I. INVESTIGATION OF THE DIRECT CURRENT

DETERMINATION OF ELECTROLYTIC CONDUCTIVITY

II. MEASUREMENT OF STRAIN POTENTIALS

by

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ABSTRACT - part I

The cell constant of a direct current conductivity cell was measured using as a standard 0.1M and 0.01M potassium chloride solutions and specific conductivity data obtained by G. Jones and M. Prendergast.[23] The results obtained for either of the solutions were exact to within one or two parts in ten thousand, but a difference of 0.6% existed between the two cell constant values. In order to investigate more exactly the nature of this variation, other concentrations were measured using as a standard the data obtained by T. Shedlovsky, A.S. Brown, and D.A. MacInness.[24]

Certain factors in the design of a direct current cell have been considered and suggestions for future work offered.

ABSTRACT - part II

Studies have been made of the anodic properties of strained copper wire in the cell

$$Cu \text{ (strained)} \quad | \quad CuSO_4 \quad | \quad Cu \text{ (normal)}.$$
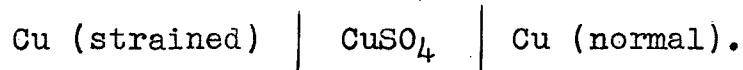
Two copper wires were immersed in copper sulphate solution. Weights were added to one of these and the potential difference measured potentiometrically or with a vacuum tube volt-meter. The results obtained show that

(1) the relaxation of this potential is approximately exponential,
(2) very little potential is developed until a critical strain is applied,
(3) after a certain strain has been applied the peak potential developed becomes constant with increasing strain,
(4) the magnitude of the effect is dependent on the concentration of the solution,
(5) the magnitude and direction (anodic or cathodic) of the potential is dependent upon the components of the electrolyte.

ACKNOWLEDGEMENT

CONTENTS

TABLES

ILLUSTRATIONS

INVESTIGATION OF THE DIRECT CURRENT

DETERMINATION OF ELECTROLYTIC CONDUCTIVITY

I. INTRODUCTION

In a consideration of the electrolytic properties
of solutions, one of the most fundamental types of exper-
imental evidence has been that of conductivity. Modern
theories of solutions of electrolytes, most notably the
Debye-Hückel theory of interionic attraction, must there-
fore be considered in the light of experimental conduc-
tance measurements. The main emphasis to date has been
in the exploration of very dilute solutions where theore-
tical calculations from modern theories are possible. An
insight regarding the effects of concentration, type of
electrolyte, and type of solvent is gradually being made.
In this regard, since most measurements have been made
using H_2O as a solvent, one of the more interesting poss-
ibilities is a study of solutions in D_2O, a solvent with
the same chemical properties as H_2O but with many differ-
ent physical properties. This research has therefore been
planned to develop a direct current method of conductiv-
ity measurement, and apply it to the measurement of pot-
assium chloride solutions in D_2O. The success obtained to
date with the development and testing of a direct current
method for conductivity measurement is reported in this
thesis.

HISTORY

In 1888, a comparison between alternation and direct current methods of measuring conductivity was made by Sheldon[1]. The irreproducibility of a resistance measurement using direct current was shown to be due to the polarization produced at the electrodes. Thus today, although some research has been done by direct current methods, most existing conductance data have been obtained by using an alternating current source.

The first research paper on direct current conductance was published by E. Newbery[2] in 1918. Using a cell with four calomel electrodes, two acting as current carriers and two as probes to measure a voltage drop, he measured the conductivity of several concentrated electrolytes but obtained agreement with the existing alternating current data only within six tenths of one percent. Two years later, E.D. Eastman[3] used a modified bridge adapted to both alternating and direct current to measure the conductivity of a one normal potassium chloride solution. He observed a difference of about seven parts in one hundred between alternating and direct current values but this difference can be attributed to the effects of polarization that had not been fully eliminated. Another approach to direct current measurement was made in 1921 by C. Marie and W.A. Noyes Jr.[4] The effect of polarization was partially removed by using hydrogen electrodes on platinized platinum

and measuring the resistance directly. However, the results
obtained deviated about one percent from Kohlrausch's data.
In 1935, J.N. Brönsted and R.F. Nielsen[5] used this method to
measure solutions of hydrochloric acid at concentrations as
low as 0.002N. Although the effects of polarization were fur-
ther eliminated by closing the circuit for less than one-
half of a second, the results varied about fifteen one-hund-
redths of one percent from the best existing alternating
current data. Another method was used by L.V. Andrews and
W.E. Martin[6] to study the conductance of potassium chloride
solutions down to 0.0005N; their technique, however, is open to
criticism and their results are of doubtful accuracy accord-
ing to modern standards. The best conductivity values
obtained by a direct current method are those reported by
A.R. Gordon[7] and his collaborators since 1941. By redesigning
the cell used by Newbery, and replacing the calomel electrodes
by silver-silver chloride electrodes, conductivity values
have been reported for several electrolytes at various
temperatures agreeing within two or three one-hundreths of a
percent with the best alternating current data. Another
direct current determination of potassium chloride solutions
has been made recently by R.F. Palmer and A.B. Scott[8] but
several precautions were overlooked and their results are not
as accurate as those reported by Gordon.

THEORY

The Debye-Hückel Theory.

In the early considerations of the theory of solutions of electrolytes the decrease of equivalent conductance as the concentration increased was attributed to a decreasing number of ions. This theory led to the equation used for the degree of dissociation proposed by Arrhenius which is

$$\propto = \frac{\Lambda_c}{\Lambda_o}$$

in which $\propto$ is the classical degree of dissociation and Λ_c and Λ_o are respectively the equivalent conductance at concentration "c" and at infinite dilution. Although this equation held well for weak electrolytes, it could not be used with data obtained for strong electrolytes, and so it became evident to many observers that a new theory should be proposed. The successful introduction of such a theory was due to P. Debye and E. Hückel[9] who interpreted electrolytic phenomena by considering the properties to be due to an interplay of the thermal forces and the coulombic forces existing in the electrolyte. They applied certain fundamentals of electrostatics and statistical mechanics to the electrolytic system and by making suitable approximations arrived at proper mathematical expressions.

The Ionic Atmosphere. It was shown by Debye and Hückel that a statistical charge distribution of opposite sign, called the ionic atmosphere, existed around any given ion in a solution. This ionic atmosphere is centrally symmetrical

and its presence causes the potential due to the considered
ion to be lowered by an amount given by the expression

$$\psi_i = - \frac{\epsilon \mathcal{K}}{D}$$

where ψ_i is the potential due to the ionic atmosphere, ϵ
is the electronic unit charge, "D" is the dielectric const-
ant of the solvent and $\mathcal{K}$, an important quantity in the
Debye-Hückel theory is defined by the equation

$$\mathcal{K} = \sqrt{\frac{8 \pi n \epsilon^2}{D k T}}$$

in which "n" is the number of ions of each kind in a unit
volume, "k" is the Boltzmann constant and "T" is the absol-
ute temperature. $\mathcal{K}$ has the dimensions of reciprocal
length, and according to Debye and Falkenhagen,[10] $1/\mathcal{K}$ is the
distance at which the ionic atmosphere is most dense. Thus,
$1/\mathcal{K}$ is called the thickness of the ionic atmosphere.

The Electrophoretic Force. When an external potential
is applied to an electrolytic solution, a selected ion will
move with a velocity "v_i" which is dependent only on the
limiting ion conductance λ_o. However, the ionic atmosphere
must move in the opposite direction, so that each element of
it will be acted on by a force per unit volume, which de-
pends on the applied potential and on the electrical density.
This causes a retardation force, termed the electrophoretic
force, which is equivalent to an increase in the viscosity
of the medium. By applying Stokes' Law, Debye and Hückel
calculated the magnitude of this resistance.

The Relaxation Force. Another mechanism tending to decrease the equivalent conductance of an electrolyte is the relaxation force. This force arises from the fact that when a central ion moves, the ion atmosphere moves with it, but there is a time lag or relaxation time involved which gives the unit an asymmitrical form. This is illustrated in figure 1 where the central ion, initially at "a" has now moved to "b", but the atmosphere has remained stationary. The magnitude of this time lag is only of the order of 10^{-8} seconds, but it is sufficient to cause an electrostatic force, independent of the viscosity of the medium, which opposes the motion of the ion.

FIGURE 1
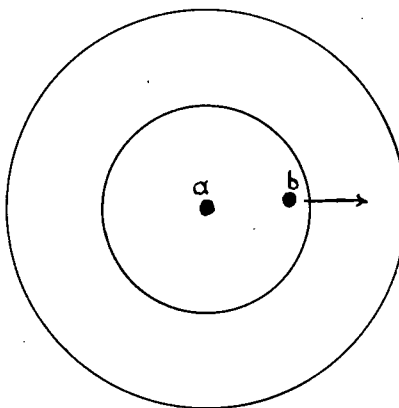
The derivation of the exact mathematical relationship for the relaxation force is quite elaborate, but it is worthy to note that the actual value of it depends on λ_o.

The Debye-Hückel-Onsager Equation.

