
Masters Theses

Student Theses and Dissertations

1966

Anodic dissolution of lead in aqueous solutions

Christopher Kuo-chieh Wu

Follow this and additional works at: https://scholarsmine.mst.edu/masters_theses



Part of the [Chemical Engineering Commons](#)

Department:

Recommended Citation

Wu, Christopher Kuo-chieh, "Anodic dissolution of lead in aqueous solutions" (1966). *Masters Theses*. 2944.

https://scholarsmine.mst.edu/masters_theses/2944

This thesis is brought to you by Scholars' Mine, a service of the Missouri S&T Library and Learning Resources. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

ANODIC DISSOLUTION OF LEAD IN
AQUEOUS SOLUTIONS

BY

CHRISTOPHER KUO-CHIEH WU-1935

A

THESIS

submitted to the faculty of the

UNIVERSITY OF MISSOURI AT ROLLA

in partial fulfillment of the requirements for the

Degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

Rolla, Missouri

1966

Approved by

James A. Johnson (Advisor)
W. R. Straub

T1965
628
c.1
W. J. James
J. E. Straub

123711

ABSTRACT

The apparent valence of lead was determined in one normal solutions of potassium nitrate, ammonium acetate, lead nitrate, and lead acetate at temperatures of 25 and 50°C. The current density was varied from 0.001 to 1.00 amp·cm⁻². The apparent valence of lead ranged between 1.90 and 2.00 in all solutions. The lower valences were reached at higher current densities. The amount of disintegration was very small, and was dependent upon film formation on the surface of the anode.

Potential-current density relationships for the anodic dissolution of lead were obtained in the electrolytes mentioned above. In potassium nitrate and ammonium acetate solutions, the Tafel slopes were 0.030 volts. The proposed dissolution mechanism is

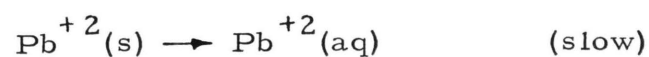
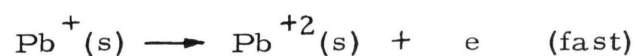
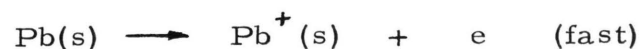


TABLE OF CONTENTS

	Page
TITLE PAGE	i
ABSTRACT	ii
TABLE OF CONTENTS	iii
LIST OF FIGURES	vi
LIST OF TABLES	vii
I. INTRODUCTION	1
II. LITERATURE REVIEW	3
A. Anodic Dissolution of Lead in Aqueous Solutions	3
B. The Relationship between the Current Density and the Potential of the Lead Anode in Aqueous Solutions	7
III. EXPERIMENTAL	12
A. The Effect of Current Density on the Apparent Valence of Lead Undergoing Anodic Dissolution in Various Electrolytes	13
1. Apparatus	13
2. Preparation of Samples	13
3. Procedure	16
4. Data and Results	17

a. Potassium Nitrate	18
b. Ammonium Acetate	18
c. Lead Nitrate	21
d. Lead Acetate	21
Sample Calculations	21
a. Calculation of the Apparent Weight of Lead Dissolved from Coulombic Data	22
b. Calculation of the Apparent Valence	23
B. The Potential of the Lead Electrode Under- going Anodic Dissolution in Various Electrolytes	24
1. Apparatus	24
2. Procedure	24
3. Data and Results	24
IV. DISCUSSION	31
A. Anodic Dissolution of Lead in Aqueous Solutions	31
B. The Relationship between the Potential of the Lead Anode and the Current Density in Aqueous Solutions	33
C. Accuracy and Reproducibility	39
D. Limitations	39
E. Recommendations	40

LIST OF FIGURES

Figure	Page
1. Diagrams of the mounted and bare electrodes	14
2. Diagram of apparatus used for measurement of apparent valence of lead undergoing anodic dissolution	15
3. X-ray diffraction patterns of the metal and the black film from the lead electrode	20
4. Diagram of apparatus used for measurement of the dissolution potential of lead at various current densities	25
5. Tafel curves for the anodic dissolution of lead in 1.00 N KNO_3	27
6. Tafel curves for the anodic dissolution of lead in 1.00 N $\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)$	28
7. Tafel curves for the anodic dissolution of lead in $\text{Pb}(\text{NO}_3)_2$	29
8. Tafel curves for the anodic dissolution of lead in 1.00 N $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ at 25°C	30
9. Tafel curves for the anodic dissolution of lead in 1.00 N $\text{K}(\text{C}_2\text{H}_3\text{O}_2)$ at 25°C	37

	Page
V. APPENDICES	
Appendix I - Materials, Equipment	41
Appendix II - Standardization of Disodium EDTA ..	43
Appendix III - Apparent Valence of Lead in Various Electrolytes	44
Appendix IV - Time Behavior of the Dissolution Potential of the Lead Electrode in Various Electrolytes	50
VI. BIBLIOGRAPHY	59
VII. ACKNOWLEDGEMENTS	61
VIII. VITA	62

LIST OF TABLES

Table	Page
I. Lines of Pattern of Anodic Film Identified as Lead and Lead Mono Oxide	19
IA. Apparent Valence of Lead Dissolving Anodically in 1.00 N Solutions of Various Electrolytes	20a
II. Apparent Valence of Lead Dissolving Anodically in 1.00 N KNO_3 at 25°C	45
III. Apparent Valence of Lead Dissolving Anodically in 1.00 N KNO_3 at 50°C	46
IV. Apparent Valence of Lead Dissolving Anodically in 1.00 N $\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)$	47
V. Apparent Valence of Lead Dissolving Anodically in 1.00 N $\text{Pb}(\text{NO}_3)_2$	48
VI. Apparent Valence of Lead Dissolving Anodically in 1.00 N $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$	49
VII. Time Behavior of the Dissolution Potential of the Lead Electrode in 1.00 N KNO_3 at 25°C	51
VIII. Time Behavior of the Dissolution Potential of the Lead Electrode in 1.00 N KNO_3 at 50°C	52
IX. Time Behavior of the Dissolution Potential of the Lead Electrode in 1.00 N $\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)$ at 25°C	53
X. Time Behavior of the Dissolution Potential of the Lead Electrode in 1.00 N $\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)$ at 50°C	54

Table		Page
XI.	Time Behavior of the Dissolution Potential of the Lead Electrode in 1.00 N $\text{Pb}(\text{NO}_3)_2$ at 25°C	55
XII.	Time Behavior of the Dissolution Potential of the Lead Electrode in 0.30 N $\text{Pb}(\text{NO}_3)_2$ at 25°C	56
XIII.	Time Behavior of the Dissolution Potential of the Lead Electrode in Saturated $\text{Pb}(\text{NO}_3)_2$ at 25°C	57
XIV.	Time Behavior of the Dissolution Potential of the Lead Electrode in 1.00 N $\text{Pb}(\text{C}_{\underline{2}}\text{H}_{\underline{3}}\text{O}_{\underline{2}})_2$ at 25°C	58

I. INTRODUCTION

Lead is one of the most durable of the metals outside of the small group of so-called "noble" metals. However, it is not unsusceptible at ordinary atmospheric conditions to a combination of oxygen and water which is the ruination of ordinary iron.

Oxygen in the atmosphere attacks lead and forms a coating of rust (lead oxide) just as it attacks iron and leaves a coating of iron rust. The two oxides, ferrous and ferric, which form iron rust are mutually unstable. They will undergo partial reduction and oxidation with great facility, thereby carrying oxygen through the rust coating to the metal underneath. This action continues, until in time, no metal is left.

With lead, it is different. When exposed to ordinary atmosphere, a suboxide is formed by a union of oxygen with the lead. This further reacts with carbon dioxide in the air to form lead carbonate. Here the process stops as the film of carbonate prevents further oxidation.

When a lead anode and platinum cathode are immersed in a vessel which contains an oxygen-free electrolyte and are connected to a direct current power source, lead is dissolved. This process is called anodic dissolution. A study of the anodic dissolution of metals has been found useful for many reasons: (1) the apparent valence of

the metal undergoing dissolution can be determined, (2) a mathematical expression for the dissolution rate can be established, and (3) a dissolution reaction mechanism can be hypothesized that may aid in predicting behavior in other environments.

The purpose of this investigation was to study the anodic dissolution of lead in approximately neutral electrolytes at various current densities and temperatures and to establish a mechanism consistent with the data.

II. LITERATURE REVIEW

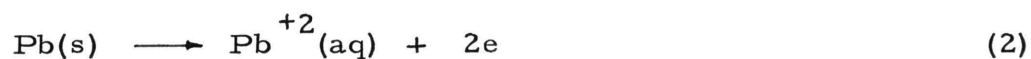
It is often found that metals dissolving anodically apparently do not go into solution according to Faraday's law. This may be due to several factors: (1) a reaction occurs in which the metal is attacked chemically by the electrolyte, (2) galvanic action takes place in which the metal is attacked by local corrosion, (3) the metal disintegrates into fine metallic particles during the dissolution process, and (4) the metal dissolves as ions with an uncommon valence. This literature review is concerned with both the anodic dissolution of lead and its current density-potential relationship in aqueous solutions.

A. Anodic Dissolution of Lead in Aqueous Solutions

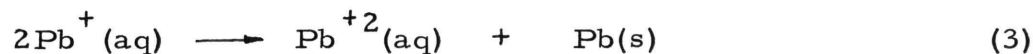
Burgess and Hambuschen (1) prepared lead hydroxide by dissolving lead anodically in a sodium nitrate solution. They found that the dissolution did not take place in the expected manner, i. e., lead ions were not produced in such quantities as Faraday's law would indicate. It was observed that some basic lead compounds caused uneven corrosion of the metal by partially or completely insulating the anode. They concluded that the current efficiency of the anode was limited by various factors such as the purity and physical

structure of the metal, the current density, and the chemical nature of the electrolyte.

Denham and Allmend (2) proposed the existence in aqueous solution of monovalent lead ions (Pb^+) in their work with the hydrogen electrode. Bell (3) studied the dissolution of lead anodically in various aqueous solutions and supported the existence of monovalent lead ions. His hypothesis was that there are two possible processes for the dissolution of the lead anode:



He assumed an equilibrium for lead similar to that for copper,



for which,

$$K = \frac{a_{\text{Pb}^{+2}}}{(a_{\text{Pb}^+})^2} \quad (4)$$

He also assumed that some aqueous solutions form complexes with Pb^+ more completely than with Pb^{+2} , just as CN^- complexes with Cu^+ when KCN is electrolyzed with a copper anode. In this case, Pb^+ would be produced at the anode in larger than normal quantities. The electrolytes used were lead acetate, sodium acetate, potassium hydrogen tartrate, hydrofluorsilicic acid, potassium bromide, and sodium thiosulphate. The amount of lead dissolved chemically was estimated by the use of a "blank anode", i. e., a second bar of pure lead immersed in the anolyte and not connected into the circuit. The current density range was 1.02 to 10.25 $\text{ma}\cdot\text{cm}^{-2}$. A calculation of the ratio of the metal actually lost from the anode to that from coulometric data is shown in the following example:

Total anodic loss	0.4736 gm
Blank loss	0.0004 gm
Loss from anode by electrolysis	0.4732 gm
Loss using coulometric data	0.4679 gm

$$\text{Ratio} = \frac{0.4732}{0.4679} = 1.011$$

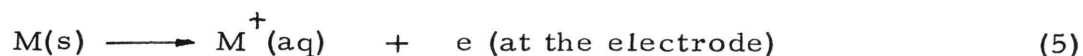
A ratio of unity would mean that the lead had dissolved as divalent ions only. Bell found, in general, that the anode lost more lead

than one would expect from Faraday's law assuming dissolution as divalent ions. In solutions of $\text{Pb}(\text{CH}_3\text{COO})_2$, $\text{KH}(\text{CHOHCO}_2)_2$, H_2SiF_6 , and KBr , the loss was due to chemical solution and mechanical detachment during cleaning and not to the lead dissolving as monovalent ions. Nevertheless, with CH_3COONa and $\text{Na}_2\text{S}_2\text{O}_3$, he calculated that 5.6 percent of the lead for the latter and 2.8 percent for the former went into solution as monovalent ions. He observed a black deposit on the anode in the sodium thiosulphate solutions. Possible explanations of this deposit were: (1) a monovalent lead compound or possibly lead sulphide, (2) finely divided lead formed by a redox reaction of the monovalent compound, or (3) a peculiar nature of the corrosion related to the crystalline structure of the metal.

