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DISSOLUTION OF TIN 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
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by

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1962

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ABSTRACT

A kinetic study of the dissolution of tin has been made by rotating tin cylinders in air-saturated hydrochloric acid solutions. The observed rate is essentially half-order with respect to the stannic tin concentration. The autocatalytic half-order rate is directly proportional to the square root of the A/V ratio and to the square root of the oxygen partial pressure in the gas phase. Above 11,000 r.p.m. the experimental energy of activation is 4.7 kcal per gram mole over the temperature range 25° - 40°C. Hydrogen ion accelerates the corrosion process over a limited range of concentration but above 0.55 N HCl the rate tends to decrease with increasing acid concentration.

The autocatalytic rate of dissolution of tin in 1 N HCl may be expressed by the empirical rate law

$$\frac{d\,[\mathrm{Sn}^{++++}]}{dt} = 4.07 \times 10^{-3}\,[\mathrm{Sn}^{++++}]^{\frac{1}{2}}\left(\frac{A}{V}\right)^{\frac{1}{2}}(P_{O_2})^{\frac{1}{2}}\,(\mathrm{r.p.m.})^{0.92}\;e^{-\frac{4700}{RT}}$$

ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to Dr. A.W. Gnyp for his valuable advice and constructive criticisms.

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I

INTRODUCTION

Comparatively little work has been reported on the dissolution of metals in aqueous solutions using time as variable. Britton and Michael (1) have investigated the local corrosion of tin in dilute chloride solutions. Ammar and Riad (2), Britton and Angles (3) have investigated the inhibition of tin dissolution by chemical addition. None of the investigators studied the effect of varying operating conditions on the dissolution mechanism. The object of this thesis is to provide more understanding of the mechanism by which metals dissolve in aerated acid solutions.

Considerable effort has been devoted to the dissolution of copper in aqueous solutions. Previous investigators have shown that over a wide range of conditions the corrosion process is autocatalytic. It is of interest and considerable importance to determine whether autocatalysis plays a significant role during the corrosion of other metals having two oxidation states. The tin-hydrochloric acid system has been chosen for study because it bears strong resemblence to the copper-hydrochloric acid system with respect to complex formation and metal-salt equilibrium. Additionally, tin provides a system capable of dissolution by hydrogen evolution.

II

LITERATURE REVIEW

To provide a smooth transition from the well studied copper-acid system and the relatively unknown tin-acid system, it will be advisable to review briefly some of the results and conclusions of earlier investigators.

Copper Dissolution

Lu and Graydon (4,5) studied the rate of copper dissolution in aqueous ammonium hydroxide and aqueous sulfuric acid solutions. Weeks and Hills (6) studied the initial corrosion kinetics in hydrochloric acid solutions. Their work was extended by Gnyp (7).

Tin Dissolution

Ammar and Riad (2) investigated the corrosion rate and corrosion potential of tin in 8 different acid, alkaline and neutral solutions. The corrosion potential measured against the saturated calomel electrode, increased with increasing solute concentration. The corrosion rate increased with increasing concentration, but this increase was not significant in sodium chloride solutions. A maximum rate of attack was observed in maleic acid solution. Pyrophosphate was found to inhibit the corrosion rate in acid and alkaline medium, but had no effect in neutral solutions.

Britton and Michael (1) studied the local corrosion of tin in chloride solutions and concluded that local corrosion is accelerated by crevices produced by surface defects and by lowering the pH of the solution below 4. However, the local corrosion of tin surfaces in dilute chloride solutions is not associated with the conditions of the surface itself.

Whitman and Russell (8) had some preliminary results on the effect of oxygen on tin dissolution in hydrochloric acid solutions. They concluded that the presence of dissolved oxygen usually increased the corrosion of the metal. Since tin evolves hydrogen gas in acids, the oxygen effect is more important in weaker acids where hydrogen evolution is slow. At higher temperatures, the corrosion by hydrogen gas evolution increases at a much more rapid rate than does the oxygen corrosion, hence the effect of oxygen corrosion becomes less important.

Claudius (9) and Lindes (10) showed that tin was dissolved by warm aqueous ammonium chloride solutions. Rammelsberg (11) found that electrolytic tin dissolves about 10 times as quickly as tin which has been melted. Presumably a greater surface area per gram of metal is exposed to the acid by the electrolytic metal.

Autoxidation of Stannous Chloride by Air

Because the autoxidation of stannous chloride may be a significant step in the heterogeneous process, it will be advantageous to discuss the information available on the homogeneous oxidation reaction. The oxidation of stannous chloride solution was first studied by Young (12) who found that the reaction was dependent upon the acidity of the solution. Lachman and Tompkin (13) studied the effect of impurities on the homogeneous oxidation of stannous chloride solutions. Haring and Walton (14, 15, 16), Filson and Walton (17) studied some additonal factors that affect the reaction. They found that increasing temperatures increased the rate of autoxidation.

Visible light had no effect on the reaction but ultra-violet was absorbed and accelerated the process. The autoxidation of stannous chloride was shown to be a photochemical chain reaction. Increase in liquid-gas interface did not increase the rate of autoxidation. The rate increased directly with increasing acid concentration and hydrogen ion concentration.

III

EXPERIMENTAL

Material

Analar grade tin bar supplied by The British Drug Houses Ltd. was machined into cylinders of 0.360 inches in diameter with a concentric hole to fit onto a rotating shaft. The analysis according to the manufacturer is given below:

TABLE 1

Tin Analysis

Lead	0.01 per cent
Copper	0.0025 per cent
Bismuth	0.002 per cent
Iron	0.002 per cent
Total Foreign Metals	0.04 per cent
Arsenic	0.0001 per cent
Antimony	0.025 per cent

All reagents used were of analytical grade, and redistilled water was used for all solutions.

Apparatus

The cylindrical tin samples were rotated on a stainless steel shaft. Plexiglas sleeves and a cap screwed tightly at the end protected the ends of the tin sample and the steel shaft from corrosion. The shaft was rotated by means of a Type 7HM Hoover vacuum motor at speeds ranging from 1,000 to 15,500 r.p.m. Figure 1 is a schematic representation of the experimental apparatus.

The reaction vessel consisted of a pyrex beaker fitted with a plexiglas cover holding three plexiglas baffle plates mounted radially.

Procedure

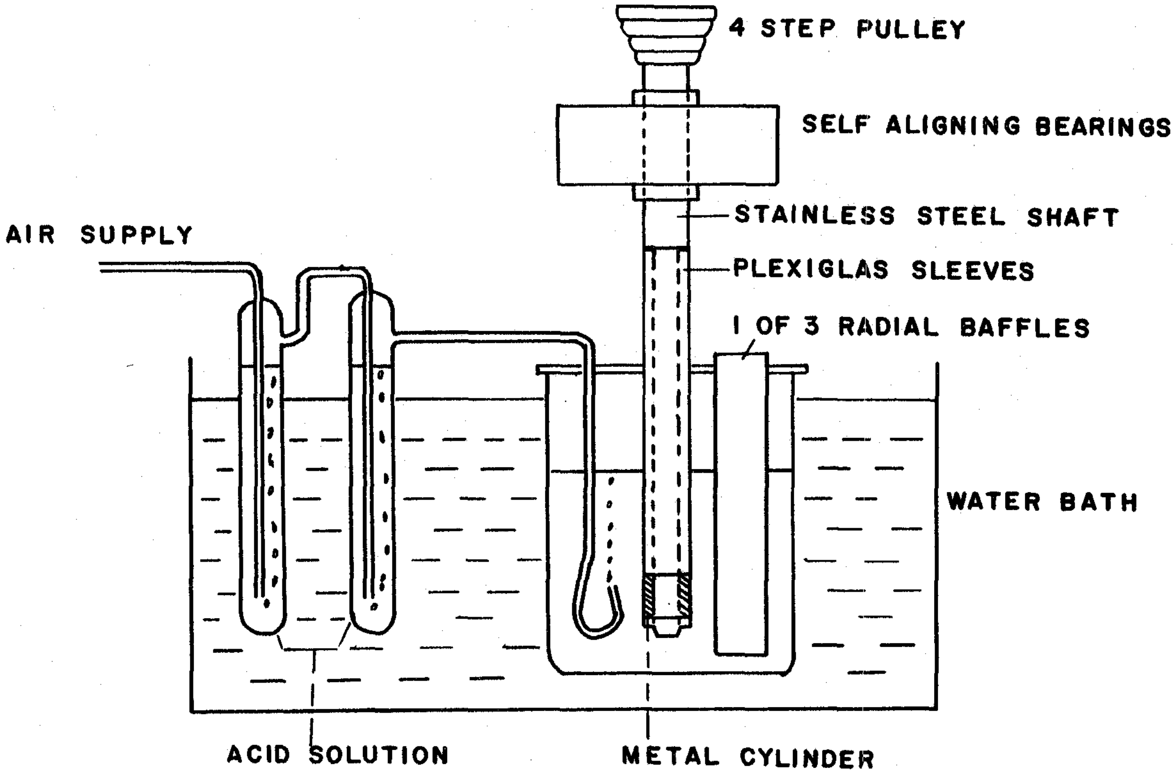
A measured volume of hydrochloric acid solution in the reaction vessel was flushed with air for approximately 10 minutes before each corrosion run. Initially, the air passed through a series of wash bottles containing hydrochloric acid of the same concentration as in the reaction beaker.

Freshly machined specimens were manually polished to a 3/0 emery paper smoothness. The polished cylinders were cleaned with distilled water and dried with filter paper. Grease stains were removed before each run with absolute alcohol. After each run, the metal samples were washed and dried, care being taken to prevent any damage to the surface film that might possibly form. A check on the material balance was maintained by weighing the clean dry specimens before and after each run.

Samples of the corroding solutions were withdrawn for analysis at convenient intervals of time. The concentration of tin was determined by a polarographic technique described in Appendix I. For every sample of solution withdrawn for analysis, an equal volume of fresh acid was added to the reaction vessel to eliminate excessive volume change during the corrosion process.

FIGURE I

ARRANGEMENT OF APPARATUS



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.

IV

RESULTS AND DISCUSSION

Rate Dependence on Stannic Ion Concentration

The first point is to establish the order of the dissolution reaction. As shown in Figure 2, all the data obtained in this research give exponential zero-order plots of $\left[Sn^{++++}\right]$ vs time. This is essentially an indication of an autocatalytic process. The zero-order plots can be approximated by straight lines for the initial corrosion as shown in Figure 3. It is evident that there may be some zero-order kinetics during the early stage of the dissolution process.

In all cases the deviation from the linear zero-order representation may be readily correlated by the half-order plot of Figure 4.

It should be possible to separate the dissolution into two separate reactions. Henry (18) has shown that tin will dissolve by hydrogen displacement according to the reaction

$$Sn + 2HCl \longrightarrow SnCl_2 + H_2$$

This is a slow reaction: Figure 5 shows typical rate data for the dissolution of tin in oxygen free solutions of hydrochloric acid at two different rotational speeds and temperatures. The results are correlated most effectively by this linear zero-order plot. It would appear that the initiation of the dissolution of tin occurs by the displacement of hydrogen.

