AN ABSTRACT OF THE THESIS OF

LE MINH HIEU for the degree of MASTER OF SCIENCE

in CHEMICAL ENGINEERING presented on September 21 1976

Title: THE KINETICS OF THE CHLORINATION OF COPPER IN

THE THIN FILM RANGE,

Abstract approved:

Robert E. Meredith

The kinetics of the chlorination of copper in the
thin film range at room temperature was studied by using
a wiped, rotating cylindrical copper cathode which was
partially submerged in an electrolyte. Experiments were
conducted at three different partial pressures: 1.00,
0.44 and 0.21 atm. of chlorine gas which was saturated
with water vapor.

The chlorination of copper was found to follow the
logarithmic equation

$$W = K_1 \ln (K_2 t + 1.0)$$

where W is the weight of copper chloride formed per unit
area during exposure time t. The constant K_1 was found
to be independent of the chlorine partial pressure while
the constant K_2 was proportional to the square root of
the chlorine partial pressure for the two pressure ranges
1.00 and 0.44 atm. The most satisfactory interpretation
of the experimental data is the mutually-blocking pores
mechanism in which the rate determining step is assumed
to be the transport of chlorine across the chloride film

through pores and paths of loosely arranged atoms.

The Kinetics of the Chlorination of Copper

in the Thin Film Range

by

Le Minh Hieu

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Completed **September 21, 1976**

Commencement June 1977

APPROVED:

Associate Professor of Chemical Engineering in Charge
    of Major

Head of the Department of Chemical Engineering

Dean of Graduate School

Date thesis is presented   September 21 1976
                            (Date of examination)

Typed by Lora Wixom—Johnny Print Shop for Le Minh Hieu

ACKNOWLEDGMENTS

The author wishes to express his sincere thanks and appreciation to:

Dr. Robert E. Meredith, for his advice, professional guidance and encouragement.

Dr. Charles E. Wicks, Head of Department of Chemical Engineering, for an excellent graduate program.

Mr. William Johnson, the machinist, for his suggestion and assistance in the construction of the apparatus.

And finally, to my parents, for their initial encouragement in my seeking higher education.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

THE KINETICS OF THE CHLORINATION OF COPPER

IN THE THIN FILM RANGE

I. INTRODUCTION

Oxidation of metal in some cases is a gas-solid reaction in which a thin layer of product forms on the surface. The most common type of metal oxidation is that in which oxygen attacks the metal. But the generalized chemical meaning of an oxidation reaction is one which involves the transfer of electrons, and the reacting gas can be any oxidizing gas. One will find most of the studies in this field are carried out using oxygen as the reacting gas. This is partly because oxygen gas is most accessible to experimentation, and partly because many of these investigations have a direct or indirect bearing on corrosion problems.

Many metals oxidize readily when exposed to oxygen, chlorine or gaseous sulfur at sufficiently low temperature. The oxidation rate is initially very rapid, but drops off to negligible values after a stable thin film is formed. Various theories have been developed for these effects by considering different limiting processes such as anion and cation diffusion through the bulk oxide, mass or electron transport across the interfaces, or electron transfer processes associated with a chemisorption step.

The objective of this thesis was the experimental study of the kinetics of the chlorination of copper in a

copper-copper chloride electrode process. The net elec-
trode reaction was the electrochemical conversion of
chlorine to chloride ions with continuous generation of a
fresh copper surface.

The chlorine-copper system was chosen because of the
following reasons: 1) chlorine and copper are common
elements in the field of corrosion; 2) the rate of reaction
is reasonably fast at room temperature; and the product
of reaction, copper chloride, has been used as electrode
material for secondary batteries.

The study was conducted by using a rotating cylindri-
cal copper strip cathode which was partially submerged in
an electrolyte. The vapor phase above the electrolyte
contained chlorine gas saturated with water. The electro-
lyte was an aqueous potassium chloride solution of 2M
concentration. The copper strip was chlorinated in the
vapor space and this was followed by an electrochemical
cathode reaction in the electrolyte in which

$$CuCl + e^- \longrightarrow Cu + Cl^- \quad . \qquad (1.1)$$
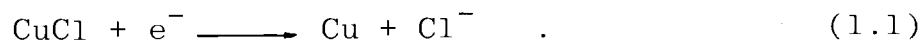
This was balanced by the anode reaction,

$$\frac{1}{2} Zn \longrightarrow \frac{1}{2} Zn^{++} + e^- \quad . \qquad (1.2)$$
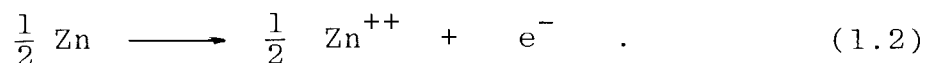
As the cathode rotated, a freshly generated copper
surface was formed and this surface was allowed to react
again with chlorine in the vapor space. Three different
chlorine partial pressures, 0.210, 0.440, and 1.000 atm.,
were examined.

II. PREVIOUS WORK

In addition to high temperature metal oxidation reactions, for which the well known classical Wagner theory[16] is usually found applicable, various theories and models have been proposed to explain the mechanism of metal oxidation at temperature near or below 25°C. Our review of previous work, however, is limited to publications which cover the oxidation of metals in the thin film range. By this we mean film thicknesses from 200 Å to several thousands Angstroms.

Theoretical Growth Equations

In general, it is often found that the average oxide film thickness can be expressed as some simple function of time—this function being known as the rate law or growth equation. However, instead of a film thickness, other units have been used in the rate law expression such as the weight of the product formed, the number of the molecular layers of oxide film, the volume of oxygen consumed, etc. As a rule, these various units are always related to each other.

Many rate laws including linear, parabolic, cubic, and logarithmic relations have been derived.

The linear rate law: Linear rate laws may result if the oxide contains macroscopic pores or cracks so that oxygen can reach the metal surface rapidly and bulk diffu-

sion through the oxide layer can be neglected.

In 1972, Ghez and Van der Meulen[8] proposed a linear growth equation in which it was assumed that neutral oxygen molecules were transported through the oxide film obeying Fick's law. The general rate relation derived from this model is rather complex, but if interface reactions are rate-determining, the linear growth rate can be expressed as

$$\frac{dX}{dt} = A \left[\alpha P - 1.0 + (1.0 + 2 \beta P)^{\frac{1}{2}} \right] \qquad (2.1)$$

where X is the average oxide thickness; t is time; P is the partial pressure of oxygen; A, α, and β are constants which are independent of oxide thickness.

Upon integration, equation (2.1) becomes

$$X = k_1 t + k_1' \qquad (2.2)$$

where k_1 and k_1' are constants.

The parabolic rate law: Cabrera and Mott[3] were among the first to postulate a mechanism for the formation of a thin oxide film in terms of the migration of ions under the influence of an electric field. Assuming that cations migrate across the n-type oxide film, Cabrera and Mott developed the following equation for the change in film thickness, X, with time, t,

$$\frac{dX}{dt} = \frac{k_2}{X} \qquad (2.3)$$

where k_2 is a constant.

Upon integration, equation (2.3) becomes

$$X^2 = k_2 t + k_2' \qquad (2.4)$$

where k_2' is integration constant.

This equation should not be confused with the well known Wagner parabolic equation[16] which is based on a different set of assumptions and is developed for the thick oxide film regime. According to Cabrera and Mott, their rate law is applicable for the thickness range of 100 – 2000 Å .

The cubic rate law: In attempting to explain the mechanism of the growth of a thin p- type semiconductor oxide such as Cu_2O, Cabrera and Mott[3] assumed that the concentration of cation vacancies near the oxide surface is proportional to the thickness of the layer. Based on this assumption, the rate of oxidation is obtained as

$$\frac{dX}{dt} = \frac{k_3}{X^2} \qquad (2.5)$$

where k_3 is a constant.
The cubic rate law follows from integration which gives

$$X^3 = k_3 t + k_3' \qquad (2.6)$$

where k_3' is integration constant.

Recently, Wagner[17] proposed a cubic rate law in which he assumed that the rate of dissociation of the absorbing oxygen molecules at the oxide-oxygen interface is rate determining, and that this rate is proportional to the local concentration of excess electrons present in the thin

oxide film next to the oxide-oxygen interface. On the basis of these assumptions he also obtained equation (2.5) and (2.6).

The logarithmic rate law: Many theories have been derived to explain the logarithmic type growth, but only the mechanism proposed by Evans[7] is significant for the thin film range.

Evans' theory is based on the formation of mechanical imperfection in the oxide layers. Pores are considered to be grain-boundaries or dislocations along which atom or ion transport can occur at temperature too low for appreciable transport through the bulk. If the decrease in the number of pores, $-d\mathcal{N}$, is proportional to the increase in oxygen consumed, dy, and the number of pores, $\mathcal{N}$, then

$$-d\mathcal{N} = k_4 \mathcal{N} \, dy \qquad (2.7)$$

or

$$\mathcal{N} = \mathcal{N}_o e^{-(k_4 y)} \qquad (2.8)$$

where $\mathcal{N}_o$ is a constant.

If the rate of oxygen consumed is determined by the number of pores then

$$\frac{dy}{dt} = -k_5 \mathcal{N} = k_6 \, e^{-(k_4 y)} \qquad (2.9)$$

where k_4, k_5, and k_6 are constants.

From this, the direct logarithmic equation of the form

$$y = K_1 \ln(K_2 t + K_3) \qquad (2.10)$$

is obtained. If equation (2.10) is obeyed from t=0, y=0,

it can be expressed as

$$y = K_1 \ln (K_2 t + 1.0) \qquad (2.11)$$

Past Experimental Work

Copper has been used in many studies designed to test various theories of oxidation. A survey of all recorded experiments conducted on the oxidation of copper, up to 1962 was made by Leidheiser[11]. The experimental work on the oxidation of copper in the thin film range are of particular interest in this investigation and are briefly reviewed here.

In 1942, Bircumshaw and Everdel[1] investigated the reaction of copper with iodine dissolved in aqueous potassium iodide and found a linear reaction rate. Later in 1947, working with an organic iodine solution, they reported that the reaction was dependent on the tarnish film thickness. These investigators attributed such behavior to wetting and penetration of the tarnish film by the aqueous solution, while the organic solution did not wet the film and the reaction proceeded only by bulk diffusion through the iodide film.

Campbell and Thomas[4] measured the reaction rate of copper, stainless steel, nickel and a large number of copper alloys at various temperatures. They found that the oxidation of copper in the temperature range 100°C-250°C obeyed the cubic rate law. At 194°C, 250°C and 300°C,

nickel and stainless steel followed a logarithmic rate law and the rest of these metals conformed to an equation of the form

$$W^n = K_n t + c \qquad (2.12)$$

where W is the weight of product formed per unit area, t is time; n, K_n and c are constants. The value of n varies from 2.50 to 4.00. The cubic rate law of copper oxidation was considered to have the same rate-controlling mechanism developed by Cabrera and Mott[3].

Brown and coworkers[2] investigated the kinetics of the reaction of fluorine with electrolytic copper powder at room temperature and 250°C at pressures of 6.0 mm and 60.0 mm Hg. They found that a logarithmic rate law was obeyed and there was no pressure effect on the reaction. According to these investigators, the reaction did not appear to be controlled by a simple diffusion process and random cracking of the corrosion film may play a role.

In 1960, Sama[15] studied the oxidation rate of silver copper and nickel with oxygen by using a rotating electrode cell. The limiting current was measured as a function of the speed of rotation of the rotating electrode. The oxidation of copper was found to follow the logarithmic rate law

$$W = K_1 \ln (K_2 t + 1.0) \qquad (2.13)$$

where W is the weight of the oxide, t is time, K_1 and K_2

are constants. K_1 was found to be independent of oxygen partial pressure, while K_2 was found to be a linear function of the square root of the oxygen partial pressure.

In 1964, O'Donnell and Spakowski[12] studied the reaction between high purity copper foil and fluorine gas at 450°C in a pressure range from 10 to 130.mm Hg. The reaction rate obeyed the logarithmic rate law

$$y = K_1 \log (at + b) + c \qquad (2.14)$$

where y is the volume of fluorine consumed; t is time; K_1, a, b and c are constants. K_1 was found to vary with the partial pressure of fluorine according to the equation

$$\log K_1 = 0.781 \log P - 6.11439 \qquad (2.15)$$

Here, fluorine was considered to be the migrating species and the reaction was considered to take place at the fluorine-metal interface. The mechanism by which fluorine migrated through the product layer was not explained.

In previous work[9], using an experimental system similar to this study, Gurian investigated the chlorination of silver at various chlorine-water partial pressures. At one atmosphere, the chlorination of silver was found to obey the linear rate law

$$W = k_1 t + k_1' \qquad (2.16)$$

where W is the weight of chloride formed, t is time, k_1 and k_1' are constants.

At lower chlorine partial pressures, the growth of the

chloride film followed a logarithmic rate law of the form

$$W = K_1 \ln t + K_2 \qquad (2.17)$$

where K_1 and K_2 are constants.

In 1969, Redfern and Wilford[13] studied the reaction between copper and iodine in iodine-acetone solutions. The rate of reaction was measured by a quartz spring balance. The parabolic rate law was observed during the initial coverage of the copper surface by a continuous film of cuprous iodide. A linear rate law was obeyed after the copper surface had been completely covered by product film. The extent of the initial parabolic behavior was governed by the temperature of reaction, the concentration of iodine in the solution and the purity of acetone. The adsorption of iodine on the product film surface was considered as the rate-determining step during the linear rate behavior.

III. EXPERIMENTAL EQUIPMENT

The equipment used in this investigation can be subdivided into the following categories:

1. the cell

2. the rotation system

3. the gas supply system

4. the electrical measurement system

The Cell

The cell was designed similar to one used in a previous study[9]. Basically, it consisted of a body which was a rectangular box constructed of 1/2 inch thick plexiglass. This box was 8 inches wide, 7-1/2 inches high and 4 inches deep. Enclosed in this volume were the rotating cathode, the anodes, the silver-silver chloride reference electrode, the wiper and the electrolyte. The detailed assembly of the cell is shown in Fig 1.

The gas was supplied to the cell through a fritted glass dispersion tube and exited through a hole in the top. The reaction was kept at room temperature and was measured with a thermometer.