The linear relationship between the equivalent conductance and the square root of the concentration had been observed in the nineteenth century by Kohlrausch but no theoretical explanation was presented. In 1927, L. Onsager[11] equated

the various forces present in a conducting electrolyte at
at equilibrium based on the Debye-Hückel concept and thus
derived the following expression for λ_o, the equivalent
ion conductance.

$$\lambda = \lambda_o - \left[\frac{0.9834 \times 10^6}{(DT)^{3/2}} w \lambda_o + \frac{28.94 z_i}{(DT)^{1/2} \eta} \right] \sqrt{(z^+ + z^-)C}$$

in which "z^+" and "z^-" are the valences, "D" and η are the
dielectric constant and viscosity of the solvent, and "T" is
the absolute temperature. Also

$$W = z^+ z^- \frac{2q}{1 + \sqrt{q}} \quad \text{and} \quad q = \frac{z^+ z^- (\lambda_o^+ + \lambda_o^-)}{(z^+ + z^-)(z^+ \lambda_o^- + z^- \lambda_o^+)}$$

If we consider a uni-univalent electrolyte in a given solvent
at a given temperature, the Onsager equation reduces to

$$\lambda = \lambda_o - \left[\theta \lambda_o + \tfrac{1}{2} \sigma' \right] \sqrt{C}$$

in which θ and σ' are constants. By applying Kohlrausch's
law of independent migration of ions, an equation for Λ_o
can be obtained. Thus,

$$\Lambda = \Lambda_o - \left[\theta \Lambda_o + \sigma' \right] \sqrt{C}$$

This equation is similar to the one proposed by Kohlrausch
for the conductance of strong electrolytes, but in the
Onsager equation the value of the constants is predicted and
assigned an exact physical significance.

A verification of the validity of this equation is only possible by making precise measurements at low concentrations. This has been successfully accomplished by many different investigators[12] for different types of salts and in almost all cases the data obtained in the laboratory agree with the theory for dilute solutions.

The Shedlovsky Equation.

Because the approximations made in deriving the Debye-Hückel-Onsager equation limit its use to dilute solutions, many additions to this equation have been proposed. The nature of these additions may be theoretical, semi-empirical or empirical. One of the more important extensions is the semi-empirical equation proposed by T. Shedlovsky[13]. In order to interpret the data obtained at higher concentrations Shedlovsky extended the Onsager equation by considering additional concentration terms. Thus for most strong electrolytes the data are adequately expressed by the equation

$$\frac{\Lambda + \sigma\sqrt{C}}{1 - \theta\sqrt{C}} = \Lambda_0 + BC$$

where "B" is an empirical constant. In some cases it is necessary to improve this equation by adding two more terms thus obtaining the equation

$$\frac{\Lambda + \sigma\sqrt{C}}{1 - \theta\sqrt{C}} = \Lambda_0 + BC + DC\log C - EC^2$$

Although the Shedlovsky equation was derived from experimental data, the terms "BC", "DC", and "log C" are of the form required by consideration of the approximations made by Debye and Hückel; hence the term "semi-empirical".

The Limiting Conductance.

In the foregoing discussion, the constant Λ_0 appeared as an important factor in the Onsager equation and so the methods of obtaining its value will be considered. The first is that suggested by Kohlrausch, where the conductance data are extrapolated to infinite dilution. This method generally gives agreement withthe theoretical Onsager slope, but has the disadvantage of depending on the data obtained from very dilute solutions. Another method of extrapolation depends on some extension of the Onsager equation, usually the one proposed by Shedlovsky. In this case, the expression $\dfrac{\Lambda + \partial\sqrt{C}}{1 - \theta\sqrt{C}}$ is plotted against the concentration and the line extended to the zero axis. Because of the semi-empirical nature of the equation, this method of obtaining Λ_0 has given excellent results. A third method of obtaining Λ_0 is realized in Kohlrausch's law of independent mobility of ions. Because the limiting conductance of an ion is a property of the ion constituent itself, we may write $\Lambda_0 = \lambda_0^+ + \lambda_0^-$. The limiting ion conductances can be obtained from transference data and the value of Λ_0 is thus secured. This method is extensively used for calculating Λ_0 for weak electrolytes.

II. EXPERIMENTAL METHODS AND RESULTS

DESCRIPTION OF APPARATUS

The Cell

The conductance cell used in this research (figure 2) is of pyrex glass and is similar to the cells used successfully by Gordon and his collaborators. It was made considerably smaller for the limited supply of solvent (D_2O) for which it was intended. The total volume of the cell is 140 milliliters. The center section is 3 centimeters in diameter and the probe electrodes, P and P', are 8.5 centimeters apart. The tube T_1 was used to fill the cell, while the tube T_2 can be used to conveniently save valuable solvent. Before use, the cell was boiled with concentrated hydrochloric acid, rinsed with doubly distilled water, and thoroughly steamed out. After this treatment the cell showed an even wetting on its surface when rinsed. It was never allowed to dry, and when not in use was always filled with the best conductance water available.

The Main Electrodes. The two main current-carrying electrodes (M and M') are made of heavy platinum foil joined to the copper leads by means of platinum wire which is fused into a soda glass rod. The platinum surfaces were silver plated and dipper into fused silver chloride with techniques described later.

The Probe Electrodes. If probe electrodes are to serve as a means of measuring potential difference it is necessary that their width, with respect to the path of the current,
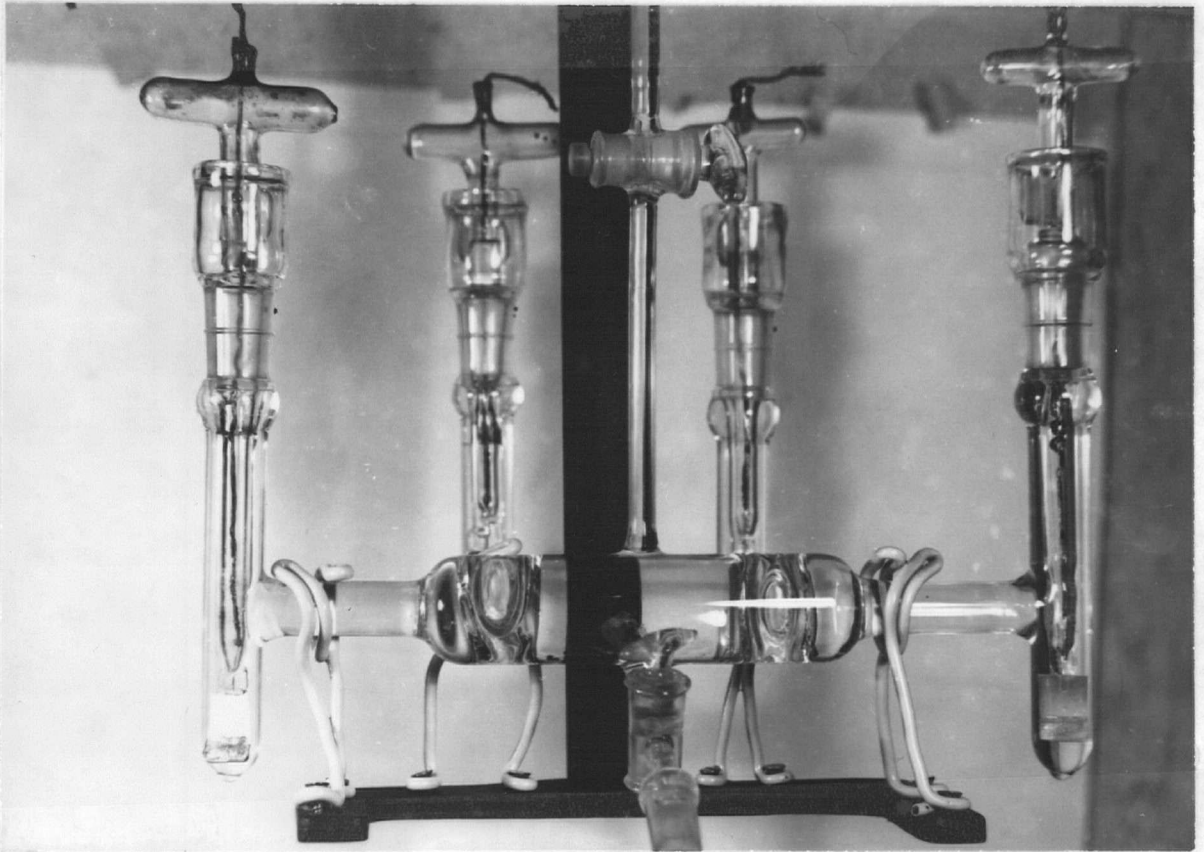
PLATE 1   THE CONDUCTANCE CELL .
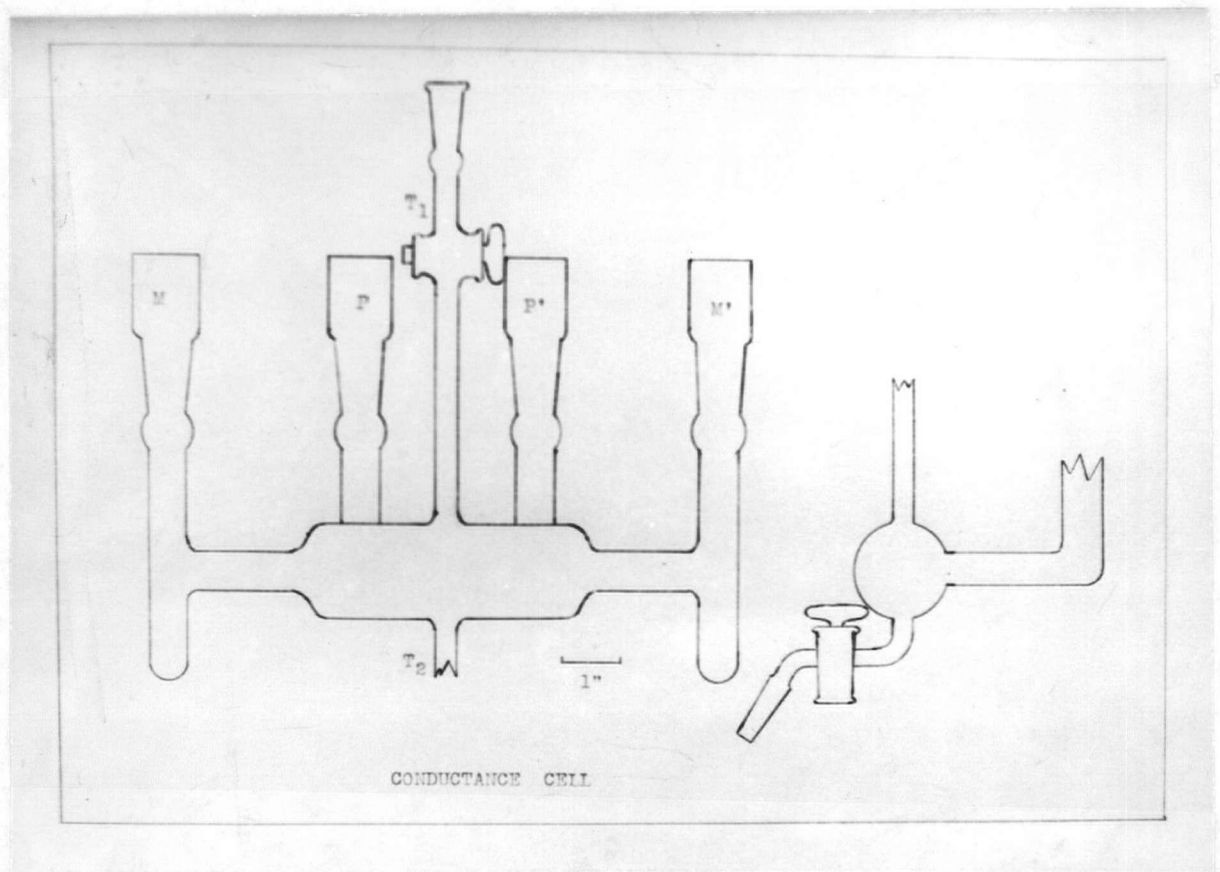
FIGURE 2   THE CONDUCTANCE CELL.