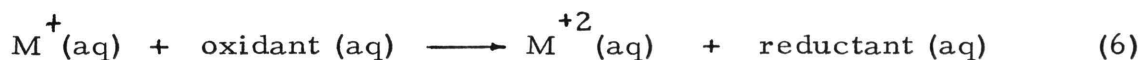
Marsh and Schaschl (4) proposed a mechanism of anodic dissolution of metals which they called the "chunk effect". They reported that when steel dissolves anodically at a high rate, the corrosion proceeds with the removal of "chunks" of iron containing many atoms. These chunks account for more iron disappearing from the anode than predicted by Faraday's law.

Davidson and coworkers (5) gave considerable support to the "uncommon valence ion" concept. This was first proposed by Epelboin (6) to explain the deviation from Faraday's law of zinc and cadmium undergoing anodic dissolution. The hypothesis is that the dissolution

of the metal is a stepwise oxidation, the first step being the oxidation of the metal to the unipositive ion at the anode:



The unipositive ion would be expected to be very unstable, readily forming the normal divalent ion as the second step. There are two ways in which the second step could occur. First, the unipositive ion could be chemically oxidized by an oxidizing agent in the solution, that is,



The alternate way is by further oxidation to the bipoisitive ion at the surface of the electrode, that is,

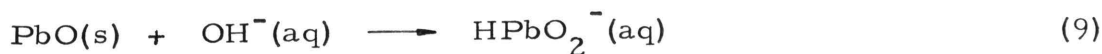


With non-reducible electrolytes, reaction (6) could not occur and consequently a valence of two would be observed according to reactions (5) and (7). With reducible electrolytes, reactions (6) and (7) would be competitive with the predominant one depending on the nature of the oxidizing electrolyte and the conditions of the experiment. Thus, a

valence between one and two would be observed.

B. The Relationship between the Current Density and Potential of the Lead Anode in Aqueous Solutions

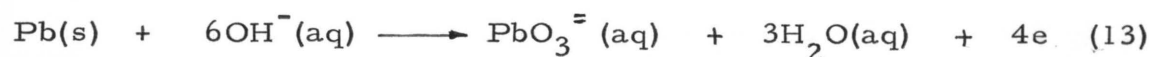
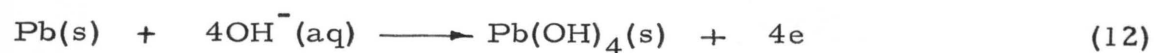
Glasstone (7) investigated the process of anodic dissolution of lead in 1.00 N NaOH by measuring the anodic potential at different current densities. In the low current density range, he found the anodic potential remained almost constant at -0.53 volts up to current densities of $0.0025 \text{ amp} \cdot \text{cm}^{-2}$. Lead was dissolved at the anode. He explained the potential as corresponding to that of the half-cell Pb, PbO in 1.00 N NaOH (-0.56 volts). The small difference was thought as probably due to concentration polarization. The reaction was proposed to occur by the discharge of OH^- ions and the dissolution of lead as plumbite ions,



A certain amount of lead also went into solution as plumbous ions,



When the current density was increased to $0.03 \text{ amp}\cdot\text{cm}^{-2}$, a dark gray film was seen on the anode surface. Coincident with this, the potential rapidly rose to 0.7 volts with no visible evolution of oxygen. It was explained that the higher potential was necessary for lead to dissolve because of passivation due to the visible oxide film. The lead was dissolving as plumbic and plumbate ions,



The presence of plumbate ions was shown in the electrolyte by precipitating them as lead dioxide with dilute nitric acid.

With a further increase in current density, a black film covered the entire surface of the anode. At this time the anode potential rose to 1.18 volts and oxygen was evolved.

Jones and Thirsk (8) investigated the process occurring at lead anodes in $2.0 \text{ N H}_2\text{SO}_4$ under conditions of constant apparent current density. They concluded that the electrode reaction could be regarded as occurring in three stages. First, a lead sulfate layer was formed on the electrode surface at a potential near the reversible Pb, PbSO_4 potential. Next, lead dioxide was formed from the lead sulfate, and finally, with the complete oxidation of the initial layer of lead sulfate to lead dioxide, the electrode seemed to function as an oxide electrode and oxygen evolution occurred at the surface.

Piontelli and Poli (9) have studied the anodic and cathodic polarization of metals. They point out that the main factors to be considered in the study of processes involving ion exchange at a metal-electrolyte interface are: (1) nature and structure of the metal, (2) nature of the electrolyte, (3) physical conditions (especially temperature), and (4) pretreatment of the electrode. They indicate that the working surface of a polycrystalline electrode is very irregular and its behavior is, therefore, a kind of rough average of contributions of various regions (with different structural characteristics) which depends not only on their area, but also on their particular electrochemical properties. For these reasons, they studied the electrode behavior of single crystals of very pure metals whose working surfaces possessed a well defined orientation. In their experiments, no evidence was obtained for the existence of differences in the electrode potential of the differently oriented surfaces when separately exposed to the same electrolyte under conditions of no external current flowing. In contrast, a definite influence of the orientation was found when an external current was passed. For the lead single crystal electrode, the electrolytes used were $\text{NH}_4\text{HSO}_3 - \text{Pb}(\text{NH}_4\text{SO}_3)_2$, $\text{HBF}_4 - \text{Pb}(\text{BF}_4)_2$, and $\text{HClO}_4 - \text{Pb}(\text{ClO}_4)_2$, each at a concentration of 0.5 M. The electrode surfaces were oriented with the (111), (110), and (100) lattice planes. In each electrolyte (on both anodic and cathodic sides), higher polarization was found on

surfaces oriented parallel to the (111) in the sulfamate solutions than in those of perchlorate and fluoborate which were similar.

Khan and Solveva (10) studied the anodic potential of pure lead in electrolytes containing 25 to 100 grams per liter of lead nitrate and 5 to 40 grams per liter of nitric acid at temperatures of 20, 35, and 50°C. The current density was varied from 0.005 to 0.1 amp·cm⁻². They found that the anodic potential was independent of concentration and temperature.

III. EXPERIMENTAL

One of the problems still unsolved is the nature of the mechanism of the anodic dissolution of metals. Discrepancies often arise between the weight loss of an electrode calculated from coulometric data and the actual value in certain salt solutions. The ratio of these two quantities is called the current efficiency. The product of this current efficiency and the normal valence of the metal gives the apparent valence of the metallic ions formed during the dissolution.

The purpose of this investigation was to study the effect of current density, electrolyte, and temperature on the apparent valence of lead. The electrolytes chosen gave approximately neutral solutions. The dissolution potentials of the lead anode were also measured.

Included for each phase of the experimentation are the apparatus, method of procedure, data, results, and sample calculations. A list of the materials and equipment used in this investigation is given in Appendix I.

A. The Effect of Current Density on the Apparent Valence of Lead Undergoing Anodic Dissolution in Various Electrolytes

1. Apparatus. The apparatus used for all apparent valence studies was similar to that described by Sanghvi (11). An electrolytic cell with separated compartments of 300 milliliter capacity, a lead anode, a platinum cathode, a sensitive milliammeter, a decade-type resistance box, a direct current power supply, a current recorder, and a knife-blade switch, were all connected in series. A diagram of this apparatus is shown in Figure 2. A timer with one-second divisions was used for measuring the elapsed time. Pipettes with capacities of 5, 10, and 25 milliliters were used to withdraw aliquots from the electrolyte which were titrated with EDTA (ethylenediamine tetraacetic acid) using a microburette of 10 milliliter capacity with 0.02 milliliter graduations. The cell was immersed in a water bath which was controlled at a desired temperature within $\pm 0.1^{\circ}\text{C}$.

2. Preparation of samples. A specimen of known cross-sectional area was prepared under vacuum by melting lead of 99.999 percent purity in a graphite mold. The exact diameter of the lead specimen was determined using a micrometer. The specimen was mounted in teflon by press fitting. Bare electrodes, i. e., a lead rod of the same purity as above, hammered into an approximate

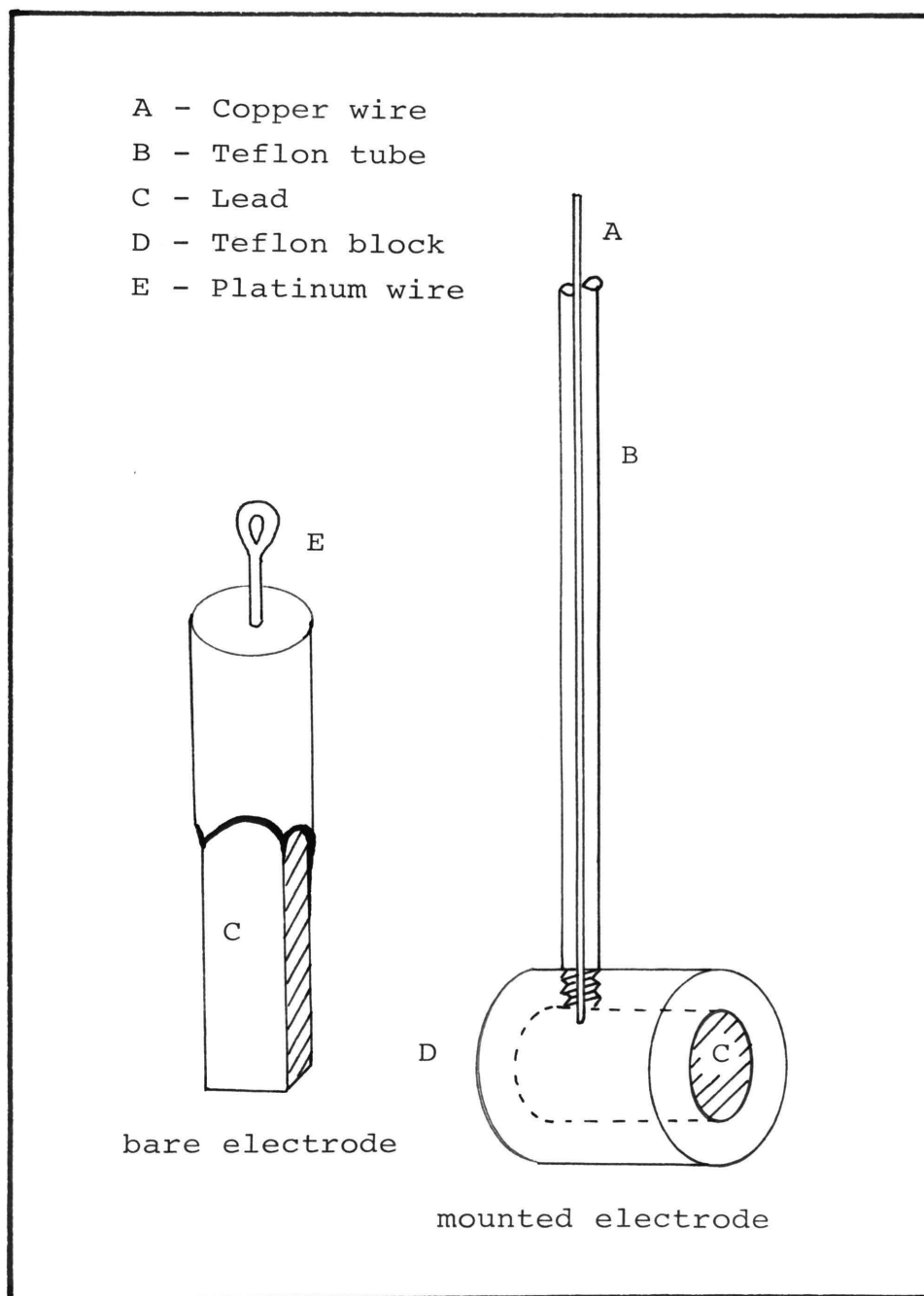


Figure 1. Diagrams of the mounted and bare electrodes.

