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Marshall L. Severson

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TRANSFERENCE NUMBERS OF CONCENTRATED MANGANOUS CHLORIDE SOLUTIONS

by

Marshall L. Severson

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in partial fulfillment of the requirements for the
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in
CHEMISTRY

APPROVED:

William J. James
Major Advisor

Dudley Thompson
Chairman of Department

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I. INTRODUCTION

Electrolytic conduction differs from metallic conduction only in the nature of the carrier of the current. In the case of metallic conduction the carrier is electrons. The passage of an electric current through an electrolyte occurs only by the movement of ions of opposite charge moving in opposite directions under an applied potential. The current carried by a particular ionic species is a direct function of the concentration, the charge on the ion, and the ionic mobility. A transference number is the fraction of the total current a given ion carries in a particular electrolyte undergoing electrolysis. The sum of the transference numbers of all the ions present in a solution must therefore add up to unity.

Transference numbers are involved in many physical chemical considerations. Calculations of ionic mobility, equivalent ion conductivities, dissociation of electrolytes, effective ion "diameters," hydration, and the electromotive force of concentration cells involve transference numbers. The presence of complex ions can be detected in solutions by the appearance of "abnormal" or negative transference numbers.

At present there are three practical methods of experimentally determining transference numbers: the electromotive force, the moving boundary, and the analytical Hittorf. The advantage of the first is speed, but it is based on rather tenuous assumptions The moving boundary method gives high precision results, but it is useless at concentrations above one molar. Therefore, the analytical Hittorf method was used in this investigation.

The objectives of this investigation were: (1) to determine transference numbers in solutions of one molar concentration and stronger; (2) to design and construct a suitable constant voltage source; (3) to assemble and make operative a coulometer for the precise measurement of faradays; (4) to determine the cation transference number of one molar potassium chloride using Findlay transference tubes and the Hittorf method, and to compare with accepted values found in the literature; (5) to find the cation transference number of manganous chloride at concentrations of one molar and higher.

II. LITERATURE REVIEW

The theory of solutions as accepted today has developed almost entirely without the use of transference data. This is due to the fact that experimental measurements have been of doubtful accuracy and validity, and also because available data has been scattered all over the literature and has appeared under improbable titles. A perusal of two good literature compilations by McBain(43) and LeRoy(32) will show the wide divergence of sources for the transference data. The experimental methods available have not permitted precision work and are difficult to carry out even for the most careful workers. The effect has been the proffering of theories of solutions in the face of contradictory transference data. MacInnes(41) points out the case of Arrhenius whose theory of dissociation claimed ion mobilities as independent of concentration even after Hittorf showed twenty years previous that transference numbers change with concentration.

The most accurate data available has been presented since 1931, after the theory of solutions was well on its way to its present development. Moving boundary measurements by MacInnes(40) Dole(10) and Longsworth(34)(35) of transference numbers (considered the most precise available) are in accord with the present theory of solutions.

Ion Mobilities. Conduction of an electric current through a solution of an electrolyte is accompanied by a transport of matter. Under an applied potential the random movement of the ions becomes directed, and at the electrodes a transfer of electrons takes place completing the electric circuit and a chemical reaction. The ability of a solution to transport current and therefore its conductance is determined by the number of ions, the charge on each, the actual velocity of the ions through a solution, and the resistance offered by the solution to movement. If no oxidation or reduction occurs in the solution the charge on a given ion is constant, so the variation in conductivity with concentration means that there is either a change in the number of ions (dissociation) or in their velocity, or in the resistance of the solution, or in some combination of the three. When a substance is 100 per cent ionized the values of conductance a various concentrations must be a function of ion mobility only. The value of the conductivity measurements give only the sum of the ion mobilities and not the individual mobilities. Figure 1 clearly shows the change in conductivity with concentration; the case of these two salts is quite typical. The figure tells nothing about the amount of current carried by each ion, only that it is a function of concentration.

