7.24	14.2	6.96
4.5	7.62	16.2	8.58
5.0	9.8	19.4	9.6

Run 32 - 35°C, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.17	1.01	0.84
1.0	0.40	1.81	1.41
1.5	0.75	3.08	2.33
2.0	1.15	3.89	2.74
2.5	1.8	5.92	4.12
3.0	2.4	7.84	5.44
3.5	3.12	9.8	6.68
4.0	4.6	12.3	7.7
4.5	5.6	14.5	8.9
5.0	6.7	17.8	11.1

Run 33 - 30°C, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.11	0.82	0.71
1.0	0.25	1.5	1.25
1.5	0.47	2.26	1.79
2.0	0.69	2.95	2.26
2.5	0.93	4.6	3.67
3.0	1.26	5.6	4.34
3.5	1.68	6.84	5.16
4.0	2.0	8.24	6.24
4.5	2.48	9.4	6.92
5.0	2.92	10.88	7.96

All Concentrations are in (Moles/litre) x 10^{-4}

Run 34 - 26°C, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.16	0.9	0.74
1.0	0.35	1.45	1.10
1.5	0.5	2.1	1.60
2.0	0.7	2.72	2.02
2.5	0.96	3.55	2.59
3.0	1.35	4.15	2.80
3.5	1.80	5.40	3.60
4.0	2.08	6.64	4.56
4.25	2.44	6.80	4.36
4.50	2.52	7.4	4.88
5.0	2.92	8.24	5.32

Run 35 - 40°C, N_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.008	1.51	1.502
1.0	0.1	2.76	2.75
1.5	0.2	4.05	3.85
2.25	0.4	7.6	7.2
2.50	0.44	8.48	8.04
3.0	0.68	10.84	10.16
3.5	0.92	14.4	13.48
4.0	1.28	16.6	15.32
4.5	1.50	21.3	19.8
5.0	1.68	24.3	22.62

Run 36 - 35°C, N_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.05	1.47	1.42
1.25	0.17	2.95	2.78
1.50	0.2	3.6	3.4
2.0	0.24	5.44	5.2
2.5	0.24	7.2	6.96
3.5	0.64	11.8	11.16
4.0	0.64	14.8	14.16
4.5	0.92	17.0	16.08
5.0	1.2	22.8	21.6

Run 37 - 30°C, N_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.01	1.30	1.29
1.0	0.02	2.3	2.28
1.5	0.07	3.55	3.48
2.0	0.17	4.25	4.08
2.5	0.20	6.24	6.04
3.0	0.24	7.84	7.6
3.5	0.25	8.8	8.55
4.0	0.28	10.48	10.2
4.5	0.44	12.32	11.88
5.0	0.68	13.80	12.12

APPENDIX VIII

2.416 N HCl Dissolution Runs

7500 r.p.m.
5.4 sq. cm.
500 ml. volume

All Concentrations are in (Moles/litre) x 10^{-4}

Run 38 - 35°C, Air				Run 39 - 46°, Air			
Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})	Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
1.0	0.53	2.80	2.33	2.0	1.18	6.2	5.02
2.0	0.825	4.0	3.175	3.0	1.25	9.15	7.90
4.5	1.26	9.8	8.54	4.0	1.375	13.6	12.225
5.0	2.1	10.92	8.82	5.0	2.59	24.78	22.19
6.0	2.98	13.20	10.22	6.5	2.64	31.44	28.80
6.5	3.65	16.0	12.35	7.0	2.80	33.0	30.2

APPENDIX IX

Effect of Area on Dissolution Rate

4500 r.p.m.
4.027 N HCl
500 ml. volume
35°C

All Concentrations are in (Moles/litre) x 10^{-4}

Run 40 - Air, 5.28 sq. cm.