be small or there will exist a sensible ohmic drop across their surface. The electrodes used as probes by Gordon (figure 3a) adhere to this requirement, but it has been found in this laboratory that a satisfactory seal of the platinum disc to the glass is not easily obtained. The result-ant contamination of the mercury contact results in extraneous potentials which invalidate any potential measurement.[14] The probe electrodes used in this research are shown in figure 3b. Platinum wire (diameter 0.081 centimeters) was sealed into soda glass and caged to prevent any mechanical disturbance on the active surface which would effect the potential of the electrodes.[15] These wires were made into silver-silver chloride electrodes according to the method of A.S. Brown.[16]
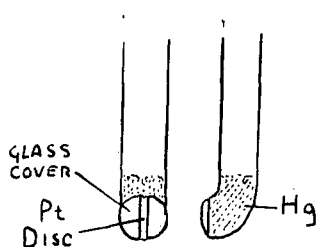
FIGURE 3a
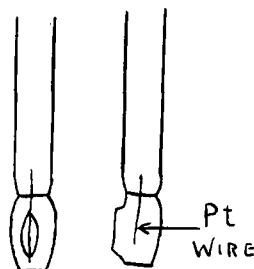
FIGURE 3b

The Thermostat.

The thermostat consisted of a rectangular vessel 46 cm. x 28 cm. x 28 cm. placed in a large wooden frame and insulated with three inches of sawdust. The vessel was filled to a constant level with Imperial D. B. oil 52 circulated by a four vane propellor placed as close to the centre of

the bath as possible. The heating element was a coil of nichrome wire, 22 gauge, with a resistance of fifty ohms wound around a cooling coil carrying a slow steady stream of water. The mercury thermostat[17] was constructed from a coil of pyrex glass in order to obtain a large surface to volume ratio. A metal to glass seal was obviated by lubricating the stopcock with graphite, the other electrical contact taking place in a capillary. The relay circuit was constructed in this laboratory and is shown in figure 4. The temperature was determined with a Beckmann thermometer calibrated at 25 ± 0.002 degrees centigrade with a platinum resistance thermometer having an N.B.S. certificate.

During a run, the bath temperature did not vary by more than 0.01 degrees and it is believed that the variation within the cell was considerably less.

The Measuring Circuit.

The resistance of the cell was obtained by measuring the voltage drop across the probe electrodes and the voltage drop across a 1000.0 ohm series resistance calibrated by the manufacturer. A Rubicon Potentiometer type B was used in conjunction with a Leeds and Northrup galvanometer type HS with a sensitivity of 1×10^{-11} amps per millimeter scale deflection. The Weston standard cell used was checked periodically with two standard cells kept for that purpose. An electronic current regulator which was a modification of the "constant current" circuit of D.J. LeRoy and A.R. Gordon,[18] gave satisfactory results after a "breaking in" period of about 100 hours.
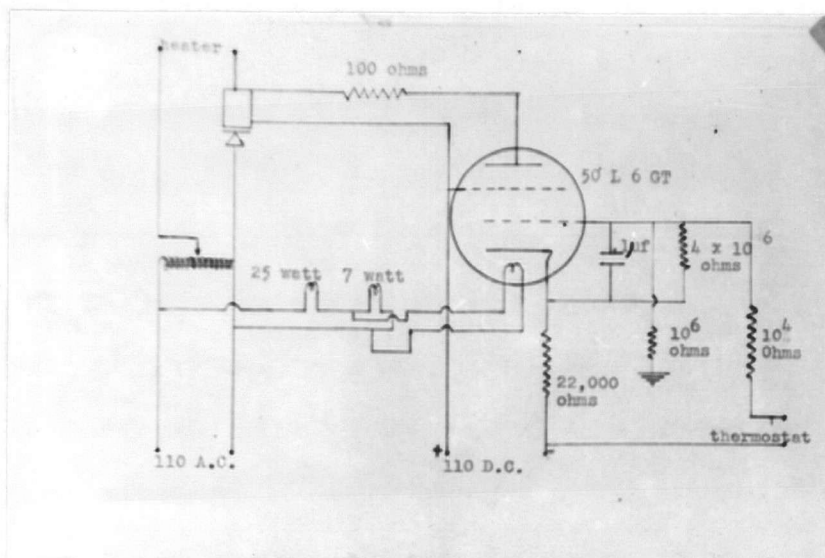
FIGURE 4   THERMOREGULATOR RELAY CIRCUIT.
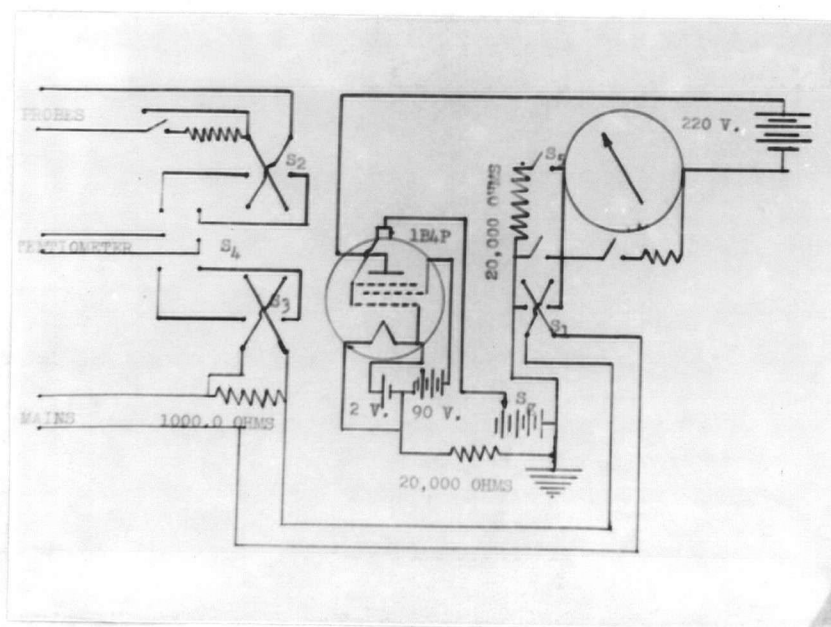
FIGURE 5   CURRENT REGULATOR AND COMPLETE

MEASURING CIRCUIT.

EXPERIMENTAL PROCEDURE.

Purification of Materials.

Conductivity Water. The conductivity water was obtained by redistilling distilled water from alkaline potassium permanganate solution in a copper still. In this apparatus the steam passed through a series of baffle plates where traces of spray were separated from the vapor. The vapor was then passed through a copper condenser where it was fully condensed and collected in a five liter pyrex flask fitted with a pyrex siphon tube for withdrawing the water. The specific conductance of the water so obtained was 3 to 3.5 x 10^{-6} mhos.

Potassium Argento Cyanide. Silver cyanide was precipitated by adding potassium cyanide solution containing 135 grams per liter dropwise to an agitated solution of silver nitrate containing 315 grams per liter maintained at 0° centigrade in an ice bath. Bakers C.P. potassium cyanide and Mallinkrodt C.P. silver nitrate were used. The precipitate was washed twenty times with conductivity water and dried in a vacuum desiccator. It was then boiled with an excess of potassium cyanide,[19] filtered through a pyrex sintered glass filtering funnel, and allowed to cool. The precipitated crystals of potassium argento cyanide were dried and recrystallized four times by dissolving 50 grams of the salt in 100 milliliters of boiling conductivity water. The hot solution was filtered and the resulting crystals dried in a vacuum desiccator and stored in a brown glass bottle. All glassware used in this and other purifications was cleaned with hot

chromic acid, washed thoroughly with water, and filled with distilled water when not in use.

Sllver Chloride. Silver nitrate solution containing 11.228 grams of the salt was added dropwise to 500 milliliters of an agitated solution containing 5.233 grams of potassium chloride. The precipitated silver chloride was protected from decomposition by keeping the reaction vessel in an ice bath and by keeping it covered with red cellophane. It was washed 18 times with distilled water, dried in a vacuum desiccator, and stored in a brown glass bottle. Both salts used had been recrystallized twice by dissolving them in conductivity water and filtering through a pyrex sintered glass funnel.

Potassium Chloride. The Merck reagent grade potassium chloride used in this research to prepare conductance solutions was recrystallized three times by dissolving 450 grams of the dry salt in a liter of conductivity water. It was filtered through a pyrex sintered glass filtering funnel each time and dried in a clean electric oven. After drying it was stored in clean glass stoppered product bottles shielded from atmospheric contamination by inverted beakers. Two different samples of the thrice recrystallized salt were prepared but no difference was observed between the conductance of their solutions.