The Cathode: The cathode was formed from a circular disk which was made of 3/4 inch thick plexiglass, the disk had $3 \frac{15}{32}$ inch diameter. A hole was drilled at the center of the disk to fit a 1/2 inch diameter Teflon shaft. A 1/8 inch hole was drilled radially through the center to the shaft and another 1/8 inch hole was drilled through

Reference Electrode

Thermometer

Gas Outlet

Wiper holder

Stainless steel screw

Luggin Capillary

Fritted glass
Dispersion tube

Electrolyte Fill
and Drain tube

Left anode

Right anode

Polyethylene shield
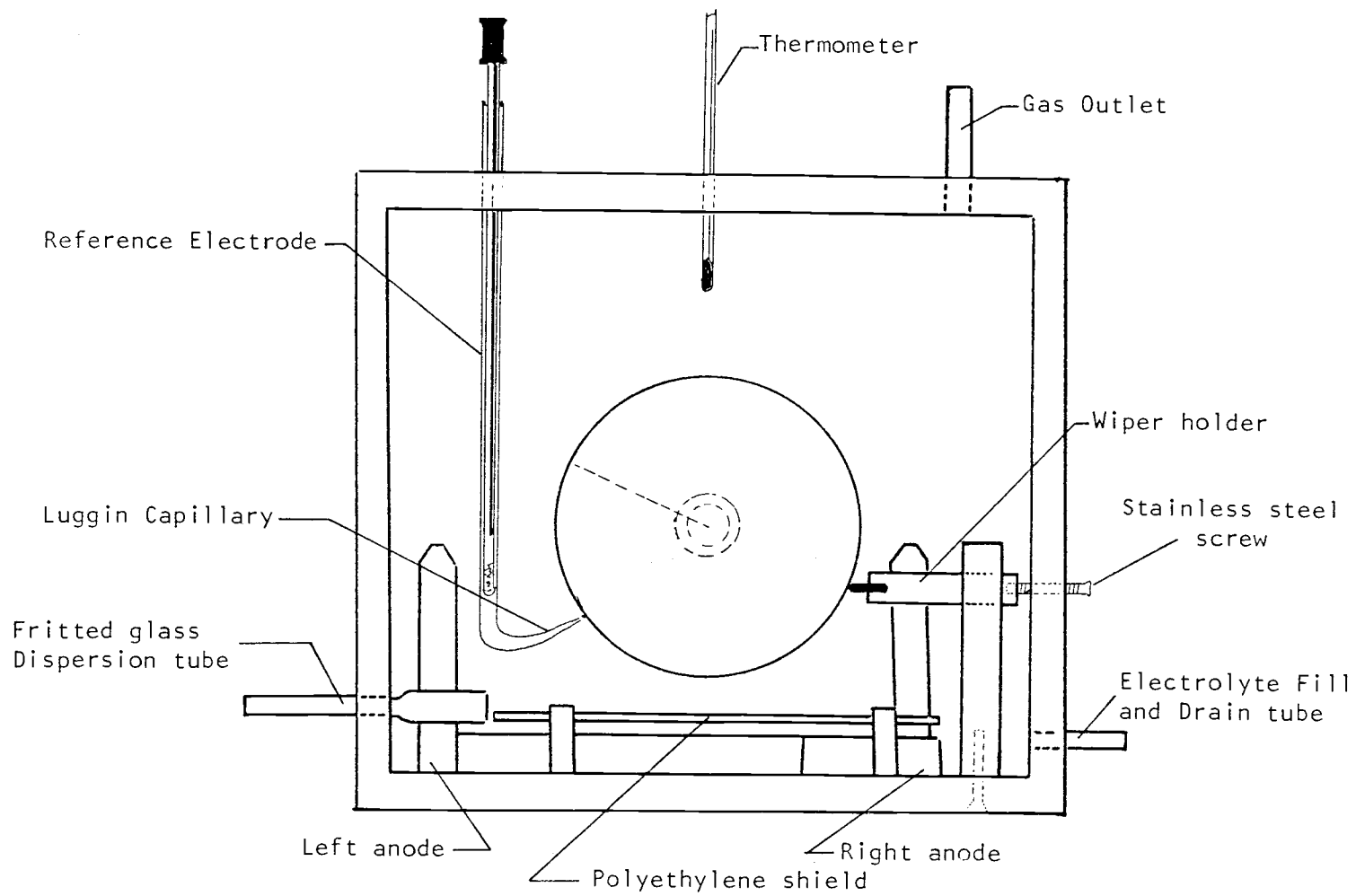
FIG. 1   PROFILE VIEW OF THE CELL

the center of the shaft. A 5/16 inch wide copper strip was cut from a 0.002 inch thick copper foil (Baker Analyzed Reagent Grade) which had the following spectrographic analysis:

Component	Composition Estimate
Copper	0.995 (by subtraction)
Antimony and Tin	0.0020
Arsenic	0.0002
Iron	0.0005
Lead	0.0005
Manganese	0.0005
Phosphorous	0.0010
Silver	0.0003

The copper strip was placed on the disk and formed a continuous band by soldering the ends together. On the opposite side, a 19 gauge silver coated copper wire was soldered to the copper strip. This wire was threaded through the disk and out the end of the shaft. A sketch of the cathode with its dimension is shown in Fig. 2 and its photograph appears in Fig. 3.

A mercury contact system was used to connect the electrical measurement system to the rotating cathode. This mercury contact system was adopted from the one used by Gurian[15] in his study. The detailed sketch of this contact appears in Fig 4.

5/16"

3/8"

1/2"

3"   1 3/6   3/4   7/8   1-3/8"

FIG. 2   THE CATHODE

FIG. 3   PHOTOGRAPH OF THE CATHODE

"O" Ring Seal

Cathode Shaft

Copper Wire

Copper disk

Brass plate

Copper contact

Mercury level

Cell Wall

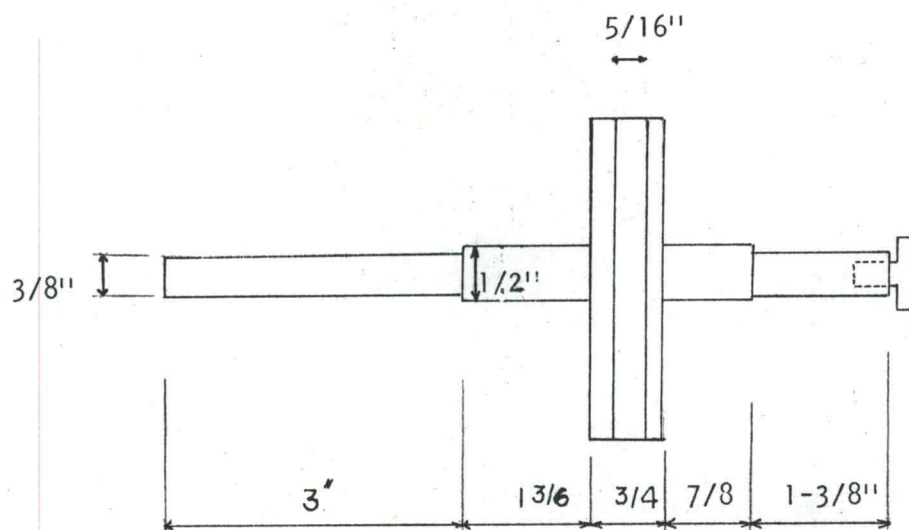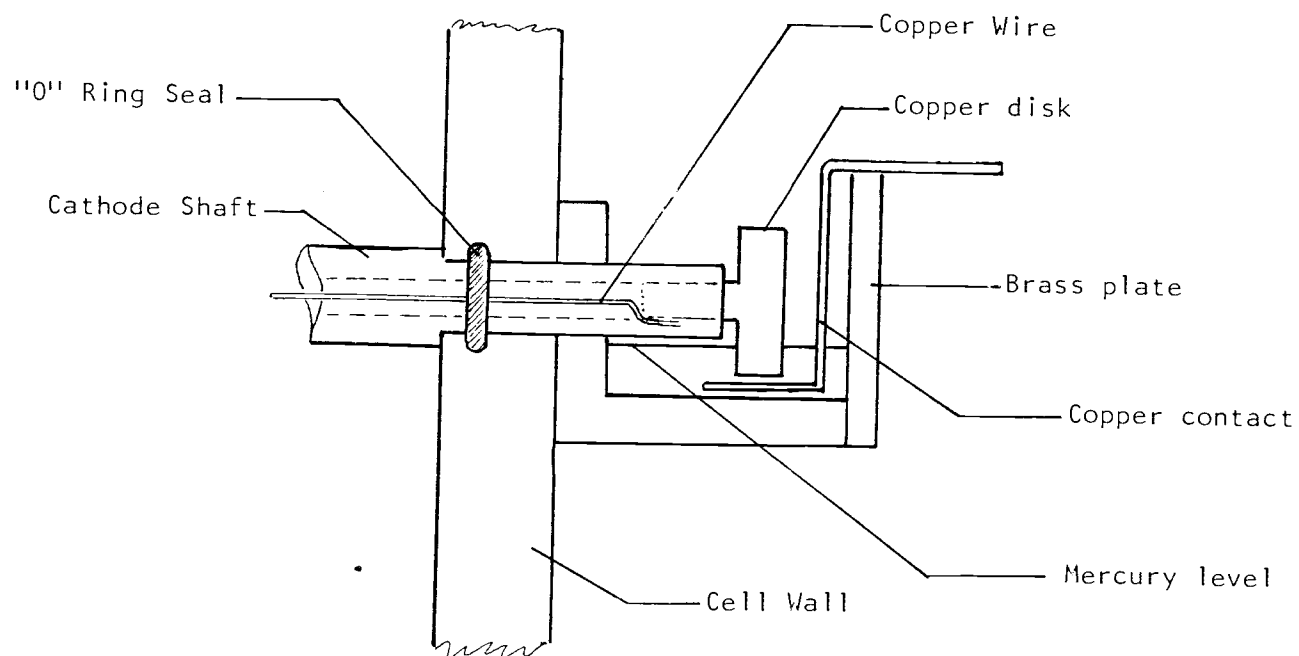FIG. 4   CONSTRUCTION OF MERCURY CONTACT

The Anode: The zinc anodes used were made from a zinc-
copper alloy strip which was 1/2 inch wide and 0.02 inch
thick containing 98% zinc and 2% copper.   The anodes were
constructed so that a maximum surface area could be ob-
tained.   Each electrode consisted of ten alloy strips
welded together in the configuration shown in Fig. 5.   A
set of anodes are shown in Fig. 6.

A 1/8 inch thick sheet of polyethylene was placed on
the top of the anodes to prevent the hydrogen gas which
was formed at the anodes from coming into contact with the
cathode surface.

The Reference Electrode: A silver-silver chloride
reference electrode was used in this investigation.   The
standard procedure for preparing the reference electrode
is as follows:

A 20-gauge silver wire, which had been cleaned with
concentrated ammonium hydroxide followed by treatment with
nitric acid and washed thoroughly with distilled water,
was chlorinated for about 30 minutes in 0.10 M HCl at a
current of 1.0 mA.   A graphite electrode was used for the
cathode in this operation.   The silver wire was then washed
well and stored in distilled water for two days after
chlorination.   It was then immersed in a beaker filled with
1.0 M KCl saturated with AgCl and tested against a commer-
cial silver-silver chloride reference electrode (Beckman
Reference Electrode, Model 39070, Beckman Instruments Inc.,
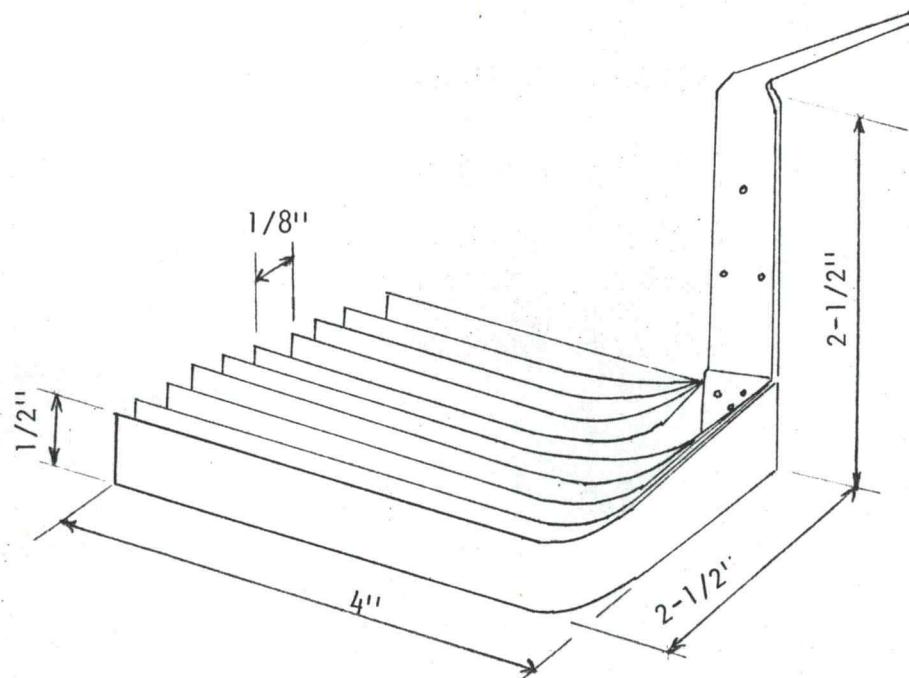Fullerton, California) in the same beaker.   The reference

FIG. 5   RIGHT ANODE CONFIGURATION
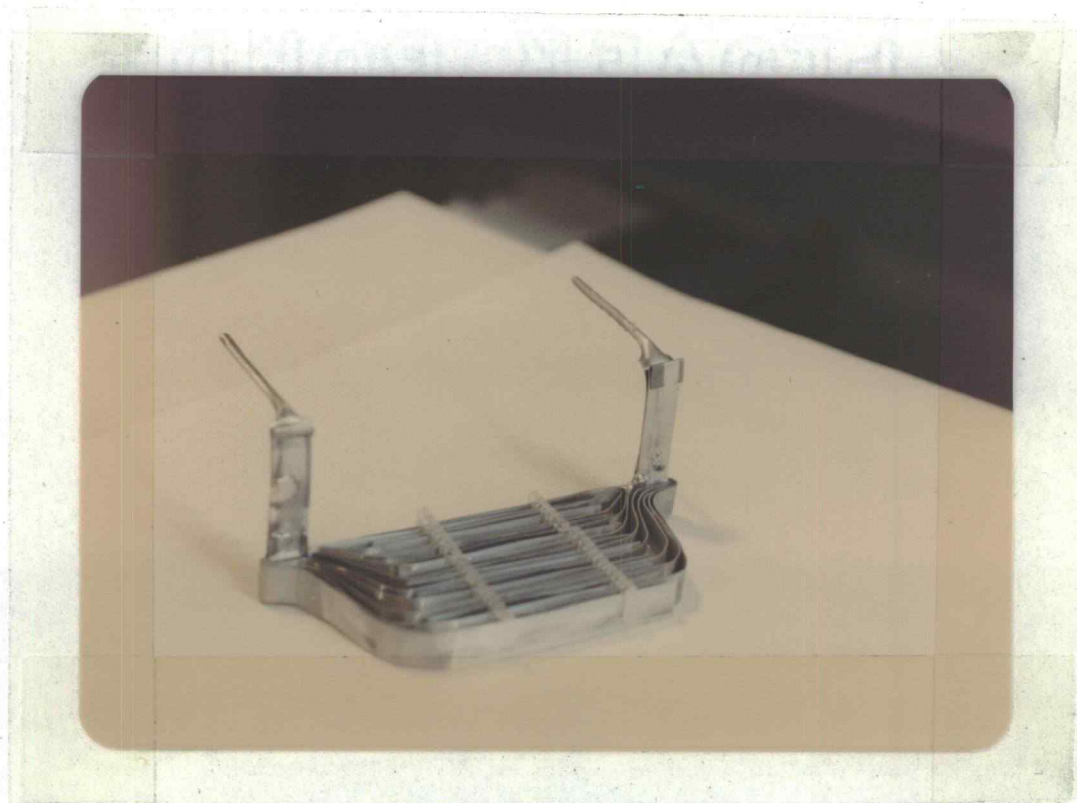
FIG. 6   A SET OF ANODES

electrode, thus prepared, exhibited a bias potential greater than $\pm$ 10 mV so it was cleaned and rechlorinated. After a reliable electrode had been formed, it was mounted in the assembly shown in Fig. 7.

The Wiper: The wiper was made of a Teflon blade cut from a 1/6 inch Teflon sheet and fitted into a plexiglass holder. The wiper holder was supported by a base which was made of 1/2 inch plexiglass. The base was 1-3/4 high and the wiper was held in the fixed position for all runs. The wiper holder was secured by a stainless steel screw which passed through the outer wall of the cell. This screw enabled the wiper to be adjusted to various horizontal positions. By this arrangement, the pressure exerted by the wiper blade on the cathode could easily be controlled by varying the position of the stainless steel screw, and a constant wiper effectiveness could be achieved during each run. The assembly of the wiper is shown in Fig. 8.

The Electrolyte: The chemicals and their concentrations used in making the electrolytes for this investigation were: 0.50 M $ZnCl_2$ and 2.00 M KCl. All electrolytes were prepared by using only analytical grade reagents and distilled water.

The Rotation System

The cathode disk electrode was driven by a variable speed motor (Model 8, Eastern Engineering Co., New Haven, Connecticut) powered by a stabilized voltage regulator (Type 116, the Superior Electric Co., Bristol, Connecticut).