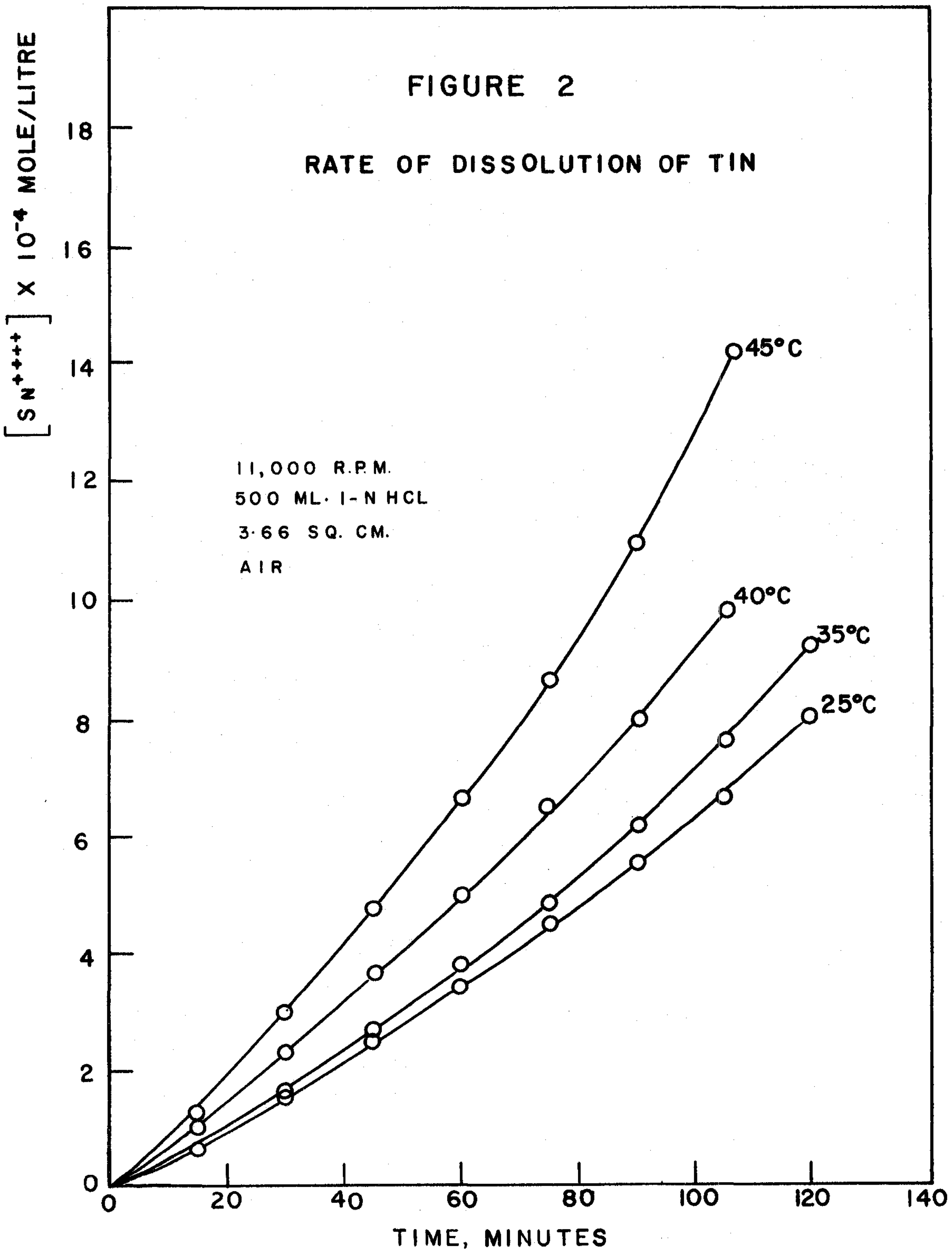


FIGURE 2

RATE OF DISSOLUTION OF TIN

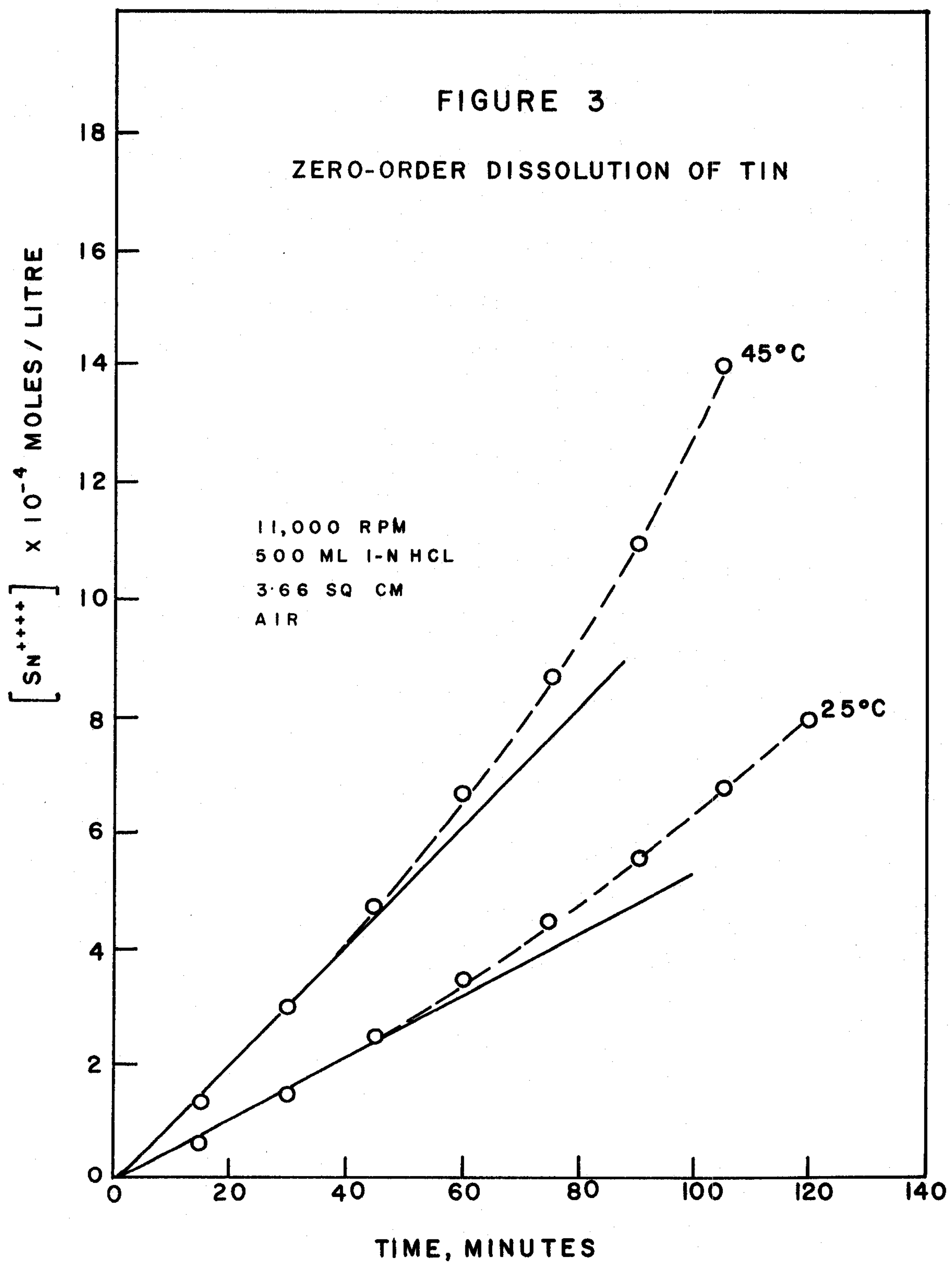
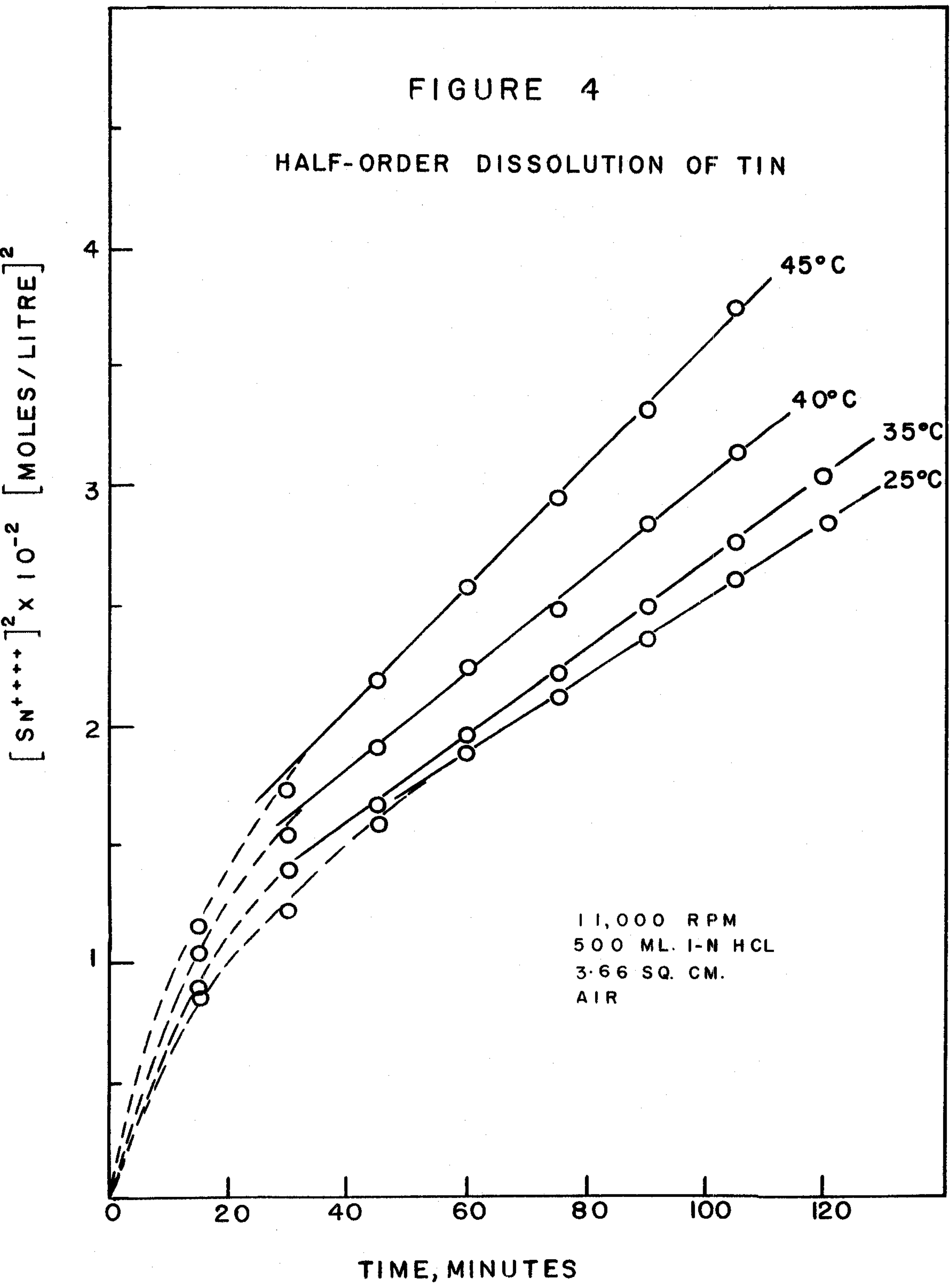


FIGURE 3

ZERO-ORDER DISSOLUTION OF TIN

FIGURE 4

HALF-ORDER DISSOLUTION OF TIN



11,000 RPM
500 ML. 1-N HCL
3·66 SQ. CM.
AIR

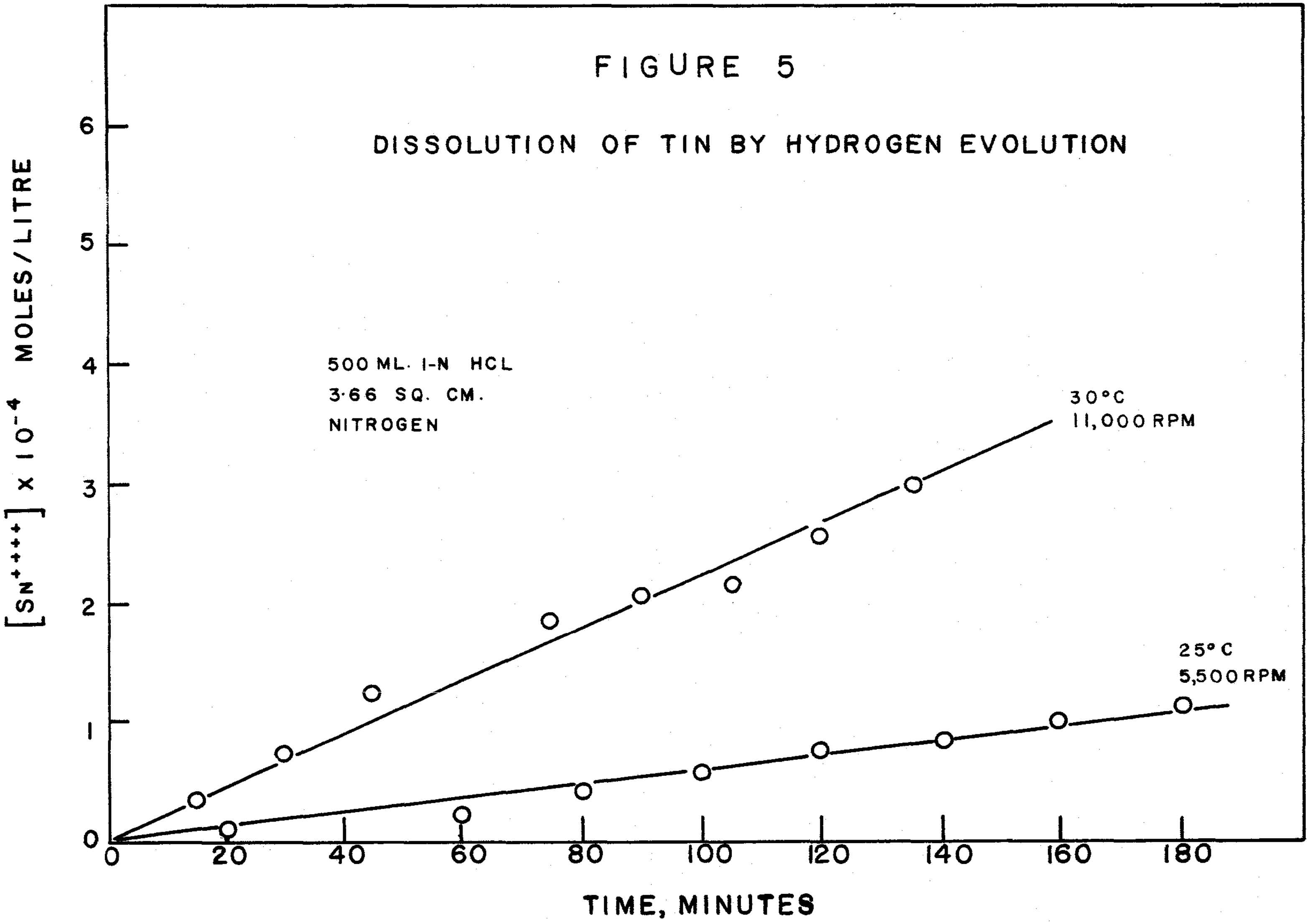


FIGURE 5

DISSOLUTION OF TIN BY HYDROGEN EVOLUTION

The half-order dependence on $[Sn^{++++}]$ suggests autocatalysis at higher metal ion concentrations. Figure 6 shows the effect of initial tin concentration on the dissolution reaction. By increasing the amount of stannic chloride added to the corroding solution it is possible to eliminate completely deviation from half-order dependence on stannic concentration.