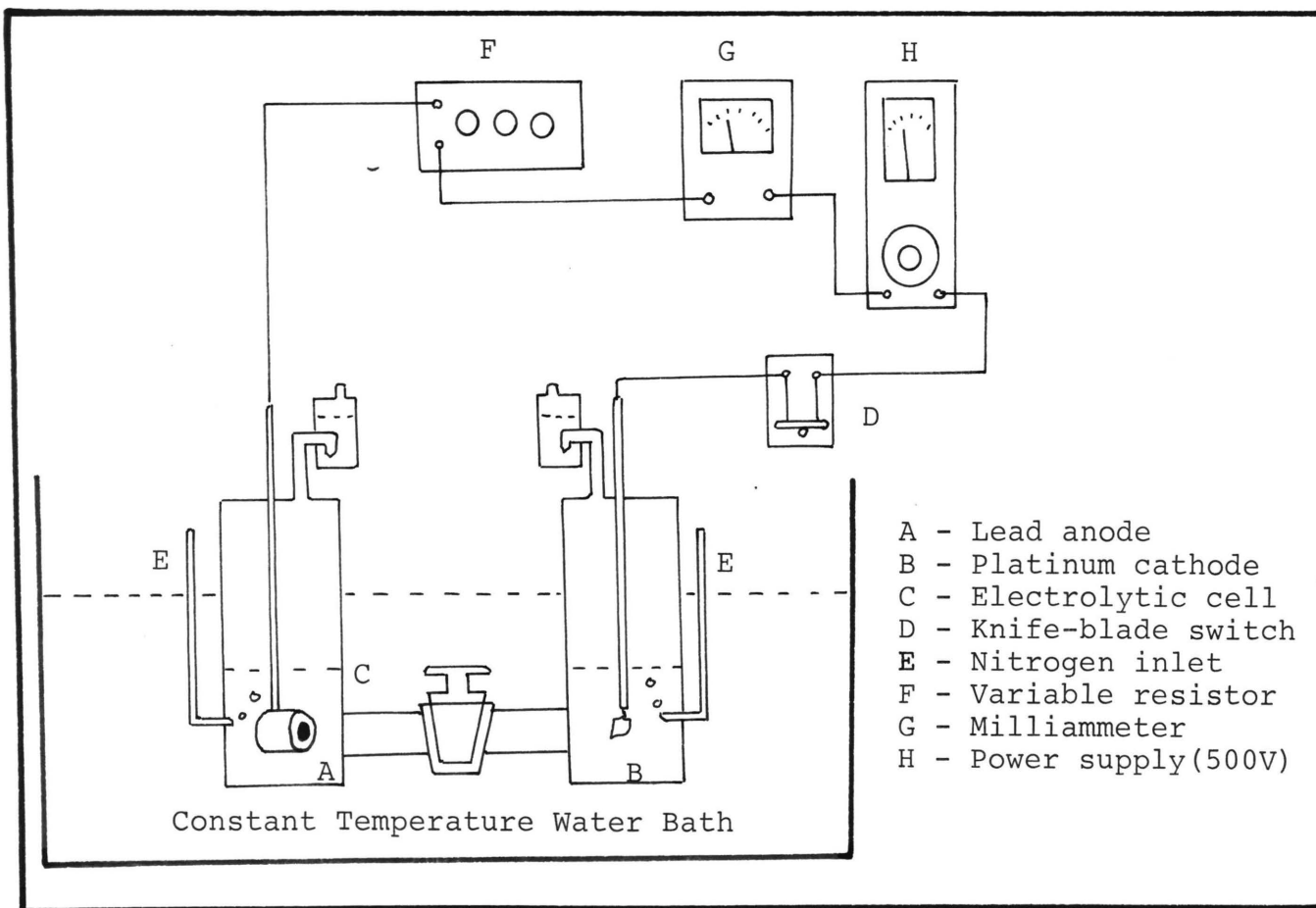


Figure 2. Diagram of apparatus used for measurement of apparent valence of lead undergoing anodic dissolution.

rectangular shape, were used in some experiments. A diagram of the mounted and bare electrodes is shown in Figure 1.

3. Procedure. Two hundred milliliters of electrolyte were transferred into the electrolytic cell. The cell was placed in the constant temperature bath so as to insure complete submergence of the solution. A nitrogen purge of the cell was begun and the system was allowed to come to constant temperature. The metal surface of the anode was ground on a belt sander until it was free of visible defects. It was then polished on a hand grinder with 240, 320, 400, and 600 abrasive grit papers until the surface was uniformly smooth. Finally the specimen was etched in dilute nitric acid for several minutes to produce a smooth clear surface. The anode and platinum cathode were then put into their respective compartments and connected into the external circuit (see Figure 2).

To begin an experiment, the knife-blade switch was closed and the current was kept at a steady value by means of the variable resistance box. The timer and milliammeter were used to measure the number of coulombs passed. At the end of a test run, the anolyte was collected in a beaker. If any visible film was on the electrode surface, it was removed with a rubber policeman and transferred into the beaker. The film in the beaker was dissolved by adding two

milliliters of concentrated nitric acid to the anolyte and warming on a hot plate. After the film was dissolved, the anolyte was poured into a volumetric flask and diluted to exactly 200 milliliters with distilled water. A 25 milliliter aliquot was withdrawn from the diluted anolyte, buffered to a pH of 10, and titrated with a standard EDTA solution using Eriochrome Black-T as an internal indicator. The EDTA solution had been previously standardized against a weighed amount of pure lead obtained from the same sample as the mounted specimen. The time of the electrolysis was recorded in seconds, the current in amperes, and the weight loss of the lead (determined by titration) in grams. The procedure employed was the same for all electrolysis experiments except in lead acetate and lead nitrate electrolytes. Here, the bare lead electrode was used and the weight loss was determined by weighing the electrode on an analytical balance. A detailed description of the procedure for standardizing the EDTA solution is included in the Appendix II.

4. Data and results. The data obtained for the anodic dissolution of lead in four different electrolytes at 25 and 50°C are shown in Tables II to VI, Appendix III. The electrolytes were potassium nitrate, ammonium acetate, lead nitrate, and lead acetate. A black film was formed on the surface of the electrode in all of the experiments. A brief summary of the results for each electrolyte follows.

a. Potassium Nitrate. The anodic dissolution of lead in 1.00 N potassium nitrate was carried out at current densities ranging from 0.0010 to 1.00 amp·cm⁻². Data from these runs are shown in Tables II and III. The black film was gradually formed on the surface of the electrode. The x-ray diffraction patterns of the film and of the lead sample are shown in Figure 3. The d values are given in Table I. The cubic pattern of metallic lead is clearly evident as well as a second phase identified as lead oxide (PbO). It can be seen that the valence does not depart appreciably from the normal value until the current density is increased above 0.150 amp·cm⁻².

b. Ammonium Acetate. Lead was dissolved anodically in 1.00 N ammonium acetate at current densities varying from 0.001 to 0.10 amp·cm⁻². The data obtained are shown in Table IV. It can be seen that the valence decreases more rapidly with current density than in potassium nitrate solutions.

TABLE I
 LINES OF PATTERN OF ANODIC FILM IDENTIFIED AS LEAD
 AND LEAD MONO OXIDE (RED)

Measured	d Calc. (Å)	d A.S.T.M. (Å)	Lines
18.36°	2.84	2.86	d,i (Pb)
21.24°	2.47	2.48	b,k (Pb)
30.61°	1.47	1.49	n (Pb)
10.27°	5.02	5.012	f,g (PbO)
16.61°	3.12	3.115	e,h (PbO)
18.72°	2.79	2.809	c,j (PbO)
27.91°	1.89	1.872	a,l (PbO)
33.10°	1.66	1.675	m (PbO)

$$\lambda_{\text{CoK}\alpha} = 1.79021 \text{ \AA}$$

$$\text{Temperature} = 25^{\circ}\text{C}$$

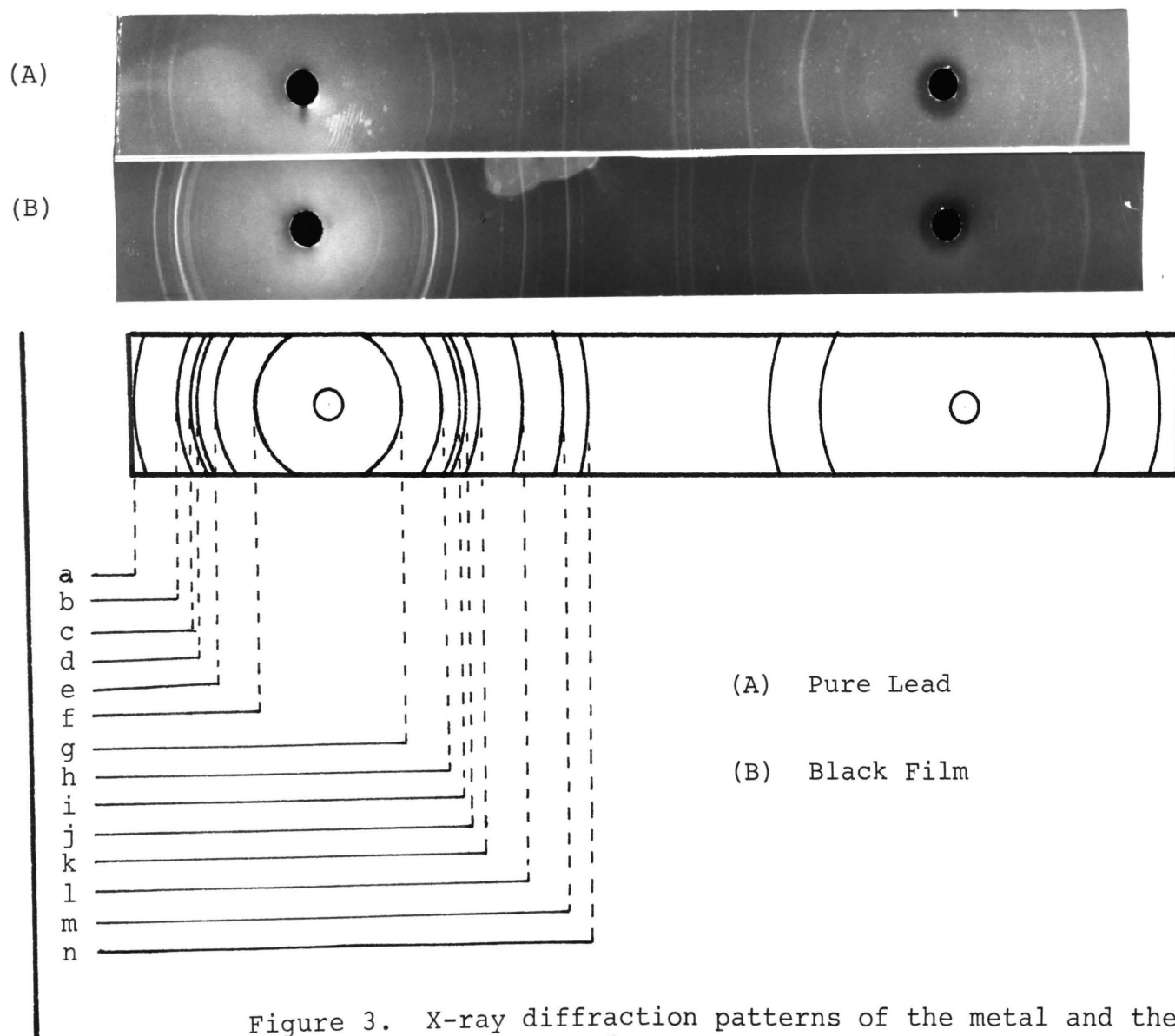


Figure 3. X-ray diffraction patterns of the metal and the black film from the lead electrode.

TABLE IA
 APPARENT VALENCE OF LEAD DISSOLVING ANODICALLY
 IN 1.00 N SOLUTION OF VARIOUS ELECTROLYTES

Electrolyte	Current Density (amp·cm ⁻²)	Apparent Valence
KNO ₃	0.0010	1.97
	0.1000	1.98
	1.0000	1.89
NH ₄ (C ₂ H ₃ O ₂)	0.0010	1.98
	0.0100	1.95
	0.1000	1.91
Pb(NO ₃) ₂	0.0010	1.93
	0.0600	1.93
	0.1000	1.93
Pb(C ₂ H ₃ O ₂) ₂	0.0010	1.91
	0.0600	1.88
	0.1000	1.83

c. Lead Nitrate. A bare lead electrode was dissolved anodically in 1.00 N lead nitrate. The current density was varied from 0.001 to 0.1 amp·cm⁻². Data from these runs are shown in Table V. The apparent valence is somewhat lower than in KNO₃ solutions. Considerable pitting was observed in these solutions. As the current density was calculated using the total electrode surface in the solution, the actual current density may have been somewhat higher than the calculated value.

d. Lead Acetate. The anodic dissolution of lead in 1.00 N lead acetate was carried out at current densities from 0.0010 to 0.10 amp·cm⁻². Data obtained from these runs are shown in Table VI. The valence measured in these solutions departs the most from the normal value. Pitting of the electrode was again noticed.

The apparent valence of lead ranged between 1.90 and 2.00 in all solutions. The current density was varied from 0.001 to 1.00 amp·cm⁻². A summarized result extracted from the Appendix Tables II to VI are shown in Table IA, page 20a.