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.32	1.52	1.20
1.0	0.58	2.4	1.82
3.0	1.45	6.56	5.11
4.0	1.90	9.0	7.1
4.5	3.88	15.84	11.96
5.0	4.1	19.5	15.4
5.5	4.3	22.5	18.2
6.5	4.5	27.0	23.5

Run 41 - 4.27 cm^2, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.16	0.55	0.39
1.0	0.26	0.90	0.64
1.5	0.36	1.342	0.982
2.0	0.45	1.88	1.43
2.5	0.53	2.5	1.97
3.0	0.65	3.24	2.59
3.5	0.72	4.20	3.48
4.0	0.82	4.84	4.02
4.5	1.0	6.0	5.0
5.0	1.2	7.0	5.8
5.5	1.4	8.22	6.82

Run 42 - 2.84 cm^2, Air

Time (hours)	(Fe^{+++})	(Fe)	(Fe^{++})
1.0	0.2	1.19	0.99
1.5	0.27	1.65	1.38
2.0	0.36	2.15	1.79
2.5	0.49	2.72	2.23
3.0	0.55	3.16	2.61
3.5	0.67	3.75	3.08
4.25	0.82	4.8	3.98
4.75	1.0	5.6	4.6
5.0	1.12	5.96	4.84
5.5	1.24	6.6	5.36

Run 43 - 1.43 cm^2, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.05	0.28	0.23
1.0	0.1	0.45	0.35
1.5	0.14	0.56	0.42
2.0	0.20	0.64	0.44
2.5	0.26	0.81	0.55
3.0	0.29	1.0	0.71
3.5	0.35	1.21	0.86
4.0	0.39	1.32	0.93
4.5	0.42	1.56	1.14
5.0	0.45	1.82	1.37
5.5	0.50	2.1	1.6

All Concentrations are in (Moles/litre) x 10^{-4}

Run 44 - 5.72 cm^2. N_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.17	1.19	1.02
1.0	0.19	1.55	1.36
1.75	0.19	2.06	1.87
2.25	0.19	2.41	2.22
2.75	0.19	2.75	2.56
3.25	0.19	3.06	2.87
4.25	0.16	3.9	3.74
4.75	0.19	4.25	4.06
5.0	0.12	4.4	4.28
5.5	0.12	4.62	4.5
6.0	0.15	5.0	4.85

Run 45 - 4.26 cm^2, N_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.01	0.73	0.72
1.0	0.05	1.2	1.15
1.5	0.02	1.73	1.71
2.5	0.04	2.5	2.46
3.0	0.04	2.97	2.93
3.5	0.04	3.16	3.12
4.0	0.04	3.5	3.46
4.5	0.04	3.75	3.71
5.25	0.04	3.96	3.92
5.5	0.05	4.2	4.15
6.0	0.05	4.9	4.85

Run 46 - 2.9 xm^2, N_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
1.0	0.2	0.96	0.76
1.5	0.2	1.17	0.97
2.5	0.2	1.55	1.35
3.0	0.2	1.83	1.63
4.0	0.2	2.18	1.98
4.5	0.2	2.35	2.15
5.0	0.2	2.58	2.38
5.5	0.2	2.73	2.53
6.0	0.24	3.16	2.92

Run 47 - 1.43 cm^2, N_2

Time (hour)	(Fe^{+++})	(Fe)	(fe^{++})
0.5	0.0	0.31	0.31
1.0	0.01	0.45	0.44
2.5	0.04	0.85	0.81
3.0	0.04	1.0	0.96
3.5	0.04	1.13	1.09
4.0	0.04	1.25	1.21
4.5	0.04	1.40	1.36
5.25	0.04	1.63	1.59
5.5	0.04	1.71	1.67
6.0	0.05	1.82	1.77

4500 r.p.m.
6.04 N HCl
500 ml. volume
35°C

All Concentrations are in (Moles/litre) x 10^{-4}

Run 48 - 5.8 cm^2, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.25	0.26	1.4	1.14
0.5	1.0	2.95	1.95
0.75	0.92	4.5	3.58
1.0	2.0	8.52	6.52
1.5	3.08	13.0	9.92
2.0	4.62	18.48	13.86
2.5	7.02	2.43	17.28
3.0	10.26	29.1	18.84
3.5	13.36	38.8	25.44
4.0	13.53	46.75	33.22
4.5	15.68	59.5	43.82
5.0	17.6	68.0	50.4
5.5	18.24	77.6	59.36