Essentially the dissolution of tin is an autocatalytic reaction that may be expressed by the rate equation

$$\frac{d[Sn^{++++}]}{dt} = k[Sn^{++++}]^{\frac{1}{2}}$$

where $[Sn^{++++}]$ represents the concentration of the complex stannic ions in solution.

Because corrosion by autocatalysis is a much more important problem, more attention will be focused on this half-order process.

The autocatalysis may be discussed in terms of the following basic assumptions.

(1) The concentration of stannic complex ion species at the metal-solution interface is equal to the concentration of the complex ions in the bulk of the solution

$$[Sn^{++++}]_i = [Sn^{++++}]_{bulk}$$

(2) The stannous species, stannic species equilibrium

$$Sn^o + Sn^{++++} \rightleftharpoons 2Sn^{++}$$

assumed to be established at all times at the metal solution interface gives

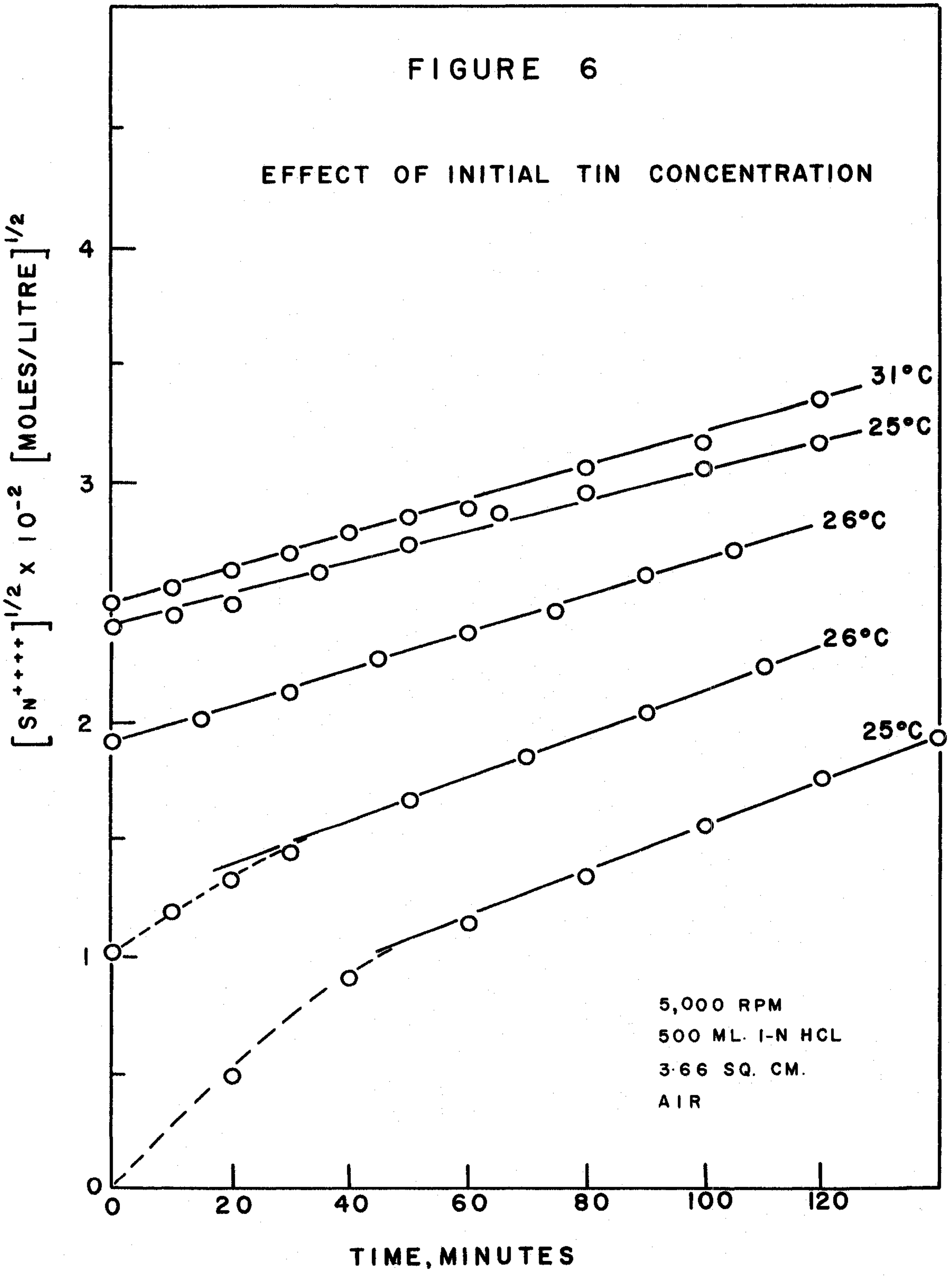


FIGURE 6

EFFECT OF INITIAL TIN CONCENTRATION

$$[Sn^{++}]_i = K_1 [Sn^{++++}]^{\frac{1}{2}}$$

Bekier and Basinski (19) have shown that metallic tin dissolves in a solution of acidic stannic chloride or aqueous stannic chloride containing ammonium chloride quite readily in the absence of oxygen.

(3) The removal of complex stannous ion species from the metal-solution interface is by a first-order process represented by

$$-\frac{d[Sn^{++}]}{dt} = k[Sn^{++}]_i$$

Since
$$\frac{d[Sn^{++++}]}{dt} = k[Sn^{++}]_i$$

it follows that

$$\frac{d[Sn^{++++}]}{dt} = k K_1 [Sn^{++++}]^{\frac{1}{2}}$$

The first-order removal of stannous species could be a chemical autoxidation reaction or a diffusional process.

It must be emphasized that the effect of an increasing initial tin concentration is a decrease in the half-order rate as shown in Table 2.

TABLE 2

Effect of Initial Tin Concentration

Temperature	Initial Concentration	Rate Constant
25°C	0 (mol/lit)	9.5×10^{-5}
25°C	5.7×10^{-4}	6.2×10^{-5}
26°C	1.05×10^{-4}	9.1×10^{-5}
26°C	3.55×10^{-4}	7.6×10^{-5}

To interpret these results it is necessary to refer to the examination of the corroding sample. At all times a blackish film appeared on the metal surface as the tin dissolved in the acidic solution. The thickness of the deposited black layer was highly dependent on the concentration of stannic tin in the corroding medium.

Vaubel (20) suggested that the black powder deposited on a polished tin sample during dissolution was essentially a modification of the original metal, produced by reduction of stannous chloride by nascent hydrogen. This surface layer dissolved only slightly even in concentrated acid.

The data in this research are consistent with Vaubel's (20) suggestions. The decrease in half-order dissolution rate at higher stannic chloride concentrations may result from the formation of the more insoluble form of tin which effectively blocks the more reactive surface beneath.

Diffusion through this layer could play a predominant role in the overall corrosion process.

Effect of Surface Roughness

The effect of the metal surface on the rate of tin dissolution has been studied by first corroding freshly polished samples and then re-running with a well developed crystalline structure. Manually polished samples having an arithmetic average surface roughness of 20 microinches were corroded for two hours until the arithmetic average roughness was of the order of 55-65 microinches. On a re-run the average roughness after two hours would be in the range of 50-100 microinches.

Figure 7 shows that the initial zero-order dissolution is dependent on the surface condition of the metal specimen. The early stage of corrosion are more rapid for samples having rougher surfaces. Table 3 provides a summary of the data in Figure 7.

TABLE 3

Effect of Surface Roughness

Sample Area	Polished Run k (zero-order)	Re-Run k (zero-order)
1.83 cm^2	0.33×10^{-5} gm mol/lit/min	0.37×10^{-5}
5.49	0.98×10^{-5}	1.00×10^{-5}
7.32	1.33×10^{-5}	1.74×10^{-5}

Figure 8 shows that the effect of surface roughness on the half-order autocatalytic process is insignificant. This behavior implies that the increase in surface area due to developing surface roughness cannot be responsible for the deviation from the zero-order dependence of Figure 3.

Consistently the data from the duplicate run lie above the initial results although both rates are equal. A valid explanation arises from a consideration of the initial zero-order dissolution discussed previously. The higher overall concentrations during the duplicate run are a direct result of the faster build up of stannic ion species during the initial corrosion process.

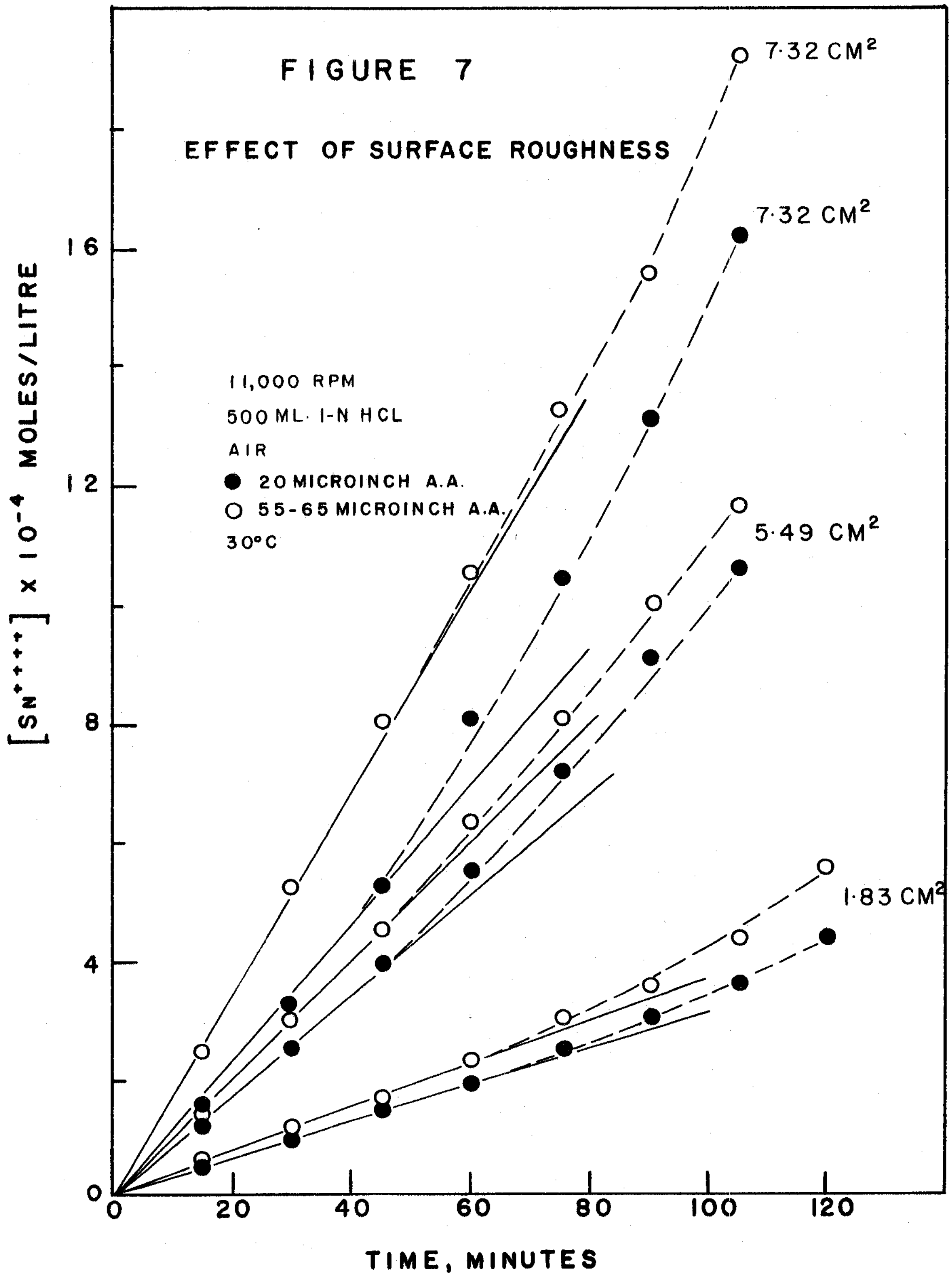


FIGURE 7
EFFECT OF SURFACE ROUGHNESS
11,000 RPM
500 ML. 1-N HCL
AIR
● 20 MICROINCH A.A.
○ 55-65 MICROINCH A.A.
30°C
7·32 CM²
7·32 CM²
5·49 CM²
1·83 CM²
[Sn⁺⁺⁺⁺] x 10⁻⁴ MOLES/LITRE
0
4
8
12
16
0
20
40
60
80
100
120
TIME, MINUTES