Preparation of Silver-Silver Chloride Electrodes.[16]

Main Electrodes. The platinum surfaces of the main electrodes were boiled in concentrated nitric acid[20] and thoroughly rinsed in conductivity water. The silver plating solution was prepared by dissolving 10 grams of the potassium argento cyanide in one liter of conductivity water. Free cyanide was reduced to a minimum by adding enough dilute silver nitrate to produce a faint cloud of silver cyanide.

The electrodes were supported in the electrolyte, contained in 125 milliliter electrolytic beakers, by inserting into holes drilled in lucite covers. Platinum anodes were used. The catholyte was gently stirred by pyrex glass rods driven by light stirring motors and protected from anode contamination by a salt bridge containing the silver plating solution.

The two main electrodes of each cell were electrolysed in series for six hours at a current density of one milli-amp per square centimeter. After plating, they were carefully rinsed and kept in concentrated ammonium hydroxide (usually overnight) in order to remove excess cyanide. They were then thoroughly rinsed with conductivity water and the bottom half of the plated foil was dipped in silver chloride fused in a platinum crucible.

Probe Electrodes. The probe electrodes were cleaned in hot chromic acid[14] (because they had been flame annealed) and boiled in conductivity water for eight hours before plating.

They were silver plated in the same manner as the main elec-
trodes at the same current density, but after standing in
ammonium hydroxide and rinsing with conductivity water, **they**
were anodized in 0.1 normal hydrochloric acid solution pre-
pared from Nichols C.P. reagent. When first used electrodes
prepared in this manner may have a potential difference as
high as 0.07 millivolts, but after continued use the potential
difference is seldom greater than 0.015 millivolts and quite
stable throughout a single run.

When not in use both the probe and main electrodes were
kept in conductivity water.

Preparation of Solutions.

Three balances were used for weighing in this research.
A large Oertling (London) balance with a capacity of two kilo-
grams and an average sensitivity of 0.3 scale divisions per
milligram was used in weighing water for the solutions. A
Henry Troemner (Philadelphia) analytical balance with an aver-
age sensitivity of 7 scale divisions per milligram was used
to weigh the potassium chloride samples for 0.1 demal and
0.01 demal standard solutions. All weighings on these two
balances were made by the transposition method, and were
corrected to vacuum using handbook values of densities.[21]
Potassium chloride samples weighing less than 0.7 grams
were weighed on a Sartorious-Werke (Göttingen) semi-micro
balance with a sensitivity of ten scale divisions per 0.1

milligrams. The weights were corrected to vacuum but were not transposed. All weights used were carefully calibrated to the same basis against a standard set of class S weights certified by Voland and Sons, October 25, 1943.

In practice a potassium chloride sample was weighed to the nearest ten milligrams in an accurately tared platinum weighing boat. The sample was then dried in a vacuum desic= cator at a pressure less than 0.1 millimeters of mercury and a temperature of 100° centigrade for not less than twelve hours. It was cooled in a clean dry desiccator and weighed to better than one part in ten thousand. After weighing, the boat and sample were immediately transferred to an accurately tared solution flask and the required solvent added to the nearest five grams by measuring it in a five hundred milliliter graduated flask. The solution was weighed and any addition- al solvent was added by means of a one milliliter pipette. The final weight of solution, corrected for vacuum, was exact to ten milligrams or one part in one hundred thousand. Where it was necessary to convert from mass to volume concentrations, the data of G.P. Baxter and C.C. Wallace[22] were employed.

All glassware used was cleaned with hot chromic acid and thoroughly rinsed with boiling conductivity water. The solution flasks were wiped with "Kleenex Tissues" before weighing. The platinum boats were cleaned by boiling first in concentrated nitric acid and then in conductivity water, and were handled

with tongs kept in a desiccator and never used for other
purposes. Before weighing a sample, the boats were wiped free
of any potassium chloride that may have adhered to the outside
using lens paper manufactured by Scientific Supplies Company.

Transfer of Solutions.

The solutions were transferred from the weighing flask
to the cell by applying air pressure to the surface of the
liquid and forcing the solution through a long tube, fitted
with a standard taper, into the filling tube of the cell.
The air used was passed through concentrated potassium
hydroxide, concentrated sulphuric acid, and finally through
conductivity water. This method of transfer effectively
prevented any possible contamination from atmospheric fumes.

Before each run, the cell and electrodes were rinsed
six to eight times with the solution to be measured. The
cell was then filled and the electrodes which had been standing
in a sample of the solution were placed in position. Because
the exact orientation of the electrodes is critical, they
were adjusted to the same position each time by means of a
fine line on the male and female members of the tapers.

When filled with solution the cell was immersed in
the thermostat, where it attained thermal equilibrium within
about twenty minutes, after which its resistance remained
constant. It was shown that refilling the cell and repeating
the measurement gave the same resistance value, and so a

second measurement was frequently omitted.

Measurement of Resistance.

The current from the thermionic regulator (figure 5) was passed through the cell in either direction by closing the reversing switch S_1. With S_1 closed S_5 connecting a 20,000 ohm plate resistance in parallel with the cell was opened to allow the full current to pass through the solution. S_2 and S_3 are reversing switches to the probes and standard resistance respectively. When set in their proper positions, either the voltage across the probes or across the standard resistance can be selected by changing S_4. In practice, the voltage across the standard resistance E_s was measured then, without changing the direction of the current, S_4 was changed so that the voltage across the probes E_p could be obtained. The current was reversed, E_s and E_p again measured, and the average values recorded. The current through the cell was varied from 0.14 to 0.29 milliamps by changing the negative grid potential from one and one-half volts to 6 volts by means of a selector switch S_g.

For the given current, the value of the resistance of the solution between the probes was calculated from the formula, $R = \dfrac{E_p}{E_s} \times 1000.0$ (1000.0 ohms being the value of the standard resistance.) The results obtained indicate that for a given solution the resistance measurement was independent of the current and easily reproduced to within 0.02%.

Solvent Conductance.

The solvent conductance was measured for each solution immediately preceding the measurement on the solution. When measuring such a high resistance the voltage across the probes exceeds the limits of the potentiometer, necessitating measurement by some other high impedance instrument or method. One method used in this research made use of calibrated galvanometer in series with a 20 megohm resistance. By knowing the characteristics of the galvanometer, one could calculate the current through the resistor and hence obtain the true voltage across the probes. Another method simply measured the voltage with a calibrated vacuum tube voltmeter. The results obtained by both methods agreed within one percent, which is the limit of accuracy possible by either method.

EXPERIMENTAL RESULTS

It was previously mentioned that a resistance measurement was independent of the current. This fact is illustrated by Table 1 showing a typical set of results obtained on a 0.02 N potassium chloride solution at 25° centigrade.

TABLE 1.

Current Mamps.	Es Volts Pos.1	Es Volts Pos.2	Es Volts Average	Ep Volts Pos.1	Ep Volts Pos.2	Ep Volts Average	R Ohms
0.29	0.30417	0.30416	0.30416	0.14332	0.14324	0.14328	471.07
	0.30420	0.30420	0.30420	0.14330	0.14330	0.14330	471.07
0.24	0.25380	0.25380	0.25380	0.11958	0.11957	0.11958	471.07
	0.25380	0.25382	0.25381	0.11957	0.11956	0.11956	471.08
0.19	0.20434	0.20436	0.20435	0.096275	0.096262	0.096268	471.09
	0.20438	0.20438	0.20438	0.096278	0.096279	0.096278	471.07

The Cell Constant.

G. Jones and M. Prendergast[23] have accurately measured the specific conductance of 1 demal, 0.1 demal, and 0.01 demal potassium chloride solutions. The standards used for calibrating the cell were the 0.1 and the 0.01 demal solutions. The solutions were prepared to within 0.1 percent of the weight required and a linear interpolation used to obtain the exact specific conductance of the salt. The solvent conduct-

ance was added to this value and the sum taken as being the specific conductance of the solution which, when multiplied by the resistance measurement on the cell, gave the cell constant. Although the results obtained for either solution are precise, (table 2) a serious inconsistency of the order of 0.6% is seen to exist between the values obtained for each solution.

TABLE 2. Cell constant Values Using 0.1 and 0.01 Molar Solutions.

0.1 Molar	0.01 Molar
1.3109	1.3043
1.3104	1.3041
1.3103	1.3045
1.3104	1.3046
1.3102	
1.3104 ± 0.0001	1.3044 ± 0.0002

This inconsistency suggested some intrinsic error in the design of the cell. In order to determine more exactly the nature of this variation, the cell constant was measured at other concentrations using the conductance data reported by T. Shedlovsky, A.S. Brown, and D.A. MacInnes.[24] A correction of 0.02% was added in order to bring the values to the standard recommended by Jones and Prendergast.

The cell constant values obtained were plotted against the specific conductivity of the solution. The resulting graph showed a minimum value of cell constant at a specific conductivity of 3.32×10^{-3} mhos. It should be pointed out that the values of the specific conductivity for solutions lower than 0.01 normal were subject to a solvent correction greater than one percent which seriously restricted the accuracy and reproducibility of those measurements.

The cell constant values obtained at various concentrations are shown in table 3 and presented graphically in figure 6.

TABLE 3. Cell "constant" values at various concentrations.