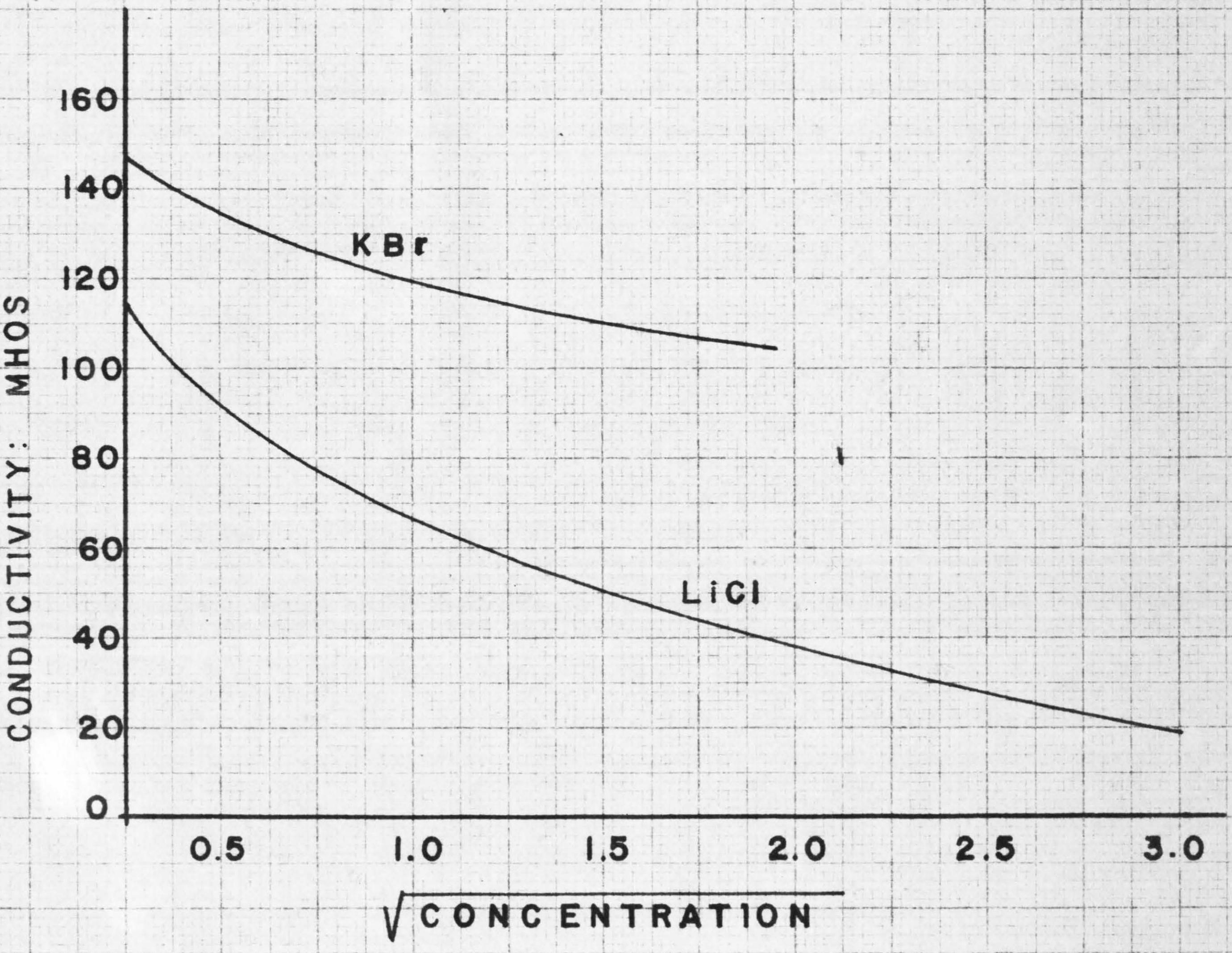


FIGURE I. EQUIVALENT CONDUCTIVITIES OF 1:1 ELECTROLYTES

STOKES, R.H. and R.A. ROBINSON: "ELECTROLYTE SOLUTIONS," p. 153, BUTTERWORTHS SCIENTIFIC PUBLICATIONS, LONDON, (1955) Methods of Measurement. The first transference number measurements of any account were made by Hittorf in 1853. His work was extended by Jahn(28) MacInnes and Dole(39) and many others. The change in equivalents of an ion is measured by chemical analysis at an electrode and divided by the number of Faradays passed through the system. Transference numbers measured in this way are limited to the accuracy of the chemical analysis.(33) The reference stationary point is the average solvent molecule. Although this method is the simplest in theory, it is the most difficult to use because of the extreme precision required in the analytical measurement.

A moving boundary transference number system was devised by MacInnes and Longsworth(41) and used with considerable success. The values obtained in this manner are the best now available. It is limited to solutions below one molar concentration in most cases and to systems where suitable indicator ions are available.(35) Attempts to operate the moving boundary apparatus with solutions of one molar concentration or stronger fail because the current required to move the boundary heats the system to the point where convection currents destroy the necessary boundary. The reference stationary point is the wall of the tube rather than the average solvent molecule. The difference in reference point is the reason for the discrepancy between "Hittorf" and moving boundary values for the same concentration of solution.

Another relatively successful method of obtaining transference data is the electromotive force method. Two concentration cells are constructed, one with and one without a liquid junction, and the potentials measured. The ratio of the two potentials obtained give the transference number of the ion to which the electrodes are not reversible.(42) It has never been decided conclusively with which concentration the transference number is involved. Attempts to get the two concentrations close together reduce the voltage output to values not accurately measureable.

Solution Effects. Of the many influences that may be exerted on a moving ion in solution only a few have been seriously considered or measured, and the effect of many is a hypothesis at best. Washburn(58) has attempted ionic hydration measurements by including a soluble sugar in the transference apparatus. After electrolysis the sugar concentration changes are believed to be due to the water carried along on the hydrated ions. The amount of sugar transfered then is a function of the relative hydration of the ion. The presence of the sugar in the solution also reduces the dielectric constant of the solvent, increases the viscosity of the solution, gets in the way of ions traveling in opposite directions, and reduces the relaxation effect. In general, the systems are not the same or equivalent when sugar is added to the pure salt solution. Robinson and Stokes(53) consider viscosity effects, electrophoresis, and the relaxation effect in a quantative manner for the dilute solutions. These effects are considered negligible for dilute solutions but not for concentrated solutions. Their studies do not attempt quantitative discussions for concentrated solutions.

The influence of temperature on the transference number is relatively small. Figure 2 shows the variation of transference numbers of the chloride ion as a function of temperature. For a temperature change of 40 °C the transference number changes only eight parts in 500. Most of the work on temperature effects has been done by Gordon(1)(2) and associates. The evidence obtained by Gordon seems to contradice the general rule by Noyes(46) that the anion and cation transference numbers tend to become equal as the temperature is increased.

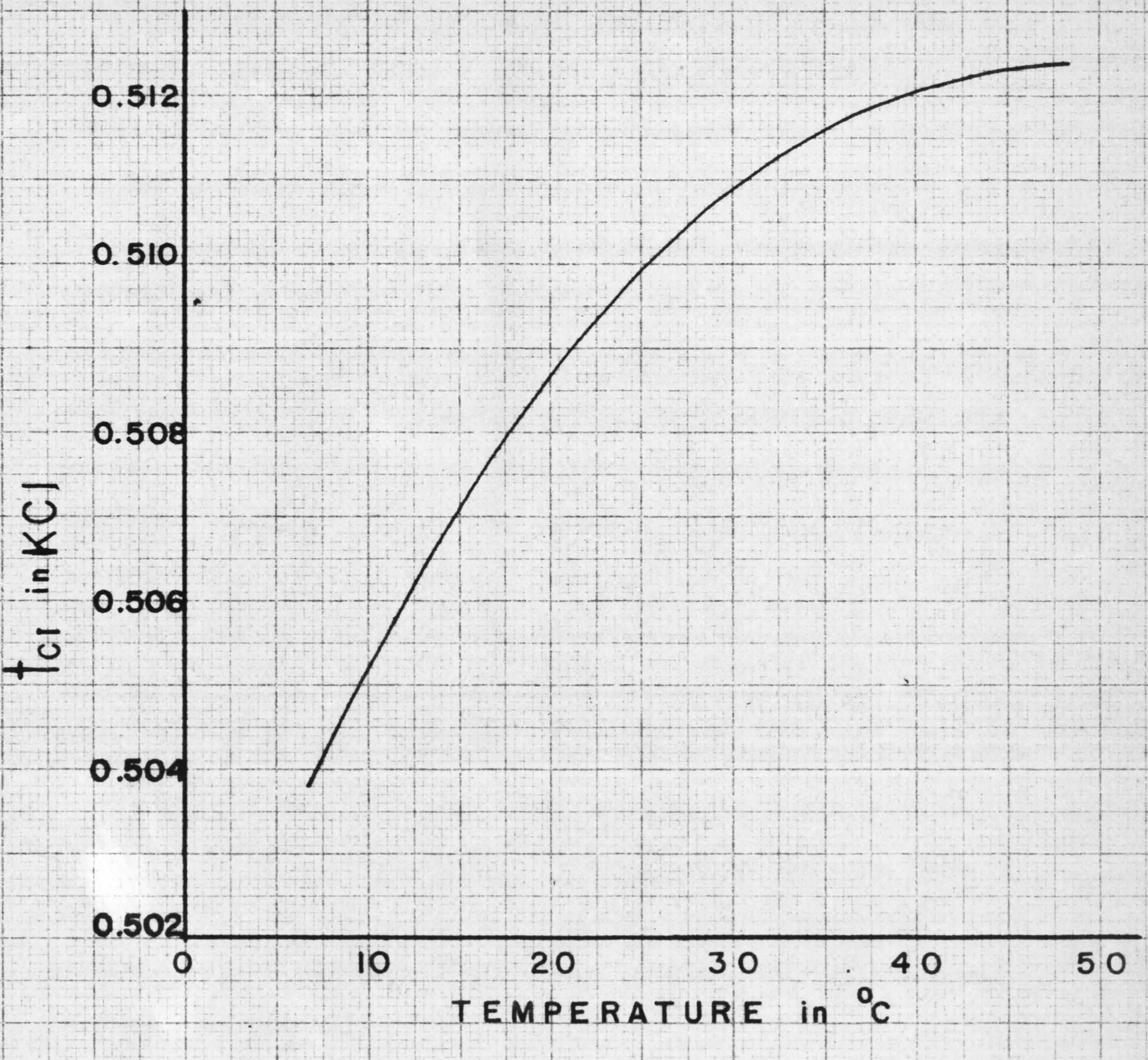


FIGURE 2. TRANSFERENCE NUMBER OF THE CHLORIDE ION IN AQUEOUS KCl AT INFINITE DILUTION AS A FUNCTION OF TEMPERATURE

STOKES, R.H. and R.A. ROBINSON: "ELECTROLYTE SOLUTIONS," p. 122, BUTTERWORTHS SCIENTIFIC PUBLICATIONS, LONDON (1955)

Concentrated Solutions. There is a great void in the literature concerning concentrated solutions. The work of Debye and Onsager, along with that of Kohlrasch, in developing equations to predict the variation of transference numbers with concentration was for extremely dilute solutions only. The concentrations involved were of the order of magnitude of 0.01 molar and less, even to infinite dilution. Figure 3 shows a typical case. Considerable variations between measured transference numbers and those predicted by theoretical equations occur at concentrations of 0.04 molar and are worthless for the consideration of solutions above one molar. No experimental work in the range of solutions of one molar concentration appear except in rare and isolated cases.(43) No theoretical considerations have appeared concerning the ionic atmosphere, the interionic attraction, viscosity, and degree of dissociation involved in ionic mobilities of concentrated solutions.