3.5M KCl solution
saturated with
AgCl

Silver wire

Glass wool

3.5M KCl solution

Luggin Capillary
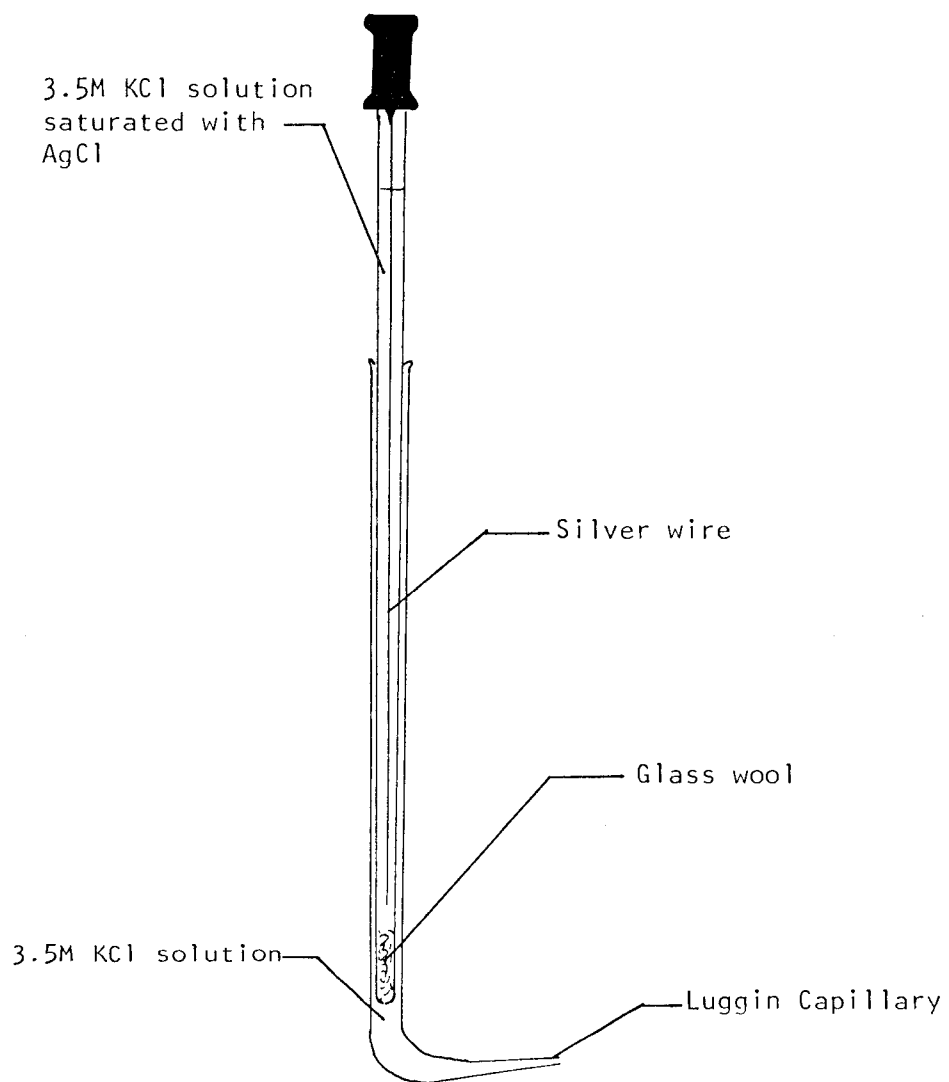
FIG. 7 CONSTRUCTION OF REFERENCE ELECTRODE

20

FIG. 8   THE WIPER

Coupling

Mercury
contact

Zero-Max
variable speed
torque converter

The cell
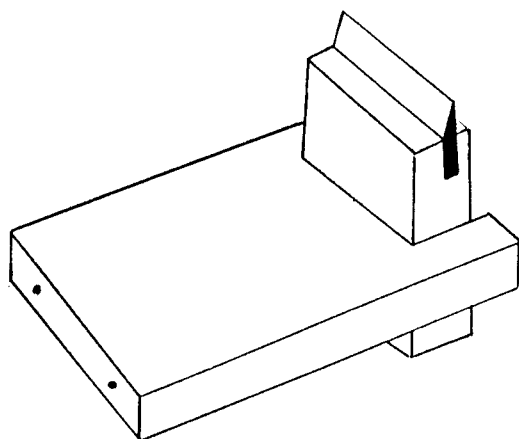
Variable speed
Stirred Motor
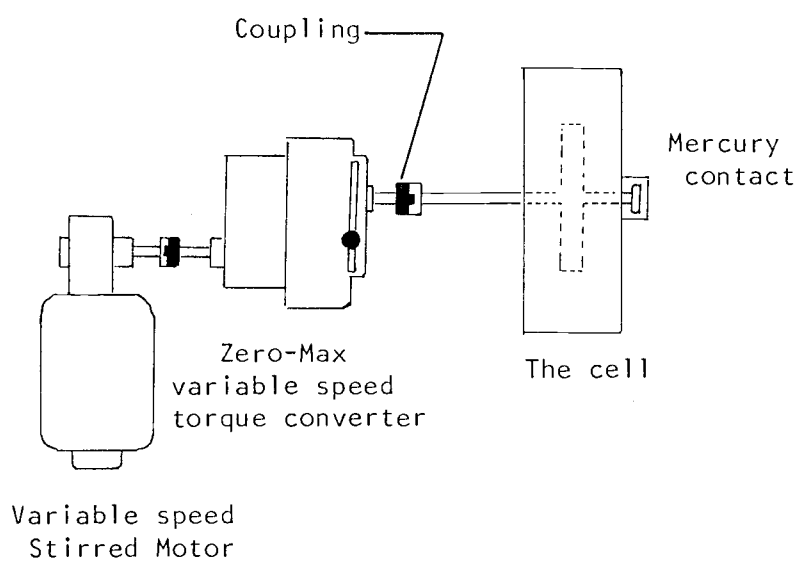
FIG. 9   TOP VIEW OF THE ROTATION SYSTEM

A "Zero-Max" variable speed torque converter (Model 142 X, Revco, Incorporated, Minneapolis, Minnesota) was connected between the variable speed motor and the shaft of the cathode electrode by two couplings (Model A050-2, Lovejoy Co., Chicago, Illinois).

The measurement of rotational speed was made by counting the number of revolutions with a reset counter (Veeder-Root, Inc., Hartford, Connecticut) during a period of time which was measured by a "Lab-Chron" electric timer.

The set up of the rotation system is shown in Fig. 9.

The Gas Supply System

The arrangement of the gas supply system is shown in Fig. 10. It consisted of

1) a cylinder of ultra high purity nigrogen gas (Liquid Air Inc.) with a pressure regulator (Model 25-100, Harris Colorific Co., Cleveland, Ohio).

2) a cylinder of chlorine gas (Jones Chemicals, Inc.) and a pressure regulator (Model B15-660, the Matheson Co., Newark, California).

3) a gas control needle valve (Model 305, the Matheson Co., Newark, California).

4) manometers which were made of 10 mm glass tubing and filled with carbon tetrachloride.

5) orifice gas flowmeters which were made by drawing a 10 mm glass tube down to a filament which was sealed
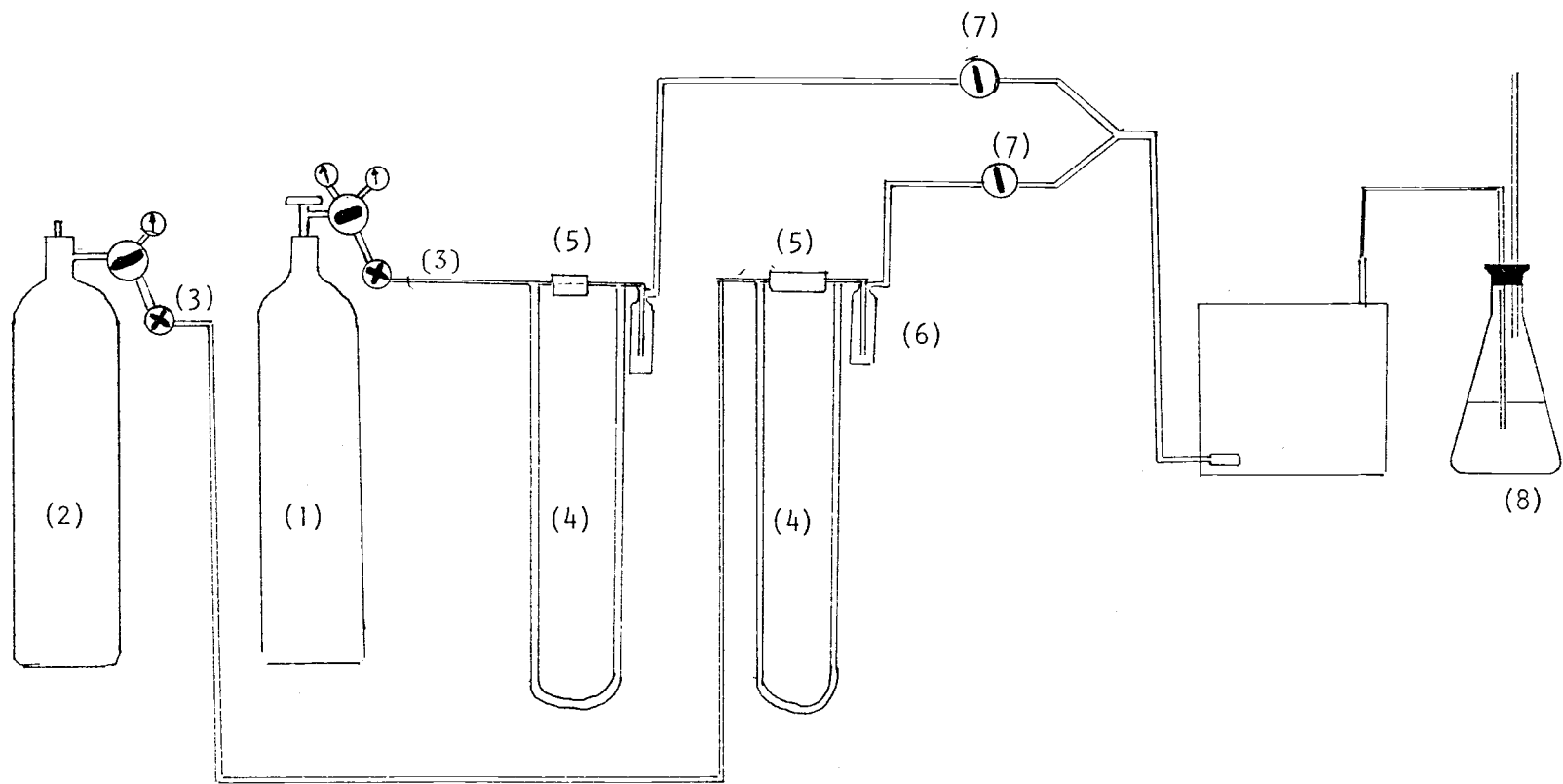
FIG. 10   GAS SUPPLY SYSTEM SCHEMATIC

within another glass tube for protection.

    6)   "Blow-out" traps.

    7)   10 mm glass stopcock valves.

    8)   a caustic wash bottle to capture the chlorine gas.

The Electrical Measurement System

The electrical measurement system schematic is shown in Fig. 11. It consisted of

    1)   Cathode reference electrode contact.

    2)   Anode contacts.

    3)   Cathode mercury contact.

    4)   DC ammeters:

        A.   0 - 50 mA (Model 1531, Weston Instrument Corp., Newark, New Jersey)

        B.   0 - 250 mA (U.S.N. Type, Simpson Electric Co., Chicago, Illinois)

        C.   0 - 3 A (Model 506, Weston Instrument Corp., Newark, New Jersey).

    5)   4 position silver contact rotary switch.

    6)   Low resistance Shunt rated 50 mV at 300 A (Type PX, Westinghouse Electric and Manufacturing Co.).

    7)   0 - 20 ohm load rheostat (#2751, The Welch Scientific Co., Chicago, Illinois).

    8)   Cell voltage strip chart recorder (Omni Scribe strip chart recorder, Houston Instrument Co., Austin, Texas).

9)   Cathode reference voltage Volmeter (Digitec Model 268, United System Corporation, Dayton, Ohio).

10)   K-3 Type Universal Potentiometer (Leeds and Northrup Co., Philadelphia, Pennsylvania).
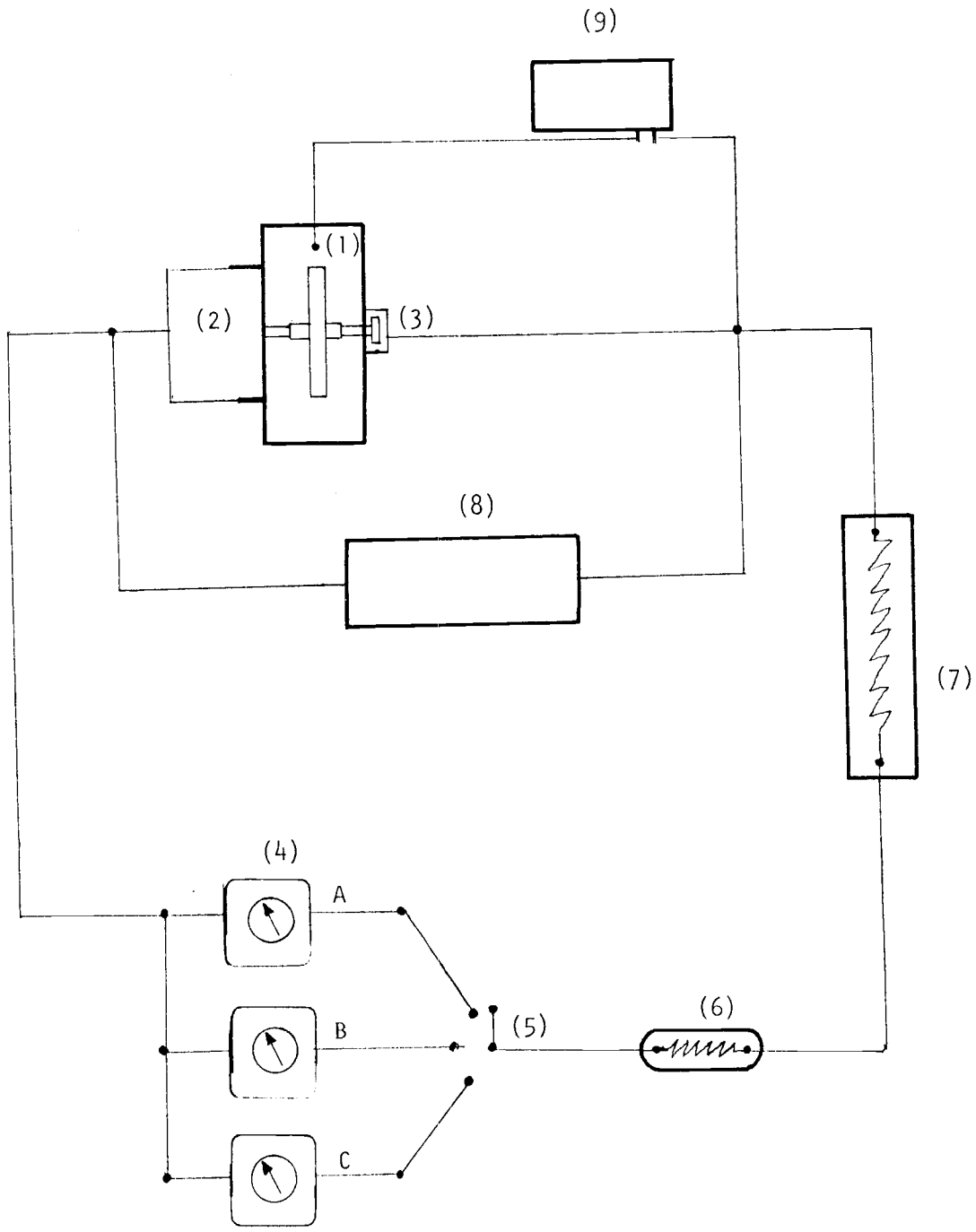
FIG. 11   THE ELECTRICAL MEASUREMENT SYSTEM DIAGRAM

IV.   EXPERIMENTAL PROCEDURE

To meet the objective of this study, the work was divided into three separate phases. Phase I involved the preparation and calibration of experimental equipment. Phase II was divided into two parts: the first part involved a verification of the cathode reaction, and the second part involved proving that the cell current was limited by the amount of chlorination of the copper cathode. In phase III, the primary thrust of this investigation, the effort was to study the chlorination rate of copper during the early stages of copper chloride film formation at various chlorine partial pressures.

The Procedure for Phase I

In phase I, the calibration of the gas supply system, the preparation of experimental runs and the start-up period were carried out.

Calibration of Gas Supply System: The equipment used to calibrate the gas supply system was basically the same as the one shown in Fig. 10, but the cell was replaced by a 100 ml buret which was modified to fit a rubber injector for the tapped fitting. The calibration was carried out in the following steps:

1. the gas flow rate was adjusted by needle valves to have a desired height difference on the manometer.

2. a soap solution was injected to the inlet of the

buret in which gas was flowing. A soap film was formed and stretched across the buret cross-section. This soap marked the flow of gas through the buret.

3. a Lab-Chron timer (Lab-line Inc., Chicago, Illinois) was used to measure the time during which the film traversed over 80, 50 and 30 cubic centimeter sections of the buret. The flow rates in cubic centimeters per second were calculated and their average value was recorded.