5. Sample calculations. The method used to calculate the apparent valence in potassium nitrate, ammonium acetate, lead nitrate, and lead acetate solutions was the same. The data from the anodic dissolution in 1.00 N KNO₃ (Table II) are used to illustrate the calculation.

a. Calculation of the apparent weight of lead dissolved from coulometric data. The apparent weight of lead dissolved according to Faraday's law, assuming a normal valence of two is calculated as follows:

$$W_P = \frac{I t A}{n F} \quad (14)$$

Where, W_P = apparent weight of lead dissolved

I = current = 0.0300 amp

t = time of run = 1,600 sec

A = atomic weight of lead = 207.19

n = normal valence of lead = 2

F = Faraday constant = 96,486 amp·sec/gm-equiv

Therefore,

$$\begin{aligned} W_P &= \frac{(0.0300) (1,600) (207.19)}{(96,486) (2)} \\ &= 0.0446 \text{ gm} \end{aligned}$$

b. Calculation of the apparent valence. The apparent valence was calculated by means of the equation:

$$V_i \text{ (apparent valence)} = \frac{\text{(wt. of lead apparent) (normal valence)}}{\text{(wt. of lead (experimental))}} \quad (15)$$
$$= \frac{(0.0446) (2)}{(0.0447)} = 1.99$$

In equation (15), the experimental weight of lead dissolved was determined from either an EDTA titration or the weight loss of the electrode.

B. The Potential of the Lead Electrode Undergoing Anodic Dissolution in Various Electrolytes

1. Apparatus. The apparatus was similar to that described previously except that the anode was also incorporated in a second circuit containing a calomel reference electrode (1N) and a high impedance electrometer. A diagram of the apparatus is shown in Figure 4.

2. Procedure. The electrode was mounted in teflon as previously described. It was polished immediately before each run and etched in dilute nitric acid. Other experimental procedure was similar to that described previously except when the lead anode and the platinum cathode were placed in the cell and connected into the external circuit, the lead anode was also connected into the reference circuit with a Luggin capillary extended up to the interface of the electrode. The potential of the anode with no applied current was measured at intervals of 15 minutes until it reached a constant value. Similar measurements were then made at increasing current densities.

3. Data and results. Dissolution potentials of the lead anode were measured in solutions of potassium nitrate, ammonium acetate, lead nitrate, and lead acetate. All solutions were 1.0 N except lead nitrate where measurements were also made in 0.3 N

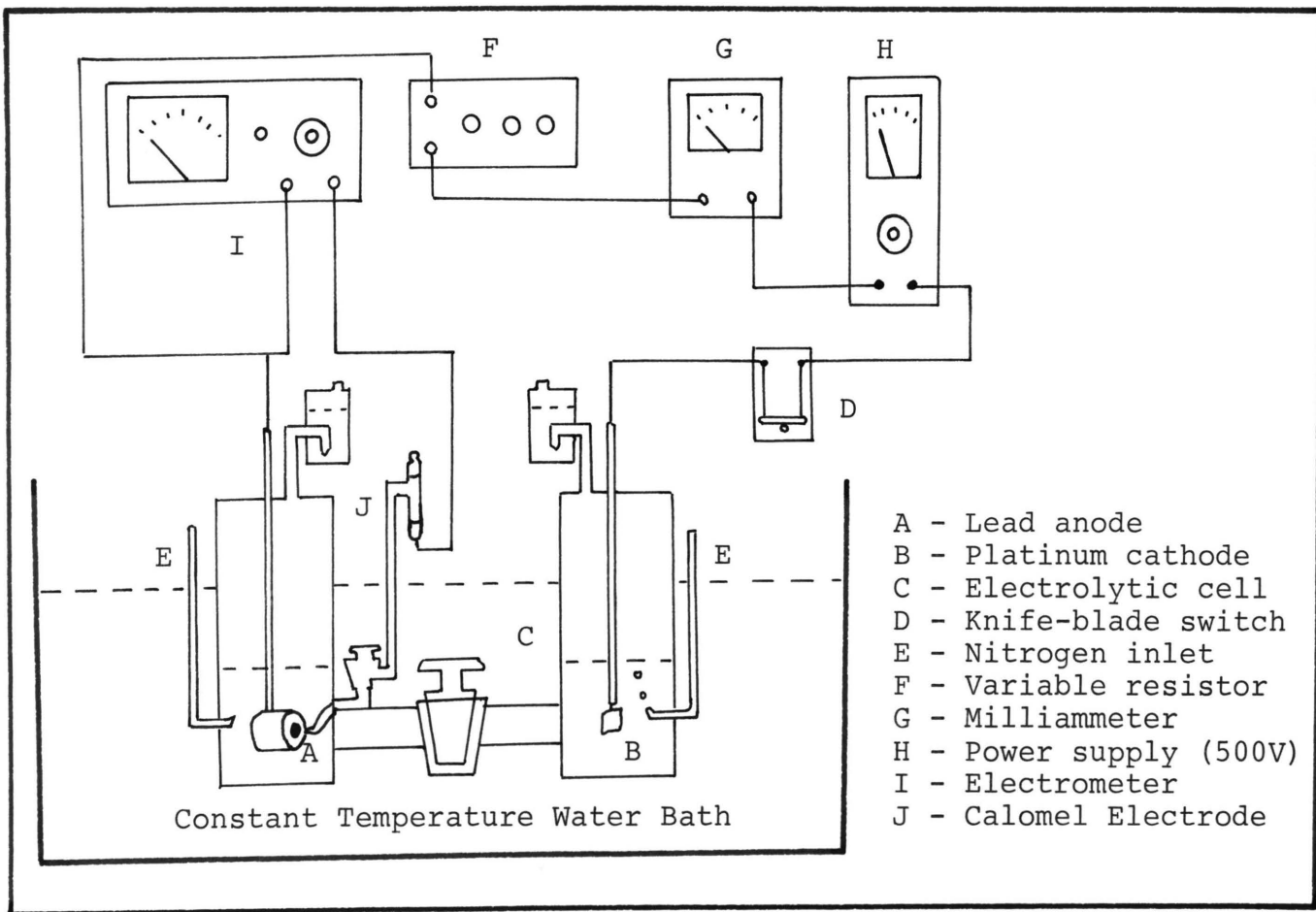


Figure 4. Diagram of apparatus used for measurement of the dissolution potential of lead at various current densities.

and saturated solutions. The solutions were prepared with triply distilled water. Measured potentials were reduced to the normal hydrogen scale. The obtained data of this studies are listed in Appendix IV. Tafel curves were also plotted and are shown in Figures 5 to 8.

In the solutions containing no lead ions, the Tafel slopes are approximately 0.030 volts per decade of current. The dissolution potentials also depart significantly from the rest potential (potential at zero current). In solutions containing lead ions, the anode is not appreciably polarized until the current density exceeds $0.01 \text{ amp}\cdot\text{cm}^{-2}$. No gas evolution was noted from the anode.

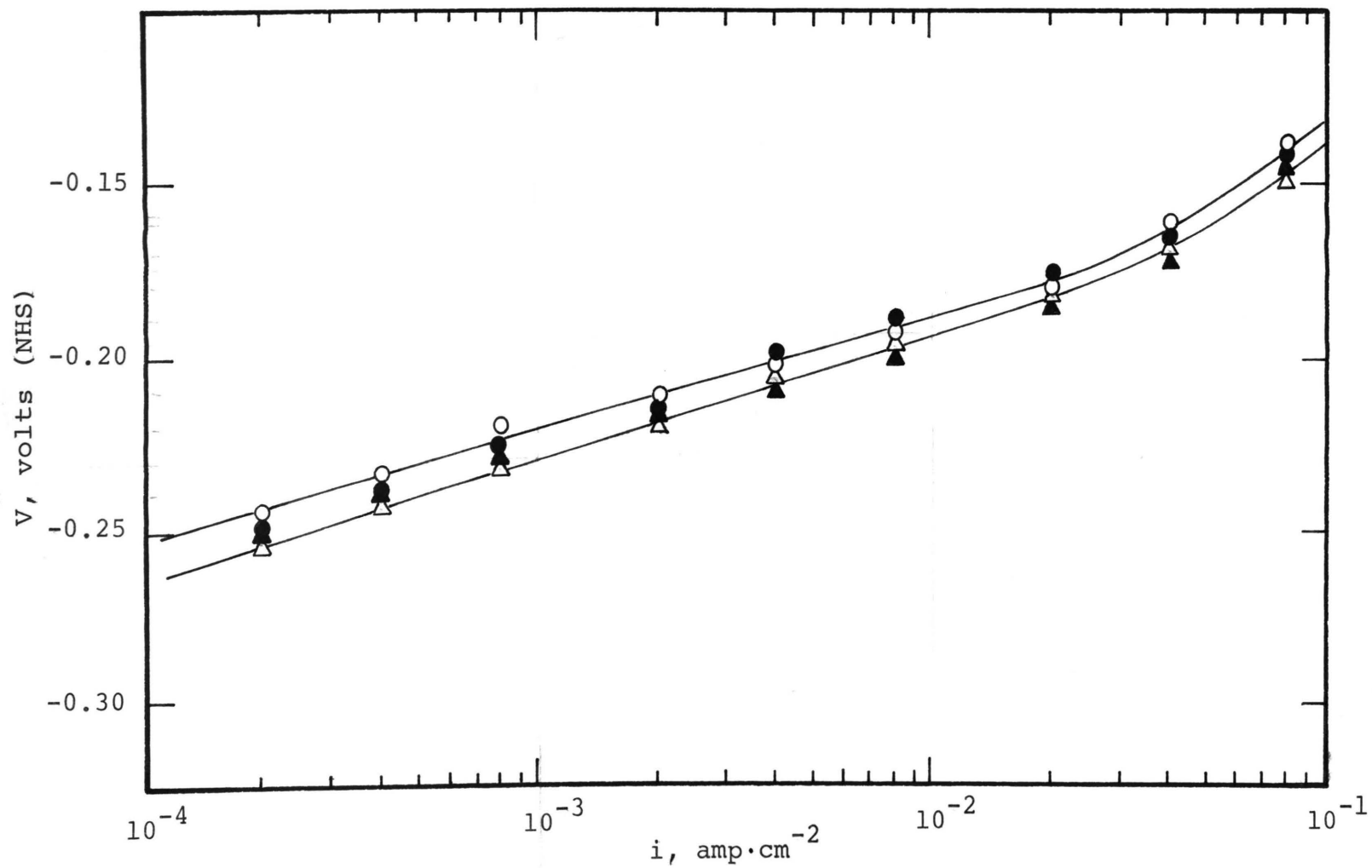


Figure 5. Tafel curves for the anodic dissolution of lead in 1.00 N KNO₃. (O, ● 25°C; Δ, ▲ 50°C)