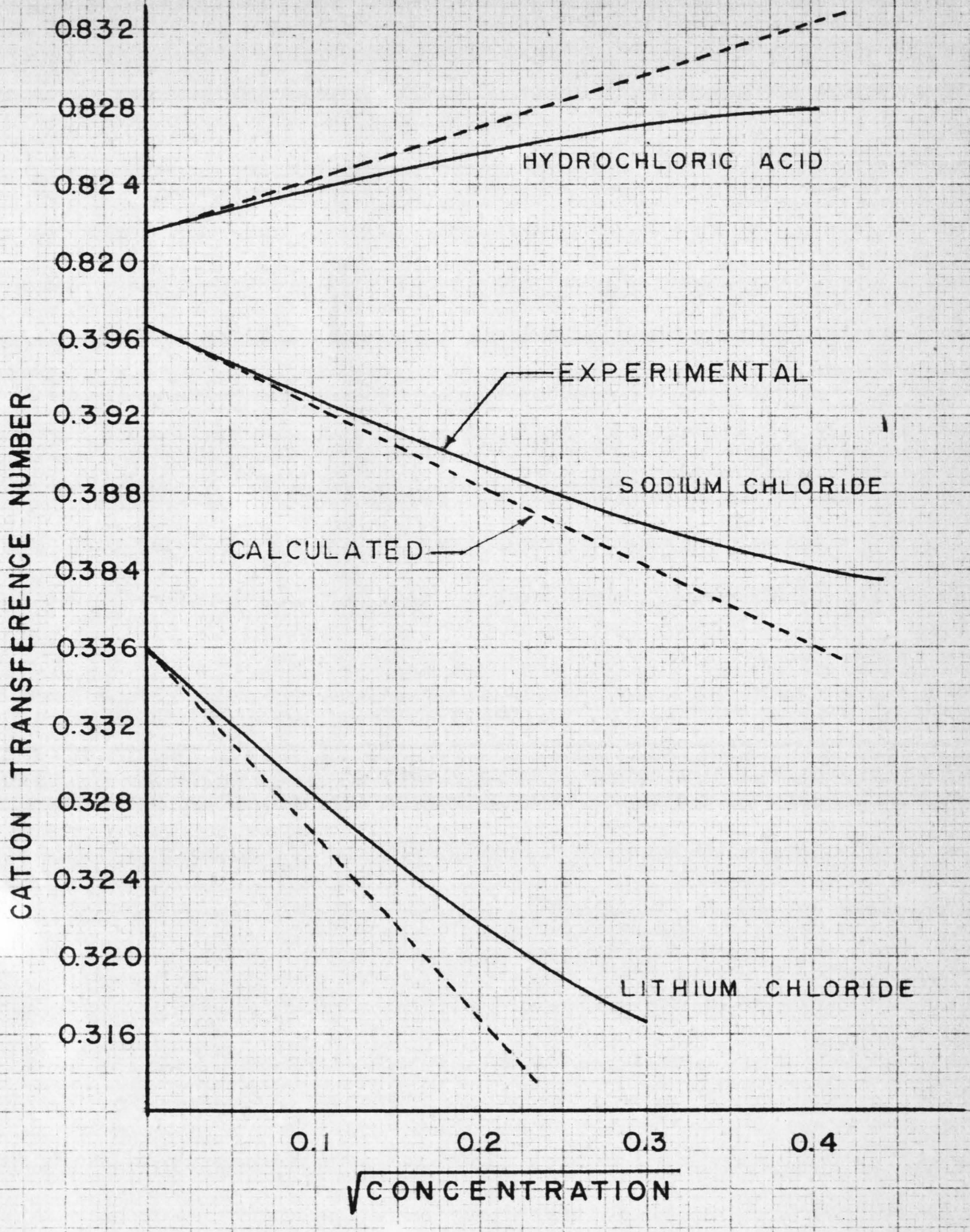


FIGURE 3. TRANSFERENCE NUMBERS AND THE ONSAGER EQUATION

LONGSWORTH, L.G.: J. AM. CHEM. SOC., 57, 1185 (1935)