4. gas flow rates were plotted versus the manometer readings and these plots were used as calibration charts for the manometers.

Preparation for a Run: The following procedure was used for the preparation of an experimental run.

1) a new set of anodes was rinsed with distilled water and installed in the cell.

2) the copper cathode was rubbed with grade 3/0 emery finishing paper until the surface was shiny. The cathode was then immersed in a 30% nitric acid solution for several minutes and rinsed with distilled water before installation.

3) the wiper was finished to a sharp edge and placed on the base. The stainless steel screw was adjusted so that a good contact between wiper and copper surface existed.

4) a new reference electrode, which was previously prepared, was installed in its place.

5) a polyethylene shield was fixed in place above

the anodes.

6)   the front plate of the cell was screwed tightly.

7)   mercury was poured into the cathode contacting system.

8)   the electrical system and rotation system were connected to the cell.

Start-up Period: The following start-up procedure was used for all runs:

1)   Electrolyte was introduced up to a marked level in the cell through a tube at one side of the cell.   The same volume of electrolyte was used for all runs in order to have the same portion of copper cathode area immersed in the electrolyte.

2)   the gas supply system was adjusted to have the desired flow rates of nitrogen and chlorine gas.   Twenty minutes was allowed to let the chlorine gas become saturated with electrolyte.

3)   the stainless steel screw was adjusted for good wiping action.

The Procedure for Phase II

In first part of Phase II, experiments were carried out to verify that the assumed electrochemical reactions had taken place in the electrolyte.   A 0.50 M $ZnCl_2$ solution was used as an electrolyte.   The open circuit cell voltage was observed and compared with the theoretical

value derived from the Nernst equation.

In the second part of Phase II, a study of the cathode polarization by a direct method was performed to prove that the cell current was limited by the amount of chlorination at the copper cathode. In the direct method, the potential dependence of the current was determined by measuring the electrode potential of the cathode relative to a reference electrode. A Luggin capillary was used to exclude the ohmic drop within the electrolyte from the potential measurements. The tip of the Luggin capillary was placed in close proximity to the cathode. The cathode polarization was defined as the difference between the cathode potential measured at zero current and the cathode potential measured during current flow through the cell.

The start-up procedure was the same as in the previous phase. Measurements were begun after it was ascertained that steady state operation was achieved. The following procedure was used to check whether steady state was obtained: the open circuit voltage of the cell was observed; the circuit was then connected for two minutes; the circuit was disconnected again; the open circuit voltage was compared with the previous value; if two readings agreed within 10 mV, it was assumed that the steady state was obtained. The external resistance was then raised stepwise in small intervals and readings of cell voltage, cathode potential,

and cell current were taken five minutes after each change. This time interval allows the system to come back to steady state conditions. Three sets of readings were taken in each interval during these tests and the average values were recorded. After the cell voltage ceased to change while increasing the external resistance, the external resistance was decreased stepwise and measurements were made in the same manner as before.

The Procedure of Phase III

The objective of the third phase of the project was the primary purpose of this study. Phase III was designed to obtain the limiting currents as a function of the speed of rotation of the copper cathode. These results were used to calculate the amount of copper chloride formed as a function of the exposure time of the cathode to the chlorine gas.

For the start-up period, the same procedure was used as in previous phases. After allowing the cell to reach the steady state, the limiting current was recorded at an intermediate speed. The speed was then set at the lowest rate and increased stepwise. To allow the current to stabilize after each change, a period of at least five minutes was allowed before the limiting current reading was taken. The reading was checked by measuring the voltage drop across the shunt with a K-2 Leeds and Northrup

Potentiometer. The readings derived by these methods were compared. If they agreed within 5%, the reading of the ammeter was assumed to be valid.

The chlorination study was carried out at three different partial pressures of chlorine: 0.210, 0.440 and 1.00 atm. In each case, the partial pressure of chlorine was calculated based on the flow rates of nitrogen and chlorine.

V. RESULTS

Results from Phases I and II

Determination of the Effectiveness of Wiping Action:
The wiper was employed to give the chlorine free excess
to the copper surface. The wiping action, of course, was
not perfect; since some entrained electrolyte always stayed
on the surface of the metal. Experiments were carried out
to determine the effectiveness of the wiper.

Fig. 12 shows results of these experiments. Three
different states of the copper cathode were studied:
totally submerged, partially-unwiped, and partially sub-
merged and wiped.

When the electrode was left unwiped, the liquid film
of the electrolyte was observed to cover the electrode
surface and the chlorination rate was reduced to a small
quantity. This is evident from the low limiting currents
obtained from the unwiped electrode case. The wiping
action improved the reaction rate considerably, because
higher limiting currents were obtained for the wiped
electrode case.

Verification of the Cathode Reaction: In the chlor-
ination of copper, the product formed in thin film layers
can be either CuCl, or $CuCl_2$, or both.

In 1966, Dagoury and coworkers[5] studied the influence
of temperature and pressure on the kinetics of the reaction
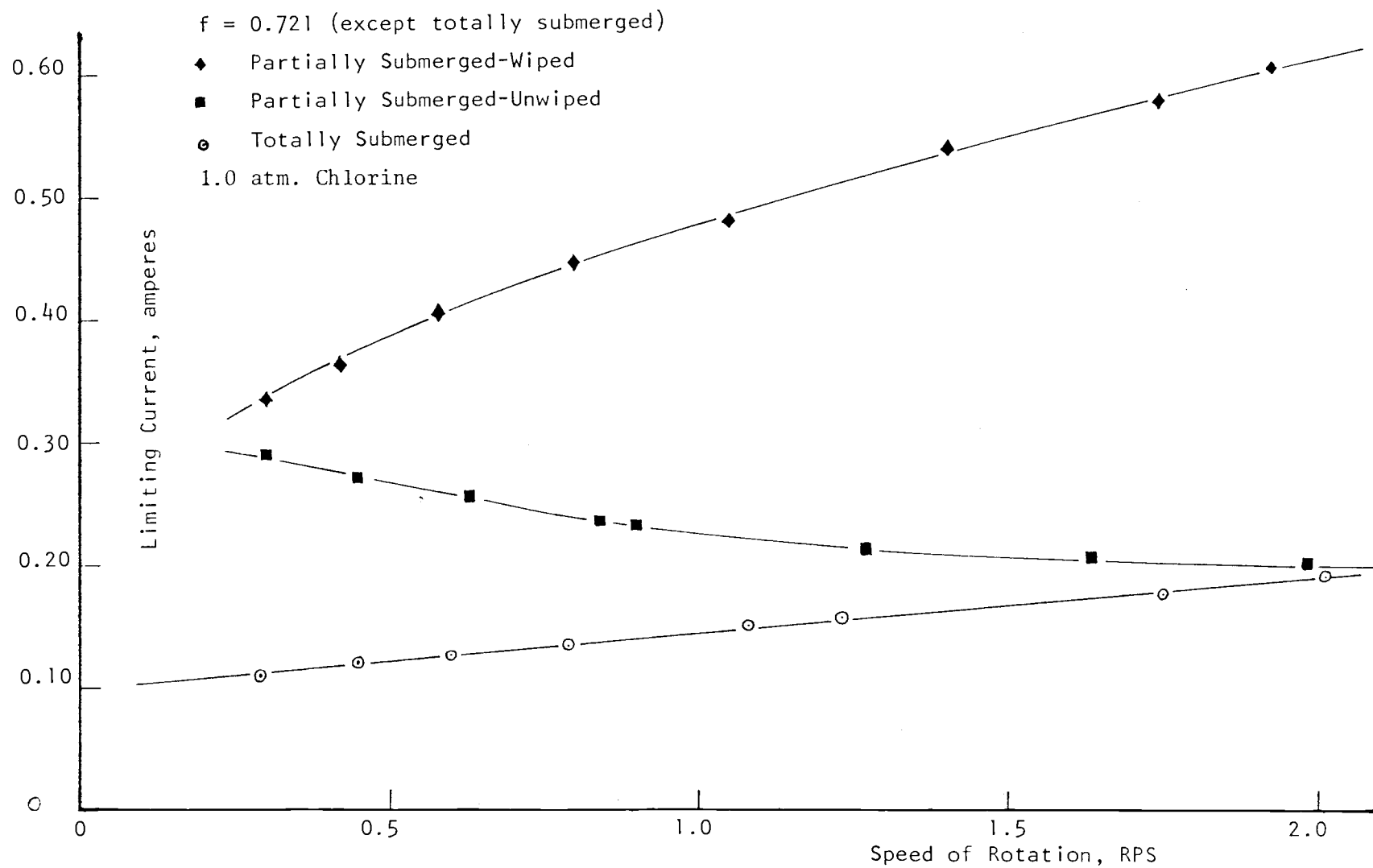
FIG. 12   EFFECTS OF WIPING THE CATHODE

33

involving pure copper and chlorine gas, and on the crystal structure of the chloride formed. They found that cuprous chloride was formed exclusively at a chlorine partial pressure of 100 mm Hg and at room temperature. An increase of temperature, however, led to the rapid formation of mixed chloride layers.

With the experimental conditions used in this investigation, cuprous chloride was the only product which was formed when the copper cathode was chlorinated by chlorine gas. The copper chloride layer was then removed by an electrochemical reaction to return the copper to the metallic state and liberate chloride ions into the electrolyte. The resulting cathode reaction was

$$2 \; CuCl \; + \; 2 \; e^- \longrightarrow 2 \; Cu \; + 2 \; Cl^- \qquad (5.1)$$
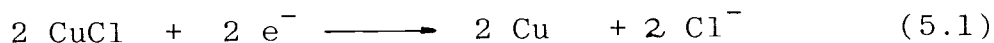
with the copper alternating between the chloride and the metallic state. This electrochemical reaction was balanced by the action of the zinc anode,

$$Zn \longrightarrow Zn^{++} \; + \; 2 \; e^- \; , \qquad (5.2)$$
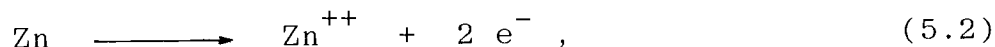
making the over-all reaction

$$Zn \; + \; 2 \; CuCl \longrightarrow Zn^{++} \; + \; 2 \; Cl^- \; + \; 2 \; Cu \; . \qquad (5.3)$$
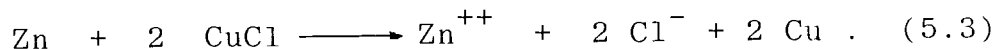
In order to verify that these reactions were taking place in the cell, one may compare the open circuit voltage of the cell with that predicted by the Nernst equation.

The Nernst equation for this particular case is

$$E_{oc} = E_O - \frac{RT}{2F} \ln \frac{a_{Zn}^{++} \; a^2_{Cl}^- \; a_{Cu}}{a^2_{CuCl} \; a_{Zn}} \qquad (5.4)$$

where E_O is the standard cell potential of 0.900 volts. This is found by adding the standard potential for

$Zn \longrightarrow Zn^{++} + 2 e^-$; $E^O = 0.763$ V, and the standard

potential for $CuCl + e^- \longrightarrow Cu + Cl^-$; $E^O = 0.137$ V.

E_{oc} is the predicted open circuit cell voltage, R is the gas constant, T the absolute temperature, F the Faraday's constant, and a_x the activity of species X.

If the activities of the solid phases are considered to be unity, equation (5.4) becomes

$$E_{oc} = E_O - \frac{RT}{2F} \ln (a_{Zn}^{++} \; a^2_{Cl}^-)$$

$$= E_O - \frac{RT}{2F} \ln (f^3_{\pm} \; C_{Zn}^{++} \; C^2_{Cl}^-) \qquad (5.5)$$

where $f_{\pm}$ is mean molar activity coefficient of $ZnCl_2$, and C_x is the molar concentration of species X.

According to Robinson and Stokes[14], the mean molar activity coefficient of 0.50 M $ZnCl_2$ is 0.394. Thus at $25^O C$

$$E_{oc} = 0.900 - \frac{0.05914}{2} \log (0.394)^3 (0.500) (1.000)^2$$

$$= 0.9448 \text{ V} \qquad (5.6)$$

The open circuit cell voltage was observed to vary between 0.930V-0.920 V for the runs with 0.50 M $ZnCl_2$ electrolyte. It was therefore considered that the assump-

tion involving cathode reaction was valid.

Proof of the Cathode Limiting Current: In order to
measure the amount of copper chloride formed during the
period in which the copper cathode was exposed to the
chlorine gas, a fresh copper surface was continually re-
generated in each revolution of the cathode rotation. In
order to do this the copper chloride layers had to be con-
verted by electrochemical reaction in the electrolyte to
metallic copper. To achieve this objective, experiments
were designed so that the rate controlling reaction was
the chlorination of the wiped electrode surface during the
exposure period to the chlorine gas, and not the electro-
chemical reduction step in the electrolyte. A study of
cathode polarization was conducted to ascertain that the
limiting current was obtained. To make the cathode the
controlling electrode, the zinc anode surface was made very
large compared to the cathode area (390 sq. cm per anode
versus the 22 sq. cm cathode). In this study, a 2 M KCl
electrolyte was used because of its high electrolytic
conductance. Specifically, this solution had a conduct-
ivity of 0.215 $ohm^{-1}cm^{-1}$.

Fig. 13 shows the results of the cathode polarization
study using 2 M KCl electrolyte and a chlorine partial
pressure of 1.0 atm. The cell voltage and cathode polar-
ization are plotted as functions of cell current. The
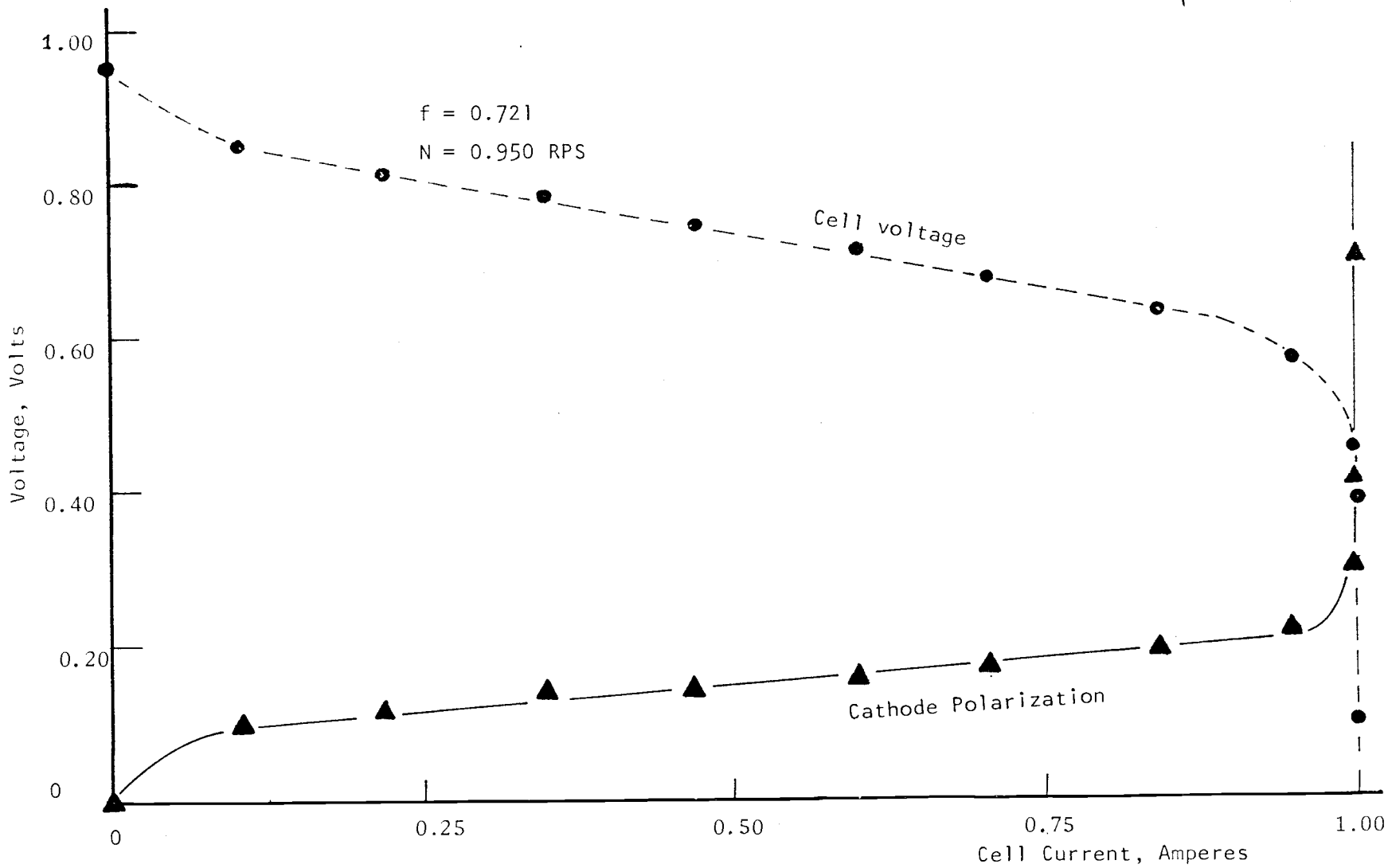
FIG. 13   CELL AND CATHODE POLARIZATION, 2M KCl

37

terminal cell voltage decreases as the current taken from the cell increases, and rapidly falls to zero when the cell current reaches the value of 1.0 amperes. This collapse of the cell voltage and the rapid increase of cathode polarization prove that limiting current was obtained and the electrochemical reaction attained at a rate equal to that of mass transfer from the copper chloride cathode.