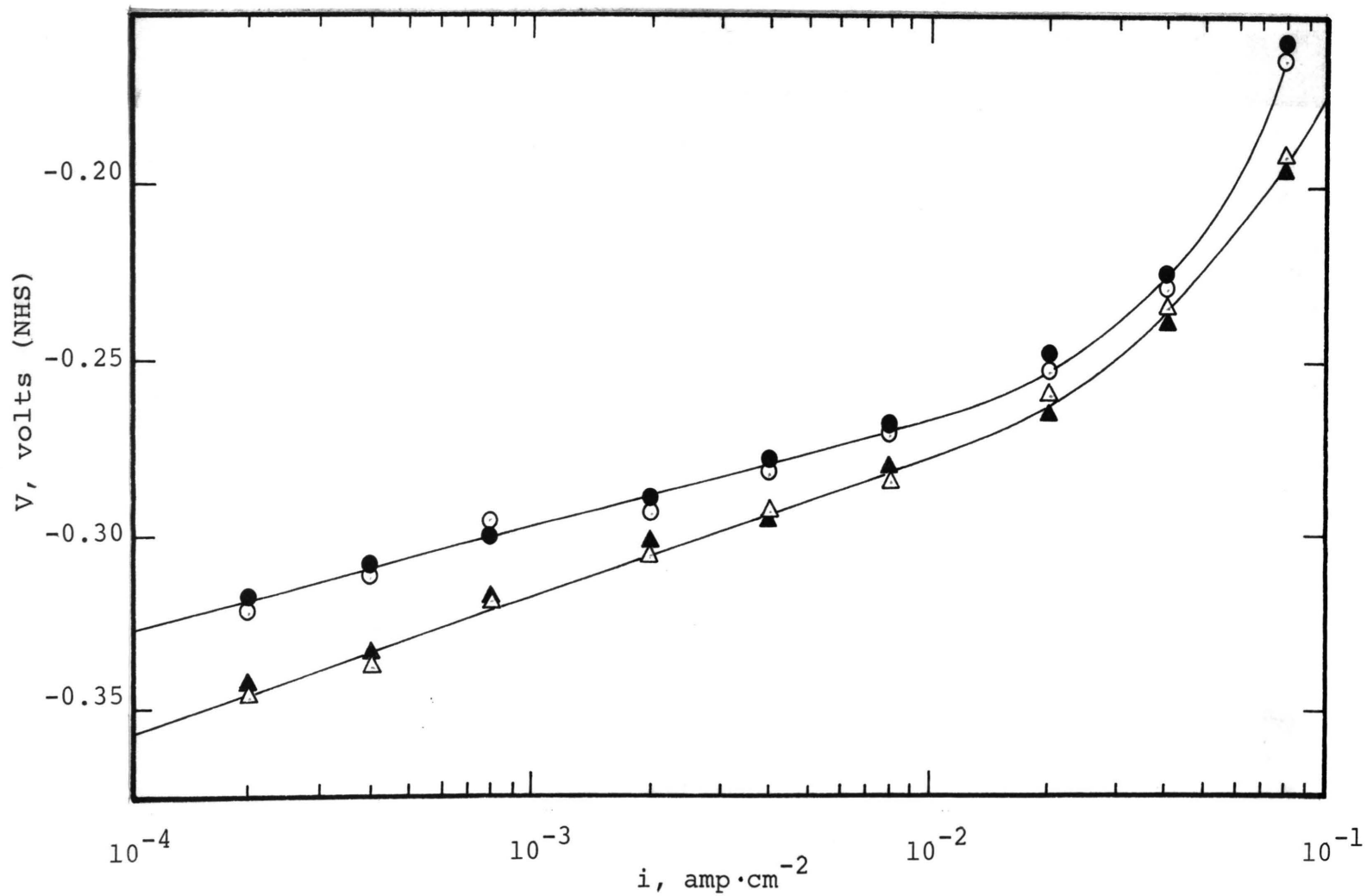


Figure 6. Tafel curves for the anodic dissolution of lead in 1.00 N $\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)$. (O,●25°C; Δ , \blacktriangle 50°C)

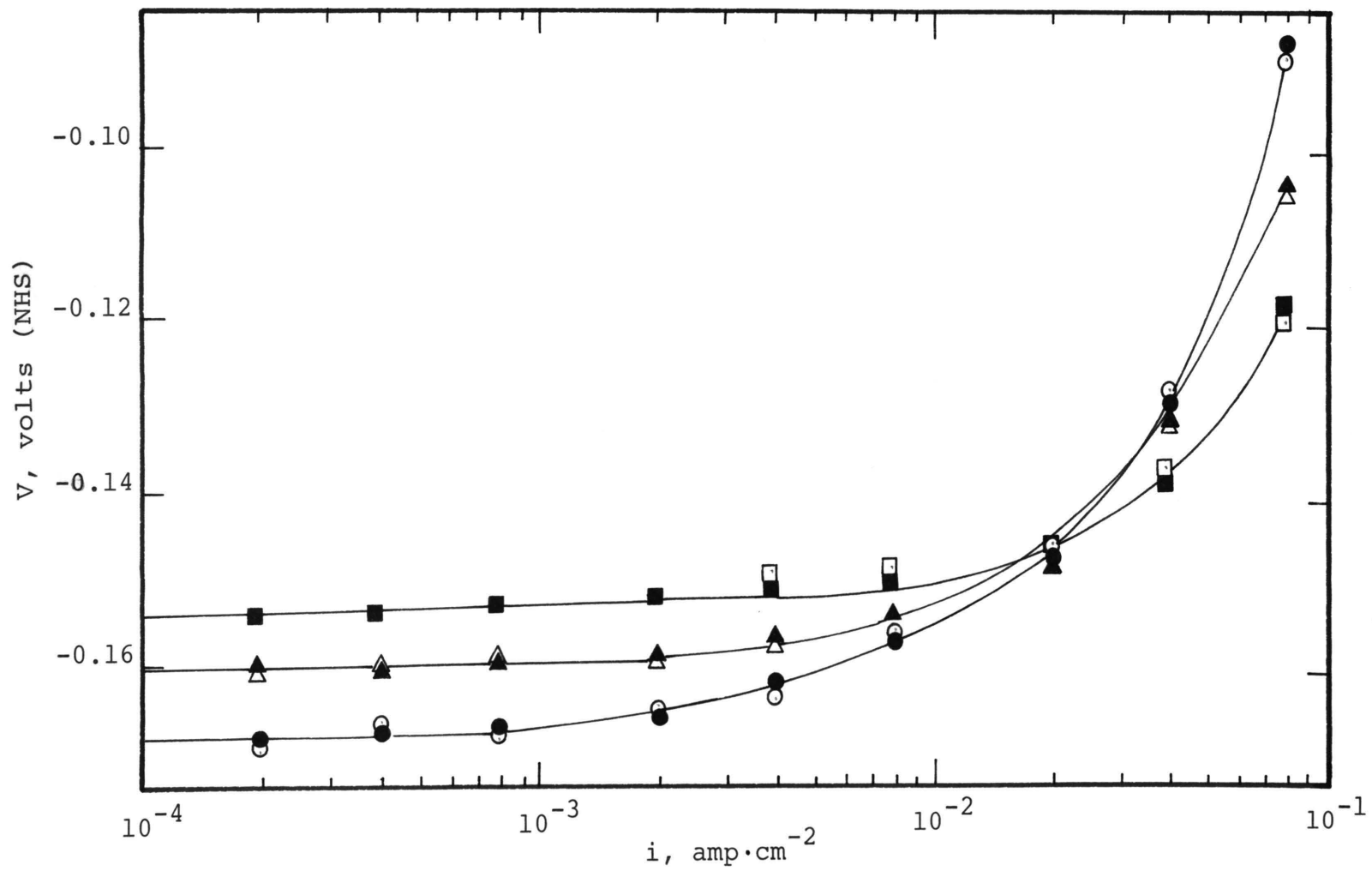


Figure 7. Tafel curves for the anodic dissolution of lead in $\text{Pb}(\text{NO}_3)_2$ at 25°C. (○, ● 0.30 N; △, ▲ 1.00 N; □, ■ Saturated)

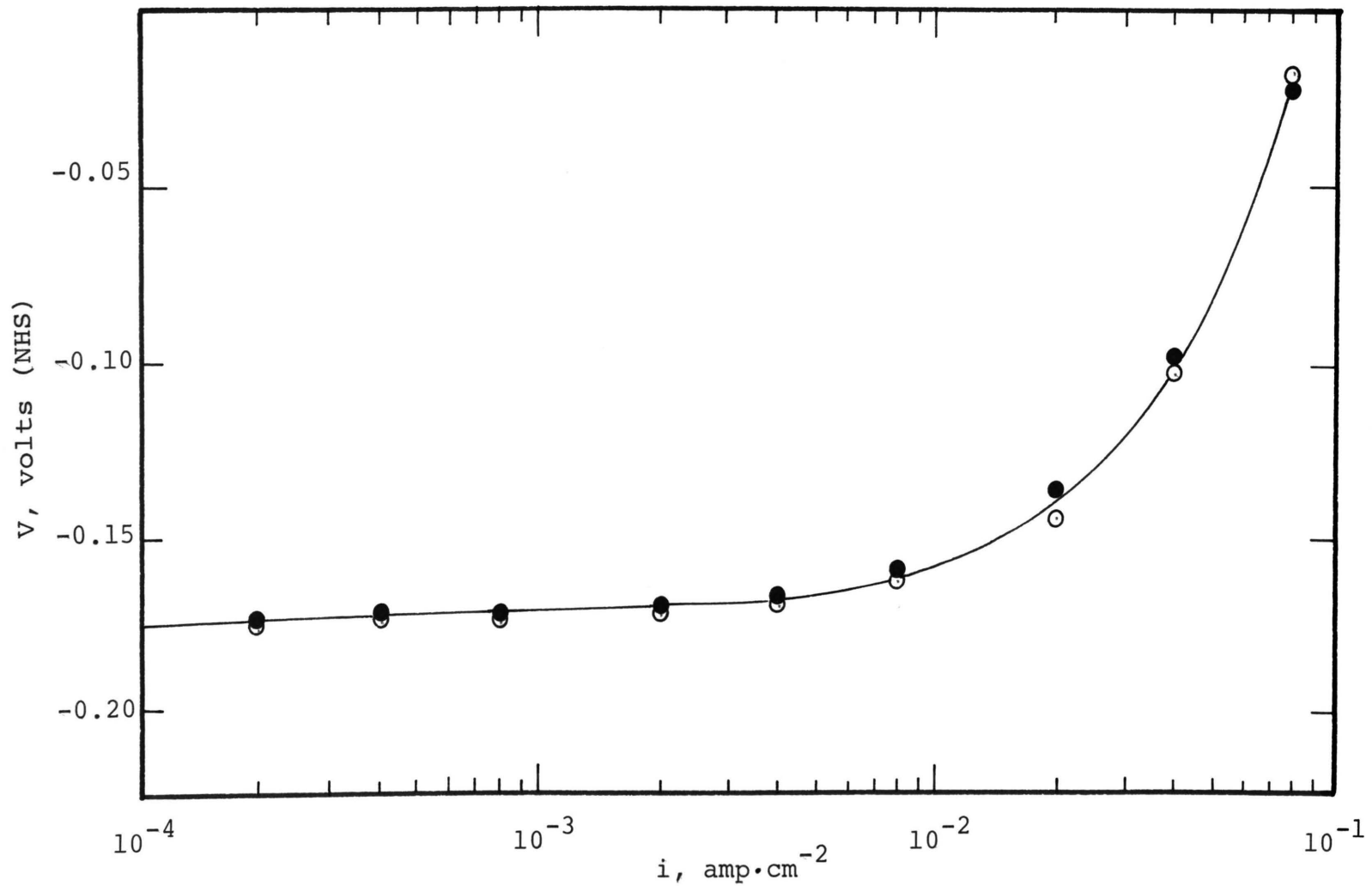


Figure 8. Tafel curves for the anodic dissolution of lead in 1.00 N $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ at 25°C. (O, ● duplicate runs)

IV. DISCUSSION

The discussion is presented in two parts: (1) the anodic dissolution of lead at various temperatures, and (2) the relationship between the dissolution potential of the lead anode and the current density in aqueous solutions.

A. Anodic Dissolution of Lead in Aqueous Solutions

The apparent valence of lead in the present investigation was found to deviate from the normal value of two. The deviation varied up to ten percent, depending upon the current density and the electrolyte. Normal valences were observed at low current densities. The observed valence seems to be associated with the formation of surface films. At low current densities, film repair would be possible, thereby giving a relatively uniform resistance to dissolution. At higher currents, inadequate film repair would lead to non-uniform film resistance, thus giving areas of differing current densities which ultimately detach particles, i. e., cause disintegration. The black film observed on the surface of the anode indicated that disintegration was occurring during anodic dissolution.

The valences and films observed agree with those reported by Bell (3). However due to results reported for magnesium (12) and beryllium (13), his postulation of monovalent lead ions does not seem acceptable. Also, the low apparent valences exhibited by some metals during anodic dissolution can be prevented by amalgamating the anode surface which casts further doubt on the existence of uncommon valence ions. Experiments by this author with lead in KClO_3 solutions gave normal valences up to current densities of $0.15 \text{ amp. cm}^{-2}$ when the electrode surface was amalgamated. Similar observations have also been made on Zn (14), Cd (15), and Sn (16).

The apparent valence of lead for the four electrolytes studied in the investigation decreased in the order: KNO_3 , $\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)$, $\text{Pb}(\text{NO}_3)_2$, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. In solutions of $\text{Pb}(\text{NO}_3)_2$ and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, hydrolysis of the cation differs, thereby altering the pH of the electrolyte which affects film formation, i. e., $\text{Pb}(\text{OH})_2$, on the anode surface. The greater film forming capability in acetate solutions would lead to a higher probability of non-uniform film resistance which would cause increased disintegration. In KNO_3 and $\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)$ solutions, the decreased Pb^{+2} concentration would further reduce the formation of $\text{Pb}(\text{OH})_2$, thus giving valences closer to the normal value. This is consistent with the observation that in KNO_3 and $\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)$ solutions, the apparent valences were higher than those in $\text{Pb}(\text{NO}_3)_2$

and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ solutions. Also after anodic dissolution, the lead surfaces were extensively pitted in the latter solutions while they were rather smooth in the former.

This explanation associates film formation on the anode surface very closely with disintegration phenomenon. If the film is insoluble and adheres well to the anodic surface, anodic disintegration can be expected. At places where the film is thin or has been damaged by metal cations forced into solution, the current density i.e., the rate of dissolution, will be high. This undermines the high resistance spots and will ultimately separate them from the anode surface.