Run 49 - 4.11 cm^2, Air

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.25	0.43	1.23	0.8
0.5	0.5	1.8	1.3
0.75	0.51	2.52	2.01
1.0	0.73	3.38	2.65
1.5	2.6	7.4	4.8
2.25	2.68	9.8	7.22
2.50	3.28	10.8	7.56
3.0	4.6	14.8	10.2
4.25	8.46	23.22	14.76
4.5	9.12	24.9	15.78
5.0	10.45	31.9	21.45
5.5	12.65	35.75	23.1

Run 50 - 5.74 cm^2, N_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.02	2.62	2.6
1.0	0.06	4.38	4.32
1.5	0.08	6.4	6.32
2.25	0.40	11.8	11.4
2.5	0.44	12.32	11.92
3.0	0.52	14.8	14.22
3.5	0.60	17.0	16.4
4.0	0.66	21.30	20.64
4.5	0.72	25.2	24.48
5.0	0.72	30.0	29.28

Run 51 - 4.26 cm^2, N_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.12	2.12	2.0
1.0	0.2	3.7	3.5
1.5	0.3	4.85	4.55
2.0	0.4	7.72	7.32
2.5	0.6	9.8	9.2
3.0	0.64	12.32	11.68
3.5	0.68	14.2	13.52
4.25	0.72	17.0	16.28
4.5	0.80	18.0	17.2
5.0	1.02	23.4	22.38

All Concentrations are in (Moles/litre) x 10^{-4}

Run 52 - 1.42 cm^2, N_2

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.008	0.8	0.792
1.0	0.01	1.37	1.36
1.5	0.04	2.0	1.96
2.0	0.07	2.62	2.55
2.5	0.10	3.23	3.13
3.0	0.12	3.95	3.83
3.5	0.4	4.25	3.85
4.0	0.48	5.88	5.4
4.5	0.52	6.6	6.08
5.0	0.6	7.72	7.12

APPENDIX X

Effect of Volume on Dissolution Rate

4500 r.p.m.
2.84 sq. cm.
6.04 N HCl
40°C
Air

All Concentrations are in (Moles/litre) x 10^{-4}

Run 53 - 400 ml. vol.

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.36	1.66	1.30
1.0	0.8	3.15	2.35
1.5	1.36	4.25	2.89
2.0	2.28	7.04	4.76
2.5	3.2	9.2	6.0
3.0	4.32	11.6	7.28
3.5	6.04	15.08	9.04
4.0	7.84	18.0	10.16
4.5	9.18	23.7	14.52
5.0	12.12	27.96	15.84

Run 54 - 500 ml. vol.

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.36	1.48	1.12
1.0	0.72	2.53	1.81
1.5	1.47	3.95	2.48
2.0	2.1	5.56	3.46
2.5	3.2	7.24	4.04
3.0	4.36	9.12	4.76
3.5	5.5	11.8	6.3
4.0	7.24	14.2	6.96
4.5	7.62	16.2	8.58
5.0	9.8	19.4	9.6

Run 55 - 600 ml. vol.

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.35	1.3	0.95
1.0	0.72	2.31	1.59
1.5	1.14	3.3	2.16
2.0	2.28	5.24	2.96
2.5	3.12	6.9	3.78
3.0	4.0	8.72	4.72
3.5	4.4	10.08	5.68
4.0	6.16	12.6	6.44
4.5	7.16	14.8	7.54
5.0	8.4	17.0	8.6

APPENDIX XI

Effect of Rotational Speed on Dissolution Rate

4.027 N HCl
2.84 sq. cm.
500 ml. volume
35°C
Air

All Concentrations are in (Moles/litre) x 10^{-4}

Run 56 - 0 r.p.m.

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
1.0	0.15	1.3	1.15
1.5	0.17	1.7	1.53
2.0	0.18	2.18	2.0
2.5	0.25	2.9	2.65
3.0	0.48	3.21	2.73
3.5	0.65	4.1	3.45
4.25	0.93	5.0	4.07
4.75	1.24	5.92	4.68
5.0	1.4	6.08	4.68
5.5	1.6	6.8	5.2

Run 57 - 6000 r.p.m.