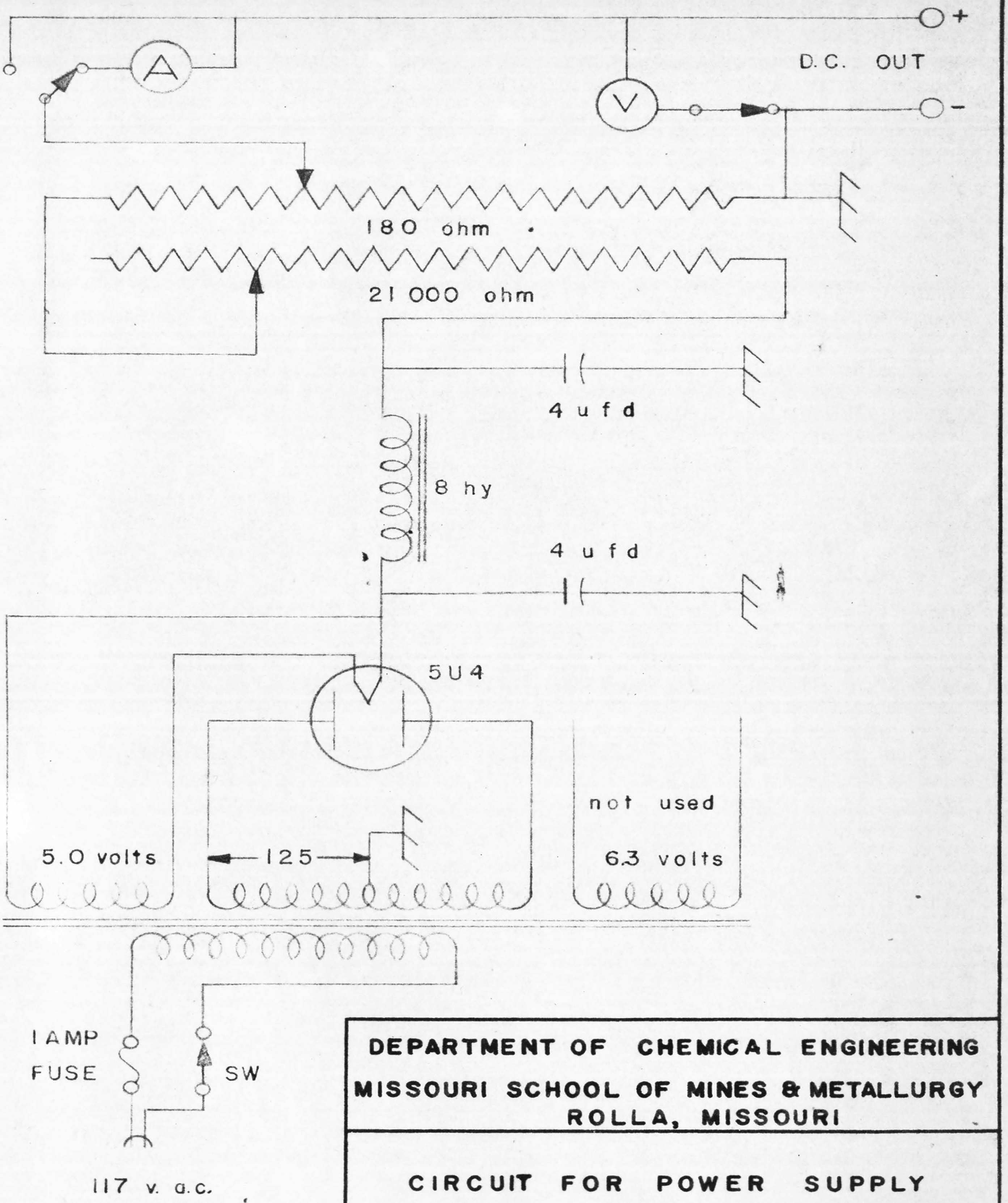
III. EXPERIMENTAL

It was decided to use the Hittorf method for concentrated solutions. This method was chosen over the moving boundary method because of the strong heating that would be involved in moving the boundary. The moving boundary method was attempted at the State College of Washington and then discarded.(7)
The electromotive force method was not elected because it was desired to find the transference number as a function of concentration and to know the concentration precisely.

The ultimate use of the equipment and knowledge gained by this investigation was to suppliment the work of Dr. G.E. Brand, who was making studies on the electromotive force of manganous chloride cells under the influence of a strong magnetic field.(6) Transference data is almost nonexistent at concentrations involved in the cells under study. The apparatus set up was to be made rigid and convenient in order that the work could be extended into different systems, provided sufficient precision was obtained.

The plan of experimental work required the construction of a constant voltage source from the diagrams shown in figures 4 and 5.

Then a modified version of Washburn's(57)(59) iodine coulometer was made, Figure 6. Since the Hittorf method was to be used, reactive electrodes (Figure 7) were prepared for the Findlay tubes (Figure 8), because potassium and manganese were unable to be plated out of solution. Two of the iodine coulometers and the Findlay tubes were placed in series with the voltage source and a one molar solution of potassium chloride was electrolyzed. The analytical work was performed on the chloride ion because it is more easily determined with precision by standard methods than either the potassium or the manganous ion. The potassium chloride transference number was to be determined until it agreed with values found in the literature. When it seemed that the apparatus was in working order to give reliable transference numbers, manganous chloride was substituted for the potassium chloride. Starting at 0.5 molar and ending at four molar, transference numbers were determined for the manganous chloride.



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CIRCUIT FOR POWER SUPPLY

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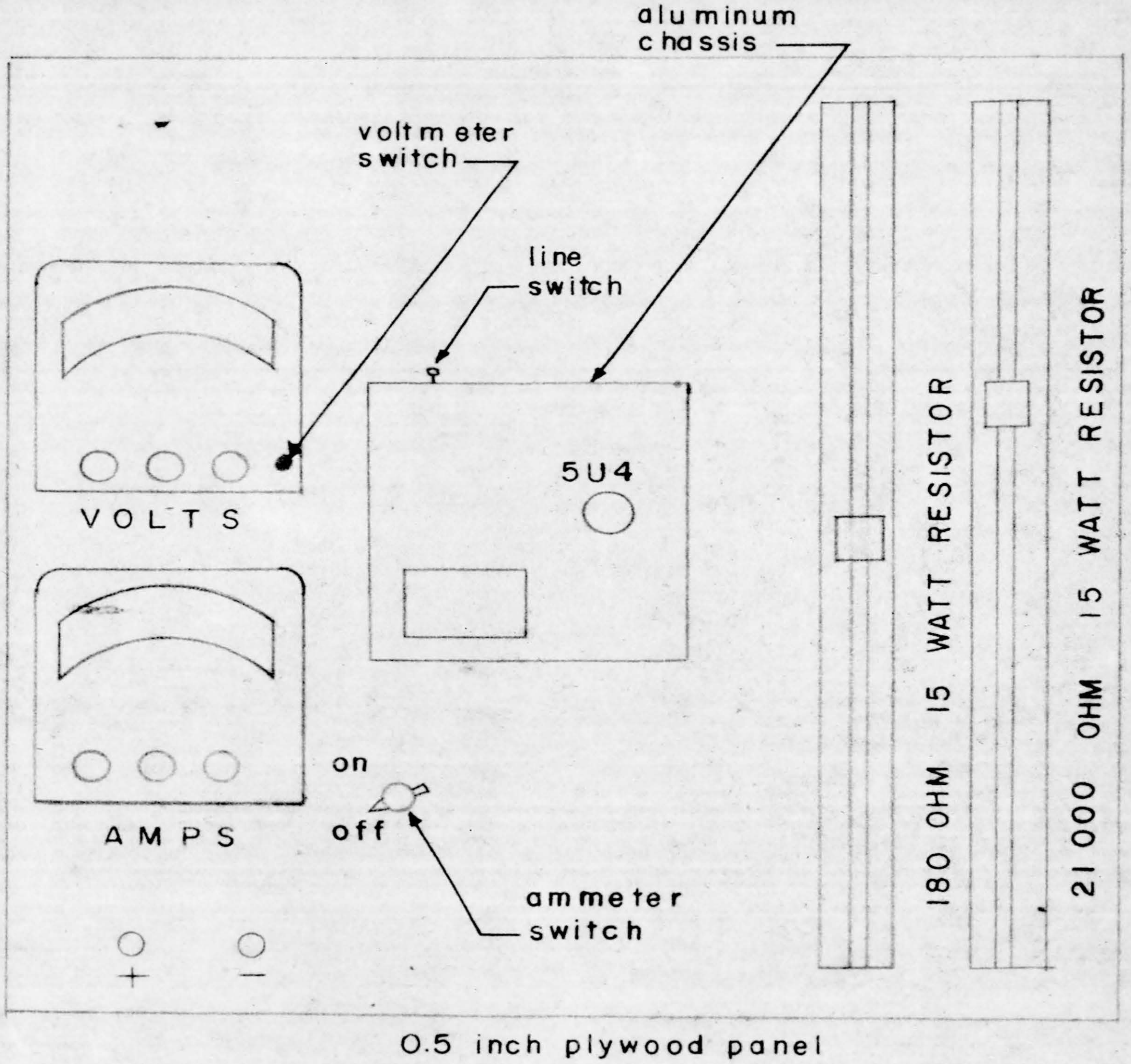
APPROVED BY W.J.J.
DATE 4/20/57
COURSE NO 490
FILE NO 1
FIGURE NO 4
SHEET NO 1