Concentration	Specific Conductance	Resistance	Cell Constant
0.1 Molar	0.012831	102.13	1.3104
0.01 "	0.0014139	922.55	1.3044
0.05 Normal	0.0066704	195.52	1.3042
0.02 "	0.0027648	471.07	1.3024
0.005 "	0.00071915	1817.7	1.3072
	0.00072030	1813.6	1.3063
0.002 "	0.00029322	4470.9	1.3110
	0.00029493	4443.2	1.3104
	0.00029462	4449.2	1.3108
	0.00029340	4460.3	1.3086
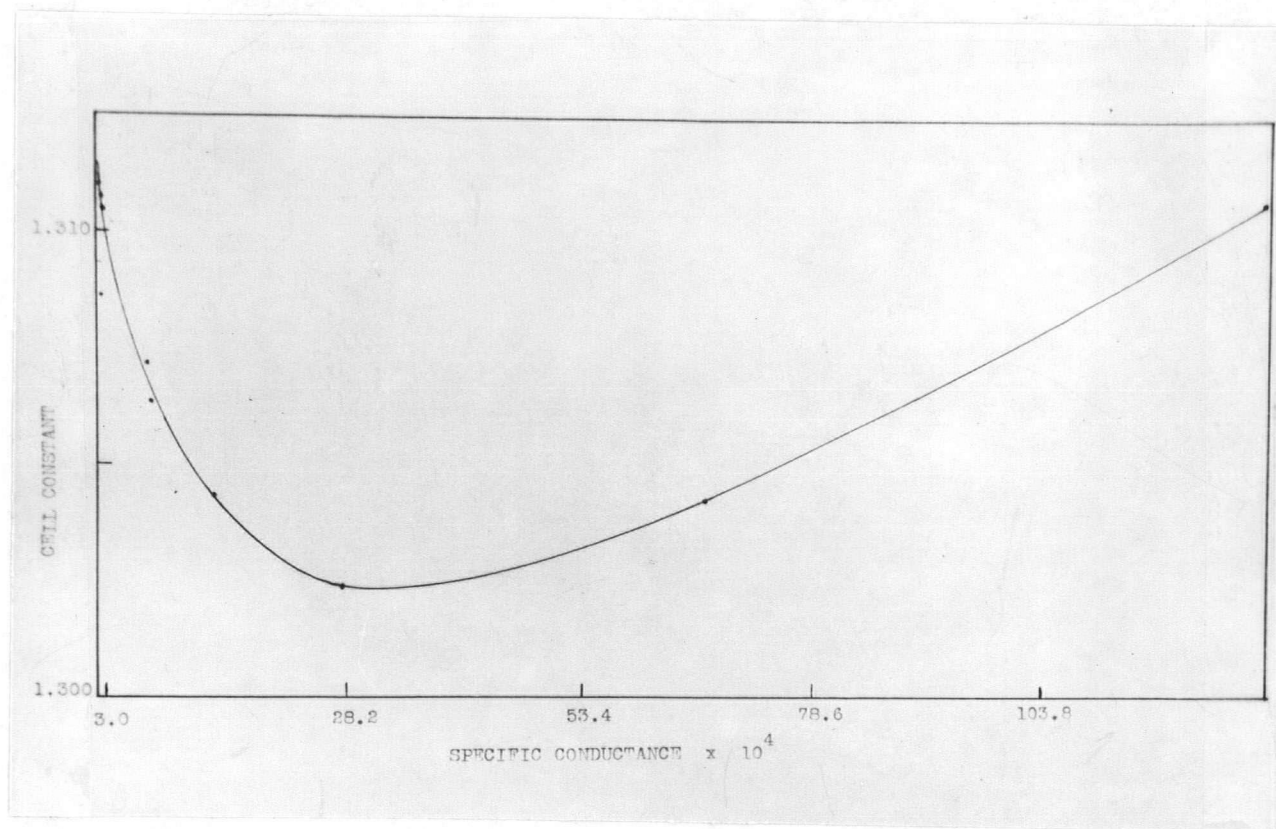
FIGURE 6 "CELL CONSTANT" VERSUS SPECIFIC CONDUCTIVITY

AT 25°C.

III. DISCUSSION OF RESULTS.

It has been shown with reasonable assurance, that the cell constant of the conductance cell used varies with the specific conductivity of the solution being measured. Of the several factors that may cause this, the design of the portion of the cell over which the voltage drop is measured is emphasised by Gordon as being the most important. The probe electrodes used by Gordon were previously described. Their design was proposed primarily to obtain narrow well defined slits across which the potential difference can be measured and for rigidity, thus ensuring an exact orientation for each run. In this research the probe electrodes were modified but the essential features have still been retained. One notable difference however is that the electrode surface of Gordon's probes existed only on one side; on our probes the complete circumferance of the wire is active. It is possible that this factor may cause, in part, the observed variation of cell constant but it is difficult to see any exact reason why it should do so.

The width of the probe electrodes was 0.081 centimeters. This corresponded to one-onehundreth of the distance between them, but it has not been possible to math-

ematically relate the IR drop across their surface to the experimental change in cell constant. In fact, since the product of the resistance and specific conductance of the electrolyte gives the cell constant, and since these are inversely proportional, to one another, it is difficult to see why the ohmic drop across the electrode surface should cause any change in cell constant.

The side extensions connecting the electrodes to the main body of the cell were designed to prevent diffusion of the electrode materials to the current-carrying electrolyte. It is possible that the error in our cell comes from the possible variation of the path of the current in these side arms. With a concentrated electrolyte one might reasonably expect the ions to flow in straight parallel lines past these extensions. However, if the number of ions available to carry current is decreased, those present in the side arms may take an active part in carrying the current thus increasing the distance across which the potential drop in the cell is measured. This possibilty however would only explain the part of the curve in which the apparent cell constant is increasing.

The foregoing discussion does not adequately account for the observed phenomena and it is evident that further work should be done to reveal what factors are operative in causing the cell constant variation.

The effect of current flowing through the side arms could be eliminated by joining them to the body of the cell with fine short capillaries. An attempt was made in this research to do so but the resulting strains in the cell caused it to be very fragile and it had to be discarded. However since then, another technique has been suggested for use in constructing such a cell and it is hoped that another of this design will soon be made and tested.

It was suggested that because the probe electrodes used in this research were active over the whole circumferance of the wire, an error might be introduced. This fact could be investigated by sealing platinum wire into a soft glass rod and covering all but a narrow slit with soft glass. Thus the electrode design of Gordon would be accurately copied but the difficult platinum disc to glass seal would be eliminated.

One can see that a considerable error exists in the solvent correction applied in these measurements because of the doubt involved in using a particular value of the cell constant. This error is probably of the order of 1 or 2% , but may be as high as 5%. However, the measurement of the solvent conductance could be facilitated by calibrating a simple cell of A.C. design and measuring

the resistance with a vacuum tube voltmeter. The meter should of course be calibrated over the necessary range using a standard resistance in order to obtain the desired accuracy. The method cannot be used with the D.C. cell described because of the resistance in the connecting arms of the probe electrodes.

Although the calibrated cell does not have a constant cell factor for all values of specific conductance, it has been shown that for a particular solution reproducable results can be obtained within one or two parts in ten thousand. It is believed that the cell could be used to measure unknown solutions with specific conductances in the range calibrated. Preliminary tests would of course be necessary on known solutions, and if accurate results were obtained, measurements could be carried out on D_2O solutions as was originally intended.

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PART II.

MEASUREMENT OF STRAIN POTENTIALS

MEASUREMENT OF STRAIN POTENTIALS

I. INTRODUCTION

HISTORY

Most metals or alloys of industrial importance are attacked by the common environments and deposit solid corrosion products that are compounds of that metal. It has been shown that when metallic couples are introduced to corroding environments, one of the metals will corrode, the other assuming cathodic properties. This phenomenon is also observed between two portions of a single metal when one of these portions is subjected to mechanical strain. The work undertaken has accurately indicated the magnitude of this behaviour for #18 A.W.G. soft drawn copper wires subjected to various straining loads.

The development of the electrolytic theory of corrosion has stimulated research in the field of strain potentials. This subject, dealing with the resulting change in the electrode potential of a metal under mechanical strain, was first investigated in 1894 by T. Andrews[1] but since that time very little research has been carried forth. The results of early workers[2,3,4] are haphazard and difficult to reproduce. Even the more recent experimental conclusions differ in many respects. An effort has been

made in this research, therefore, to develop consistent techinques that can be easily copied.

The investigation reported is concerned, for the most part, with the results obtained on #18 A.W.G. soft drawn copper wire. Previous researches of this type on copper wire were preformed by L.V. Nikitin[5] L.R. Gautam and J.B. Jha[6] O.K. Miniato[7] B. McDonnell[8] and R.D. Jamieson[9] The results of Nikitin are in reasonable agreement with ours. The paper of Gautam and Jha, however, reports that the strained wire became more cathodic in copper sulphate solution which contradicts our observations[#] The other works mentioned are the results of thesis investigations carried on at the University of British Columbia. The first of these, performed by O.K. Miniato, utilized a ballistic galvanometer as a detecting instrument. The results reported by Miniato have not been confirmed by other investigators however, and it appears that some lamentable error, possibly in the calibration of the galvanometer, has occurred. The results of McDonnell have been shown to be quite valid for runs similar to ours, but in most cases the exact values obtained were considerably lower than those obtained in this investigation. In Jamieson's work the main considerations were given to the change of potential over long periods of time and do not readily compare with our results.

[#]The abstract reported by A.O. Allen, Chem. Abs., $\underline{38}$, 5459[8] (1944), states that the strained wire became more anodic.