Increasing the temperature from 25 to 50°C. was found to have a very small effect on the apparent valence of lead. As $\text{Pb}(\text{OH})_2$ is very insoluble, this change would not significantly affect film formation. The primary influence seems to be the pH of the electrolyte.

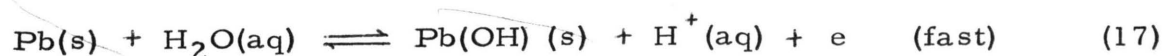
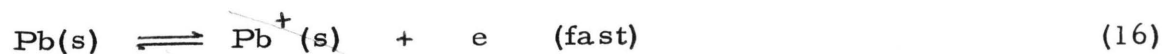
B. The Relationship between the Potential of the Lead Anode and the Current Density in Aqueous Solutions

Linear Tafel regions were obtained where the currents became steady almost immediately and remained thus. The slopes of the curves in ^{1. NO₃} potassium nitrate and ammonium acetate were approximately 0.030 volts per unit of logarithm of current density. In lead ^{Pb(NO₃)₂} nitrate and lead acetate electrolytes, the slopes were less than 0.002 volts. This indicated a possible difference in mechanism for the solutions containing

appreciable concentrations of lead ions.

Tafel slopes of 0.030 volts are associated with electrochemical mechanisms which have a rate determining chemical step preceded by two equilibrium charge transfer steps. For the solutions of potassium nitrate and ammonium acetate, there are several likely mechanisms which will give the observed slope. They fall into two types, those in which water discharge (film formation by reaction) is involved and those in which cation expulsion (film formation by precipitation) is involved.

The first mechanism type is postulated to occur as represented by equations (16) through (18). This also is representative of other types in which water discharge is involved in steps prior to the rate determining step.



It should be noted in this scheme that the surface film is periodically removed by the chemical reaction. The rate equations for each of the steps in the mechanism can be formulated as shown in equations (19) through (21).

$$i_{16} = Fk_{16} \theta_{\text{Pb}} \exp\left(\frac{(1-B)FE}{RT}\right) - Fk'_{16} \theta_{\text{Pb}^+} \exp\left(\frac{-BFE}{RT}\right) \quad (19)$$

$$i_{17} = Fk_{17} a_w \theta_{\text{Pb}} \exp\left(\frac{(1-B)FE}{RT}\right) - Fk'_{17} a_{\text{H}^+} \theta_{\text{PbOH}} \exp\left(\frac{-BFE}{RT}\right) \quad (20)$$

$$i_{18} = Fk_{18} \theta_{\text{PbOH}} \theta_{\text{Pb}^+} \quad (21)$$

where,

i = current density, amp·cm⁻²

θ = fractional surface coverage of indicated species

B = symmetry factor, assumed to be 0.5

a = activity

k = rate constant

K = equilibrium constant

F = Faraday's constant 96,486 coulomb/equivalent

E = electrode potential, volts

R = gas constant 8.314 joules/gm-mole^{°K}

T = Temperature, °K

Equations (19) and (20) can be assumed to be at equilibrium since they precede the rate controlling step. Thus,

$$\theta_{\text{Pb}^+} = K_{16} \theta_{\text{Pb}} \exp\left(\frac{FE}{RT}\right) \quad (22)$$

$$\theta_{\text{PbOH}} = K_{17} \frac{a_w}{a_{\text{H}^+}} \theta_{\text{Pb}} \exp\left(\frac{FE}{RT}\right) \quad (23)$$

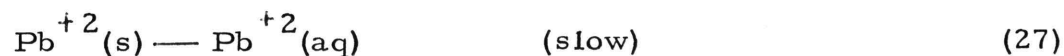
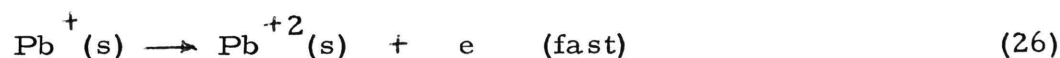
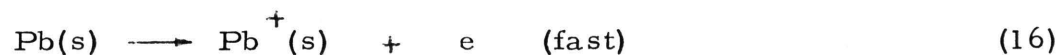
substituting equations (22) and (23) into (21), the over-all rate expression is

$$i = k_{18} \frac{F K_{16} K_{17}}{a_{\text{H}}^2} \theta_{\text{Pb}} \frac{a_{\text{w}}}{a_{\text{H}}^+} \exp\left(\frac{2FE}{RT}\right) \quad (24)$$

$$\frac{\partial E}{\partial \log i} = \frac{RT}{2F} = 0.0295 \text{ volts (25}^\circ\text{C)} \quad (25)$$

Equation (24) indicates that the current is dependent upon the pH of the solution, as well as other things. A further experiment in potassium acetate solution, pH 9 to 10, was made. The Tafel slope remained the same as in ammonium acetate solution and the curve was not shifted significantly. Since no pH effect was observed, all mechanisms involving water discharge can be eliminated.

A second mechanism type can be postulated in which charge transfer involves only lead ions as represented by equations (16), (26), (27)



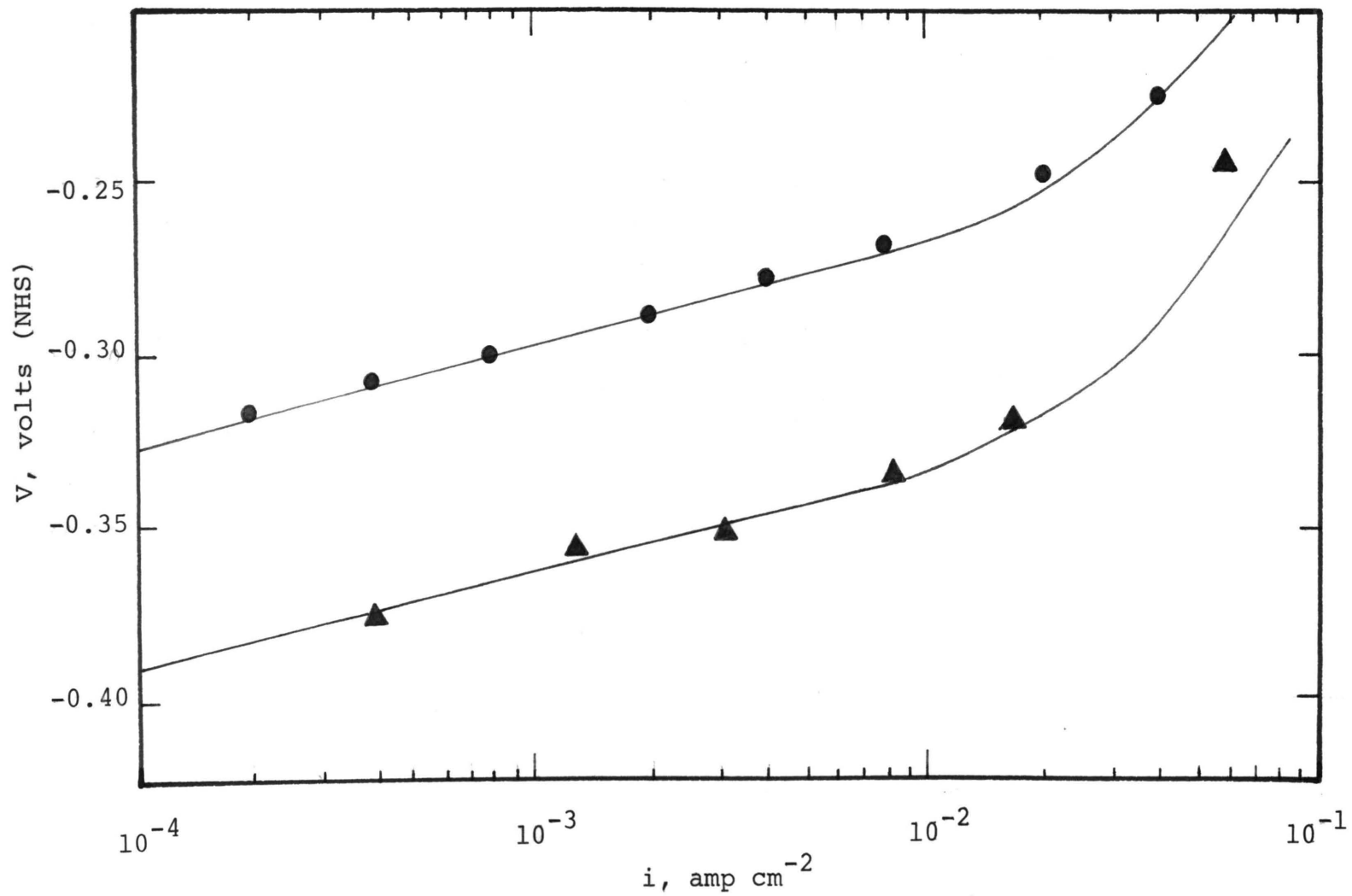


Figure 9. Tafel curves for the anodic dissolution of lead in 1.00 N $\text{K}(\text{C}_2\text{H}_3\text{O}_2)$ at 25°C. (▲, $\text{K}(\text{C}_2\text{H}_3\text{O}_2)$; ●, $\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)$)

Using the method described above,

$$\theta_{\text{Pb}^+} = K_{16} \theta_{\text{Pb}} \exp\left(\frac{FE}{RT}\right) \quad (28)$$

$$\theta_{\text{Pb}^{+2}} = K_{26} \theta_{\text{Pb}^+} \exp\left(\frac{FE}{RT}\right) \quad (29)$$

we obtain

$$i_{27} = k_{27} F K_{16} K_{26} \theta_{\text{Pb}}^2 \exp\left(\frac{2FE}{RT}\right) \quad (30)$$

$$\frac{\partial E}{\partial \log i} = \frac{RT}{2F} = 0.0295 \text{ volts (25}^\circ\text{C)} \quad (31)$$

The slope is correct and no pH dependence is present which is in qualitative agreement with experimental observations. Therefore, it is assumed that the second mechanism is more probable. An indirect influence of pH could be seen here through the precipitation of Pb(OH)_2 on the electrode surface. This would normally cause an abrupt increase in the potential due to the resistance added by the film.

In solutions containing appreciable concentrations of lead ions, lead behaves much as a non-polarizable electrode. This means the potential is controlled by the concentration of Pb^{+2} and not by the current. Under these conditions, no kinetic interpretations are possible.

C. Accuracy and Reproducibility

For valence measurements, the accuracy depended on measurements of the current, time of electrolysis, and the determination of dissolved lead by EDTA titration. The time of electrolysis was recorded within ± 1 second, giving a maximum error of ± 0.5 percent. The accuracy of the current measured depended on the scale of the milliammeter and could be estimated at ± 2.0 percent. The total volume of EDTA used was three to five milliliters. An error of one drop in titration could introduce a relative error of 2 percent.

Reproducibility of the valence measurements was within ± 2.0 percent. In potential measurements, reproducibility was ± 0.005 volts. The potential of the electrode depended on the surface preparation, etching, and the flow rate of nitrogen bubbling through the electrode. A constant flow rate was used throughout the experiments.

D. Limitation

Because the activity of Pb^{+2} was uncertain due to complex ion formation, the reversible potentials of the electrode could not be calculated. The high resistance of the stop-cock in the electrolytic cell limited the current densities to less than $0.10 \text{ amp} \cdot \text{cm}^{-2}$ for the valence and potential studies.

E. Recommendations

It is recommended that valence studies under the present experimental conditions be made using amalgamated lead electrodes and at temperatures greater than 50°C to see if further disintegration of lead occurs.

The mechanism of the anodic dissolution of lead in mixed electrolytes of potassium nitrate and ammonium acetate at constant ionic strength should be studied further for comparison with the proposed mechanism.

APPENDIX I

Materials

The following is a list of the major materials used in this investigation:

1. Potassium Nitrate. Reagent grade, meets ACS specifications. Fisher Scientific Company, Fair Lawn, N.Y.
2. Ammonium Acetate. Reagent grade, meets ACS specifications. Fisher Scientific Company, Fair Lawn, N.Y.
3. Lead Nitrate. Reagent grade, meets ACS specifications. Fisher Scientific Company, Fair Lawn, N.Y.
4. Lead Acetate. Reagent grade, meets ACS specifications. Fisher Scientific Company, Fair Lawn, N.Y.
5. Ethylenediamine Tetraacetic acid, Disodium salt. Reagent grade, Distillation Products, Eastman Organic Chemicals, Rochester 3, N.Y.
6. Eriochrome Black-T. Reagent grade, Fisher Scientific Company, Fair Lawn, N.Y.
7. Mercurous Chloride. Reagent grade, meets ACS specifications. Merck and Company Inc., Rahway, N.J.
8. Mercury. Continuous vacuum triple distilled, Bethlehem Apparatus Co., Inc., Hellertown, Pa.
9. Lead. 99.999 percent purity, Fisher Scientific Company, Fair Lawn, N.Y.