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POWER SUPPLY PANEL BOARD

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CHECKED BY W.J.J. FIGURE NO 5
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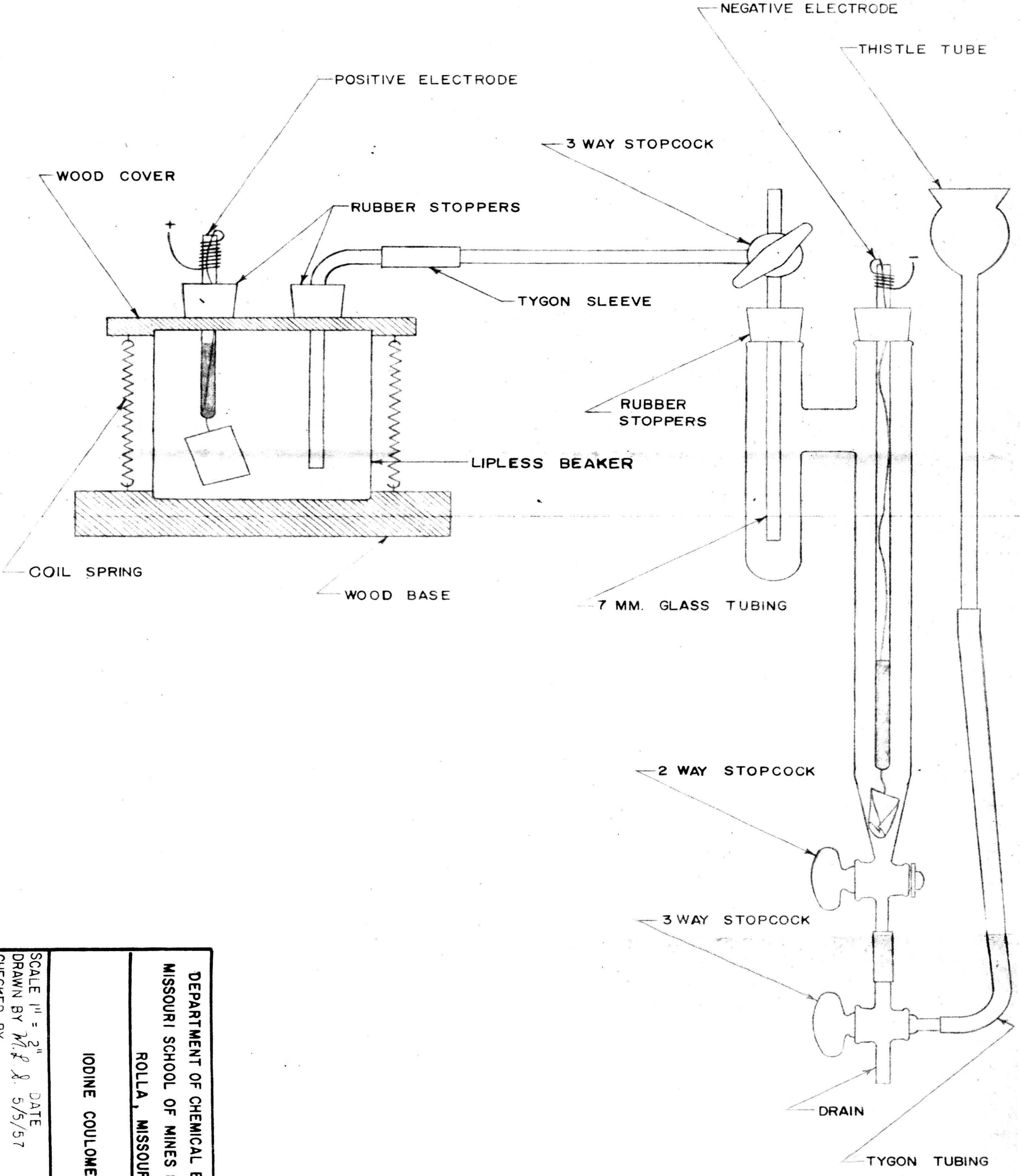

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IODINE COULOMETER

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FIGURE NO. 6
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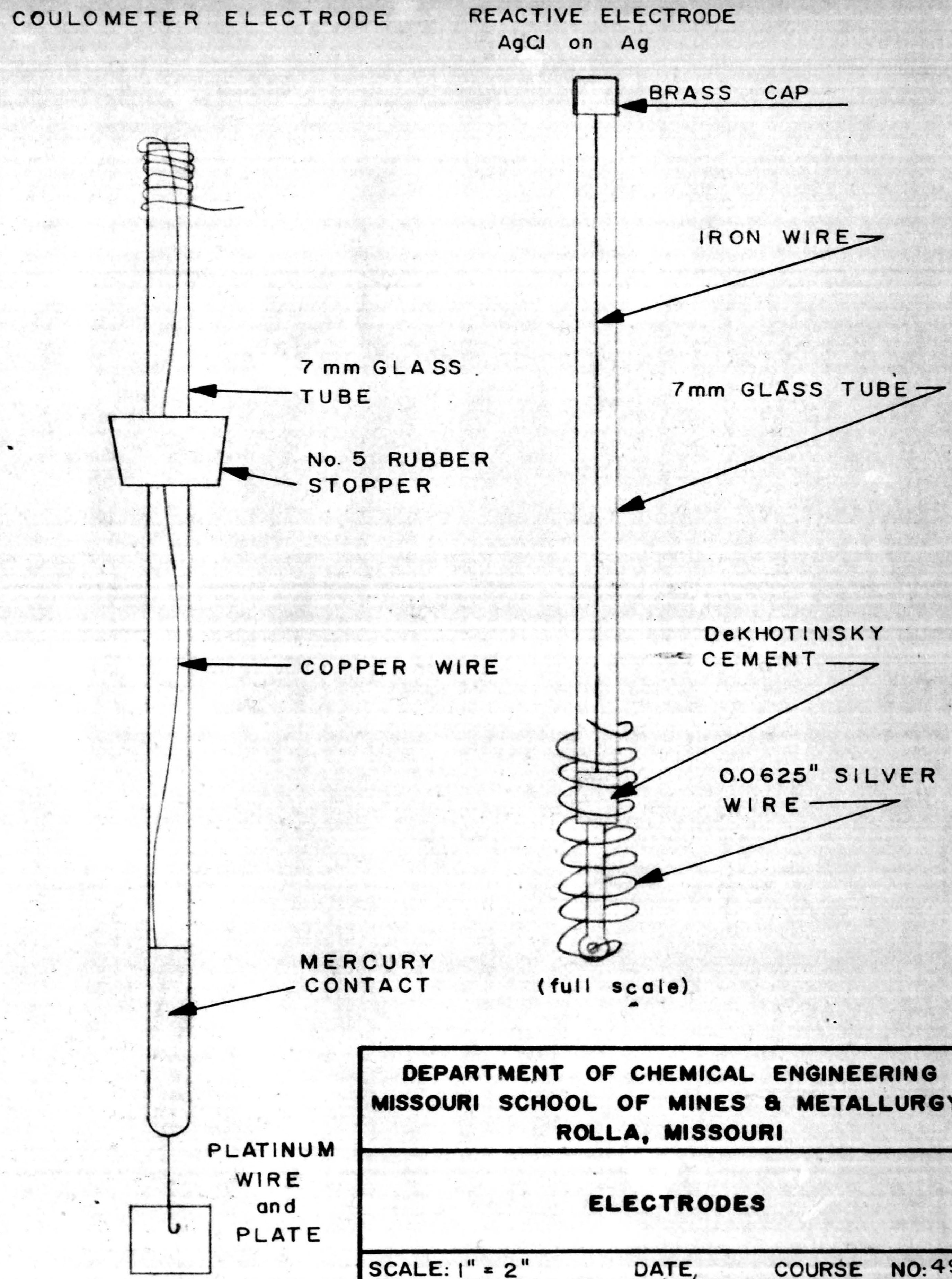