THEORY

Theoretical considerations of strain potentials have been as haphazard as the experimental work. Efforts have been made to correlate the magnitude of the developed potential to such concepts as solution pressure, modulus of elasticity, and free energy, but little progress has been achieved. The greatest error apparent in these efforts is the assumption that all the energy is stored as potential energy. R.W. Gorensen[10] has quite clearly contradicted this assumption by stating that the energy of deformation is stored as potential energy and heat energy. The latter would, in this case, be rapidly transmitted through the body of the electrolyte and thus be unavailable.[#]

Other theoretical approaches are possible however. Goranson has outlined in detail theoretical considerations of stressed solids. It is possible that the concepts presented by Goranson could be applied to the particular case under consideration and, in conjunction with the modern theories of electrode potentials, quantitatively explain the phenomenon observed. One might also consider the fact that corrosion of metals has been observed to take place preferably on a particular crystal plane,[11]

A discussion by Prof. J.W. Richards and Mr. W.H. Walker (Trans. Elchem. Soc. 11, 168, (1907)) concluded that this heating effect could not cause the observed change in potential. However, the results obtained by Nikitin on copper and silver wires suggests that the momentary change in temperature should be investigated.

thus suggesting a different potential belonging to each plane. Perhaps in stretching the metal, the less inert plane or planes are exposed and give rise to the observed change. The restoration of the electrode to approximately its original value would correspond then to the reorientation of the crystals to positions of greater stability. Another theoretical approach considers the potential to be due to ruptures produced in a surface film on the metal thus exposing a new surface to the electrolyte. The results presented in this thesis indicate qualitatively that this may be the correct theory, but the other factors are very likely contributing also.

Although an exact theory has not been presented here, it is hoped that the suggestions made may lead to a quantitative explanation of strain potentials in the future. Such a theory would undoubtably contribute to our knowledge of the nature of metals and their corrosion, and possibly contribute to our knowledge of electrode potentials.

II. EXPERMINTAL TECHNIQUES AND RESULTS

DESCRIPTION OF APPARATUS AND EXPERIMENTAL PROCEDURE

Preparation of Solutions. The solutions were prepared by weighing the required amount of copper sulphate to the nearest milligram and adding it to distilled water in a volumetric flask. No corrections were applied to the weights or the flask.

The Cell and Straining Apparatus. The all glass cell, shown in plate 2, was constructed from a 500 milliliter round bottom florence flask. The design is considered an improvement over previous types of cells used since contamination from rubber parts is eliminated. The cell illustrated was made so that an atmosphere of nitrogen could be conveniently kept over the solution if desired.

During a run, the two copper wires investigated were supported on a wooden frame by heavy insulated hooks and passed into the solution through the capillaries on the cell. Scale pans were attached to the free ends and the weights added by hand. Considerable care had to be taken in adding the weights since any slight dropping would appreciably invalidate the measurements.

The Potentiometer and Electronic Voltmeter. The potential difference between the strained and unstrained wires was measured by two methods. The first method
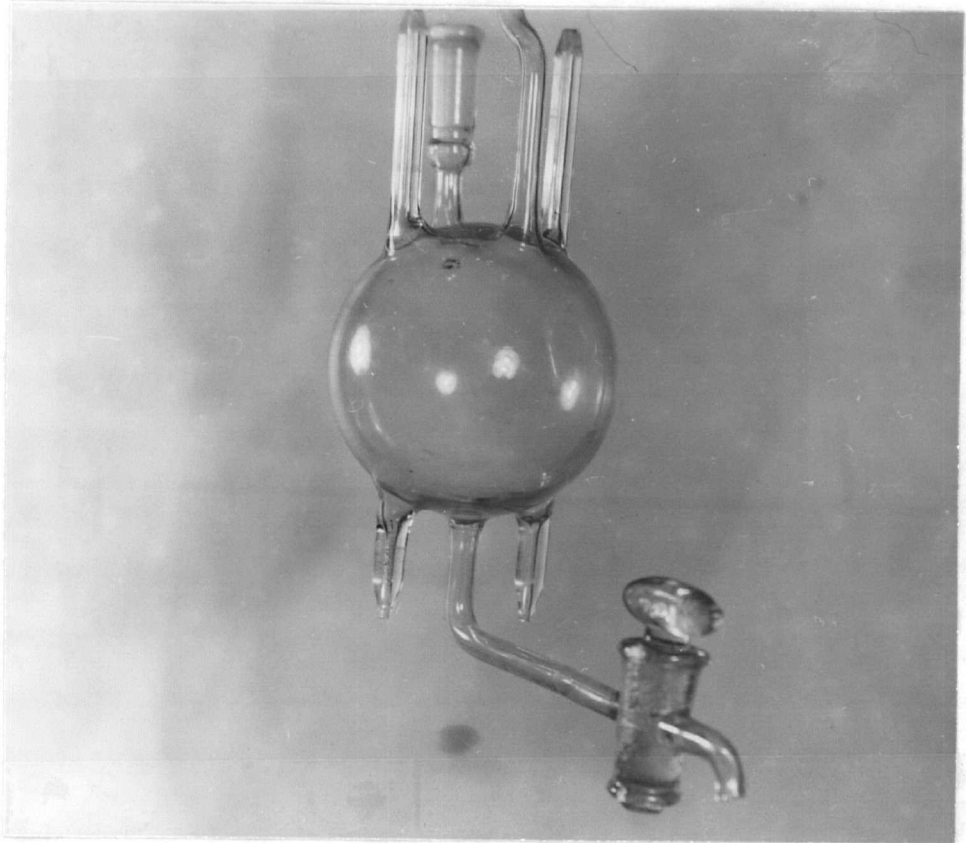
PLATE 2   THE STRAIN POTENTIAL CELL

utilized a Leeds and Northrup portable potentiometer with
a range of either zero to fifteen or zero to seventy-five
millivolts and a built in galvanometer. A preliminary run
was necessary to indicate the approximate peak potential.
Having obtained this value the potentiometer was set and t he
weights added to new wires. The potentiometer was balanced
at all times during a run thus eliminating any possibility
of imposing an excess voltage on the wires from the pot-
entiometer circuit. In the second method the potential
difference was measured with an electronic millivoltmeter
constructed in this laboratory. The instrument, illustrat-
ed in figure 7, is a modification of the voltmeter suggest-
ed by H.S. Burr, C.T. Lane, and L.F. Nims[12] for the measure-
ment of small potentials. In operation, the instrument was
found to be extremely unstable and any small electrical
disturbances would destroy its balance. However, some runs
were conducted successfully with it which agreed with the
potentiometric measurements.
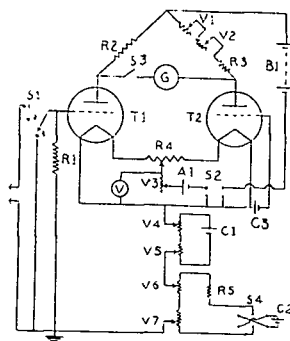
A_1 -- $1\frac{1}{2}$ volts	R_5 -- 0.1 megohms
B_1 -- 90 "	T_1, T_2 -- 1G4GT
C_1 -- 3 "	V_1 -- 20 ohms (w.w.)
C_2 -- $1\frac{1}{2}$ "	V_2 -- 3,000 " "
C_3 -- $1\frac{1}{2}$ "	V_3 -- 25 " "
R_1 -- 10 megohms	V_4 -- 25,000 " (linear)
R_2 -- 10,000 ohms	V_5 -- 1,000 " (w.w.)
R_3 -- 6,800 "	V_6 -- 500 " "
R_4 -- 6 " (wire wound)	V_7 -- 20 " "

FIGURE 7   ELECTRONIC MILLIVOLTMETER CIRCUIT

EXPERIMENTAL RESULTS

Electrode Potential versus Time. Three preliminary runs were made to study the decay of the developed potential using 0.05N $CuSO_4$ solution. Weights were added and the potential recorded at short intervals of time. Any initial emf. was subtracted from the recorded values and the resultant difference called the change in the electrode potential. The results obtained are tabulated below, and presented graphically in figure 8. For convenience, the points obtained in periods of time corresponding to a few seconds have not been listed in the table.

The abscissa (time) for run #5 has been distorted in order to correlate the data obtained with a 7 kilogram straining weight with the data obtained with the same weight in run #6.

These three runs were measured with the potentiometer, but later two similar runs were made using the potentiometer on one and the vacuum tube voltmeter on the other. The results (not presented here) are consistent with the previous determinations.