Equipment

Surface Preparation of Lead Specimen

1. Belt Surfacers. Buehler No. 1250, Buehler Ltd., Evanston, Illinois.

2. Hand Grinder. Handimet, 4 stages, Buehler No. 1470, Buehler Ltd., Evanston, Illinois.

Apparatus for the Electrolysis and Potential Measurements

1. Power Supply. Model 711 A, DC regulated voltage (0 to 500 volts), Hewlett-Packard Company, Loveland, Colorado.

2. Electrometer. Model 610 B, Keithley Instruments, Inc., Cleveland, Ohio.

3. Ammeter. Model 931, Weston Electric Instrument Corporation, Newark, N.J.

APPENDIX II

Standardization of Disodium EDTA

The procedure for this part of the experimentation follows as a step by step operation.

1. Accurately weigh out approximately three-tenths of a gram of lead metal of 99.999 percent purity.
2. Transfer to a 100 milliliter volumetric flask and dissolve in 10 ml of concentrated HNO_3 and distilled water.
3. Withdraw 5 ml aliquot by means of a pipette.
4. Dilute to 50 ml with distilled water and heat to about 40°C .
5. Add 5 ml pH 10 buffer solution.
6. Add one drop of Eriochrome Black-T indicator solution.
7. Titrate with 0.05 M EDTA in a micro burette until one drop turns solution blue.
8. Determine the lead equivalent of EDTA in gm lead/ml.

APPENDIX III

Apparent Valence of Lead in Various Electrolytes

TABLE II
 APPARENT VALENCE OF LEAD DISSOLVING ANODICALLY IN
 1.00 N KNO₃ AT 25°C

Time (sec)	Current Density (amps · cm ⁻²)	Weight of Lead		Apparent Valence
		Calc. (gm)	Expt. (gm)	
43,500	0.0010 ^a	0.0407	0.0404	1.97
17,700	0.0030	0.0505	0.0506	1.99
18,600	0.0030	0.0587	0.0606	1.94
5,080	0.0100	0.0472	0.0482	1.96
5,080	0.0100	0.0472	0.0483	1.96
1,600	0.0300	0.0446	0.0454	1.97
1,600	0.0300	0.0446	0.0447	1.99
5,020	0.1000	0.4531	0.4561	1.98
5,150	0.1000 ^b	0.3600	0.3568	2.01
5,000	0.1500	0.5261	0.5262	1.99
7,060	0.1500	0.7428	0.7624	1.95
3,000	0.2000 ^c	0.6441	0.6674	1.93
3,000	0.2000	0.6441	0.6686	1.93
2,000	0.4000	0.8588	0.8899	1.92
2,000	0.4000	0.8588	0.8917	1.92
1,500	0.6000	0.9660	1.0063	1.92
1,500	0.6000	0.9660	1.0078	1.92
1,500	0.8000	1.2882	1.3418	1.92
1,500	0.8000	1.2882	1.3436	1.92
1,000	1.0000	1.0735	1.1300	1.90
1,000	1.0000	1.0735	1.1359	1.89

^aElectrode area = 0.87 cm² (mounted)

^bElectrode area = 0.64 cm² (mounted)

^cElectrode area = 1.00 cm² (mounted)

TABLE III
 APPARENT VALENCE OF LEAD DISSOLVING ANODICALLY IN
 1.00 N KNO₃ AT 50°C

Time (sec)	Current Density (amp·cm ⁻²)	Weight of Lead		Apparent Valence
		Calc. (gm)	Expt. (gm)	
72,000	0.0010 ^a	0.0579	0.0584	1.98
20,000	0.0030	0.0483	0.0492	1.96
20,000	0.0030	0.0483	0.0492	1.96
4,000	0.0100	0.0643	0.0663	1.94
4,000	0.0100	0.0643	0.0666	1.93
2,000	0.0300	0.0483	0.0494	1.95
2,000	0.0300	0.0483	0.0499	1.94
1,000	0.1000	0.0804	0.0820	1.96
5,000	0.2000 ^b	1.0091	1.0457	1.93
5,000	0.2000	1.0091	1.0460	1.93
3,000	0.4000	1.2109	1.2613	1.92
3,000	0.4000	1.2109	1.2679	1.91
2,000	0.6000	1.2109	1.2609	1.92
2,000	0.6000	1.2109	1.2613	1.92
1,500	0.8000 ^c	1.2882	1.3489	1.91
1,500	0.8000	1.2882	1.3418	1.92
1,000	1.0000	1.0735	1.1359	1.89
1,000	1.0000	1.0735	1.1420	1.88

^aElectrode area = 0.75 cm² (mounted)

^bElectrode area = 0.94 cm² (mounted)

^cElectrode area = 1.00 cm² (mounted)

TABLE IV
 APPARENT VALENCE OF LEAD DISSOLVING ANODICALLY IN
 1.00 N $\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)$

Time (sec)	Current Density (amps · cm ⁻²)	Weight of Lead		Apparent Valence
		Calc. (gm)	Expt. (gm)	
25°C				
50,000	0.0010 ^a	0.0335	0.0338	1.98
67,000	0.0030 ^b	0.1719	0.1723	1.99
42,500	0.0050 ^a	0.1825	0.1869	1.95
30,000	0.0100 ^b	0.2593	0.2653	1.95
30,000	0.0100	0.2593	0.2659	1.95
15,000	0.0300 ^c	0.3704	0.3796	1.96
15,000	0.0300	0.3704	0.3768	1.97
10,000	0.0600 ^a	0.5099	0.5398	1.89
10,000	0.1000	0.8430	0.8822	1.91
50°C				
77,700	0.0010 ^d	0.0601	0.0602	1.99
25,000	0.0030	0.0580	0.0589	1.97
10,000	0.0100	0.0773	0.0785	1.97
17,000	0.0300 ^e	0.1825	0.1882	1.94
17,000	0.0300	0.1825	0.1868	1.95
8,700	0.0600	0.1868	0.1938	1.93
8,700	0.0600	0.1868	0.1959	1.92
6,500	0.0800	0.1884	0.1965	1.91
6,500	0.0800	0.1884	0.1974	1.91
5,000	0.1000	0.1660	0.1738	1.91

^aElectrode area = 0.785 cm² (mounted)

^bElectrode area = 0.805 cm² (mounted)

^cElectrode area = 0.767 cm² (mounted)

^dElectrode area = 0.332 cm² (mounted)

^eElectrode area = 0.270 cm² (mounted)

TABLE V
 APPARENT VALENCE OF LEAD DISSOLVING ANODICALLY IN
 1.00 N $\text{Pb}(\text{NO}_3)_2$

Time (sec)	Current Density (amp·cm ⁻²)	Weight of Lead		Apparent Valence
		Calc. (gm)	Expt. (gm)	
25°C				
40,000	0.0010 ^a	0.0858	0.0880	1.93
9,000	0.0100 ^b	0.0965	0.1006	1.92
4,000	0.0300	0.1286	0.1319	1.95
4,000	0.0300	0.1286	0.1339	1.92
2,000	0.0600	0.1286	0.1325	1.94
2,000	0.0600	0.1286	0.1336	1.93
1,000	0.1000	0.1072	0.1111	1.93
50°C				
40,000	0.0010 ^a	0.0858	0.0884	1.94
9,000	0.0100 ^b	0.0965	0.0900	1.95
4,000	0.0300	0.1286	0.1337	1.93
4,000	0.0300	0.1286	0.1333	1.93
2,000	0.0600	0.1286	0.1313	1.96
2,000	0.0600	0.1286	0.1328	1.93
1,000	0.1000	0.1272	0.1117	1.92

^aElectrode area = 2.0 cm² (bare)

^bElectrode area = 1.0 cm² (bare)

TABLE VI
 APPARENT VALENCE OF LEAD DISSOLVING ANODICALLY IN
 1.00 N $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$

Time (sec)	Current Density (amps \cdot cm ⁻²)	Weight of Lead		Apparent Valence
		Calc. (gm)	Expt. (gm)	
25°C				
34,000	0.0010 ^a	0.0551	0.0578	1.91
8,600	0.0100	0.1385	0.1458	1.90
3,500	0.0300 ^b	0.1879	0.1983	1.90
3,000	0.0600	0.3221	0.3438	1.88
1,600	0.1000 ^c	0.1717	0.1896	1.83
50°C				
35,000	0.0010 ^d	0.1012	0.1060	1.91
15,000	0.0100	0.4841	0.5096	1.91
2,700	0.0300	0.1391	0.1459	1.90
2,000	0.0600 ^a	0.1288	0.1351	1.90
1,000	0.1000 ^e	0.1288	0.1365	1.89

^aElectrode area = 1.50 cm² (bare)

^bElectrode area = 1.65 cm² (bare)

^cElectrode area = 1.00 cm² (bare)

^dElectrode area = 1.60 cm² (bare)

^eElectrode area = 1.20 cm² (bare)

APPENDIX IV

Time Behavior of the Dissolution Potential of the
Lead Electrode in Various Electrolytes

TABLE VII
 TIME BEHAVIOR OF THE DISSOLUTION POTENTIAL OF THE
 LEAD ELECTRODE IN 1.00 N KNO₃ AT 25°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
Run 1			Run 2		
0.00	15	-0.331	0.00	15	-0.345
0.00	30	-0.339	0.00	30	-0.348
0.00	45	-0.340	0.00	45	-0.348
0.00	60	-0.349	0.00	60	-0.350
0.00	75	-0.349	0.00	75	-0.350
0.20	15	-0.247	0.20	15	-0.247
0.20	30	-0.246	0.20	30	-0.247
0.40	15	-0.235	0.40	15	-0.237
0.40	30	-0.235	0.40	30	-0.237
0.80	15	-0.224	0.80	15	-0.225
0.80	30	-0.223	0.80	30	-0.224
2.00	15	-0.213	2.00	15	-0.214
2.00	30	-0.212	2.00	30	-0.213
4.00	15	-0.202	4.00	15	-0.204
4.00	30	-0.202	4.00	30	-0.203
8.00	15	-0.194	8.00	15	-0.193
8.00	30	-0.192	8.00	30	-0.193
20.00	15	-0.181	20.00	15	-0.179
20.00	30	-0.180	20.00	30	-0.179
40.00	15	-0.165	40.00	15	-0.164
40.00	30	-0.163	40.00	30	-0.164
80.00	15	-0.138	80.00	15	-0.139
80.00	30	-0.139	80.00	30	-0.136

^aArea = 0.365 cm²

^bNormal hydrogen scale

TABLE VIII
 TIME BEHAVIOR OF THE DISSOLUTION POTENTIAL OF THE
 LEAD ELECTRODE IN 1.00 N KNO_3 AT 50°C

$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts)	$I \times 10^3$ (amp·cm ⁻²) ^a	t (min)	E (volts) ^b
Run 1			Run 2		
0.00	15	-0.349	0.00	15	-0.353
0.00	30	-0.349	0.00	30	-0.359
0.00	45	-0.349	0.00	45	-0.360
			0.00	60	-0.361
0.20	15	-0.249	0.20	15	-0.251
0.20	30	-0.250	0.20	30	-0.253
0.40	15	-0.238	0.40	15	-0.244
0.40	30	-0.239	0.40	30	-0.243
0.80	15	-0.229	0.80	15	-0.230
0.80	30	-0.229	0.80	30	-0.231
2.00	15	-0.215	2.00	15	-0.218
2.00	30	-0.216	2.00	30	-0.218
4.00	15	-0.209	4.00	15	-0.207
4.00	30	-0.209	4.00	30	-0.207
8.00	15	-0.199	8.00	15	-0.197
8.00	30	-0.199	8.00	30	-0.197
20.00	15	-0.184	20.00	15	-0.182
20.00	30	-0.185	20.00	30	-0.182
40.00	15	-0.175	40.00	15	-0.172
40.00	30	-0.173	40.00	30	-0.170
80.00	15	-0.149	80.00	15	-0.153
80.00	30	-0.147	80.00	30	-0.149

^aArea = 0.365 cm²

^bNormal hydrogen scale

TABLE IX
 TIME BEHAVIOR OF THE DISSOLUTION POTENTIAL OF THE
 LEAD ELECTRODE IN 1.00 N $\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)$ AT 25°C