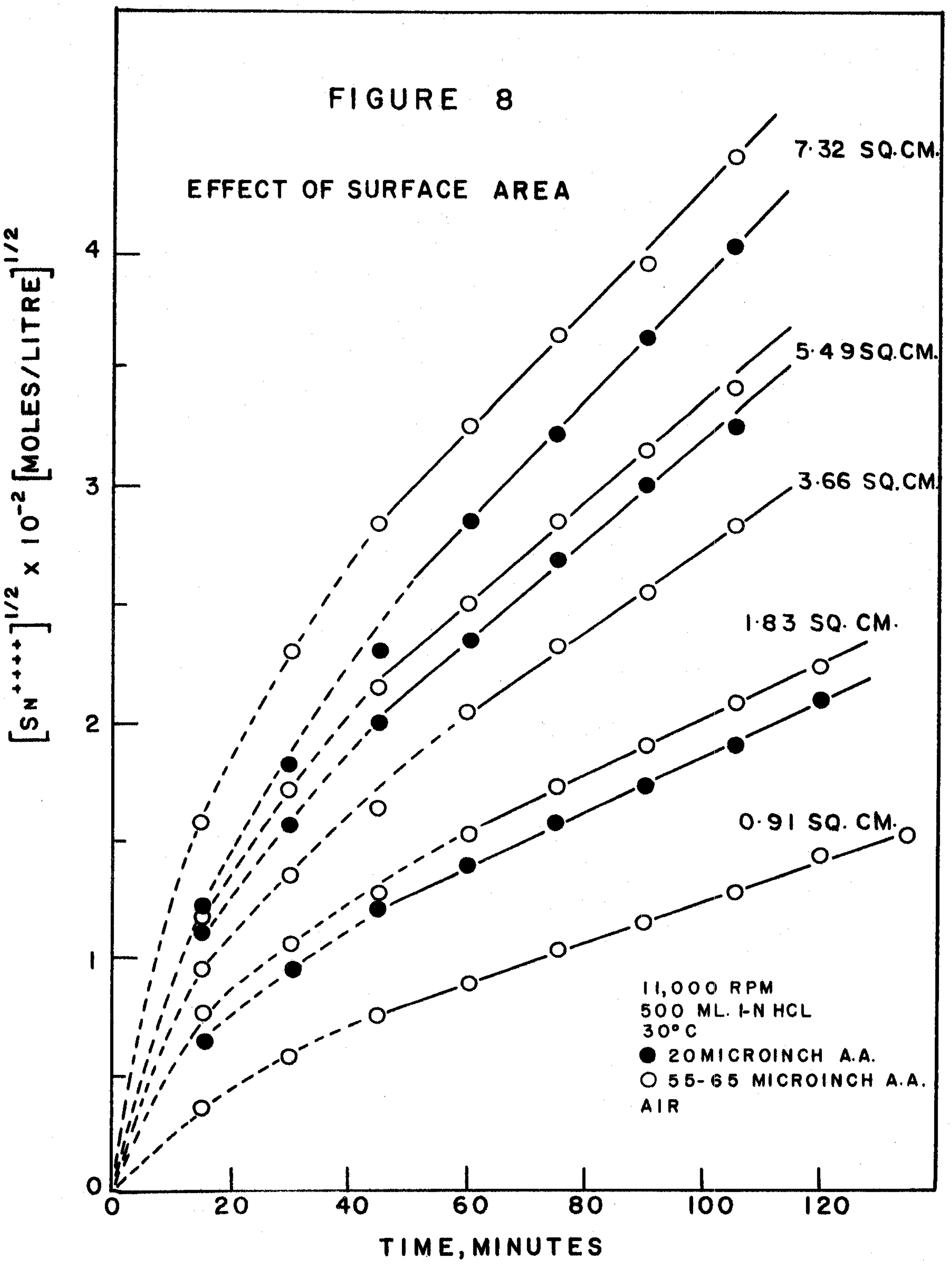


FIGURE 8
EFFECT OF SURFACE AREA
$[Sn^{++++}]^{1/2} \times 10^{-2}$ [MOLES/LITRE]$^{1/2}$
0
1
2
3
4
TIME, MINUTES
0
20
40
60
80
100
120
7·32 SQ.CM.
5·49 SQ.CM.
3·66 SQ.CM.
1·83 SQ. CM.
0·91 SQ. CM.
11,000 RPM
500 ML. 1-N HCL
30° C
● 20 MICROINCH A.A.
○ 55-65 MICROINCH A.A.
AIR

Rate Dependence on Sample Area and Corroding Solution Volume

Although there is no half-order rate dependence on actual surface area, Figure 8 suggests that there must be some relationship between the rate of dissolution of tin and the apparent surface area of the sample as measured by a micrometer. If the corrosion of tin is truly autocatalytic some dependence on solution volume must be expected also.

Figure 9A shows that the half-order rate is a linear function of the apparent surface area. This plot implies that there is a finite half-order rate at zero surface. This apparent contradiction may be resolved in terms of the black film that forms during dissolution. Samples of large surface area produce higher stannic concentrations which favour the film formation. The net result is a lowering of the half-order rate well below that for a clean tin surface of the same area. Figure 9B shows that the autocatalytic rate is directly proportional to the square root of the apparent sample area.

Figure 10A and Figure 10B support the contention that there is a loss of effective area available for dissolution under conditions of high tin concentrations in solution. Small samples corroding in large volumes of solution are still shiny after a two hour dissolution period.

According to Figure 10B the autocatalytic rate is directly proprotional to the square root of the A/V ratio.

Figure 11 indicates that in general the initial zero-order rate is essentially directly proportional to the apparent surface area and inversely to the reaction volume.

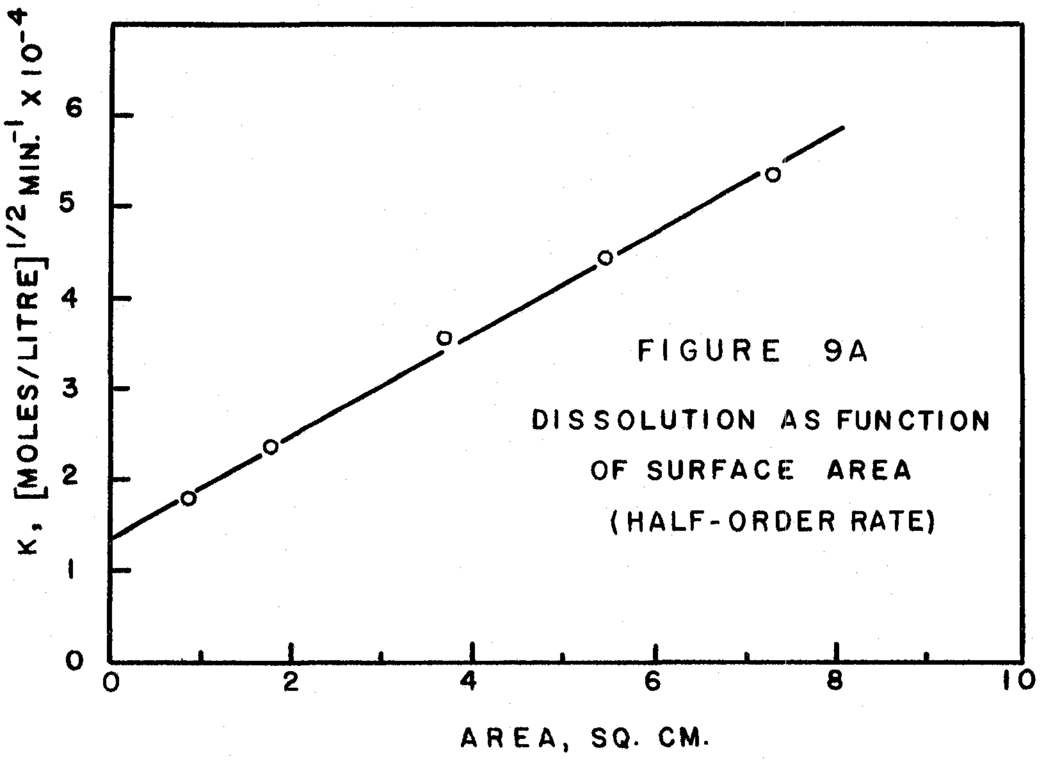


FIGURE 9A

DISSOLUTION AS FUNCTION OF SURFACE AREA (HALF-ORDER RATE)

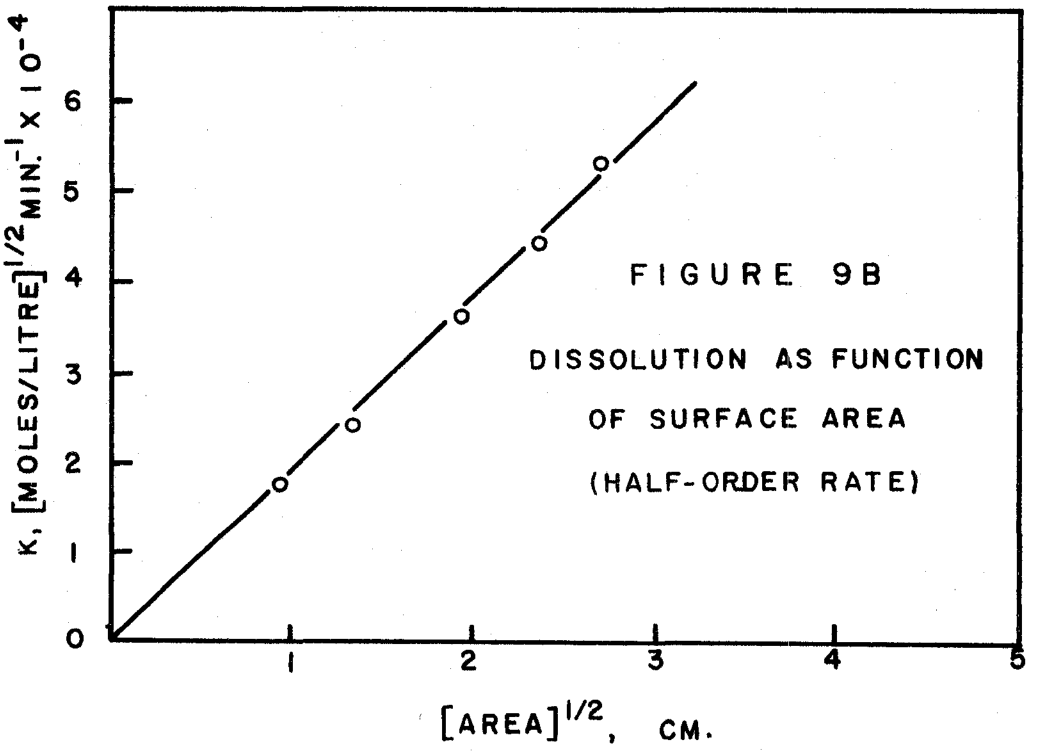


FIGURE 9B

DISSOLUTION AS FUNCTION OF SURFACE AREA (HALF-ORDER RATE)

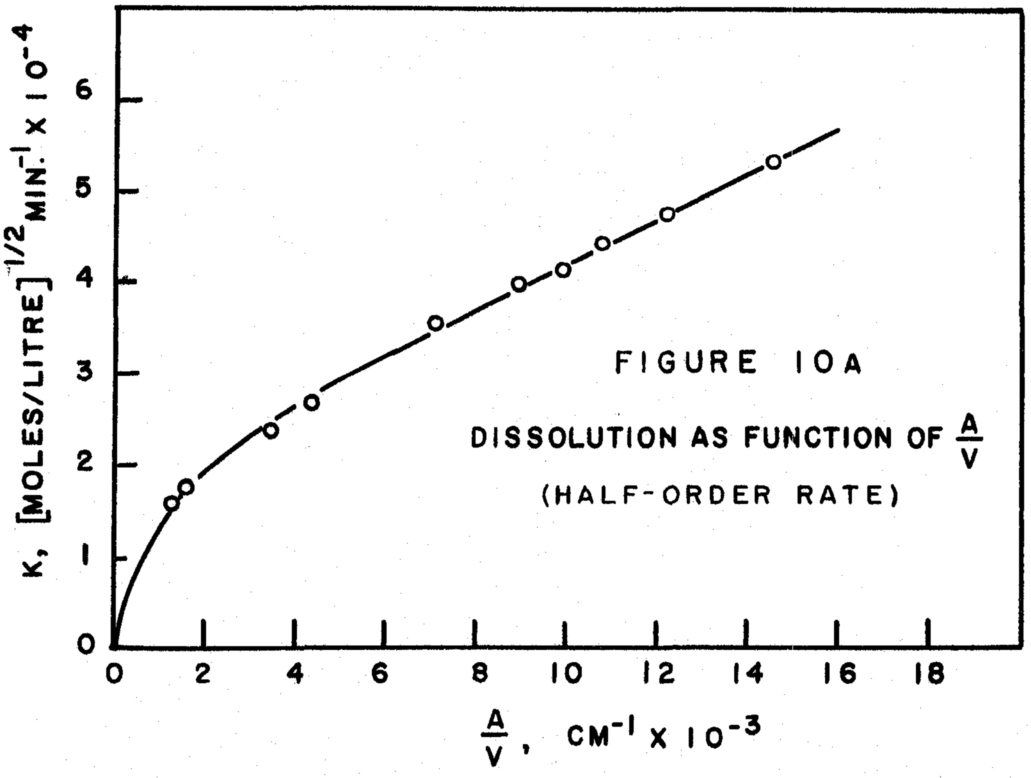


FIGURE 10A

DISSOLUTION AS FUNCTION OF $\frac{A}{V}$

(HALF-ORDER RATE)