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ELECTRODES

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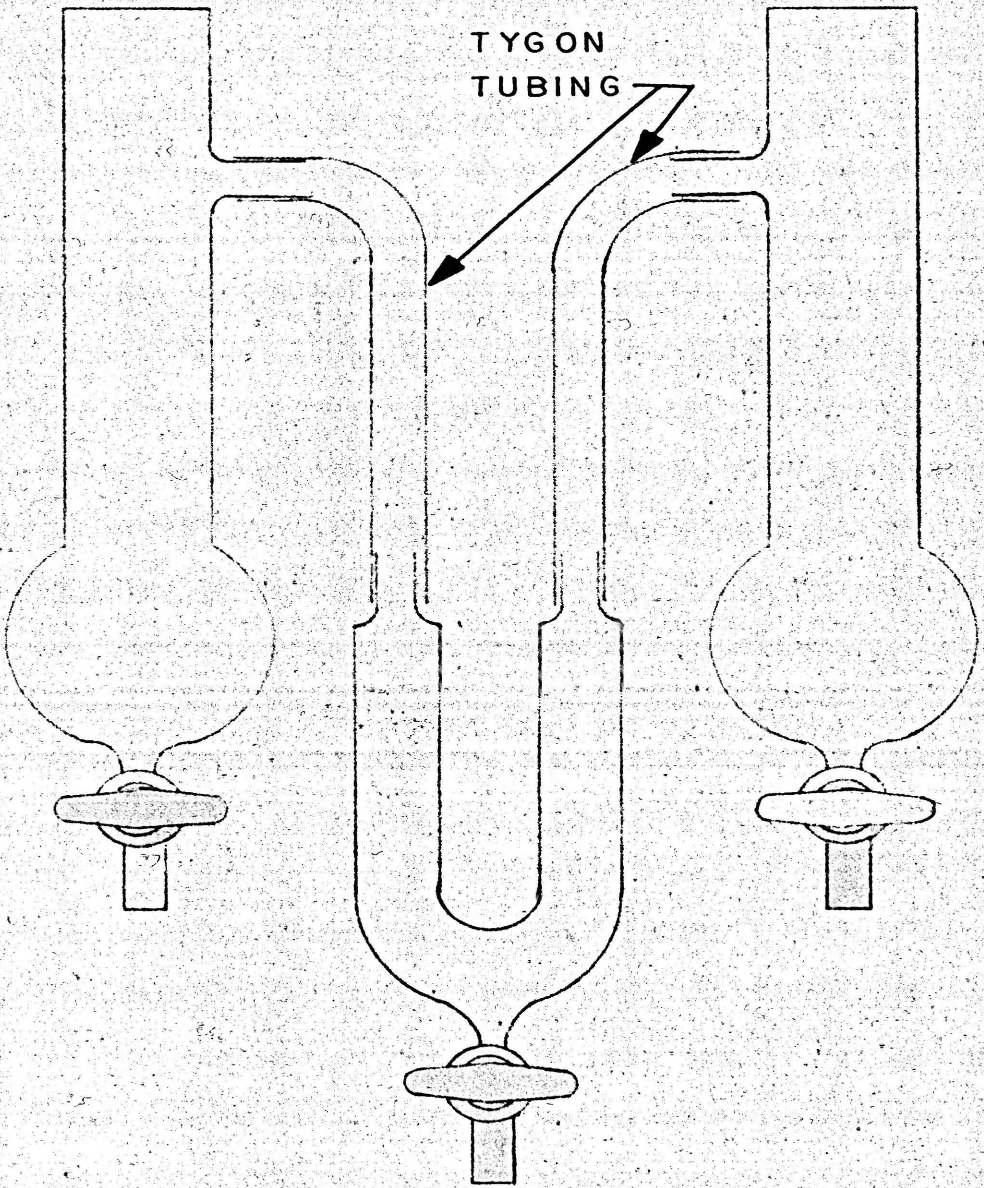

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FINDLAY TRANSFERENCE TUBE

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APPROVED BY: J. J. Y. SHEET NO: 1

APPARATUS

Findlay Tubes. The transference tubes were the Findlay tubes commonly available and shown in Figure 8. When it was desired to stop the electrolysis the tygon tubing was pinched together with clamps and the anode and cathode compartments drained into weight burettes. The clamps were removed and the middle portion also drained. It was necessary to measure the middle portion and compare it with the original solution.

The direct current voltage sourde was made from standard radio power supplies, and the electrical constants are not critical. The large load resistors permit almost any desirable voltage output from full 100 volts to nothing. The filtered direct current was free from harmonics and pulses, and could be held constant for the period of time (10 to 20 hours) needed. The ammeter (0-50 milliamperes) and voltmeter (0-150 volts) were switched in and out of the circuit when necessary and were a check on the power being drawn by the system. The usual current load was 14 milliamperes drawn by two coulometers and the Findlay tubes. The meters were also used as a check to determine if the apparatus was operative. A bubble or leak might break the circuit and not be readily apparent. Excessive currents would mean that a short circuit had developed and current was by-passing part of the system. When the electrolysis of a solution was terminated the number of faradays was determined from the iodine coulometer, The meters read only instantaneous values and were not high precision instruments. The coulometer also integrated out all the variations that might have occurred during peak and light loads on the city mains.

Iodine Coulometer. The iodine coulometer was developed from the coulometer of Washburn.(59) It was desired to have a precision instrument that was more convenient to operate than the one described by Washburn. The accuracy of the coulometer, the arsenic-iodine titration, and the reversibility of the electrodes was proven by Washburn in his article. As long as the electrodes were equivalent only the anode compartment where iodine is formed from potassium iodide was analyzed. This relieved the necessity of preparing a standard iodine solution. The only standard solution was arsenious acid, which reacted with all the iodine found in the anode. Starch was not used for observing the end point because the ionic strength was too strong for starch and one drop of 0.25 normal arsenious acid completely discharged the color at the end point.

The coulometer was assembled as shown in Figure 6. The 600 milliliter lipless anode beaker was filled with about 250 milliliters of ten per cent potassium iodide. The rest of the apparatus held about 200 milliliters. A four molar iodine in potassium iodide solution was introduced into the cathode chamber through the thistle tube by the threeway stopcock in the base. The turbulent flow became smooth in the space between the two stopcocks, and if the boundary was allowed to rise slowly, all the bubbles were forced out without mixing the iodine solution with the ten per cent potassium iodine. The iodine was allowed to rise until it covered the electrode and about half an inch of the glass tip. It was desireable to have an interface between the iodine and the potassium iodide solution above it. A colorless space must exist between the anode and cathode compartments for all the iodine in the anode must have been formed there. The experiment was worthless if iodine diffused into the anode chamber. Generally, after 15 hours the interface at the cathode became diffused about two inches above the platinum electrode plate; the rest of the solution was clear and colorless. When the current was stopped the threeway stopcock on the top of the "H" tube was turned to let the liquid drain out of the salt bridge. The junction of the anode and salt bridge was separated at the rubber slieve. The top of the anode was removed and the glass leg of the salt bridge and the platinum electrode rinsed with a wash bottle. The iodine solution was then titrated with arsenious acid. This coulometer proved to be most convenient and was easily manipulated without spilling concentrated iodine solutions. Both coulometers agreed to within the limits of experimental accuracy, or about 0.2 per cent.