TABLE 4. Electrode Potential versus Time

| TIME	RUN #5		RUN #6		RUN #7	
	LOAD	$-\triangle$E.P.	LOAD	$-\triangle$E.P.	LOAD	$-\triangle$E.P.
0 min.	5 Kgm.	1.75 mv.	5 Kgm.	0.50 mv.	5 Kgm.	1.66 mv.
1		1.40		0.39		1.28
2		1.12		0.33		1.11
3		0.99		0.30		0.99
4		0.86		0.30		0.87
5		0.81		0.29		0.84
6		0.74		0.28		0.77
7		0.69		0.27		0.73
8		0.65		0.26		0.69
13		0.52		0.01		0.56
20				0.14		0.46
21			7 Kgm.	3.27		
22		0.36		2.86		
23				2.51		
24				2.32		
25				2.12		
26				1.98		
27		0.33		1.87		
28				1.79		
29				1.70		
30			8 Kgm.	3.04		
31				2.72		
32				2.45		
33				2.24		
34				2.10		0.42
35				1.99		
36				1.88		0.44
37	7 Kgm.	2.85	9 Kgm.	3.12		
38		2.61		2.61		
39		2.33		2.31		
40		2.08		2.13		
41		1.90		1.98		
42		1.77		1.89		
43		1.66		1.78		
44	9 Kgm.	2.86		1.70		
45		2.33		1.53		
50				1.35		
55				1.14	7 Kgm.	5.6
56						4.38
57						3.60
58						3.26
59						3.02
60						2.85
62						2.53
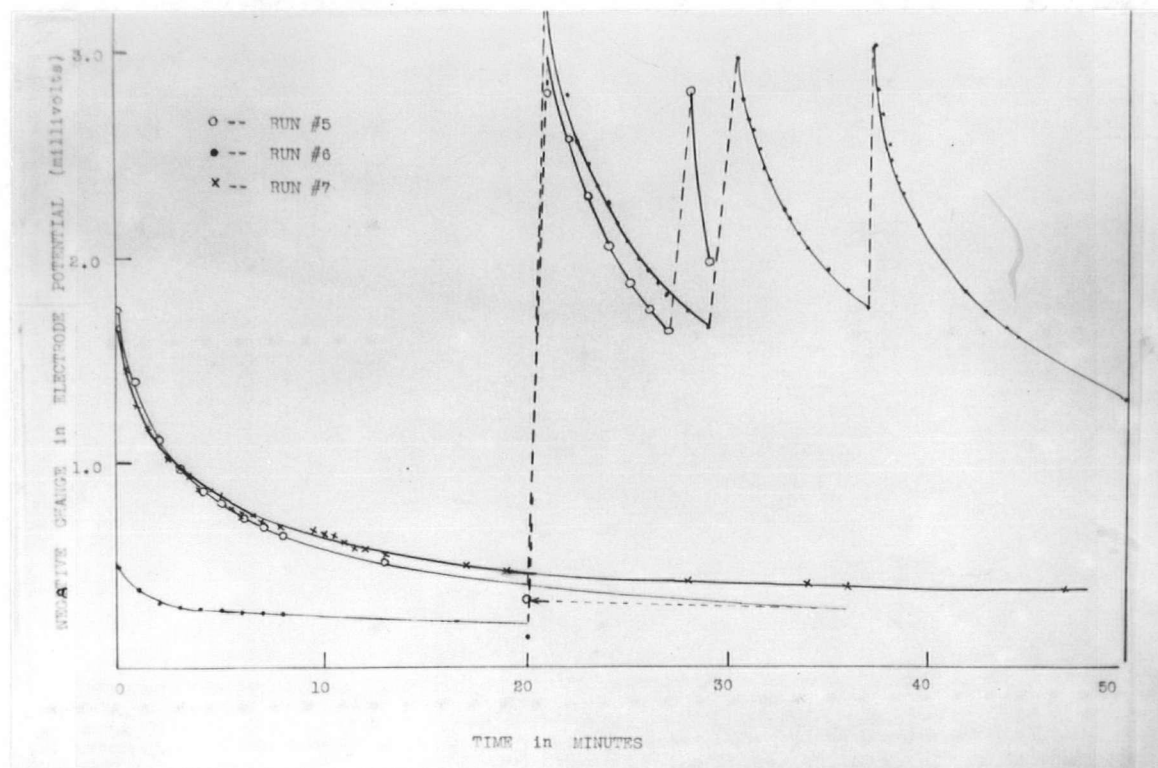
FIGURE 8 NEGATIVE CHANGE IN ELECTRODE POTENTIAL

VERSUS TIME IN 0.05 N CuSO$_4$ SOLUTIONS

Peak Potential versus Strain. Using 0.05N $CuSO_4$ solution as the connecting electrolyte, the instantaneous effect of sudden strains was observed by adding increments of weight at definite time intervals and recording the peak potential. As is shown in figure 9 the exact values do not always correspond, but this is expected to be due to differences in the various samples of wire. The data are tabulated in table 5.

TABLE 5. Peak Potential versus Strain

TOTAL LOAD	RUN #8 $-\triangle$E.P.	RUN #11 $-\triangle$E.P.	RUN #13 $-\triangle$E.P.	RUN #15 TOTAL LOAD	$-\triangle$E.P.
1 Kgm.	0.0 mv.		0.02 mv.	2 Kgm.	0.00 mv.
2	0.0	0.06 mv.		3	0.11
3	0.0		0.08	3.5	0.18
4	0.35	0.27	0.17	4	0.26
5	2.35	1.21	1.80	4.5	0.35
6	4.49	4.12	2.66	4.7	0.44
7		5.09		4.9	0.70
8	5.60	4.83	3.65	5.1	1.11
9				5.3	1.54
10	5.72	4.89	3.65	6.3	2.10
				7.3	4.07
				8.3	4.71
				9.3	4.63

Effect of Concentration and Electrolyte. The peak potentials developed for various straining loads were compared using 0.5N, 0.05N, and 0.0005N $CuSO_4$ solutions. The results presented in table 6 and figure 10, show that as
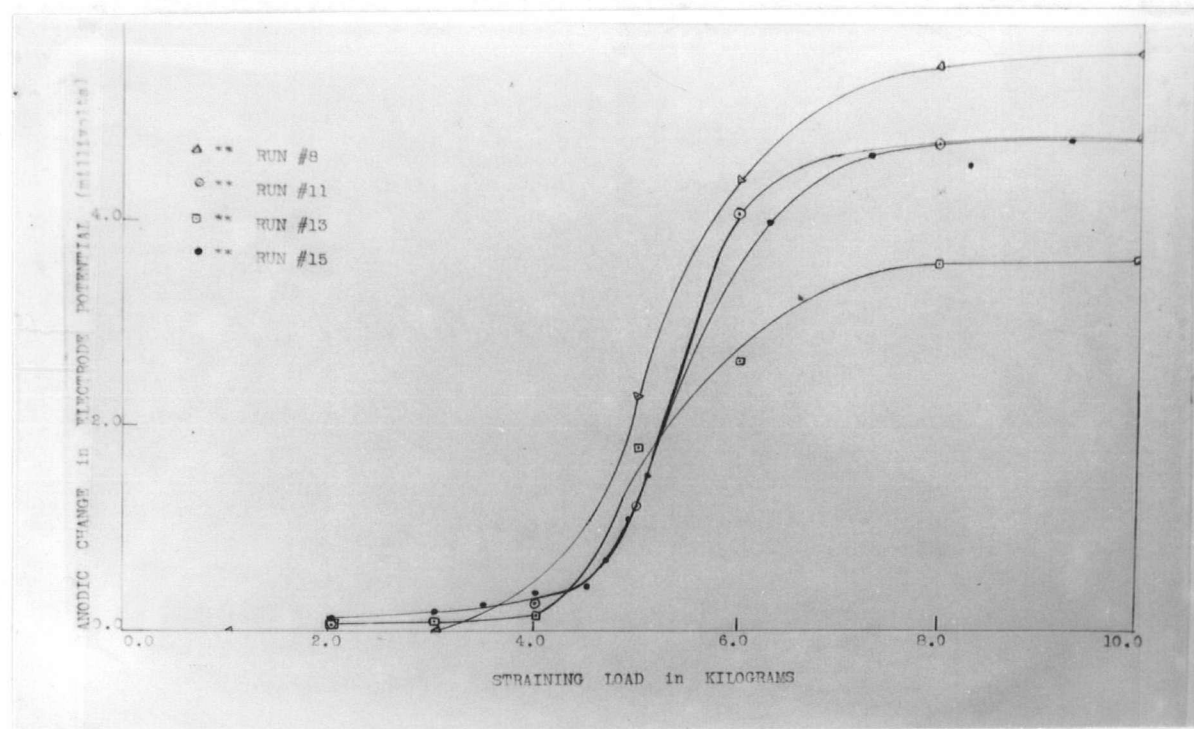
FIGURE 9.   PEAK POTENTIAL VERSUS STRAINING LOAD

(Weights added every 30 seconds)

the concentration decreases, the anodic property of the strained wire is enhanced.

TABLE 6. Effect of Concentration on Electrode Potential

TIME min.	TOTAL LOAD Kgm.	$-\Delta$E.P. 0.5N CuSO$_4$			$-\Delta$E.P. 0.05N CuSO$_4$			$-\Delta$E.P. 0.0005N CuSO$_4$	
		POT. mv.	POT. mv.	VTVM. mv.	POT. mv.	POT. mv.	VTVM. mv.	POT. mv.	POT. mv.
0	3	0.03	0.11	0.12	0.10	0.07	0.27	0.40	0.16
2	3	0.06	0.02	0.12	0.06	0.05	0.14	0.65	0.15
2.15	4	0.03	0.02	0.12	0.10	0.04	0.32	1.00	0.12
4.15	4	0.03	0.01	0.24	0.81	0.03	0.37	1.00	0.12
4.30	6	0.17	0.32	0.365	1.49	0.86	1.94	2.40	2.16
6.30	6	0.14	0.18		0.91	0.45	1.76	2.35	1.83
6.45	7	0.58	0.60	3.11	2.61	1.98	6.13	7.10	9.62
8.45	7	0.35	0.33	1.57	1.71	1.03	4.41	4.85	7.51
9.00	8	0.75	0.70	3.61	3.31	2.18	8.30	9.90	12.51
9.45	8	0.59	0.49	2.50	2.81	1.53	7.22	7.80	10.68