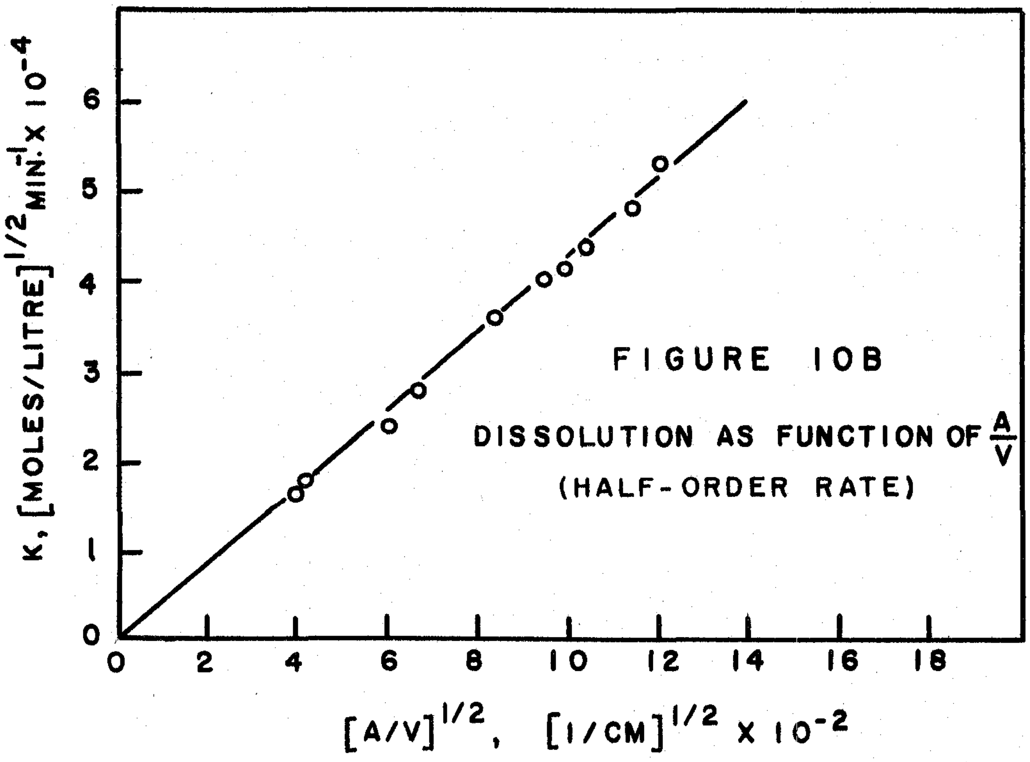


FIGURE 10B

DISSOLUTION AS FUNCTION OF $\frac{A}{V}$

(HALF-ORDER RATE)

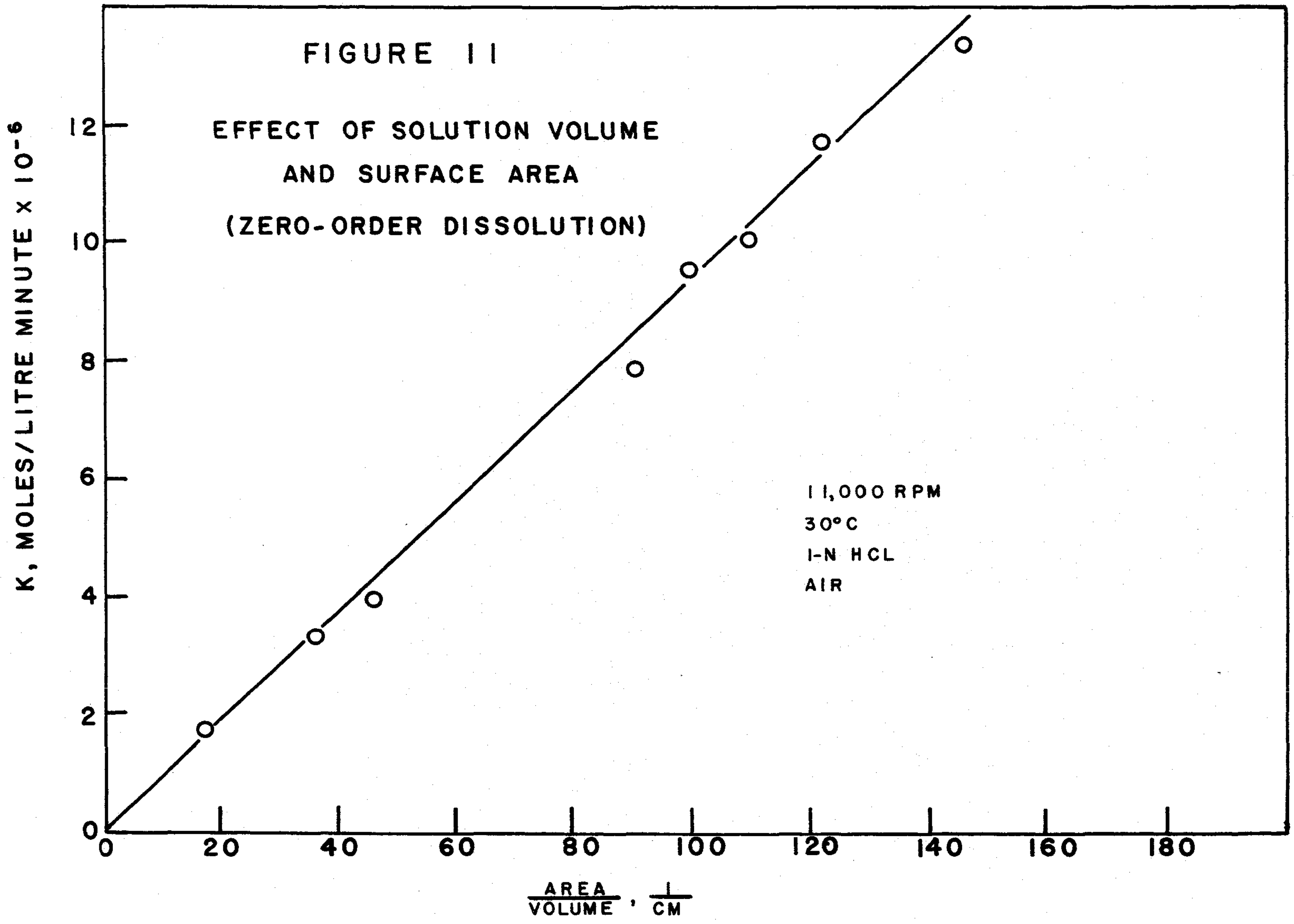


FIGURE 11

EFFECT OF SOLUTION VOLUME AND SURFACE AREA

(ZERO-ORDER DISSOLUTION)

Rate Dependence on Temperature

The half-order rate dependence on temperature has been studied over a wide range of rotational speeds. The temperature coefficient evaluated as an Arrhenius activation energy from Figure 12 is a linear function of rotational speed up to 11,000 r.p.m. Figure 13 shows that above this speed the apparent activation energy is essentially constant at 4.7 kcal per gram mole.

The low value of the activation energy suggests that the controlling step in the dissolution of tin is a physical process rather than a chemical one. In view of the number of equilibria involved and the complications presented by the deposited layer on the dissolving tin surface it is doubtful that this activation energy is a real measure of the controlling process.

Rate Dependence on Rotational Speed

Figure 14A indicates that the half-order rate of tin dissolution increases considerably with increasing rotational speeds. Over the temperature range 20-45°C the rate dependence on r.p.m. varied from 0.55 to 0.72 power as shown in Table 4. This range of values is acceptable for a simple diffusional process (21) and is quite consistent with the low activation energies evaluated in the preceding section.

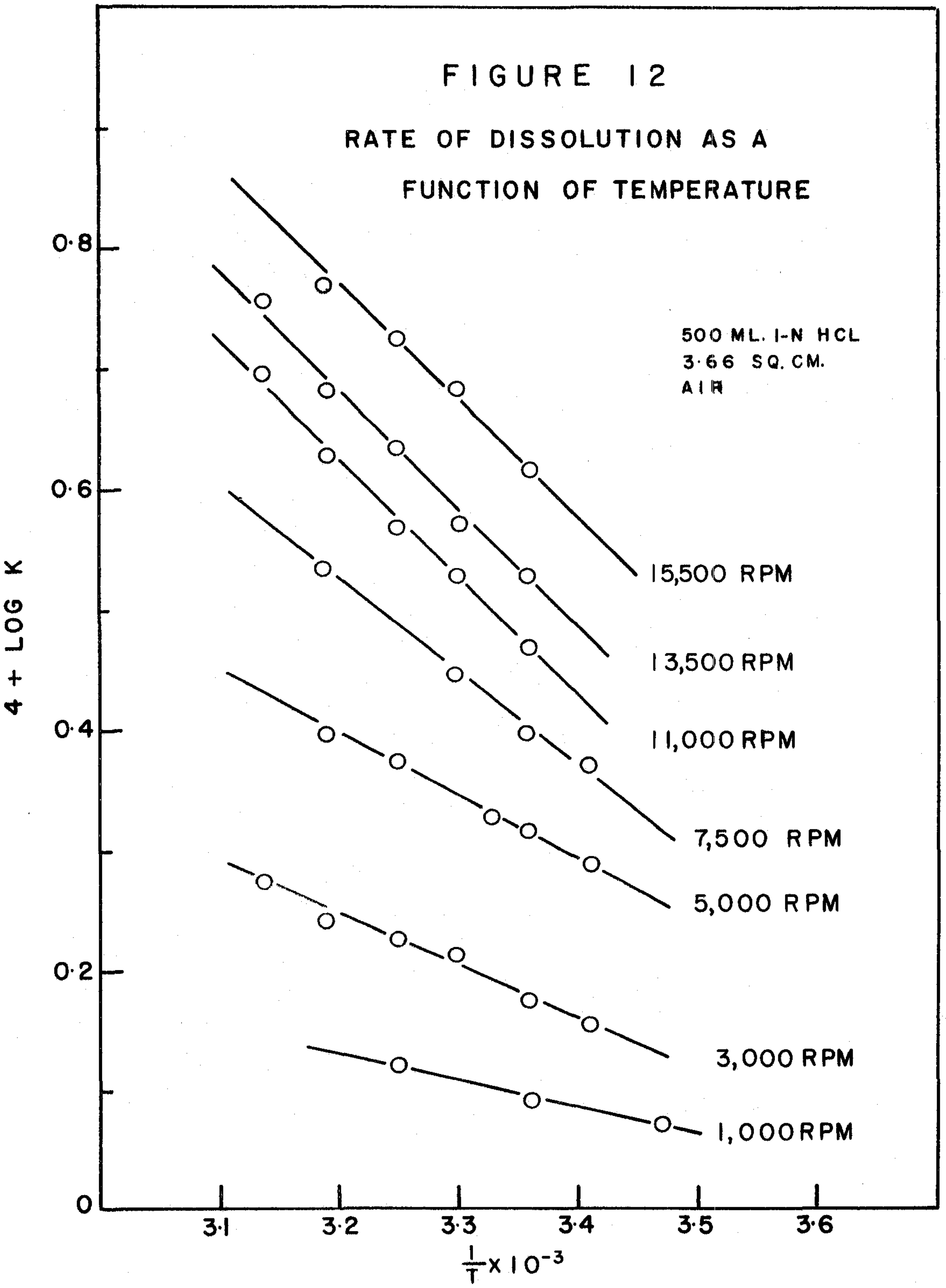


FIGURE 12
RATE OF DISSOLUTION AS A FUNCTION OF TEMPERATURE
500 ML. 1-N HCL
3·66 SQ. CM.
AIR
15,500 RPM
13,500 RPM
11,000 RPM
7,500 RPM
5,000 RPM
3,000 RPM
1,000 RPM
4 + LOG K
0·8
0·6
0·4
0·2
0
3·1
3·2
3·3
3·4
3·5
3·6
$\frac{1}{T} \times 10^{-3}$

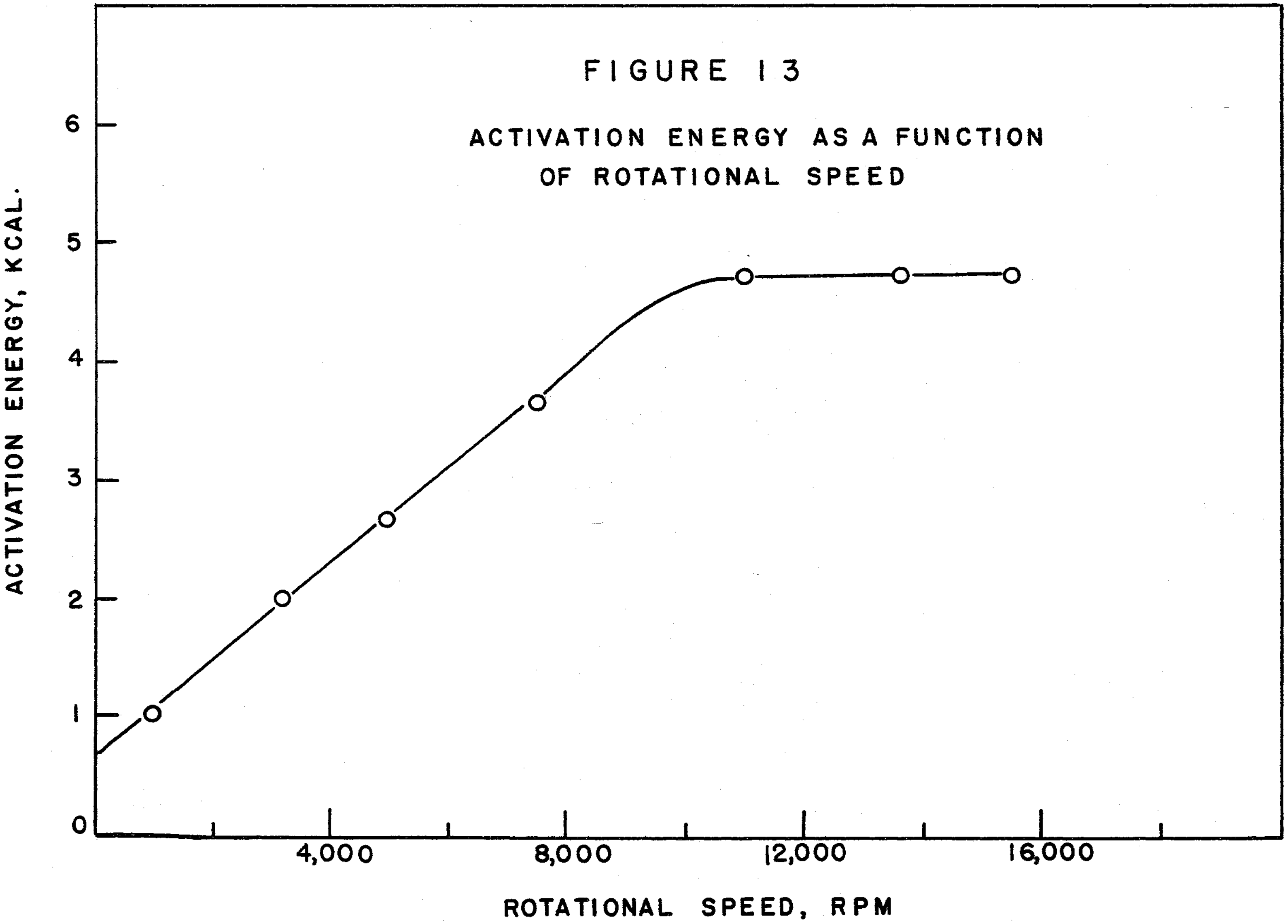


FIGURE 13

ACTIVATION ENERGY AS A FUNCTION OF ROTATIONAL SPEED

TABLE 4

Dissolution Rate as Function of R.P.M.