Electrodes. The iodine coulometer requires an inert electrodes of platinum. A piece of seven millimeter glass tubing was welded shut at one end with a two centimeter piece of platinum wire protruding. The platinum wire made contact with mercury inside the tube and copper wire was used as an electric lead from the mercury. The terminal was made by wrapping the copper wire around the top a few times. A drop of glue on top prevented the mercury from falling out if the electrode was ever inverted during cleaning, rinsing, etc. The 2.5 centimeter square platinum plate was welded to the platinum wire so that a larger reactive surface would be available.

The plate is very necessary because the wire alone will reduce the iodine so quickly that the iodine would be exhausted near the electrode and hydrogen would be given off. This causes mixing and destroys the boundary, and usually invalidates the determination. In order to weld platinum wire to platinum plate, it was necessary to heat the wire and plate together on an anvil in the flame of a bunsen burner. When the two pieces were red hot at the point of contact, they were struck a blow with a hammer. Four welds of this nature took normal abuse for 18 months without separating. After welding, the electrodes were cleaned in aqua regia and thereafter required almost no attention.

The Findlay electrodes had to be the reactive type. Since it was not feasible to plate out potassium and manganese in aqueous solution, these cations had to be in effect neutralized upon reaching the cathode. An electrode with chlorine on it would give up the chloride to the cation upon arrival, thereby only increasing the concentration in the vicinity of the electrode without side reactions taking place. If this one reaction would take place alone, it would be accounted for in the calculations.

The electrodes were made of silver wire and were spiraled up the stem about three centimeters. They were cleaned in nitric acid a few times and rinsed with distilled water. Then they were plated with silver for a few hours until the surface became pebbled. The cathode was electrolyzed as an anode in a 600 milliliter beaker with one molar potassium chloride over a silver chloride mud about two centimeters thick serving as a cathode. This allowed more silver chloride to be put on the surface of the electrode than was necessary for the transference tubes. The experiment would be worthless if all of the silver chloride came off and the cathode compartment started evolving hydrogen. The anode was used as is. When an experiment was completed, the anode was covered with bare spots on it. These electrodes were then electrolyzed to remove the chlorine from the anode and to replace it on the cathode in the 600 milliliter beaker with the one molar potassium chloride. When the anode was bare again it was removed and the mud was used as the cathode to put excess chlorine on the cathode electrode. The electrodes were rinsed several times with distilled water. Before a determination was made on a manganous or potassium chloride solution, the electrodes were allowed to soak for several hours in a sample of the solution. The surface area of these electrodes was considerable and if taken immediately from distilled water and placed into the Findlay tubes with a solution in them, the solution would be diluted. Convection currents were observed when the electrodes were placed in the solution for the first time.

Analytical. The analytical apparatus included the usual 50 milliliter burettes, and analytical balance, four 50 milliliter weight burettes, and assorted glassware. The weight burettes were necessary because the basis of analysis had to be molality due to the density changes in the Findlay transference tubes. All reagents used were chemically pure analytical reagent grade chemicals.

PROCEDURE

The coulometers were filled with solutions as described being careful not to destroy the iodine boundary. The Findlay tubes were filled with the chloride solution to be examined and the prepared electrodes placed in their compartments. There is no difference between the anode and the cathode compartments so the placement of the electrodes is arbitrary. The system was placed in series with the voltage source and electrolyzed with 14 milliampered at 80 volts for 15 to 20 hours. At the end of the electrolysis the Findlay tubes were drained into weight burettes and the anode was separated from the rest of the iodine coulometer. The solutions were then analyzed and the transference humber was calculated.

Method of Analysis. Arsenious oxide was used as a primary standard. A weighed sample was dissolved in sodium hydroxide, neutralized with hydrochloric acid, and then buffered with dibasic sodium phosphate, and then diluted in a volumetric flask. This solution of known concentration was titrated into the anode beaker with the solution additionally buffered with sodium bicarbonate. The chemistry of the titrations is described by Washburn in his original article. This method gives excellent results with a minimum of analytical manipulations and more than the required precision.

A weighed sample of the electrolyzed chloride was placed in a volumetric flask and diluted. This dilution was necessary because it was desired to titrate the sample with one burette full of 0.2 or 0.1 Normal silver nitrate. The weight of the sample of concentrated solution was adjusted such that when diluted to 500 milliliters the concentration of the resulting solution was slightly less than that of the silver nitrate solution. Fifty milliliter aliquots were withdrawn from the volumetric flask and analyzed by the Mohr (50) method. The silver nitrate was standardized against weighed samples of sodium chloride.

Table I, II, and III show the results of the experimental work and a comparison with the available similar work found in the literature.

TABLE I

Potassium Chloride Experiments

		Change in eq.		t of Cl in KCl			Deviation
Molal	Faradays	Anode	Cathode	Anode	Cathode	Average	from 0.510
0.9941	0.01029	0.00562	0.00536	0.547	0.534	0.540	4.7%
0.9840	0.01070	0.00536	0.00535	0.500	0.500	0.500	0.2%
1.0269	0.006819	0.00315	0.00353	0.462	0.518	0.495	2.9%

I.C.T. vol VII p.310	Gravemetric method	t of Cl in KCl	0.510
I.C.T. vol VII p.311	EMF method	t of Cl in KCl	0.504
Chem Rev <u>11</u>, 209 (1932)	Moving Boundary	t of Cl in KCl	0.512