A similar study was made using 0.05N solutions of CuSO$_4$, CuCl$_2$, MgSO$_4$, and MgCl$_2$. The results obtained using the MgCl$_2$ solution were incoherent, but considerable variation was observed in the normal bias potential between two unstrained electrodes and it is believed that this effect was operative during the runs. With the other solutions the results obtained (figure 11, table 7) show that the anodic potential in MgSO$_4$ solution is considerably greater than for CuSO$_4$ solution, but when using CuCl$_2$ solution a cathodic potential is developed in the strained electrode.
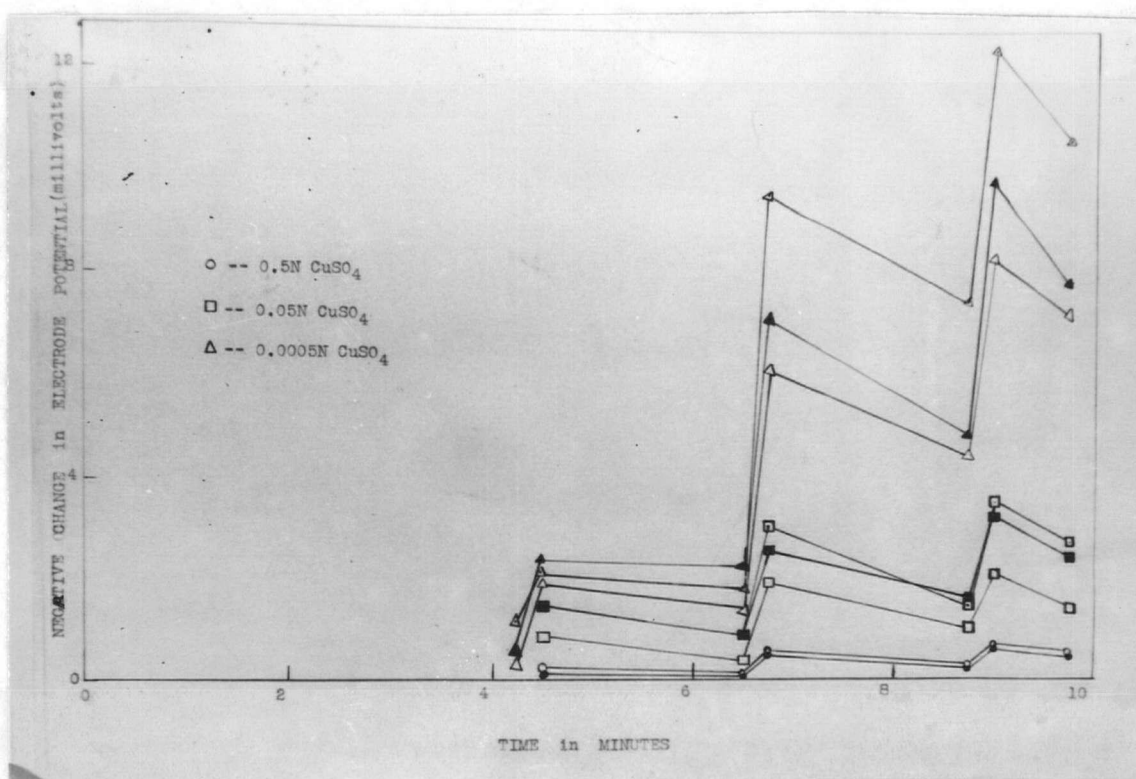
FIGURE 10   NEGATIVE CHANGE IN ELECTRODE

POTENTIAL FOR VARIOUS CONCENTRATIONS

OF $CuSO_4$

(Weights added every 120 seconds)

TABLE 7. Effect of Different Electrolytes on Electrode Potential.

| TIME min.	TOTAL LOAD Kgm.	0.05N CuSO₄ VTVM. mv.	POT. mv.	POT. mv.	0.05N MgSO₄ VTVM. mv.	POT. mv.	POT. mv.	0.05N CuCl₂ VTVM. mv.	POT. mv.	POT mv
0	3	0.12	0.10	0.07	0.55	0.17	0.12	0.12	0.20	0.15
2	3	0.12	0.06	0.05	0.70	0.15	0.37	0.24	0.25	0.17
2.15	4	0.12	0.10	0.04	0.90	0.65	0.30	0.55	0.36	0.26
4.15	4	0.24	0.81	0.03	1.55	0.16	0.49	0.52	0.27	0.13
4.30	6	0.36	1.49	0.86	4.0	2.83	2.8	5.7	4.46	3.55
6.30	6		0.91	0.45	3.70	2.37	1.41	3.83	2.74	2.14
6.45	7	3.11	2.61	1.98	12.25	12.1	11.05	5.25	5.38	5.75
8.45	7	1.57	1.71	1.03	7.95	6.70	6.30	4.63	3.70	4.17
9.00	8	3.61	3.31	2.18	15.35	11.33	13.05	5.70	4.71	5.20
9.45	8	2.50	2.81	1.53	10.78	9.03	9.90	5.25	4.12	4.66
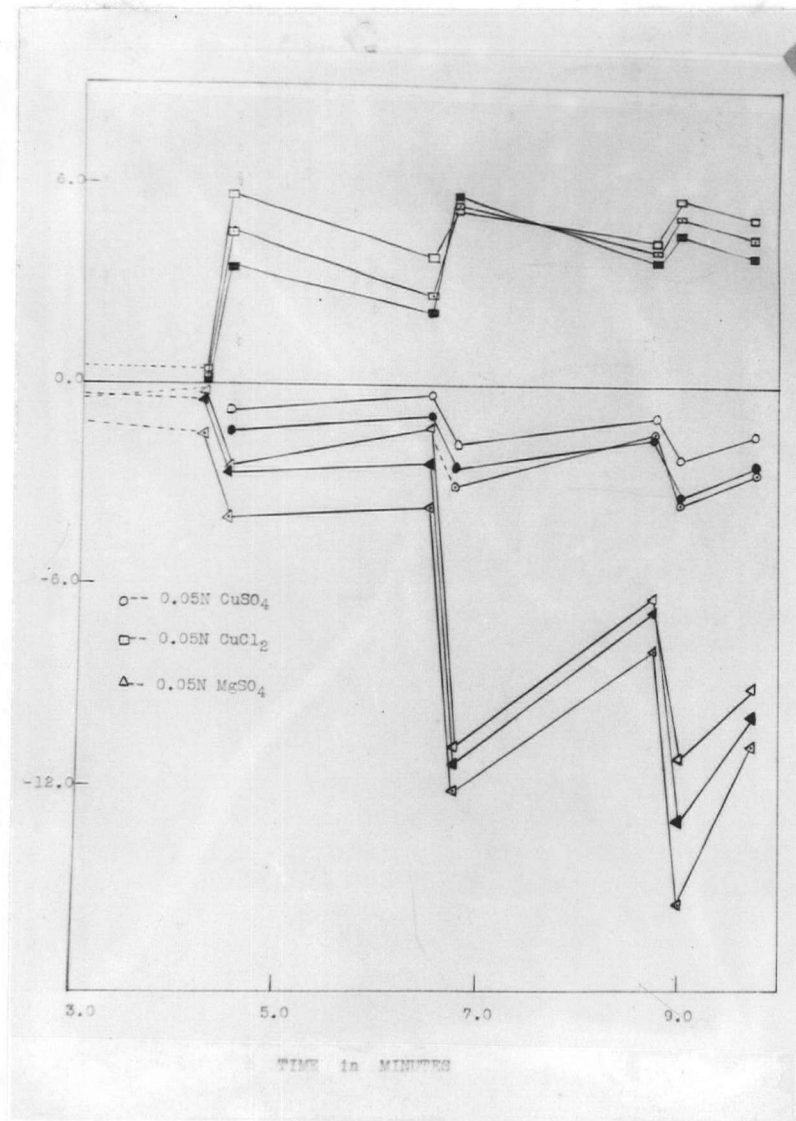
FIGURE 11. NEGATIVE CHANGE IN ELECTRODE
POTENTIAL FOR VARIOUS ELECTROLYTES.
(Weights added every 120 seconds)

III. DISCUSSION OF RESULTS

It has been shown that when a copper wire immersed in an electrolyte is subjected to mechanical strains an electromotive potential is produced dependent on the magnitude of the straining load, the concentration of the electrolyte, and the components of the electrolyte. The first runs performed in this research have demonstrated that the relaxation of this potential is approximately exponential thus suggesting some kinetic process in operation. It it is assumed that in $CuSO_4$ solution a surface layer of copper oxide exists on the metal which is ruptured when the wire is stretched, this process could be the renewal of the oxide film by the equations

$$2 \, Cu^o + 2OH^- \longrightarrow Cu_2O + H_2O + 2(e)$$

$$Cu_2O + 2OH^- \longrightarrow 2CuO + H_2O + 2(e)$$
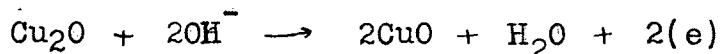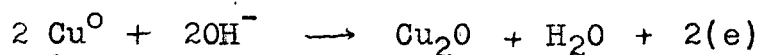
This theory is also supported by the data plotted in figure 9. It is seen that below 4 kilograms very little potential difference is developed and above 7 kilograms the potential developed (approximately 5 millivolts in 0.05N $CuSO_4$ solution) is independent of the straining load. If one postulates that the surface film stretches with the wire up to a critical straining load after which fractures appear in the film, the evidence supports the possible

theory suggested above. However, this evidence could also point to the possible disorientation of the crystals in the metal, but since it has been established that the effect is dependent on the concentration of the electrolyte and the components of the electrolyte, the surface film theory seems more probable.

The measurements made using 0.05N $CuCl_2$ solution show a cathodic increase in the potential of the strained wire. This fact can be explained by assuming that when the surface film of oxide is broken exposing the pure copper, a new surface film of $CuCl_2$ is produced by the equation

$$2 \ Cu^o + \ 2 \ Cl^- \longrightarrow Cu_2Cl_2 + 2(e).$$
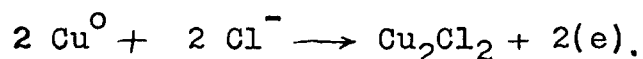
The observed change in the direction of the electrode potential corresponds then to a different electrode reaction and it appears that such theories as may be derived from consideration of the energy stored in the metal, modulus of rigidity, or corrosion on a particular crystal plane can be disregarded. An interesting confirmation could be made on this electrode or surface film theory by substituting for the electrolyte a resistance large enough to prevent any appreciable current from flowing between the two wires. One would intuitively expect a potential difference to be developed, but it is difficult to estimate what the magnitude or direction of this potential might be.

Work in this field has been continued by Mr. R.S. Dudley, who has measured the potential developed at various temperatures and so established a temperature coefficient for the phenomena. The author would like to suggest that in future work an emphasis should be placed on variation of electrolyte with consideration given to the possible electrode processes taking place. Some interesting possibilities not previously considered are solutions of copper complexes such as the copper-ammonium complex or the copper-cyanide complex. Because of the low concentration of copper ions present in such solutions, the resultant potential should be highly anodic, but it is possible that other factors may give unexpected results. Profitable measurements could also be made using different metals. Because of the widespread use of iron and steel, measurement of strain potentials on such couples could be of great industrial importance.

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