Temperature	Rate
20°C	$k \propto (\text{r.p.m.})^{0.55}$
25°C	$k \propto (\text{r.p.m.})^{0.57}$
30°C	$k \propto (\text{r.p.m.})^{0.62}$
40°C	$k \propto (\text{r.p.m.})^{0.69}$
45°C	$k \propto (\text{r.p.m.})^{0.72}$

A closer examination of the data above 11,000 r.p.m. according to Figure 14B reveals that the effect of rotational speed is essentially constant at different temperatures. In this region of constant activation energy the rate of dissolution of tin is related to the speed of rotation by the expression

$$k \propto (\text{r.p.m.})^{a}$$

where a = stirring coefficient = 0.92.

Many investigators have confirmed this value for the transport controlled dissolution of metal cylinders in various solvents. Table 5 provides a summary of some of the basic work in this field.

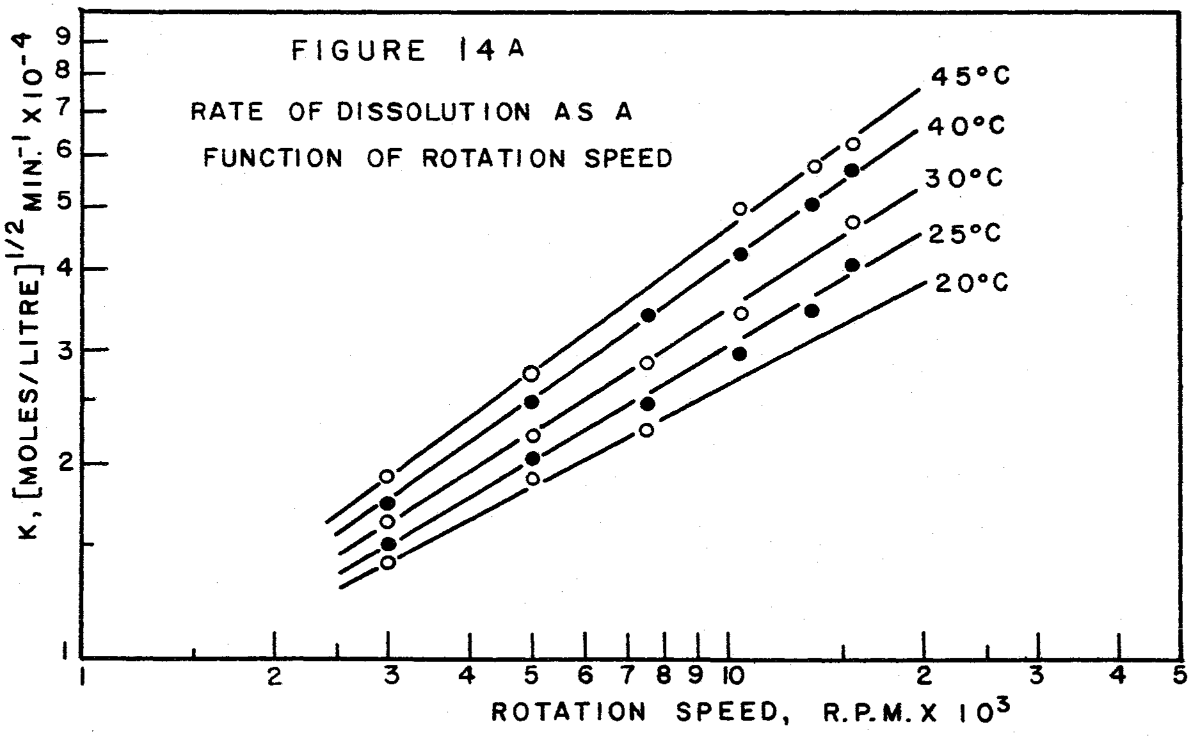


FIGURE 14A

RATE OF DISSOLUTION AS A FUNCTION OF ROTATION SPEED

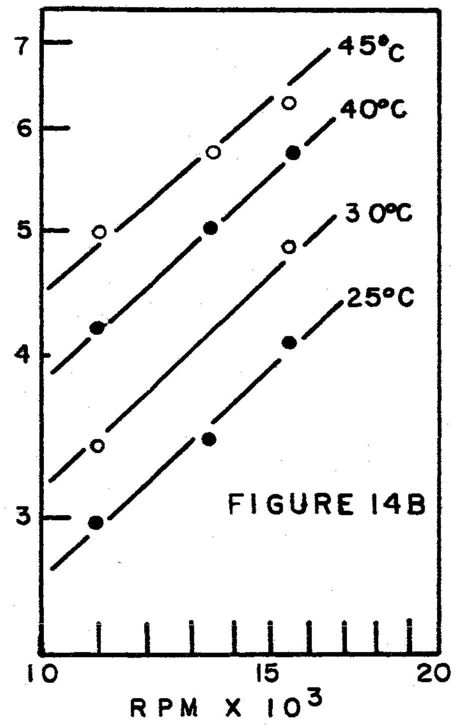


FIGURE 14B

TABLE 5

Values of a, Stirring Coefficient
(Cylindrical Metal Samples)

System	R.P.M.	a	Ref.
Dissolution of Mg in HCl	350-700	< 1	22
	700-2730	1	
Dissolution of Mg in HCl	0-1000	< 1	23
	1000-5600	~ 1	
Dissolution of Na in liquid NH_3	116-834	1	24
Dissolution of Zn in acetic acid	450-26400	1	25

At lower stirring rates the value of the coefficient is usually between 0.42 to 0.8

Rate Dependence on Oxygen Concentration

The effect of oxygen on the half-order rate was determined by passing different mixtures of oxygen-nitrogen gas through the corroding solution. Figure 15 indicates that the rate of dissolution is most effectively correlated in term of the square root of the oxygen partial pressure in the gas phase with which the solution is equilibrated. This dependence could imply oxygen dissociation in the liquid phase. In view of the square root dependence on surface area and solution volume it seems unlikely that this is a possibility. It is most reasonable to associate this relationship with the formation of the surface film and loss of effective area at higher stannic ion concentrations.

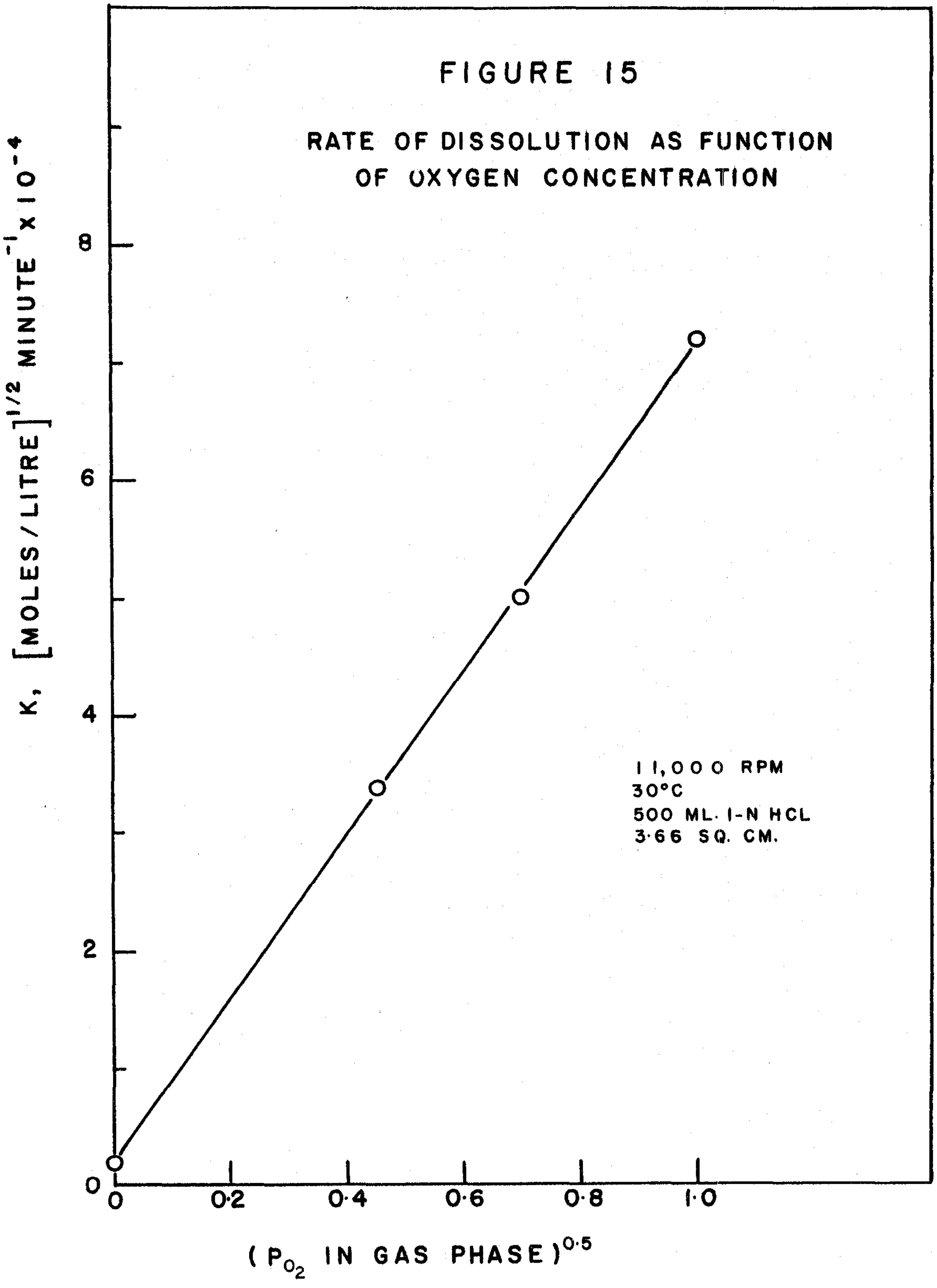


FIGURE 15

RATE OF DISSOLUTION AS FUNCTION OF OXYGEN CONCENTRATION

Effect of Hydrochloric Acid Concentration

The rate of dissolution of tin appears to be a complex function of acid concentration as shown in Table 6.

TABLE 6

Effect of HCl on Tin Dissolution

$[\text{HCl}]$	$k_{\text{(half-order)}}$
0.3233	3.22 $\frac{(\text{mol/lit})^{\frac{1}{2}}}{\text{min}}$
0.4009	3.50
0.5458	4.32
0.8018	3.96
1.0135	3.28

The rate increases with increasing hydrogen ion concentration until a maximum is attained at 0.55 N HCl. Further increase in acid concentration tends to decrease the corrosion rate. This behaviour parallels the formation of the black surface film. At low acid concentrations there is little tendency for the film to develop during a two hour period. At higher acid concentrations the decrease in rate due to film formation offsets the increase due to the increasing hydrogen ion concentration.

Ammonium chloride has virtually little effect on the rate of solution of tin in 0.1 N HCl. Figure 16 shows the slight inhibition by ammonium chloride in the concentration range 0.1 to 1.0 M.

At all acid concentrations ammonium chloride favors the formation of a looser type of surface film.