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.14	0.7	0.56
1.0	0.25	1.02	0.77
1.5	0.33	1.45	1.12
2.0	0.42	1.87	1.45
2.5	0.54	2.12	1.58
3.0	0.6	2.5	1.9
3.5	0.68	3.06	2.38
4.25	0.81	3.75	2.94
4.5	0.85	4.1	3.25
5.0	1.0	4.5	3.5
5.5	1.11	5.85	4.74

Run 58 - 10500 r.p.m.

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.16	0.65	0.49
1.0	0.24	1.06	0.82
1.5	0.30	1.32	1.02
2.0	0.38	1.39	1.01
2.5	0.45	2.1	1.65
3.0	0.51	2.6	2.09
4.0	0.66	3.45	2.79
4.5	0.75	3.80	3.05
5.0	0.8	4.25	3.45
5.5	0.89	4.75	3.86

6.04 N HCl
2.26 sq. cm.
500 ml. volume
35°C
Air

All Concentrations are in (Moles/litre) x 10^{-4}

Run 59 - 0 r.p.m.

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.7	3.0	2.7
1.0	1.36	5.8	4.44
1.5	3.28	8.9	5.72
2.0	4.48	12.2	7.72
2.5	6.84	16.2	10.36
3.0	8.4	19.9	11.5
3.5	11.22	24.3	13.08
4.0	14.49	30.8	16.31

Run 60 - 2300 r.p.m.

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.25	0.28	0.4	0.12
0.75	0.63	1.3	0.67
2.0	1.6	3.55	2.95
2.5	2.3	5.3	3.0
3.0	3.0	6.08	3.08
3.5	3.6	6.8	3.2
4.0	3.66	7.8	4.14
4.5	4.02	9.0	4.98
5.0	4.62	10.5	5.88
5.5	5.5	11.88	6.38

Run 61 - 4500 r.p.m.

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.25	0.2	0.8	0.6
0.50	0.245	1.02	0.775
0.75	0.42	1.35	0.93
1.0	0.5	1.75	1.25
1.5	0.72	2.62	1.9
2.0	1.15	3.55	2.4
2.5	1.67	4.38	2.71
3.0	2.4	6.76	4.36
4.25	5.44	12.4	6.96
4.5	6.04	14.48	8.44
5.0	7.2	17.0	9.8
5.5	7.6	19.4	11.8

Run 62 - 8300 r.p.m.

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.42	1.6	1.18
1.5	1.26	3.1	1.84
2.0	1.7	4.6	2.9
2.5	2.08	6.24	4.16
3.0	2.52	7.4	4.88
3.5	3.08	8.8	5.72
4.0	3.6	10.48	6.88
4.5	4.4	12.0	7.6
5.0	5.04	14.0	8.96

All Concentrations are in (Moles/litre) x 10^{-4}

Run 63 - 11000 r.p.m.

Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
0.5	0.5	1.75	1.25
1.0	0.89	2.77	1.88
1.5	1.6	4.2	2.6
2.0	2.0	5.44	3.44
2.5	2.4	6.84	4.44
3.0	3.0	8.82	5.82
3.5	3.72	10.8	7.08
4.0	4.32	12.78	8.46

3.04 N HCl
2.90 sq. cm.
500 ml. volume
35°C
Nitrogen

All Concentrations are in (Moles/litre) x 10^{-4}

Run 64 - 3300 r.p.m.				Run 65 - 6500 r.p.m.			
Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})	Time (hour)	(Fe^{+++})	(Fe)	(Fe^{++})
1.0	0.16	2.1	1.94	1.0	0.03	0.82	0.79
1.5	0.2	2.34	2.14	1.5	0.03	1.04	1.01
2.0	0.22	2.54	2.32	2.0	0.03	1.38	1.35
2.5	0.20	2.6	2.4	2.75	0.05	1.7	1.65
3.5	0.23	2.96	2.73	3.5	0.20	1.92	1.72
4.0	0.16	3.1	2.94	4.0	0.12	2.16	2.04
4.5	0.14	3.3	3.16	4.75	0.02	2.34	2.32
6.0	0.12	3.9	3.78	6.0	0.05	2.70	2.67
6.5	0.11	4.04	3.93	6.5	0.12	2.92	2.80
7.5	0.11	4.6	4.5	7.5	0.16	3.3	3.14

VITA AUCTORIS

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