$I \times 10^3$ (amp cm^{-2}) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp cm^{-2}) ^a	t (min)	E (volts) ^b
Run 1			Run 2		
0.00	15	-0.341	0.00	15	-0.316
0.00	30	-0.344	0.00	30	-0.339
0.00	45	-0.348	0.00	45	-0.349
0.00	60	-0.348	0.00	60	-0.350
0.20	15	-0.320	0.20	15	-0.318
0.20	30	-0.320	0.20	30	-0.317
0.40	15	-0.311	0.40	15	-0.308
0.40	30	-0.310	0.40	30	-0.308
0.80	15	-0.300	0.80	15	-0.300
0.80	30	-0.300	0.80	30	-0.300
2.00	15	-0.291	2.00	15	-0.289
2.00	30	-0.290	2.00	30	-0.290
4.00	15	-0.279	4.00	15	-0.280
4.00	30	-0.277	4.00	30	-0.279
8.00	15	-0.269	8.00	15	-0.269
8.00	30	-0.268	8.00	30	-0.269
20.00	15	-0.248	20.00	15	-0.250
20.00	30	-0.247	20.00	30	-0.249
40.00	15	-0.228	40.00	15	-0.226
40.00	30	-0.227	40.00	30	-0.225
80.00	15	-0.161	80.00	15	-0.159
80.00	30	-0.161	80.00	30	-0.158

^aArea = 0.325 cm^2

^bNormal hydrogen scale

TABLE X
 TIME BEHAVIOR OF THE DISSOLUTION POTENTIAL OF THE
 LEAD ELECTRODE IN 1.00 N $\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)$ AT 50°C

$I \times 10^3$ (amp cm^{-2}) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp cm^{-2}) ^a	t (min)	E (volts) ^b
Run 1			Run 2		
0.00	15	-0.373	0.00	15	-0.367
0.00	30	-0.376	0.00	30	-0.369
0.00	45	-0.375	0.00	45	-0.374
0.00	60	-0.375	0.00	60	-0.375
0.20	15	-0.347	0.20	15	-0.341
0.20	30	-0.347	0.20	30	-0.341
0.40	15	-0.337	0.40	15	-0.334
0.40	30	-0.337	0.40	30	-0.334
0.80	15	-0.318	0.80	15	-0.318
0.80	30	-0.317	0.80	30	-0.318
2.00	15	-0.304	2.00	15	-0.303
2.00	30	-0.305	2.00	30	-0.303
4.00	15	-0.294	4.00	15	-0.293
4.00	30	-0.293	4.00	30	-0.293
8.00	15	-0.282	8.00	15	-0.282
8.00	30	-0.284	8.00	30	-0.282
20.00	15	-0.259	20.00	15	-0.264
20.00	30	-0.258	20.00	30	-0.264
40.00	15	-0.234	40.00	15	-0.238
40.00	30	-0.233	40.00	30	-0.237
80.00	15	-0.191	80.00	15	-0.193
80.00	30	-0.190	80.00	30	-0.193

^aArea = 0.325 cm^2

^bNormal hydrogen scale

TABLE XI
 TIME BEHAVIOR OF THE DISSOLUTION POTENTIAL OF THE
 LEAD ELECTRODE IN 1.00 N $\text{Pb}(\text{NO}_3)_2$ AT 25°C

$I \times 10^3$ (amp cm^{-2}) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp cm^{-2}) ^a	t (min)	E (volts) ^b
Run 1			Run 2		
0.00	15	-0.160	0.00	15	-0.160
0.00	30	-0.160	0.00	30	-0.160
0.00	45	-0.160	0.00	45	-0.160
0.20	15	-0.160	0.20	15	-0.160
0.20	30	-0.160	0.20	30	-0.160
0.40	15	-0.160	0.40	15	-0.160
0.40	30	-0.160	0.40	30	-0.160
0.80	15	-0.159	0.80	15	-0.159
0.80	30	-0.159	0.80	30	-0.159
2.00	15	-0.159	2.00	15	-0.159
2.00	30	-0.159	2.00	30	-0.159
4.00	15	-0.156	4.00	15	-0.157
4.00	30	-0.156	4.00	30	-0.157
8.00	15	-0.154	8.00	15	-0.155
8.00	30	-0.154	8.00	30	-0.155
20.00	15	-0.147	20.00	15	-0.148
20.00	30	-0.147	20.00	30	-0.148
40.00	15	-0.131	40.00	15	-0.131
40.00	30	-0.131	40.00	30	-0.130
80.00	15	-0.104	80.00	15	-0.107
80.00	30	-0.104	80.00	30	-0.105

^aArea = 0.365 cm^2

^bNormal hydrogen scale

TABLE XII
 TIME BEHAVIOR OF THE DISSOLUTION POTENTIAL OF THE
 LEAD ELECTRODE IN 0.30 N $\text{Pb}(\text{NO}_3)_2$ AT 25°C

$I \times 10^3$ (amp cm^{-2}) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp cm^{-2}) ^a	t (min)	E (volts) ^b
Run 1			Run 2		
0.00	15	-0.164	0.00	15	-0.162
0.00	30	-0.166	0.00	30	-0.163
0.00	45	-0.166	0.00	45	-0.165
			0.00	60	-0.165
0.20	15	-0.168			
0.20	30	-0.168	0.20	15	-0.169
			0.20	30	-0.169
0.40	15	-0.168			
0.40	30	-0.168	0.40	15	-0.168
			0.40	30	-0.168
0.80	15	-0.167			
0.80	30	-0.167	0.80	15	-0.168
			0.80	30	-0.168
2.00	15	-0.166			
2.00	30	-0.166	2.00	15	-0.166
			2.00	30	-0.166
4.00	15	-0.162			
4.00	30	-0.162	4.00	15	-0.163
			4.00	30	-0.163
8.00	15	-0.157			
8.00	30	-0.158	8.00	15	-0.157
			8.00	30	-0.157
20.00	15	-0.147			
20.00	30	-0.147	20.00	15	-0.147
			20.00	30	-0.147
40.00	15	-0.129			
40.00	30	-0.128	40.00	15	-0.129
			40.00	30	-0.129
80.00	15	-0.087			
80.00	30	-0.087	80.00	15	-0.089
			80.00	30	-0.089

^aArea = 0.365 cm^2

^bNormal hydrogen scale

TABLE XIII
 TIME BEHAVIOR OF THE DISSOLUTION POTENTIAL OF THE
 LEAD ELECTRODE IN SATURATED $\text{Pb}(\text{NO}_3)_2$ AT 25°C

$I \times 10^3$ (amp cm^{-2}) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp cm^{-2}) ^a	t (min)	E (volts) ^b
Run 1			Run 2		
0.00	15	-0.154	0.00	15	-0.161
0.00	30	-0.154	0.00	30	-0.160
0.00	45	-0.154	0.00	45	-0.156
0.00	60	-0.154	0.00	60	-0.155
0.20	15	-0.154	0.20	15	-0.154
0.20	30	-0.154	0.20	30	-0.154
0.40	15	-0.154	0.40	15	-0.153
0.40	30	-0.154	0.40	30	-0.153
0.80	15	-0.153	0.80	15	-0.153
0.80	30	-0.153	0.80	30	-0.153
2.00	15	-0.152	2.00	15	-0.152
2.00	30	-0.152	2.00	30	-0.152
4.00	15	-0.149	4.00	15	-0.151
4.00	30	-0.149	4.00	30	-0.151
8.00	15	-0.149	8.00	15	-0.150
8.00	30	-0.149	8.00	30	-0.150
20.00	15	-0.146	20.00	15	-0.147
20.00	30	-0.146	20.00	30	-0.147
40.00	15	-0.137	40.00	15	-0.138
40.00	30	-0.137	40.00	30	-0.138
80.00	15	-0.118	80.00	15	-0.118
80.00	30	-0.118	80.00	30	-0.118

^aArea = 0.365 cm^2

^bNormal hydrogen scale

TABLE XIV
 TIME BEHAVIOR OF THE DISSOLUTION POTENTIAL OF THE
 LEAD ELECTRODE IN 1.00 N $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ AT 25°C

$I \times 10^3$ (amp cm^{-2}) ^a	t (min)	E (volts) ^b	$I \times 10^3$ (amp cm^{-2}) ^a	t (min)	E (volts) ^b
Run 1			Run 2		
0.00	15	-0.199	0.00	15	-0.204
0.00	30	-0.200	0.00	30	-0.200
0.00	45	-0.200	0.00	45	-0.200
0.00	60	-0.200	0.00	60	-0.200
0.00	75	-0.200			
			0.20	15	-0.200
0.20	15	-0.200	0.20	30	-0.200
0.20	30	-0.200			
			0.40	15	-0.200
0.40	15	-0.200	0.40	30	-0.200
0.40	30	-0.200			
			0.80	15	-0.199
0.80	15	-0.200	0.80	30	-0.199
0.80	30	-0.200			
			2.00	15	-0.197
2.00	15	-0.200	2.00	30	-0.197
2.00	30	-0.200			
			4.00	15	-0.193
4.00	15	-0.193	4.00	30	-0.193
4.00	30	-0.193			
			8.00	15	-0.186
8.00	15	-0.186	8.00	30	-0.186
8.00	30	-0.186			
			20.00	15	-0.163
20.00	15	-0.172	20.00	30	-0.163
20.00	30	-0.172			
			40.00	15	-0.124
40.00	15	-0.129	40.00	30	-0.124
40.00	30	-0.129			
			80.00	15	-0.047
80.00	15	-0.043	80.00	30	-0.047
80.00	30	-0.043			

^aArea = 0.365 cm^2

^bNormal hydrogen scale

VI. BIBLIOGRAPHY

1. Burgess, C. F., and Hambuschen, C., *Electrochemical Society Transactions*, Vol. III, 689 (1903).
2. Denham and Allmand, F. C. S., 93, 424 (1908).
3. Bell, N. M., *Faraday Soc.*, 17, 79, (1916).
4. March, G. A., and Schaschl, E., *J. Electrochem. Soc.*, 109, 960 (1960).
5. Sorensen, D. T., Davidson, A. W., and Kleinberg, J., *J. Inorg. Nucl. Chem.*, 13, 64 (1960).
6. Epelboin, I., *F. Electrochim*, 59, 689 (1955).
7. Glasstone, S., *J. Chem. Soc.*, 121, 2091 (1922).
8. Jones, P., and Thirsk, H. R., *Faraday Society Transactions*, 50, 732 (1954).
9. Piontelli, R., Poli, G., *Electrochemical Society Trans. of the Symposium on Electrode Processes* 67 (1961).
10. Khan, O. A., and Solveva, V. I., *Zhur Priklad Khim* 34, 1793 (1961).
11. Sanghvi, J. S., Anodic Dissolution of Silver in Aqueous Solutions, M.S. Thesis, Library, University of Missouri at Rolla, Rolla, Missouri (1965).
12. Straumanis, M. E., and Bhatia, B. K., *J. Electrochem. Soc.*, 110, 347 (1963).

13. Straumanis, M. E. and Mathis, D. L., *ibid.*, 109, 434 (1962).
14. Stoner, G. E., The Anodic Dissolution of Zinc in Aqueous Solutions, M.S. Thesis, Library, University of Missouri at Rolla, Rolla, Missouri (1963).
15. Sun, Y. C., The Anodic Dissolution of Cadmium in Aqueous Solutions, M.S. Thesis, Library, University of Missouri at Rolla, Rolla, Missouri (1964).
16. Straumanis, M. E. and Dutta, M., *J. Inorganic Chemistry* 5, 992 (1966).

VII. ACKNOWLEDGEMENTS

The author wishes to express his gratefulness to Dr. J. W. Johnson, Associate Professor of Chemical Engineering, who served as research advisor, and Dr. W. J. James, Director of Graduate Center for Research Material. Their guidance, assistance, and encouragement are sincerely appreciated.

A further word of appreciation is extended to the Departments of Chemical Engineering and Chemistry for the use of their equipment.

He would also like to express his thanks to Dr. M. E. Straumanis, Professor of Metallurgy and Research Professor of Materials, for his help and to the Office of Naval Research for financial assistance.

VIII. VITA

Wu Christopher Kuo-chieh was born April 3, 1935, in Canton, China. In 1950, he migrated to Taipei, Taiwan, where he attended Taiwan Provincial Ching-kung High School. In 1958, he entered National Taiwan University, receiving a Bachelor of Science degree in Chemical Engineering in June of 1962.

In January, 1964, he came to the University of Missouri at Rolla for advanced studies.

He was a graduate assistant in Chemistry from September 1964 to June 1965. He also received a research assistantship from June 1965 to June 1966 supported by the Office of Naval Research.

123711