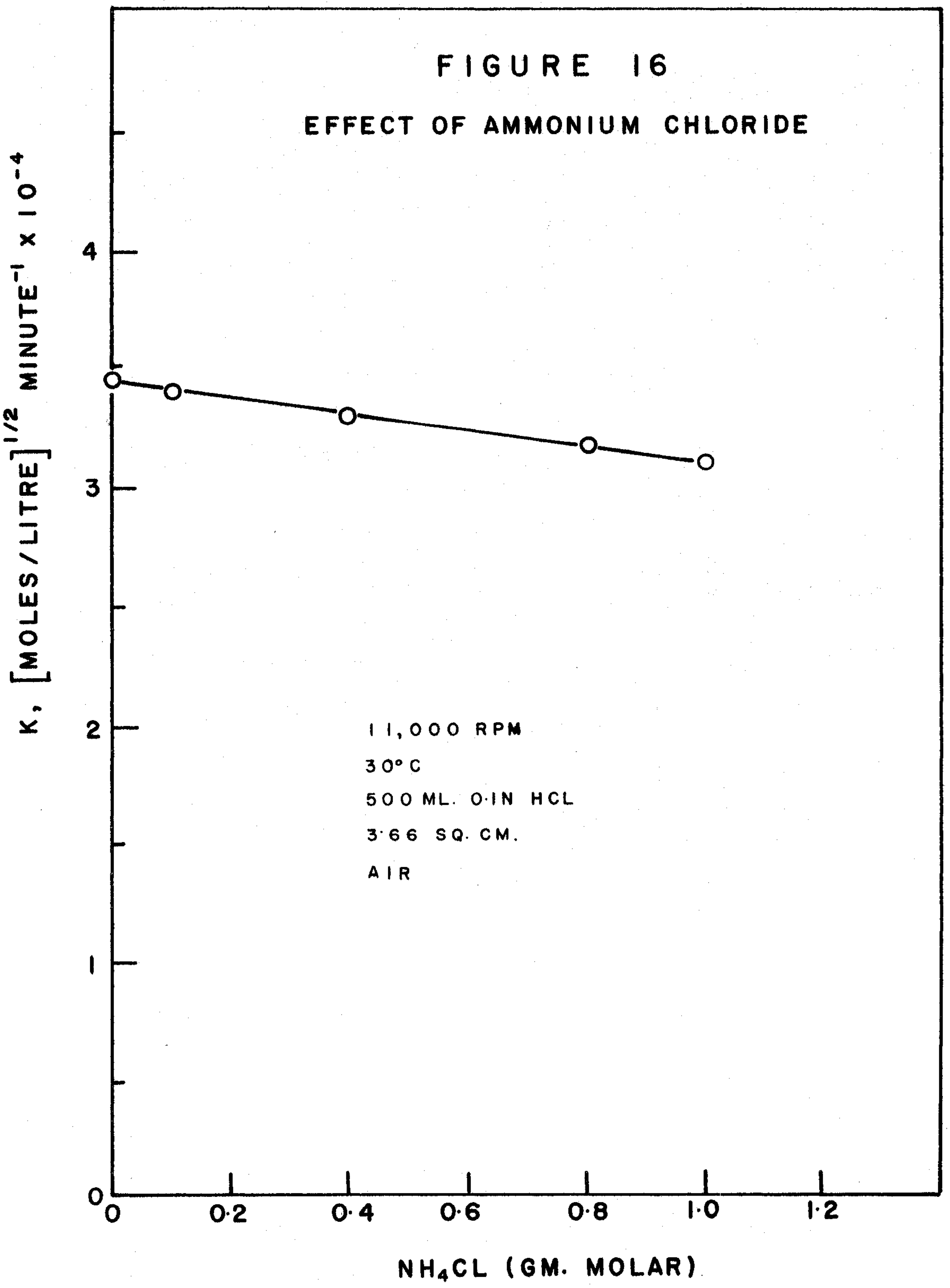


FIGURE 16

EFFECT OF AMMONIUM CHLORIDE

11,000 RPM
30° C
500 ML. 0·1N HCL
3·66 SQ. CM.
AIR

Empirical Equation for Tin Dissolution

The data may be summarized by the relationship

$$\frac{d\left[Sn^{++++}\right]}{dt} = k\left[Sn^{++++}\right]^{\frac{1}{2}}\left(\frac{A}{V}\right)^{\frac{1}{2}}\left(P_{O_2}\right)^{\frac{1}{2}}(R.P.M.)^{0.92}\; e^{-\frac{4700}{RT}}$$

for the conditions

$\left[Sn^{++++}\right]$ = $3 - 20 \times 10^{-4}$ moles/litre of complex stannic ions

T = 293° - 318° K

A = 0.91 - 7.32 cm^2

V = 400 - 600 ml

t = 0 - 180 min

P_{O_2} = 0 - 1 atm

HCl = 1.0 M

r.p.m. > 11,000

The value of k has been calculated in Table 7 giving a mean of 4.07×10^{-3} with an average deviation of ± 5%.

TABLE 7

Evaluation of Velocity Constant

$$k = 2\,\frac{d\left[Sn^{++++}\right]^{\frac{1}{2}}}{dt}\left(\frac{V}{A}\right)^{\frac{1}{2}}\left(\frac{1}{P_{O_2}}\right)^{\frac{1}{2}}\left(\frac{1}{R.P.M.}\right)^{0.92}\; e^{\frac{4700}{RT}}$$

$\frac{d\left[Sn^{++++}\right]^{\frac{1}{2}}}{dt}$	R.P.M.	T (°C)	V (ml)	A (cm^2)	P_{O_2} (atm)	k
0.895×10^{-4}	11,000	30°	500	0.91	0.21	4.31×10^{-3}
1.19				1.83		4.05
1.79				3.66		4.30

$\frac{d[\mathrm{Sn}^{++++}]^{\frac{1}{2}}}{dt}$	R.P.M.	T ($^{\circ}$C)	V (ml)	A (cm^2)	P_{O_2} (atm)	k
2.22×10^{-4}	11,000	30°	500	5.49	0.21	4.36×10^{-3}
2.65				7.32		4.50
0.83			550	0.91		4.10
1.38			400	1.83		4.20
2.00			400	3.66		4.30
2.06			550	5.49		4.25
2.39			600	7.32		4.45
1.48	11,000	25°	500	3.66	0.21	3.95
1.85		35°				3.91
2.10		40°				3.91
2.50		45°				4.16
1.70	13,500	25°	500	3.66	0.21	3.91
1.86		30°				3.84
2.16		35°				3.95
2.50		40°				4.02
2.85		45°				4.08
2.06	15,500	25°	500	3.66	0.21	3.91
2.42		30°				4.15
2.66		35°				4.00
2.88		40°				3.82
3.10		45°				3.74
3.61	11,000	30°	500	3.66	1.00	3.98
2.50					0.50	3.90

mean value of $k = 4.07 \times 10^{-3}$

V

CONCLUSION

There seems little doubt that the mechanism of tin dissolution in hydrochloric acid solutions will depend on experimental conditions.

In the absence of oxygen there is a slow rate due to simple hydrogen displacement.

Initially, when the sample is first immersed into air-saturated hydrochloric acid, dissolution will occur by hydrogen evolution. As the concentration of tin in the solution increases the corrosion shows autocatalytic behaviour with the rate being dependent on the square root of the stannic concentration.

For corrosion periods not much longer than an hour the rate of dissolution of tin may be quite adequately correlated in term of a zero-order dependence on stannic ion concentration. Extrapolation of these short term data to longer corrosion times, as is generally done in reporting corrosion data, could lead to serious errors.

The dissolution by autocatalysis appears to be somewhat inhibited by the formation of a black film at the tin surface. The effect of rotational speeds and low activation energies suggest that diffusion controls the heterogeneous dissolution reaction.

The half-order rate is directly proportional to the square root of the partial pressure of oxygen in the gas phase with which the solution is equilibrated.

The action of hydrochloric acid appears to be complex and requires further study. Concentrations above 0.55 N HCl tend to inhibit the dissolution presumably by the formation of thicker surface films.

The half-order rate of dissolution of tin in [illegible] HCl may be correlated with a precision of ± 5% by the empirical rate law

$$\frac{d\left[Sn^{++++}\right]}{dt} = 4.07 \times 10^{-3}\left[Sn^{++++}\right]^{\frac{1}{2}}\left(\frac{A}{V}\right)^{\frac{1}{3}}\left(P_{O_2}\right)^{\frac{1}{2}}(\text{r.p.m.})^{0.92}\ e^{-\frac{4700}{RT}}$$

for rotational speeds above 11,000 r.p.m.

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APPENDIX I

Polarographic Technique

Tin Ion Analysis

A Sargent model XV polarograph was employed for the analysis of tin concentrations. The general theory and procedure have been reviewed by Lingane (26). The polarography of tin has been studied by Phillips (28) and Phillips and Morgan (29).

A stock 2×10^{-3} M stannic chloride solution was prepared by dissolving Analar Grade tin in 1N HCl. Standard stannic solutions were prepared by diluting aliquot samples of the stock solution with 1N HCl and 4M NH_4Cl. The dropping mercury electrode calibration curve (Figure 17) was made with this supporting electrolyte of 1N HCl and 4M NH_4Cl containing 0.05% gelatin.

The polarographic cell containing the solution was immersed in a constant temperature bath kept at 25°C and the sample solution was flushed with nitrogen for approximately 10 minutes before a polarographic reading (27) was taken. For high tin concentrations, the solution was diluted and a corresponding amount of gelatin and ammonium chloride were added.

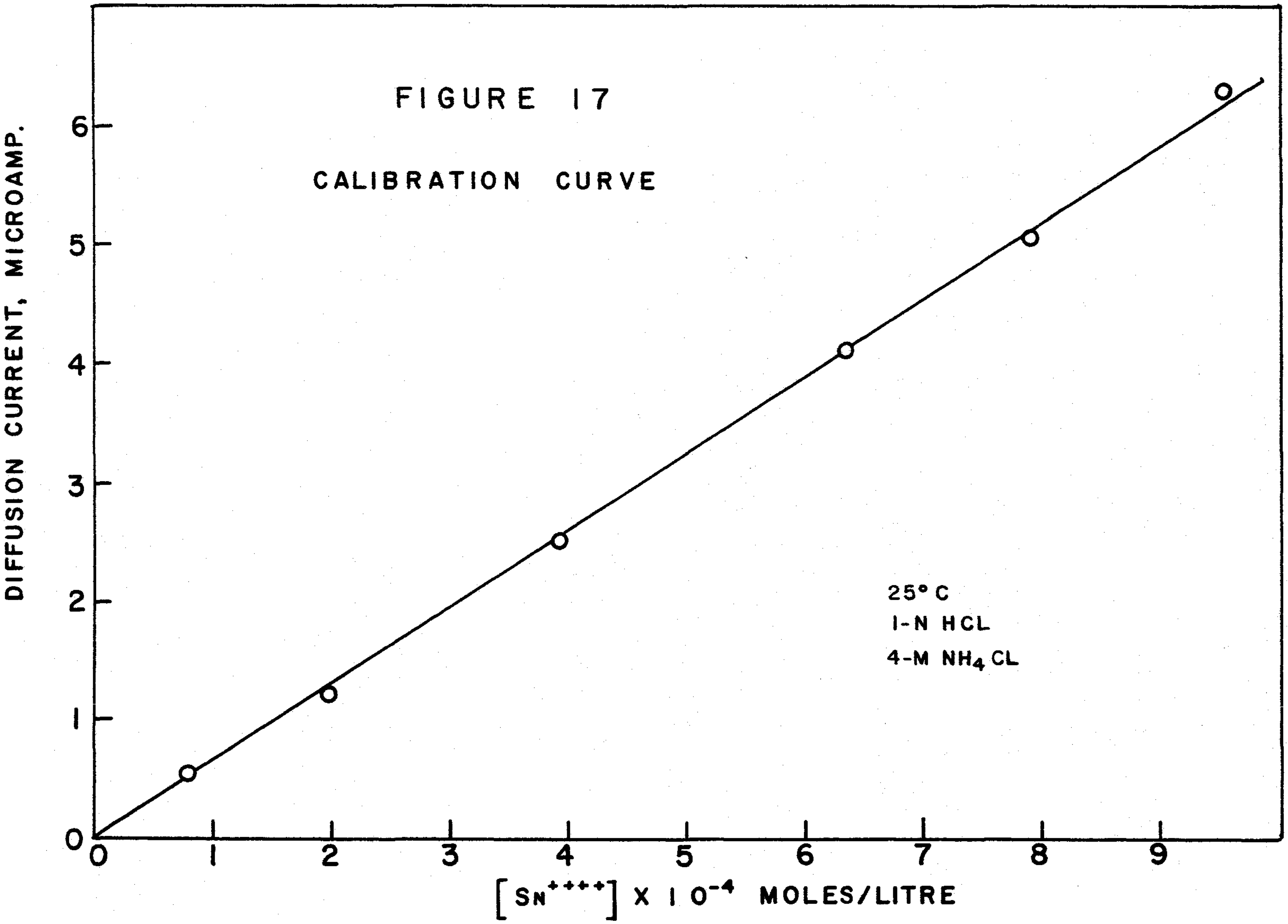

FIGURE 17

CALIBRATION CURVE

APPENDIX II

Variation or Rotational Speed and Temperature

1,000 R.P.M.
500 ml 1N HCl
3.09 sq cm
Air

Run 1 - 25°C		Run 2 - 35°C		Run 3 - 15°C	
Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)
0		0		0	
20	$0,35 \times 10^{-4}$	15	$0,20 \times 10^{-4}$	20	$0,30 \times 10^{-4}$
40	0,65	30	0,50	40	0,75
60	1,05	45	0,75	60	1,05
80	1.45	60	0,95	90	1,60
100	1,65	80	1,25	120	2,07
120	2,10	100	1,50	150	2,75
140	2,30	120	1,85	180	3,20
160	2,80	140	2,20		
180	3,20	160	2,60		
200	3.55	180	2,95		