The fact is further proved by the observation that a much higher current was obtained if the cell was left at open circuit for several minutes and suddenly short circuited. This high current lasted only for a short time. This indicates that the electrochemical reaction at the cathode in the electrolyte could go to a higher rate if the chlorination reaction would support it.

Results from Phase III

In phase III, the limiting current of the cell was measured as a function of the speed of the rotation of the copper cathode at three different chlorine partial pressures. These data are plotted in Fig. 14, 15 and 16. The rate of chlorination of copper can be calculated directly from these limiting currents, the rotational speed and the area of the cathode.

Calculations of the rate of chlorination: The calculations were carried out by using equations developed in the following paragraphs.
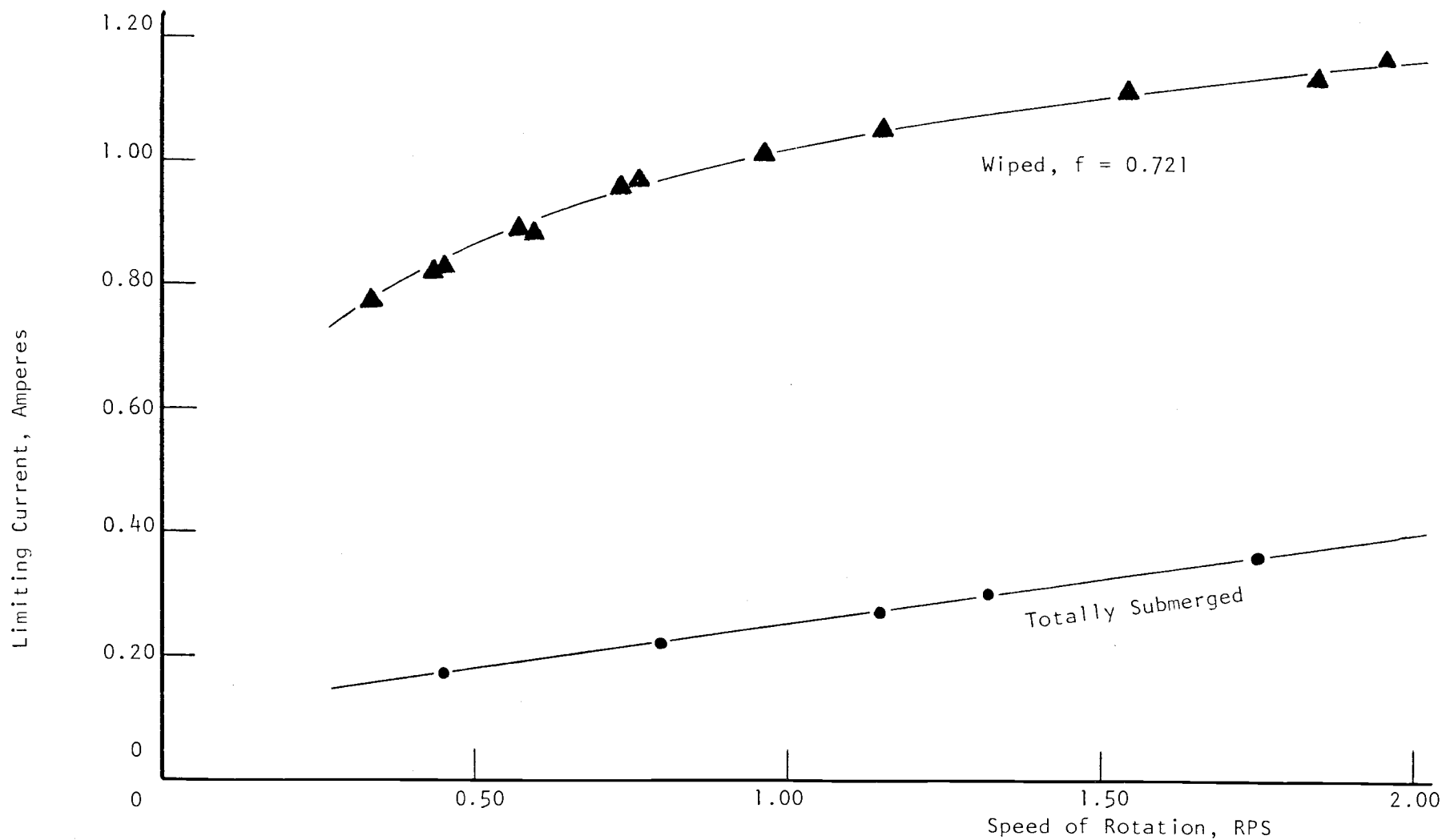
FIG. 14   LIMITING CURRENT - SPEED OF ROTATION 1.00 atm. Chlorine

39
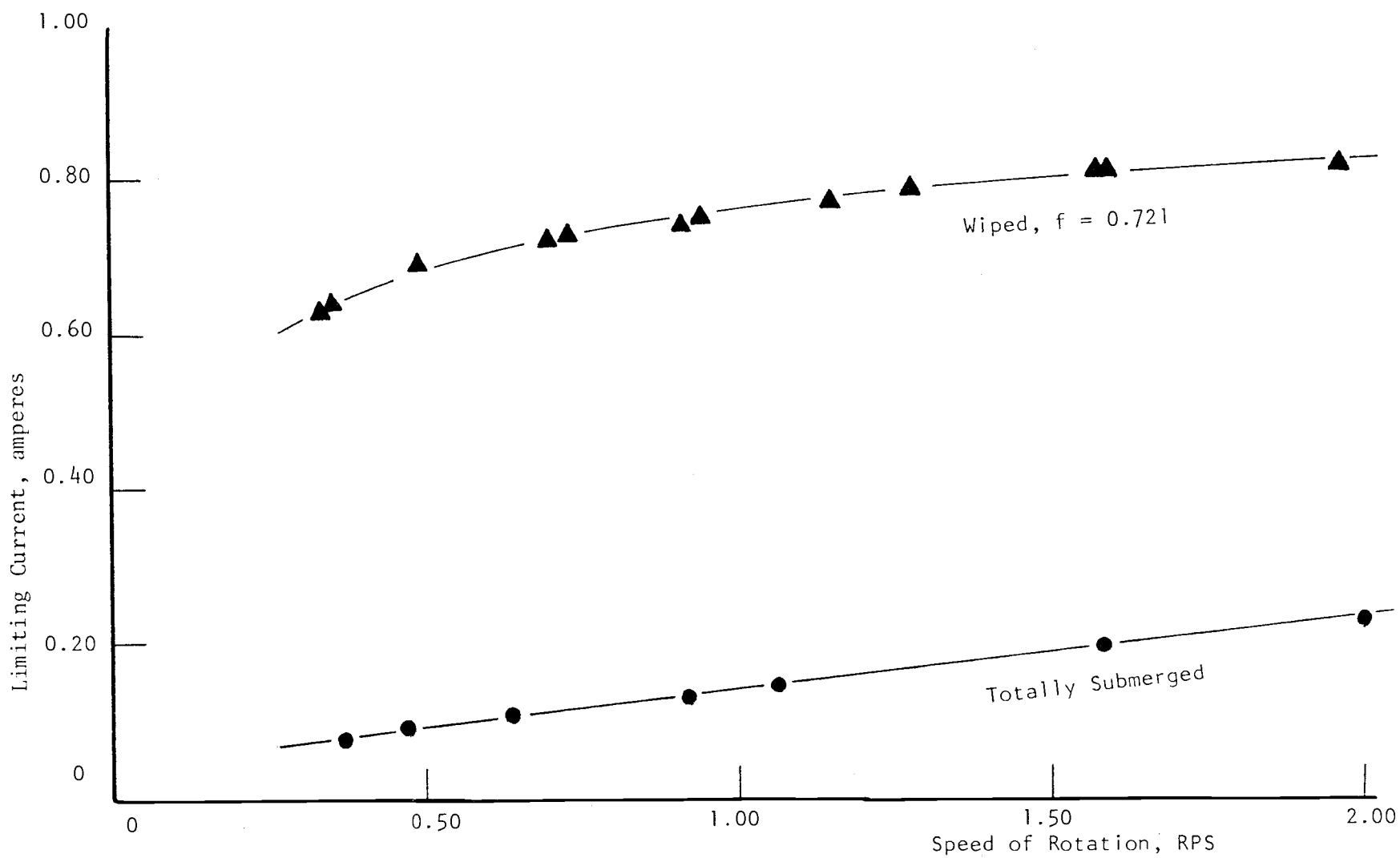
FIG. 15   LIMITING CURRENT - SPEED OF ROTATION 0.440 atm Chlorine
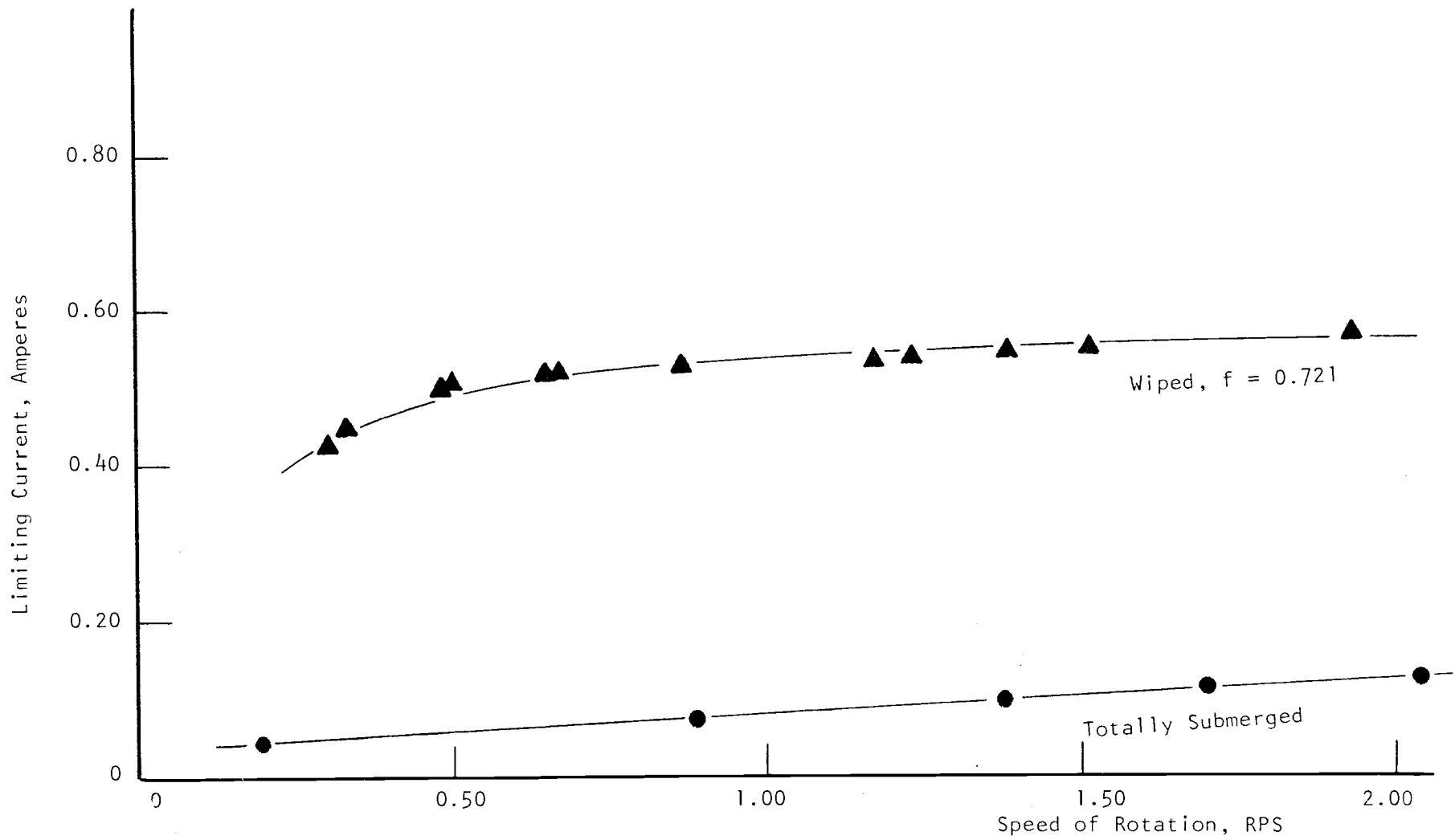
FIG. 16   LIMITING CURRENT - SPEED OF ROTATION   0.210 atm. Chlorine

The time, t, in seconds, during which the copper cathode was exposed to the chlorine gas is calculated from the equation

$$t = f / N \qquad (5.7)$$

where f is the fraction of the cathode exposed to the gas and N is the rotational speed of the cathode in RPS.

The current due to the gas phase reaction, I_G, is equal to the total limiting current, I, minus the portion of current due to diffusion of dissolved chlorine to the submerged cathode, I_D. It is given by the equation

$$I_G = I - I_D = I - I_o(1-f) \qquad (5.8)$$

where I_o is the limiting current of the totally submerged cathode at the rotational speed. The rate of formation of cuprous chloride due to the gas phase reaction, μ, is given by

$$\mu = \frac{I_G}{\mathscr{F}} = \frac{I - [I_o(1-f)]}{\mathscr{F}} \qquad (5.9)$$

where $\mathscr{F}$ is the Faraday's constant. Since the surface velocity, V cm/sec, is given by the following equation

$$V = \pi D N \qquad (5.10)$$

where D is the diameter of the cathode in centimeters, the rate of reaction per unit length can be calculated by:

$$\frac{\mu}{V} = \frac{I - [I_o(1-f)]}{\pi \mathscr{F} D N} \qquad (5.11)$$

The amount of cuprous chloride formed per unit area, W, on the surface of the copper cathode exposed to the chlorine gas in a period of time, t, is given by the equation

$$W = \frac{I - [I_O (1 - f)]}{\pi \, \mathcal{F} \, D \, w \, N} \qquad (5.12)$$

where w is the width of the cathode in centimeters and W has the units of gram-moles/cm^2.

The calculated values of t, I_D, I_G, and W are shown in Tables 1, 2 and 3 using equations 5.7, 5.8 and 5.12. The rate of chlorination is shown in Fig. 17.

Curve Fitting Procedure: As mentioned in the previous sections, the oxidation of metals at room temperature can lead to various rate laws, such as linear, parabolic, cubic or logarithmic. In order to test these rate laws, the method of least squares was applied to the experimental data. The Statistic Interaction Program System (SIPS) developed and made available through the Computer Center of Oregon State University was used to evaluate the constants of the best fit lines. The closeness of fit can be judged from the values of coefficient of determination R^2, which is defined as the fraction of the variance of dependent variable that may be ascribed to the effect of the independent variable[6]. For a perfect fit, R^2 is equal to

1.00.

The fitting procedure for the linear, parabolic and cubic rate laws was directly applied by using W, W^2 or W^3 as dependent variable and t as independent variable. The results from the least squares fitting process are shown in Tables 4, 5 and 6; and Fig. 18, 19 and 20 represent the best lines.

An iterative method was used in application of least squares method to evaluate the constants, K_1 and K_2, in the logarithmic rate law. In this method, the fitting process involved choosing a value for constant K_2, the quantity Z which is equal to ln (K_2 t + 1.0) was then calculated. The logarithmic rate law now can be expressed in the linear form

$$W = K_1 \ Z + K_3 \qquad\qquad (5.13)$$

SIPS was used to get the best fit equation and the coefficient of determination R^2 was calculated. The value of K_2 which gave the highest R^2 would be considered the best fit constant. The best equations for the logarithmic rate law are shown in Table 7. A comparison of values estimated from these equations with experimental data is shown in Table 8. Fig. 21, 22 and 23 represent the best fit lines.

TABLE 1.   Rate of the Chlorination of Copper
in 1.00 atm Chlorine

$f \quad = 0.721$

$1-f \quad = 0.279$

$\pi\, D_W \quad = 22.0 \text{ cm}^2$

N (RPS)	t (sec.)	I_D (amperes)	I_G (amperes)	$W \times 10^7$ (gram-mole $CuCl/cm^2$)
0.330	2.185	0.0421	0.7329	10.46
0.430	1.677	0.0469	0.7731	8.468
0.450	1.602	0.0474	0.7826	8.191
0.570	1.265	0.0525	0.8375	6.921
0.590	1.222	0.0536	0.8274	6.605
0.730	0.988	0.0586	0.8964	5.784
0.760	0.949	0.0600	0.9000	5.578
0.960	0.751	0.0678	0.9422	4.623
1.150	0.627	0.0751	0.9749	3.993
1.540	0.468	0.0907	1.0193	3.118
1.840	0.392	0.1032	1.0568	2.705
1.950	0.370	0.1069	1.0631	2.568

TABLE 2.   Rate of the Chlorination of Copper
in 0.440 atm Chlorine

$$f \quad = \quad 0.721$$
$$1-f \quad = \quad 0.279$$
$$\pi\,Dw \quad = \quad 22.0 \ cm^2$$

N (RPS)	t (sec.)	I_D (amperes)	I_G (amperes)	$W \times 10^7$ (gram-moles $CuCl/cm^2$)
0.330	2.185	0.0206	0.6094	8.697
0.350	2.060	0.0209	0.6191	8.331
0.490	1.471	0.0246	0.6654	6.396
0.700	1.030	0.0301	0.6899	4.642
0.730	0.988	0.0307	0.6923	4.467
0.910	0.792	0.0349	0.7051	3.650
0.940	0.767	0.0363	0.7107	3.561
1.150	0.627	0.0413	0.7287	2.985
1.260	0.572	0.0446	0.7404	2.768
1.580	0.456	0.0502	0.7598	2.265
1.590	0.453	0.0533	0.7567	2.242
1.960	0.368	0.0628	0.7572	1.820

TABLE 3. Rate of the Chlorination of Copper
in 0.210 atm. Chlorine

$$f = 0.721$$
$$1-f = 0.279$$
$$\pi Dw = 22 \text{ cm}^2.$$

N (RPS)	t (sec.)	I_D (amperes)	I_G (amperes)	$W \times 10^7$ (gram-moles $CuCl/cm^2$)
0.300	2.403	0.0120	0.4180	6.563
0.330	2.185	0.0126	0.4474	6.386
0.480	1.502	0.0140	0.4861	4.769
0.500	1.442	0.0142	0.4958	4.670
0.650	1.109	0.0173	0.4997	3.621
0.670	1.076	0.0179	0.5021	3.530
0.870	0.829	0.0204	0.5096	2.759
1.170	0.616	0.0232	0.5088	2.048
1.230	0.586	0.0248	0.5152	1.973
1.380	0.522	0.0265	0.5195	1.773
1.510	0.477	0.0285	0.5225	1.630
1.930	0.374	0.0338	0.5352	1.306

FIG. 17   RATE OF THE CHLORINATION OF COPPER

The chart shows three data series plotted as $W \times 10^7$, gram-mole cucl/cm^2 versus t, seconds:

- 1.00 atm Cl$_2$
- 0.44 atm Cl$_2$
- 0.210 atm Cl$_2$
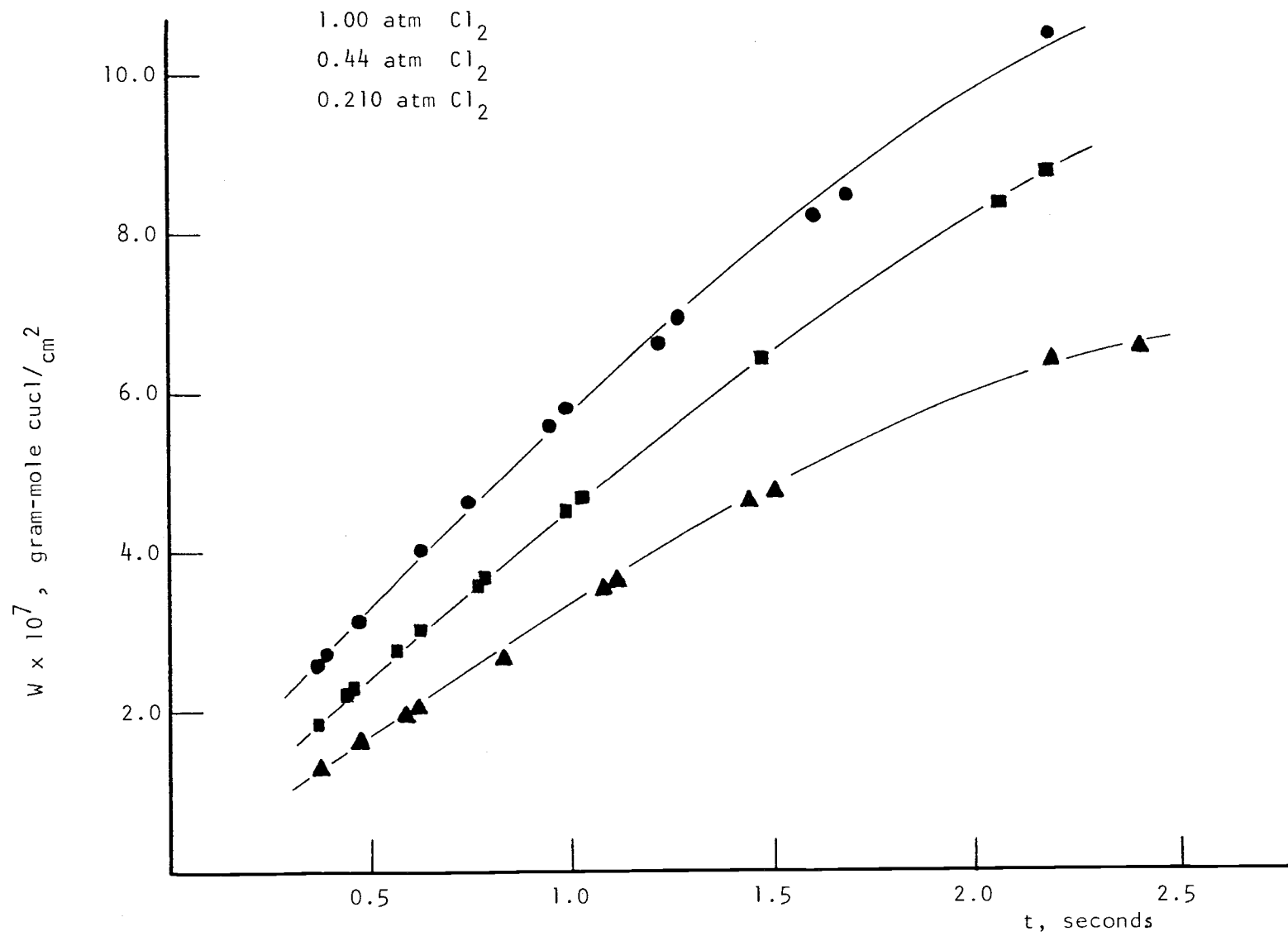
TABLE 4. Results of Curve Fitting Process for the Rate Law of the Form $W = k_1 t + k_1'$

Partial Pressure of Chlorine	Equation of Best Fit Line	R^2
1.00 atm.	$W = (4.358 \times 10^{-7})t + (1.214 \times 10^{-7})$	0.9942
0.44 atm.	$W = (3.783 \times 10^{-7})t + (0.609 \times 10^{-7})$	0.9972
0.21 atm.	$W = (2.708 \times 10^{-7})t + (0.458 \times 10^{-7})$	0.9883

TABLE 5. Results of Curve Fitting Process for the Rate Law of the Form $W^2 = k_2 t + k_2'$

Partial Pressure of Chlorine	Equation of Best Fit Line	R^2
1.00 atm.	$W^2 = (5.442 \times 10^{-13})t - (1.790 \times 10^{-13})$	0.9846
0.44 atm.	$W^2 = (4.047 \times 10^{-13})t - (1.607 \times 10^{-13})$	0.9853
0.21 atm.	$W^2 = (2.154 \times 10^{-13})t - (0.879 \times 10^{-13})$	0.9894

TABLE 6. Results of Curve Fitting Process for the Rate
Law of the Form $W^3 = k_3 t + k_3'$

Partial Pressure of Chlorine	Equation of Best Fit Line	R^2
1.00 atm.	$W^3 = (5.607 \times 10^{-19})t - (2.908 \times 10^{-19})$	0.9181
0.44 atm.	$W^3 = (3.599 \times 10^{-19})t - (1.983 \times 10^{-19})$	0.9425
0.21 atm.	$W^3 = (1.434 \times 10^{-19})t - (0.823 \times 10^{-19})$	0.9465

TABLE 7. Results of Curve Fitting Process for the Rate
Law of the Form $W = K_1 \ln (K_2 t + 1.0)$

Partial Pressure of Chlorine	Equation of Best Fit Line	R^2
1.00 atm.	$W = 1.58 \times 10^{-6} \ln (0.40t + 1.0)$	0.9993
0.44 atm.	$W = 1.82 \times 10^{-6} \ln (0.28t + 1.0)$	0.9998
0.21 atm.	$W = 1.33 \times 10^{-6} \ln (0.28t + 1.0)$	0.9966

FIG. 18   BEST FIT LINES TO THE RATE LAW OF THE FORM $W = k_1 t + k_1'$
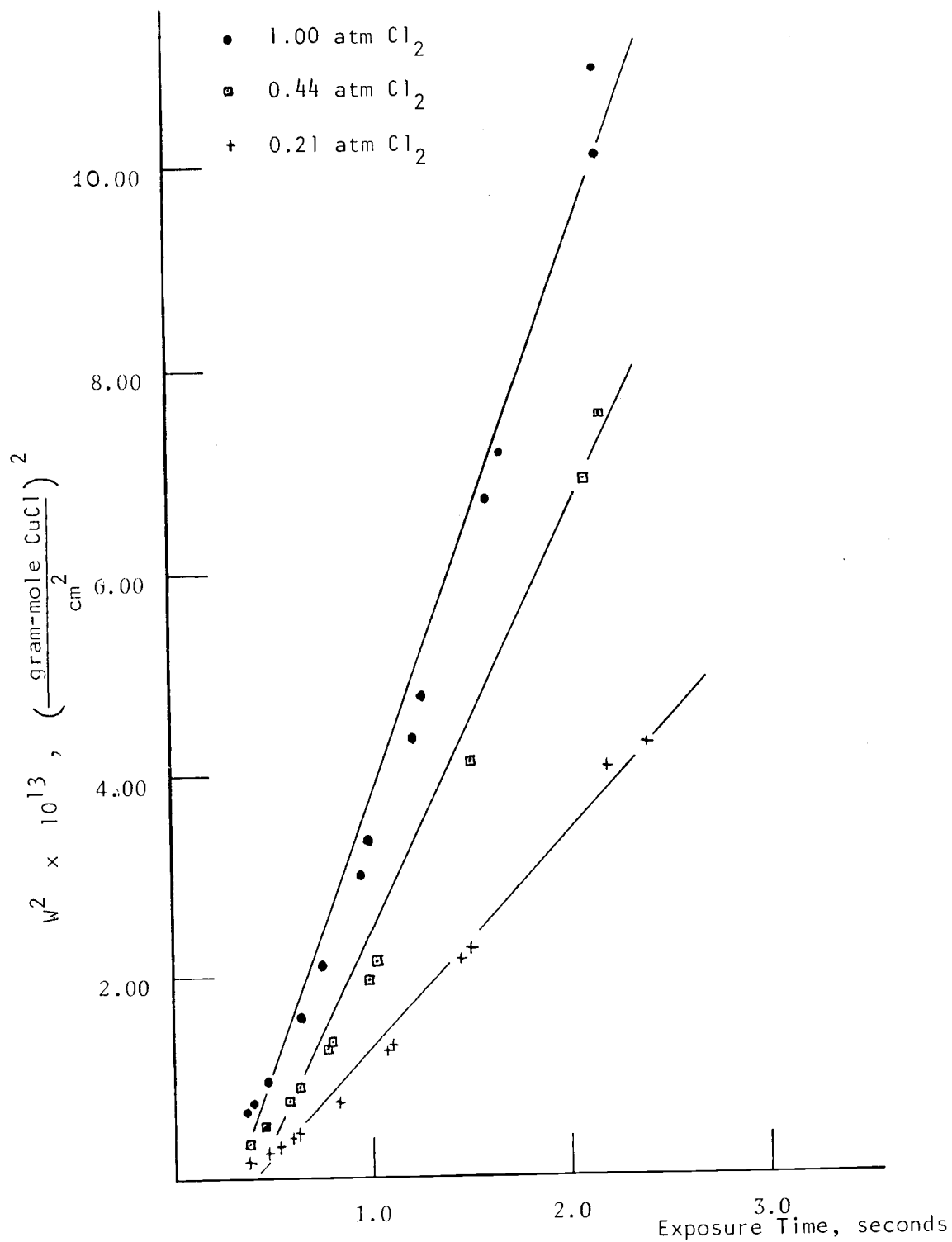
FIG. 19   BEST FIT LINES TO THE RATE LAW OF THE FORM
$$W^2 = k_2 t + k_2'$$
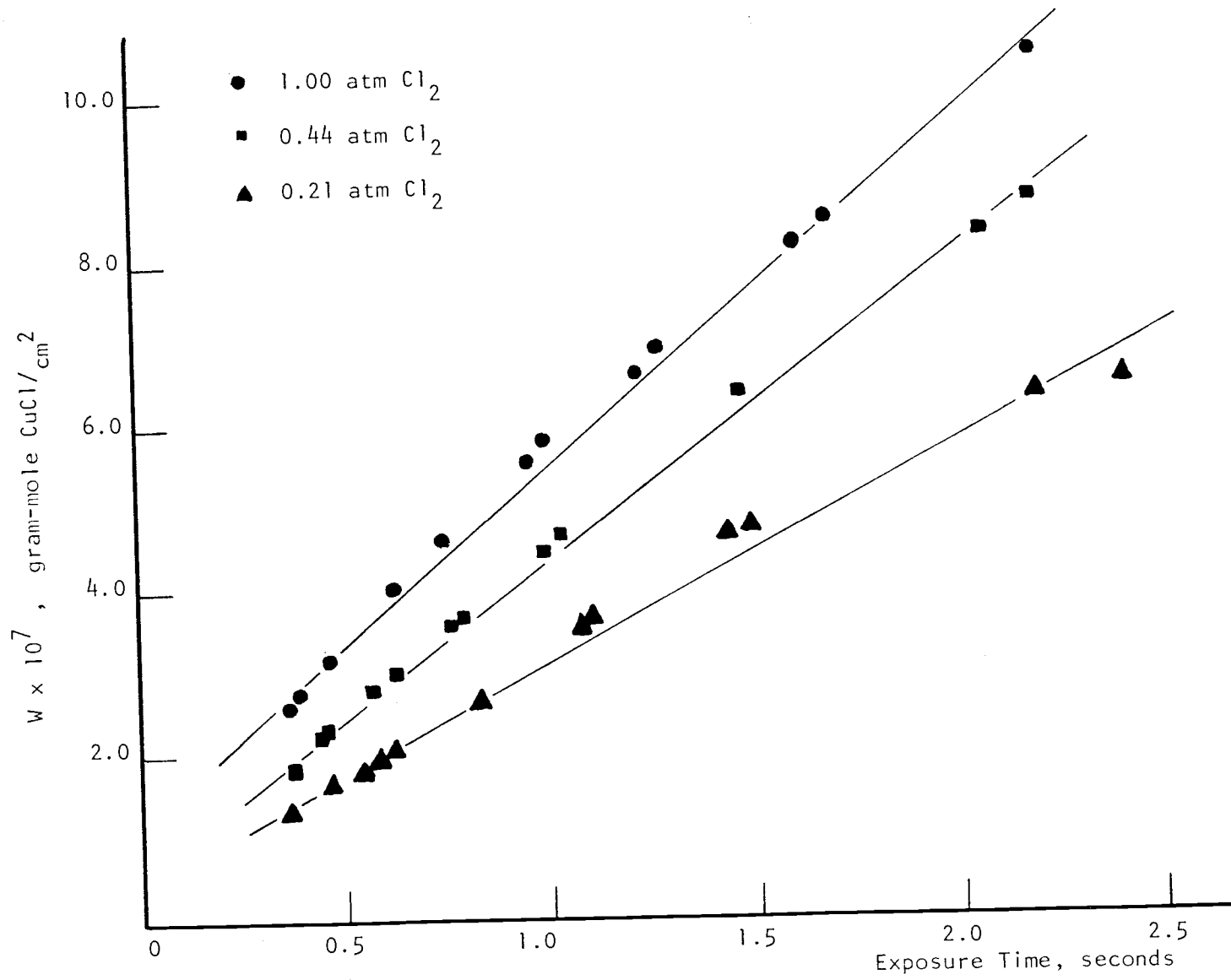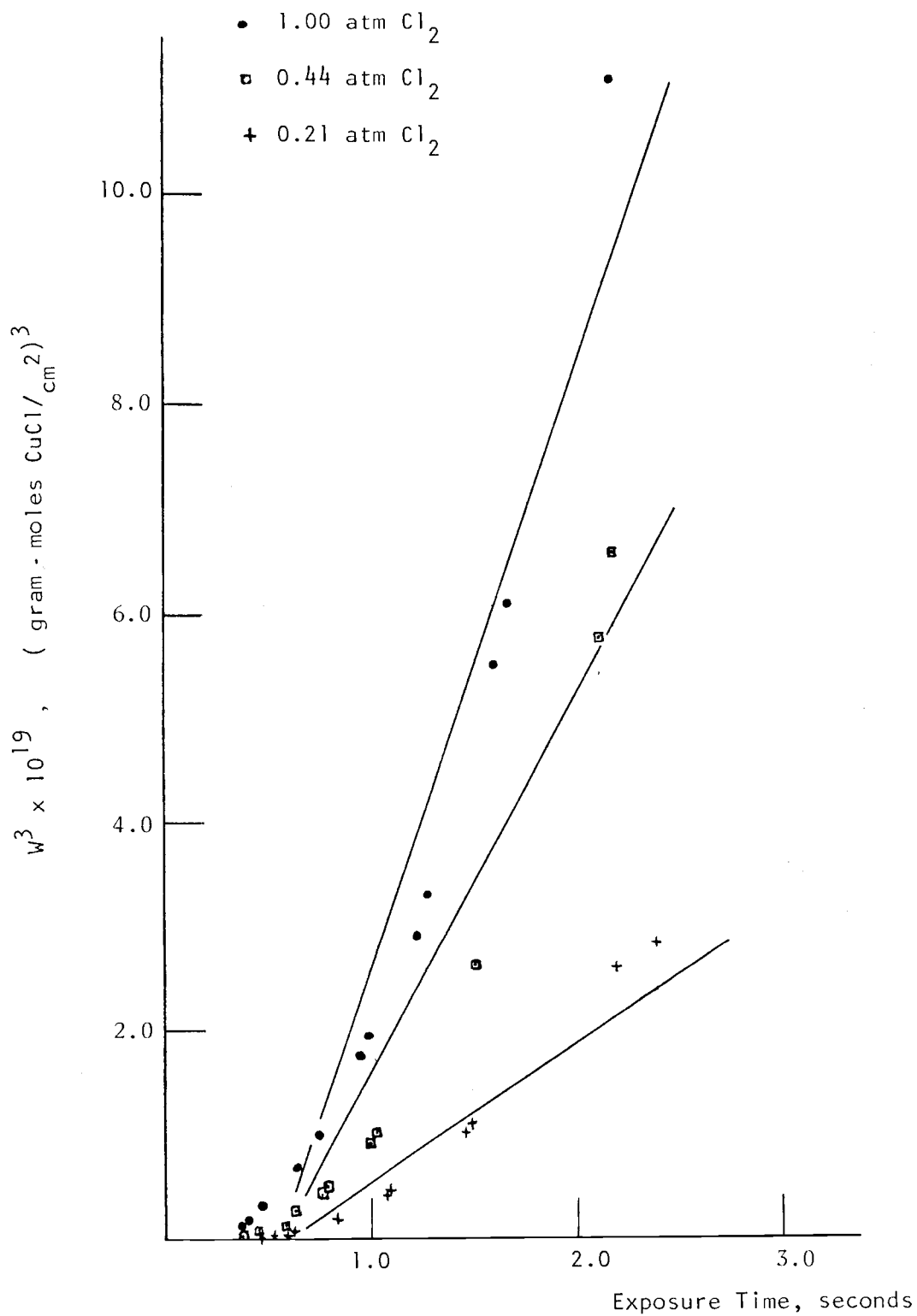
FIG. 20. BEST FIT LINES TO THE RATE LAW OF THE FORM