3,000 R.P.M.
500 ml 1N HCl
3.65 sq cm
Air

Run 4 - 25°C		Run 5 - 35°C		Run 6 - 45°C		Run 7 - 40°C		Run 8 - 30°C		Run 9 - 20°C	
Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)
0		0		0		0		0		0	
10	0.1×10^{-4}	15	0.35×10^{-4}	20	0.50×10^{-4}	15	0.35×10^{-4}	15	0.25×10^{-4}	20	0.45×10^{-4}
30		30	0.75	42	1.20	30	0.65	30	0.75	40	1.00
55	0.65	50	1.30	60	1.60	50	1.15	50	1.20	60	1.40
70	0.90	70	1.75	80	2.40	70	1.65	70	1.70	80	1.90
90	1.20	95	2.30	100	3.00	90	2.10	90	2.10	100	2.35
110	1.60	120	2.95	120	3.55	110	2.65	110	2.70	120	2.85
130	2.00			140	4.40	130	3.15	130	3.20	140	3.35
								150	3.85	160	3.85

5,000 R.P.M.
500 1N HCl
3.66 sq cm
Air

Run 10 - 20°C		Run 11 - 25°C		Run 12 - 30°C		Run 13 - 35°C		Run 14 - 40°C		Run 15 - 45°C	
Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)
0		0		0		0		0		0	
20	0.50×10^{-4}	20	0.50×10^{-4}	20	0.30×10^{-4}	20	0.75×10^{-4}	20	0.75×10^{-4}	20	0.75×10^{-4}
40	1.05	40	0.80	40	1.25	40	1.60	40	1.60	40	2.10
60	1.60	60	1.30	60	1.85	60	2.30	60	2.50	60	3.05
80	2.25	80	1.75	80	2.60	80	3.40	80	3.30	80	4.00
100	2.60	100	2.40	100	3.35	100	4.30	100	4.10	100	5.30
120	3.80	120	3.05	120	4.10	120	5.30	120	5.25	120	6.50
140	4.30	140	3.70	140	4.85	140	6.10	140	6.25	140	8.10
160	4.90										

7,500 R.P.M.
500 ml 1N HCl
3.66 sq cm
Air

Run 16 - 40°C		Run 17 - 35°C		Run 18 - 25°C		Run 19 - 20°C	
Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)
0		0		0		0	
20	0.80×10^{-4}	20	1.20×10^{-4}	20	0.90×10^{-4}	20	0.80×10^{-4}
40	1.60	40	2.50	40	1.80	40	1.70
60	2.45	60	3.80	60	2.65	60	2.25
80	3.65	80	5.05	80	3.60	80	3.65
100	4.95	100	6.40	100	4.65	100	4.70
120	7.10	120	7.85	120	5.55	120	5.60
140	8.60	140	9.80	140	6.75	140	6.30

11,000 R.P.M.
500 ml 1N HCl
3.66 sq cm
Air

Run 20 - 25°C		Run 21 - 35°C		Run 22 - 45°C		Run 23 - 30°C		Run 24 - 40°C	
Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)
0		0		0		0		0	
15	0.75×10^{-4}	15	0.75×10^{-4}	15	1.35×10^{-4}	15	0.90×10^{-4}	15	1.10×10^{-4}
30	1.50	30	1.95	30	3.00	30	1.85	30	2.35
45	2.50	45	2.70	45	4.75	45	2.70	45	3.70
60	3.55	60	3.75	60	6.70	60	4.20	60	5.10
75	4.45	75	4.95	75	8.70	75	5.40	75	6.60
90	5.60	90	6.20	90	11.00	90	6.55	90	8.10
105	6.75	105	7.55	105	14.00	105	7.95	105	9.80
120	8.05	120	9.25	120	-	120	-	120	-

13,500 R.P.M.
500 ml 1N HCl
3.66 sq cm
Air

Run 25 - 25°C		Run 26 - 35°C		Run 27 - 45°C		Run 28 - 30°C	
Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)
0		0		0		0	
15	1.25×10^{-4}	15	1.30×10^{-4}	15	1.60×10^{-4}	20	1.40×10^{-4}
30	2.60	30	2.85	30	3.00	30	2.15
45	4.10	45	4.50	45	4.75	45	3.40
60	5.60	60	6.30	60	6.70	60	4.70
75	7.10	75	7.85	75	8.70	75	6.05
90	8.75	90	9.90			90	7.30
105	10.30	105	11.50			105	8.60

15,500 R.P.M.
500 ml 1N HCl
3.66 sq cm
Air

Run 29 - 25°C		Run 30 - 35°C		Run 31 - 30°C		Run 32 - 45°C		Run 33 - 40°C	
Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)
0		0		0		0		0	
15	1.30×10^{-4}	15	1.35×10^{-4}	15	1.85×10^{-4}	15	1.75×10^{-4}	15	1.35×10^{-4}
30	2.70	30	2.95	30	2.80	30	3.65	30	2.85
45	4.25	45	4.75	45	4.45	45	5.95	45	4.55
60	5.70	60	6.60	60	6.35	60	8.50	60	6.70
75	7.15	75	8.80	75	8.10	75	11.10	75	8.75
90	8.85	90	11.20	90	10.20	90	13.50	90	11.80
100	9.90			105	12.20				

APPENDIX III

Variation of Surface Roughness

11,000 R.P.M.
500 ml 1N HCl
30°C
Air

Run 34A - 7.32 cm^2		Run 34B - 7.32 cm^2		Run 35A - 5.49 cm^2		Run 35B - 5.49 cm^2		Run 36A - 1.83 cm^2		Run 36B - 1.83 cm^2	
Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)
0		0		0		0		0		0	
15	1.35×10^{-4}	15	2.50×10^{-4}	15	1.25×10^{-4}	15	1.45×10^{-4}	15	0.40×10^{-4}	15	0.50×10^{-4}
30	3.30	30	5.30	30	2.50	30	2.95	30	0.90	30	1.10
45	5.30	45	8.05	45	3.90	45	4.55	45	1.45	45	1.60
60	8.10	60	10.50	60	5.50	60	6.30	60	1.95	60	2.30
75	10.40	75	13.20	75	7.15	75	8.10	75	2.45	75	3.00
90	13.10	90	15.50	90	9.05	90	10.00	90	3.00	90	3.55
105	16.20	105	19.20	105	10.90	105	11.50	105	3.60	105	4.35
								120	4.35	120	5.05
20 microinch A.A.		55-65 microinch A.A.		20 microinch A.A.		55-65 microinch A.A.		20 microinch A.A.		55-65 microinch A.A.	

APPENDIX IV

Variation of A/V

11,000 R.P.M.
1N HCl
30°C
Air

Run 37 - 3.66 cm^2/500 ml		Run 38 - 3.66 cm^2/400 ml		Run 39 - 1.83 cm^2/400 ml		Run 40 - 7.32 cm^2/600 ml	
Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)
0		0		0		0	
15	0.90×10^{-4}	15	1.10×10^{-4}	15	0.50×10^{-4}	15	1.70×10^{-4}
30	1.85	30	2.05	30	1.10	30	3.70
45	2.70	45	3.30	45	1.70	45	5.35
60	4.20	60	4.65	60	2.35	60	7.65
75	5.40	75	6.00	75	3.05	75	9.60
90	6.55	90	7.40	90	3.85	90	12.10
105	7.95	105	9.15	105	4.50	105	14.90

APPENDIX IV
(Continued)

11,000 R.P.M.
1N HCl
30°C
Air

Run 41 - 5.40 cm^2/550 ml

Time (min)	$[Sn^{++++}]$ (mole/lit)
0	
15	1.40×10^{-4}
30	2.85
45	4.35
60	6.05
75	7.55
90	9.40
105	10.90

Run 42 - 0.91 cm^2/500 ml

Time (min)	$[Sn^{++++}]$ (mole/lit)
0	
15	0.10×10^{-4}
30	0.35
45	0.55
60	0.75
75	1.1[illegible]
90	1.50
105	1.65
120	2.05
135	2.30

Run 43 - 0.91 cm^2/550 ml

Time (min)	$[Sn^{++++}]$ (mole/lit)
0	
15	0.25×10^{-4}
30	0.50
45	0.80
60	1.15
75	1.45
90	1.75
105	2.05
120	2.40

APPENDIX V

Variation of [HCl]

11,000 R.P.M.
500 ml
30°C
Air

Run 44 - 1.014-N Hcl		Run 45 - 0.802 N HCl		Run 46 - 0.546 N HCl		Run 47 - 0.401 N-HCl		Run 48 - 0.323 N-HCl		Run 49 - 0.101 N-HCl	
Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)
0		0		0		0		0		0	
15	0.90 10^{-4}	15	1.00×10^{-4}	15	1.15×10^{-4}	15	1.00×10^{-4}	15	1.00×10^{-4}	15	1.10×10^{-4}
30	1.85	30	2.10	30	2.45	30	2.35	30	2.20	30	2.40
45	2.70	45	3.20	45	3.65	45	3.05	45	3.40	45	3.50
60	4.20	60	4.25	60	5.20	60	4.95	60	4.20	60	4.80
75	5.40	75	5.55	75	6.65	75	6.40	75	6.00	75	6.00
90	6.55	90	7.20	90	8.05	90	7.85	90	7.60	90	6.80
105	7.95	105	8.85	105	10.20	105	9.30	105	8.70	105	8.50
						120	10.90	105	10.20		

APPENDIX VI

Effect of Ammonium Chloride

11,000 R.P.M.
500 ml 0.1 N HCl
35°C
5.56 sq cm
Air

Run 50 - 0.1 M-NH_4Cl		Run 51 - 0.4 M-NH_4Cl		Run 52 - 0.8 M-NH_4Cl		Run 53 - 1.0 M-NH_4Cl	
Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)
0		0		0		0	
15	1.00×10^{-4}	15	0.90×10^{-4}	15	0.90×10^{-4}	15	0.90×10^{-4}
30	2.60	30	2.00	30	1.41	30	1.81
45	3.50	45	3.10	45	1.80	45	2.70
60	4.60	60	4.40	60	2.05	60	4.00
75	6.60	75	5.60	75	2.30	75	5.20
90	7.10	90	6.80	90	2.59	90	6.10
105	8.50	105	7.90	105	2.79	105	7.30
120	9.80	120	9.10	120	3.00	120	9.10

APPENDIX VII

Variation of Initial Tin Concentration

11,000 R.P.M.
500 ml 1N HCl
Area
3.66 sq cm

Run 54 - 31°C		Run 55 - 26°C		Run 56 - 26°C		Run 57 - 25°C	
Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)
0	6.35×10^{-4}	0	1.05×10^{-4}	0	3.55×10^{-4}	0	5.7×10^{-4}
10	6.50	10	1.40	15	4.00	10	5.85
20	6.90	20	1.75	30	4.50	20	6.20
30	7.30	30	2.05	45	5.10	35	6.75
40	7.70	50	2.75	60	5.55	50	7.65
50	8.00	70	3.40	75	6.00	65	8.20
60	8.20	90	4.10	90	6.70	80	8.70
80	9.30	110	4.90	105	7.10	100	9.20
100	9.90					120	10.00
120	11.10						

APPENDIX VIII

Variation of Oxygen Concentration

11,500 r.p.m.
30°C
500 ml 1 N HCl
3.66 sq cm

Run 58 - P_{O_2} = 1.0 atm		Run 59 - P_{O_2} = 0.50 atm		Run 60 - P_{O_2} = 0.21 atm		Run 61 - P_{O_2} = 0. atm	
Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)	Time (min)	$[Sn^{++++}]$ (mole/lit)
0		0		0		0	
15	3.20×10^{-4}	15	1.10×10^{-4}	15	0.90×10^{-4}	15	0.35×10^{-4}
30	6.30	30	2.35	30	1.85	30	0.75
45	10.30	45	3.70	45	2.70	45	1.30
60	14.80	60	5.45	60	4.20	60	1.85
75	18.00	75	7.25	75	5.40	75	1.90
90	23.60	90	8.70	90	6.55	90	2.05
		105	12.00	105	7.95	105	2.15
						120	2.55
						135	3.00

APPENDIX IX

Dissolution by Hydrogen Evolution

500 ml 1 N HCl
3.66 sq cm
N_2

Run 61 - 11,000 rpm
30°C

Time (min)	$[Sn^{++++}]$ (mol/lit)
0	
15	0.35×10^{-4}
30	0.75
45	1.30
60	1.85
75	1.90
90	2.05
105	2.15
120	2.55
135	3.00

Run 62 - 5000 rpm
26°C

Time (min)	$[Sn^{++++}]$ (mol/lit)
0	
20	0.075×10^{-4}
40	"
60	0.15
80	0.40
100	0.55
120	0.75
140	0.80
160	1.00
180	1.25
200	1.60
220	2.00

VITA AUCTORIS

1937	Born in Hong Kong in 1937.
1957	Completed high school education in St. Joseph's College, Hong Kong with G.C.E. and the Hong Kong University Matriculation certificates.
1961	Received the Degree of Bachlor of Science in Chemical Engineering from Queen's University, Kingston, Ontario.
1962	Currently, a candidate for the degree of Master of Science in Chemical Engineering at the Assumption University of Windsor.