$$W^3 = k_3 t + k_3^1$$
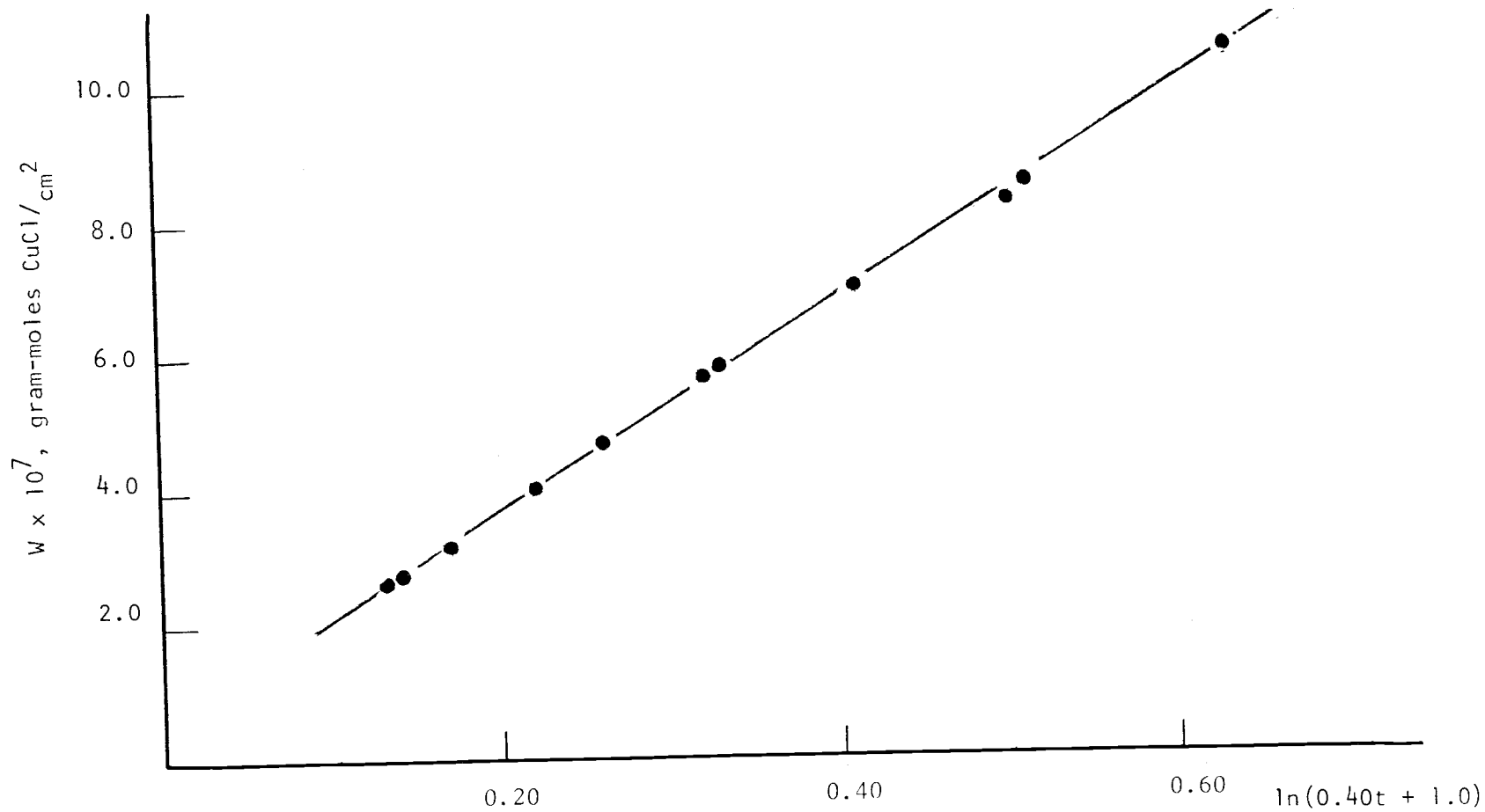
FIG. 21   BEST FIT LINE TO THE RATE LAW OF THE FORM

$$W = K_1 \ln (K_2 t + 1.0)$$

1.00 atm. Chlorine
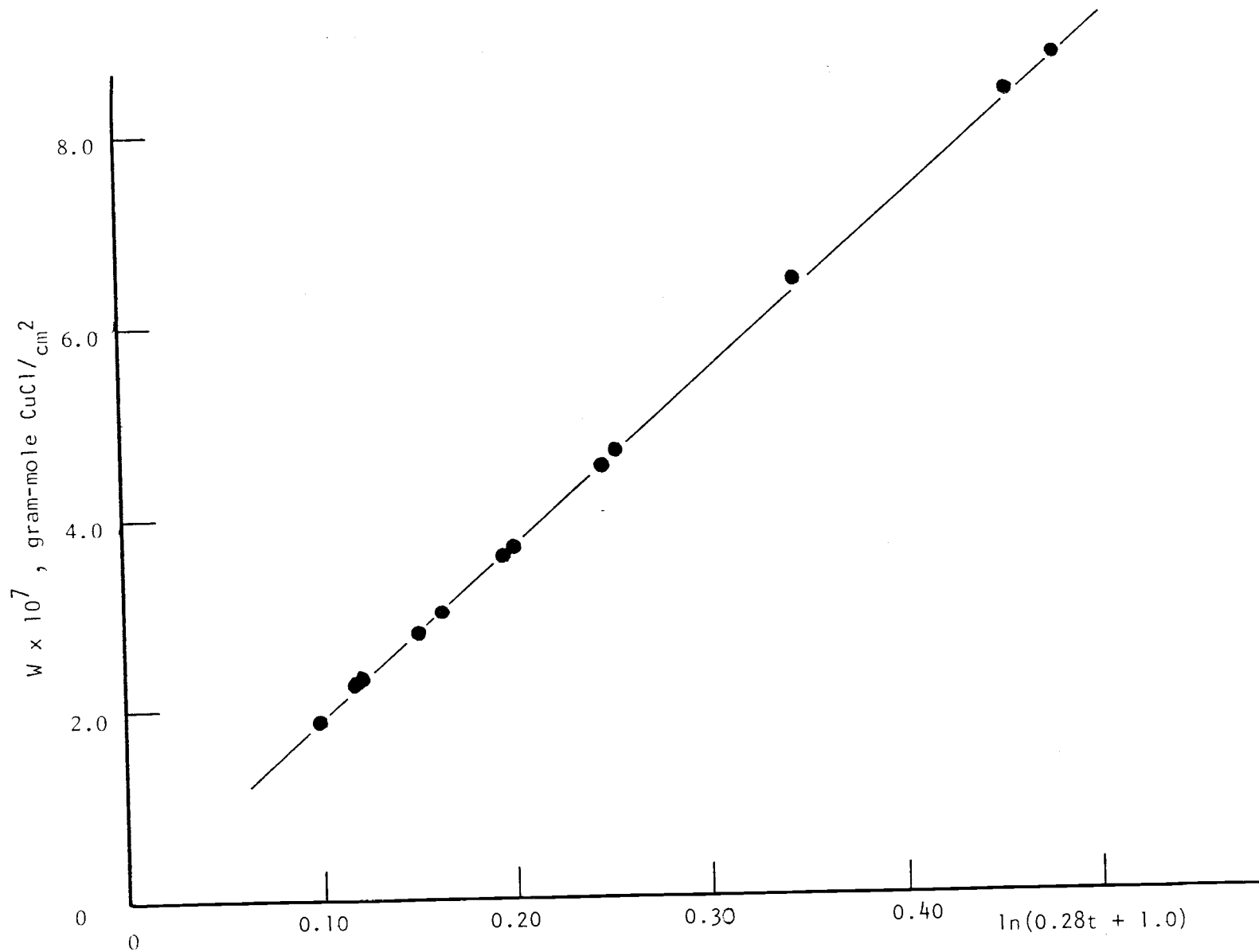
FIG. 22   BEST FIT LINE TO THE RATE LAW OF THE FORM $W = K_1 \ln (K_2 t + 1.0)$

0.440 atm. Chlorine
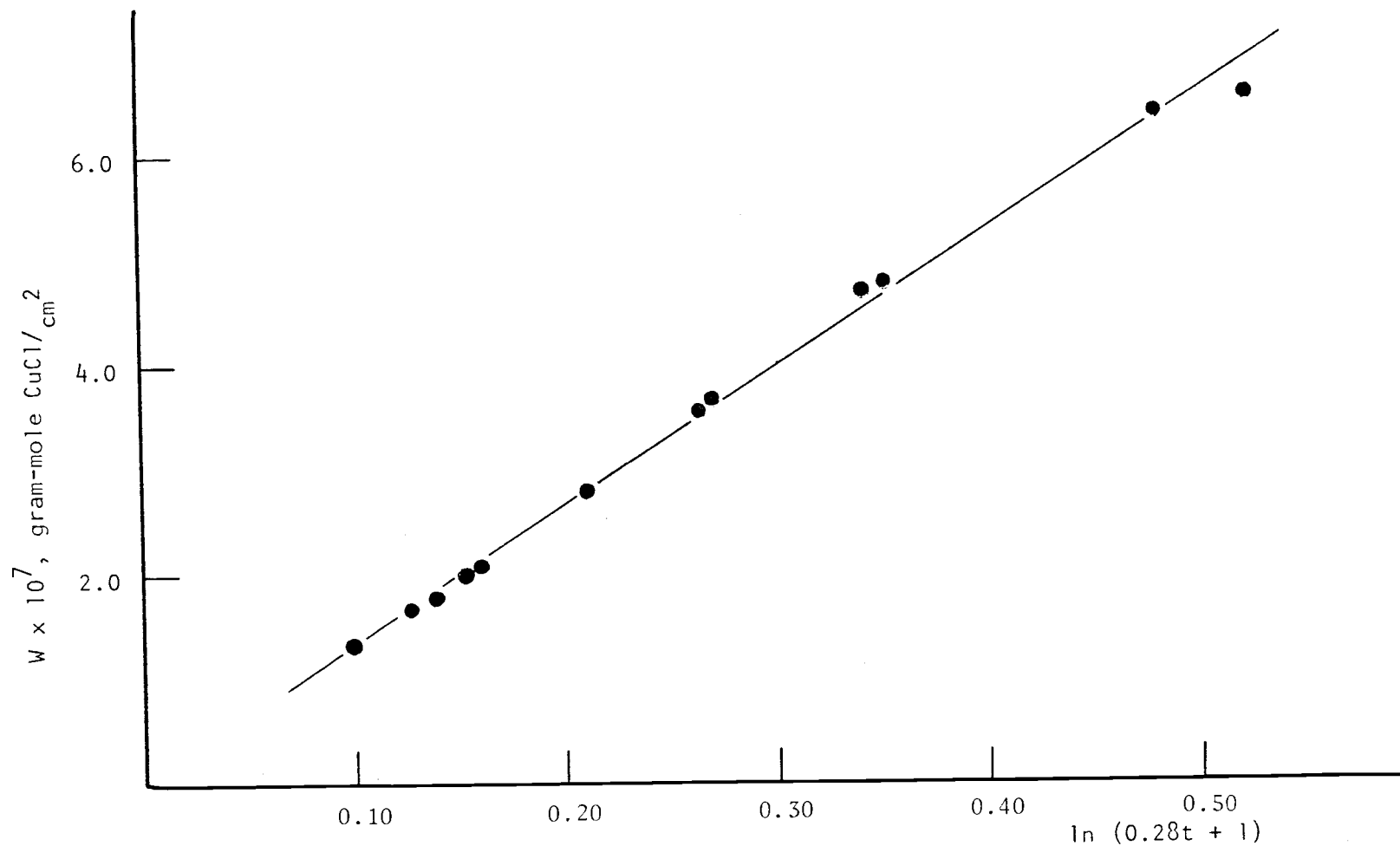
FIG. 23   BEST FIT LINE TO THE RATE LAW OF THE FORM $W = K_1 \ln (K_2 t + 1.0)$

0.210 atm. Chlorine

TABLE 8. Comparison of W estimated from best fit equations
to the experimental data. (1.00 atm chlorine)

t	$W \left(\dfrac{\text{gram-mole CuCl}}{\text{cm}^2}\right)$ x 10^7		
(sec)	Experimental	Linear	Logarithmic
0.370	2.568	2.825	2.602
0.392	2.705	2.921	2.723
0.468	3.118	3.253	3.136
0.627	3.993	3.946	3.962
0.751	4.623	4.486	4.578
0.949	5.578	5.348	5.513
0.988	5.784	5.518	5.692
1.222	6.605	6.539	6.722
1.265	6.921	6.726	6.904
1.602	8.191	8.195	8.263
1.677	8.468	8.522	8.550
2.185	10.460	10.735	10.368

VI. DISCUSSION

The treatment of the experimental data in the previous chapter shows that the parabolic and cubic rate laws are not totally satisfied since the correlation coefficients for these equations are smaller than 0.990. The linear and logarithmic rate laws both have the correlation coefficients higher than 0.990. It seems that the logarithmic rate law has a better fit compared to the linear rate law, but the differences are not significant. A comparison of the values estimated from the best fitted equations for the case 1.00 atm. with the experimantal data is shown in Table 8. However, the linear rate best fit lines do not cross the origin, e.g. at t= 0, W= 0. This is not consistent with the assumption that the product layers were completely removed by the electrochemical reaction in the electrolyte. Since it was verified that the limiting current was always obtained, the non-zero thickness at t= 0 is unlikely to be the case.

Even though good agreement between theoretical curves and experimental data does not represent unambiguous proof that the theory is applicable to the data, such agreement does represent a necessary condition for a correlation to exist. A knowledge of the pressure dependence of the rate of reaction is useful in determining the reaction mechanism.

The results from the best fitted equations give the values of K_1; 1.58 x 10^{-6}, 1.81 x 10^{-6}, 1.33 x 10^{-6}; for

the cases of 1.00 atm., 0.44 atm., and 0.21 atm. of chlorine partial pressures respectively. The variation of the rate constant, K_2, with the square root of the chlorine partial pressures is shown in Fig. 24. The data points for two pressure ranges, 1.00 atm. and 0.440 atm. form a good linear relationship according to Evans' theory. The data points in the 0.21 atm. pressure range is 51% higher than the value estimated from this straight line. Unfortunately, there is no explanation for this deviation.

A similar pressure dependence relation on the rate constant K_2 was observed by Sama[15] in his study of the oxidation of copper at room temperature by using an electrode process cell. It is well known that both copper oxide and copper chloride are p-type semiconductors. It is reasonably assumed that the crystal structure of the product layers formed in the oxygen-metal reaction or chlorine-metal reaction is similar to each other, the same mechanism would be expected to apply to both systems.

The analogy between oxygen-copper and chlorine-copper systems was observed by Dagoury and coworkers[5] in their study of reactions between gaseous chlorine and copper at room temperature.

At this point, it is believed that the chlorination of copper carried out in this investigation followed the Mutally-Blocking Pores mechanism developed by Evans.[7] According to this theory, it is assumed the slow reaction
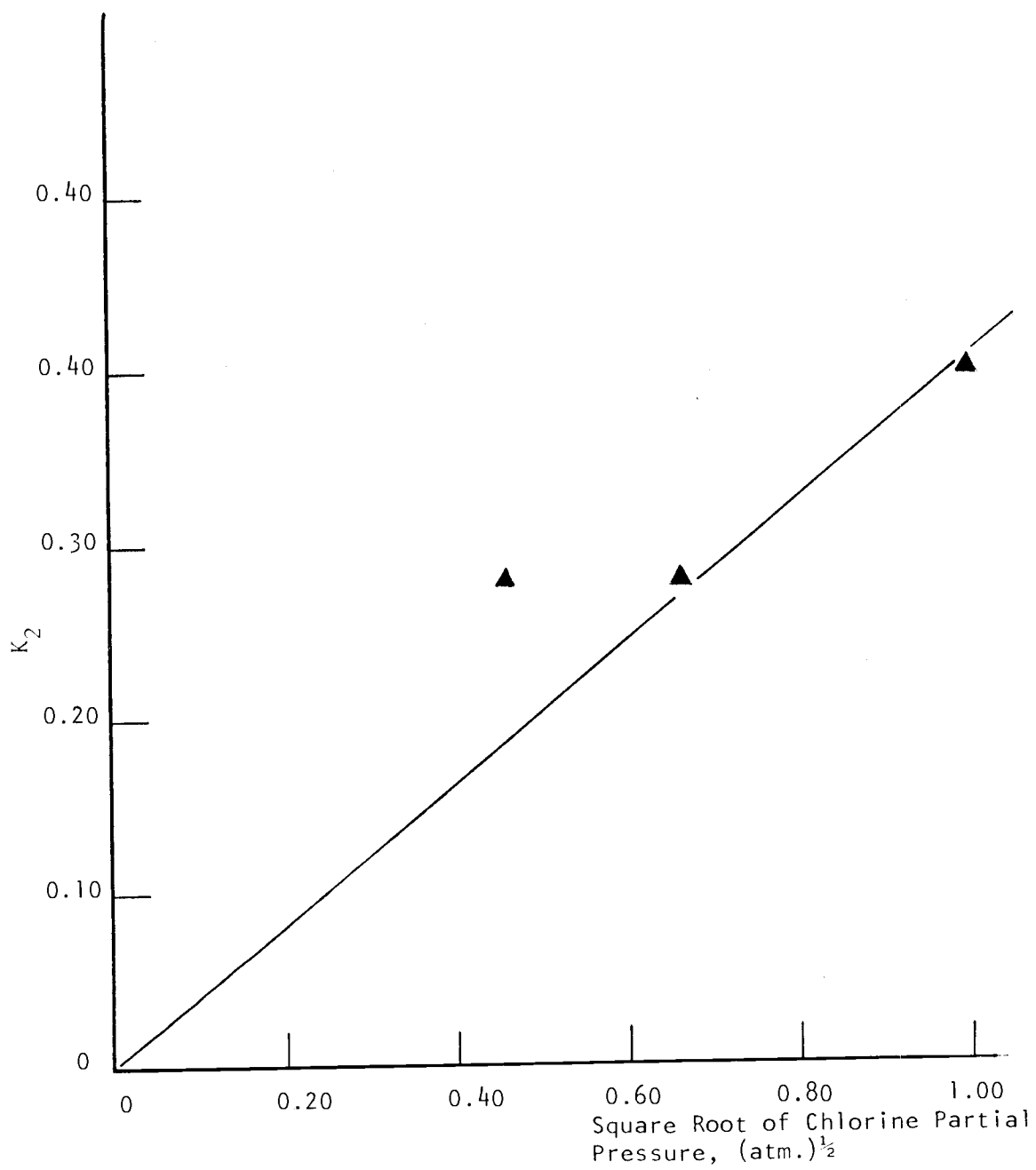
FIG. 24   PRESSURE DEPENDENCE OF THE CONSTANT K_2 OF THE LOGARITHMIC
RATE LAW

is that of the oxygen penetrating into the metal along
pores or paths of loosely arranged atoms, producing a
lateral pressure owing to the volume of the oxide being
greater than that of the metal destroyed, so that there is
progressive blockage of path as the reaction proceeds.
In the study of the structure of the oxide film on the
copper surface, Lawless and Gwathmey[10] found that at
atmospheric pressure the amount of orientation of the oxide
film decreased with increasing thickness. The decrease
was rapid at low temperatures but gradual at high temper-
atures. Randomness was observed in the formation of the
oxide film at low temperature. If the random nature of
the copper chloride existed, there was opportunity for
pore development, and the mechanism proposed by Evans is
logical. However, further knowledge of the structure
of copper chloride layers by a microscopic method would be
a stronger proof for supporting the theory.

VII. CONCLUSIONS

The following conclusions can be drawn from the study of the reaction between copper and chlorine gas at room temperature and chlorine partial pressures of 1.00, 0.44, and 0.21 atm.

1) The cuprous chloride was the only product of the reaction.

2) The kinetics of the chlorination of copper was best described by the logarithmic rate law as the followings

$$1.00 \text{ atm. } ; W = 1.58 \times 10^{-6} \ln (0.40\ t + 1.0)$$

$$0.44 \text{ atm. } ; W = 1.82 \times 10^{-6} \ln (0.28\ t + 1.0)$$

$$0.21 \text{ atm. } ; W = 1.33 \times 10^{-6} \ln (0.28\ t + 1.0)$$

where w is the weight of the copper chloride formed per unit area (gram-moles $CuCl/cm^2$) and t is exposure time in seconds. All these equations have correlation coefficients higher than 0.990. The mechanism of mutually-blocking pores developed by Evans is considered to be applicable to the growth of copper chloride layers.

NOMENCLATURE

a   constant

a_x activity of species x

A   constant

b   constant

c   constant

C_x concentration of species x (moles/liter)

D   diameter of cathode (cm)

E^O standard potential (volts)

E_O standard cell potential (volts)

E_{oc} open circuit cell voltage (volts)

f   fraction of cathode area exposed to gaseous atmospheres

$f_{\pm}$ mean molar activity coefficient

I   cell current (amperes)

I_D current due to diffusion of dissolved chlorine towards submerged cathode (amperes)

I_G current due to gas phase chlorination (amperes)

I_O limiting current of totally submerged cathode (amperes)

k_i constant

k_i' constant

K_i constant

n   constant

N   rotational speed (RPS)

P   partial pressure of oxidizing gas (mm Hg or atm.)

R   correlation coefficient

t   exposure time (seconds)

T   absolute temperature (^{O}K)

V   velocity (cm/second)

W   weight of chloride or oxide formed in film (gram-moles/cm^2)

w   width of copper cathode (cm)

X   average oxide or chloride film thickness (cm)

y   volume of oxidizing gas consumed (ml/cm^2)

Z   ln (K_2t + 1)

$\mathcal{F}$ Faradays constant

$\mathcal{N}$ number of pores

$\mathcal{N}_o$ constant

$\mathcal{R}$ gas constant

α constant

β constant

μ rate of formation of chloride (gram-moles/second)

π pi

BIBLIOGRAPHY

1. Bircumshaw, L.L. and M.H. Everdell. The Kinetics of the reaction between copper and iodine in aqueous (potassium iodide) solution. Part I. Journal of Chemical Society. 598-605. 1942

2. Brown, P.E. and coworkers. The Kinetics of the reaction of elementary fluorine with copper metal. Journal of Inorganic and Nuclear Chemistry. 1:202-212. 1955

3. Cabrera, N. and N.F. Mott. Theory of the oxidation of metals. Reports on Progress in Physics. 12: 163-184. 1948-1949

4. Campbell, W.E. and U.B. Thomas. The oxidation of metals. Transactions of the Electrochemical Society. 91: 623-640. 1947

5. Dagoury, G. and coworkers. Reactions of gaseous chlorine with copper. Metalix (Mons. Belg.) 6:173-177. 1966

6. Draper, N.R. and H. Smith. Applied regression analysis. John Wiley and Sons, Inc., 1966. 407p.

7. Evans, U.R. The corrosion and oxidation of metals. London, Edward Arnold. 1960. 1094p.

8. Ghez, R. and Y.J. Van der Meulen. Kinetics of Thermal Growth of Ultra-Thin Layers of SiO_2 on Silocon. Part II. Theory. Journal of the Electrochemical Society. 119:1100-1106. 1972

9. Gurian, M.I. Rotating silver-silver chloride electrode studies in gaseous chlorine environments. M. Sc. Thesis., Corvallis, Oregon State University. 1964 89 numb. leaves

10. Lawless, K.R. and A.T. Gwathmey. The structure of oxide films on different faces of a single crystal of copper. Acta Metallurgica. 4:153-163. 1956

11. Leidheser, H. Corrosion of copper, tin and their alloys. John Wiley and Sons, Inc., 1971 411p.

12. O'Donnell, P.M. and A.E. Spakowski. The fluorination of copper. Journal of the Electrochemical Society. 111:633-636. 1964

13. Redfern, B.A.W. and C.F. Wilford. The reaction between Cu and iodine in acetone. Corrosion Science. 4:877-885. 1969

14. Robinson, R.A. and R.H. Stokes. Electrolyte solutions. 2nd ed. London, Butterworths. 1959. 559p.

15. Sama, D.A. Metal oxide-oxygen electrodes and fuel cells. D.Sc. Thesis. Cambridge. Massachusetts Institute of Technology, 1960 129 numb. leaves

16. Wagner, C. Beitrag zur Theorie des Anlaufvorgangs. Zeitschrift fur Physikalische Chemie B21:25-41 1933

17. Wagner, C. Dissociation of molecular O_2 as the rate-determining step during the initial stage of the oxidation of Ni at 250^OC. Corrosion Science. 10:641-647. 1970

APPENDIX

Data of Polarization Run

f = 0.721

N = 0.950 RPS

2M KCl

1atm Cl_2

Cell Current (Volts)	Cell Voltage (Volts)	Cathode Polarization (Volts)
0.000	0.950	0.000
0.102	0.851	0.098
0.220	0.810	0.115
0.351	0.784	0.142
0.470	0.740	0.148
0.600	0.710	0.159
0.705	0.680	0.170
0.840	0.630	0.199
0.948	0.570	0.218
0.997	0.450	0.250
1.002	0.390	0.410
1.007	0.705	0.100

RAW DATA

* Partial Pressure of Chlorine : 1.0 atm

* f = 0.721

* Area of the cathode : 22.0 cm^2

  * TOTALLY SUBMERGED

N (RPS)	I_O (Ampere)
0.45	0.168
0.79	0.216
1.14	0.270
1.32	0.300
1.75	0.357
2.24	0.420

  * PARTIALLY SUBMERGED

N (RPS)	I (Ampere)	I_O (interpolated)
0.330	0.775	0.151
0.43	0.820	0.168
0.45	0.830	0.170
0.57	0.890	0.188
0.59	0.881	0.192
0.73	0.965	0.210
0.76	0.960	0.215
0.96	1.010	0.243
1.15	1.050	0.269
1.54	1.110	0.325
1.84	1.160	0.370
1.95	1.170	0.383

RAW DATA

* Partial Pressure of Chlorine = 0.440 atm
* f = 0.721
* Area of the cathode = $22.0cm^2$

  * TOTALLY SUBMERGED

N (RPS)	I_o
0.37	0.072
0.47	0.086
0.61	0.103
0.92	0.129
1.06	0.144
1.58	0.192
2.00	0.225

  * PARTIALLY SUBMERGED

N (RPS)	I (Ampere)	I_o (interpolated) (Amperes)
0.33	0.630	0.074
0.35	0.640	0.075
0.49	0.690	0.088
0.70	0.720	0.108
0.73	0.723	0.110
0.91	0.740	0.125
0.94	0.747	0.130
1.15	0.770	0.148
1.26	0.785	0.160
1.58	0.810	0.189
1.59	0.810	0.190
1.96	0.820	0.225

RAW DATA

* Partial Pressure of Chlorine = 0.210 atm.
* f = 0.721
* Area of the cathode = 22.0 cm^2

TOTALLY SUBMERGED

N (RPS)	I_o (Amperes)
0.19	0.042
0.89	0.072
1.38	0.096
1.70	0.111
2.04	0.126

PARTIALLY SUBMERGED

N (RPS)	I (Amperes)	I_o (interpolated) (Amperes)
0.30	0.430	0.043
0.33	0.460	0.045
0.48	0.500	0.050
0.50	0.510	0.051
0.65	0.517	0.062
0.67	0.520	0.064
0.87	0.530	0.073
1.17	0.532	0.083
1.23	0.540	0.089
1.38	0.546	0.095
1.51	0.551	0.102
1.93	0.569	0.121