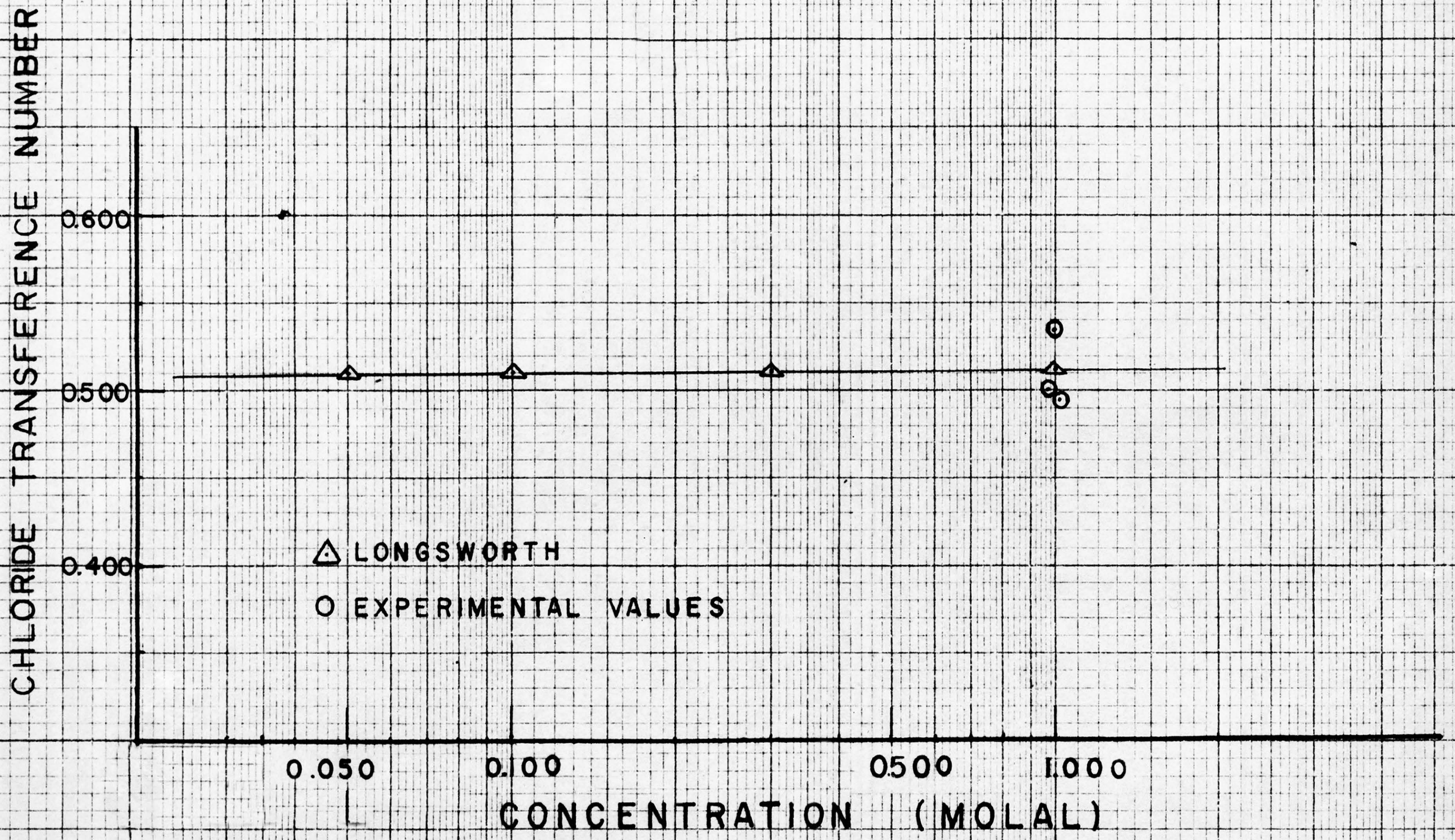

FIGURE 9. KCl TRANSFERENCE NUMBERS

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TABLE II

Manganous Chloride Experiments

Nominal			Change in eq.		t of Cl in $MnCl_2$		
Molar	Molal	Faradays	Anode	Cathode	Anode	Cathode	Average
0.5	0.7025	0.011786	0.008306	0.008587	0.704	0.729	0.716
1.	1.005	0.01260	0.01040	0.00845	0.825	0.671	0.748
2.	1.763	0.00990	0.00745	0.00871	0.753	0.880	0.816
3.	2.480	0.01228	0.01079	0.01169	0.879	0.952	0.916
4.	3.070	0.01972	0.01972	0.01456	1.000	0.810	0.905

TABLE III

Manganous Chloride Transference Numbers as Found in the Literature (43)

Molal	Name	Year	Transference No. of Cl
2.41	Hittorf	1859	0.758
0.0419	Hittorf	1859	0.682
0.0568	Bein	1898	0.613

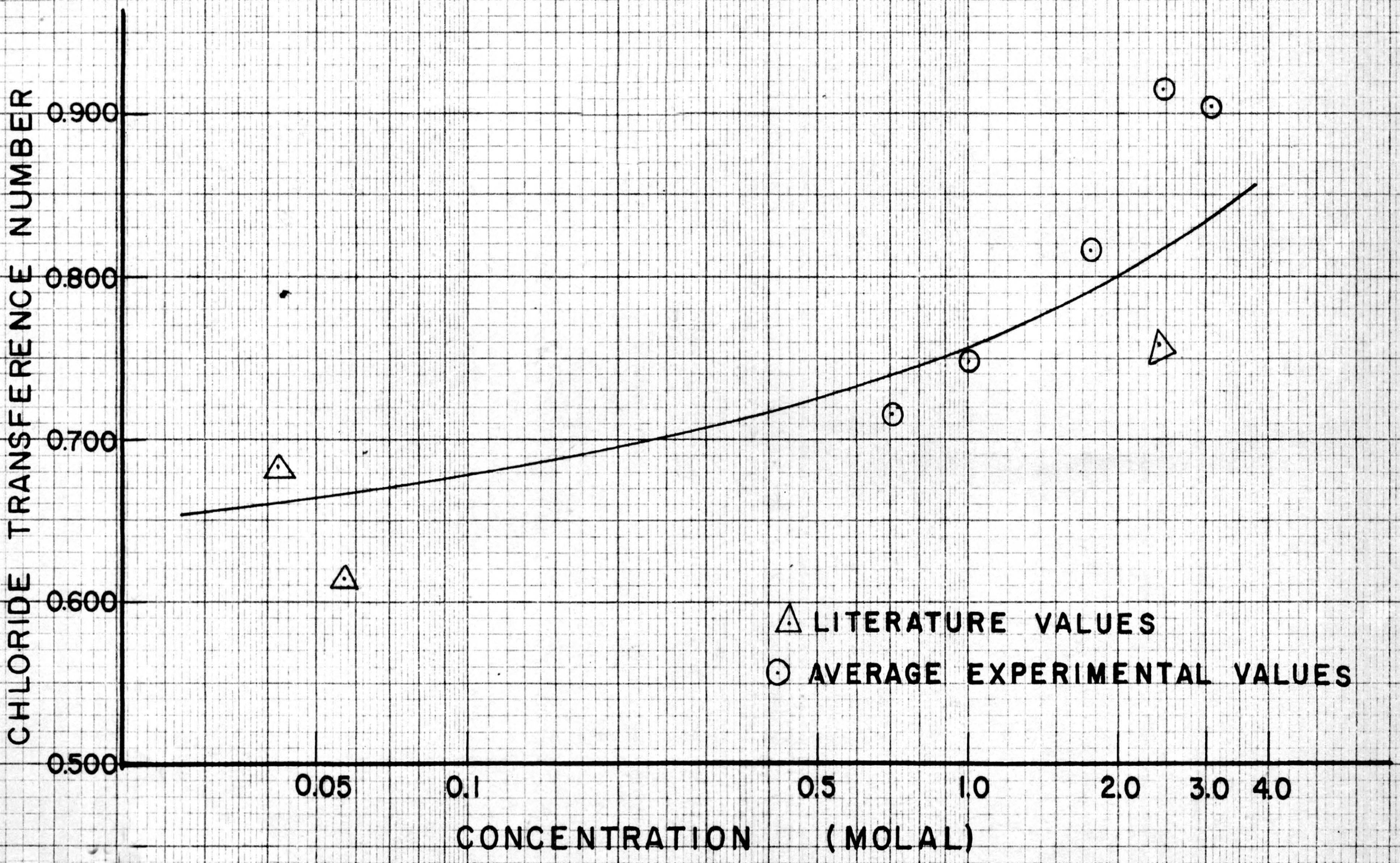

FIGURE 10 $MnCl_2$ TRANSFERENCE NUMBERS

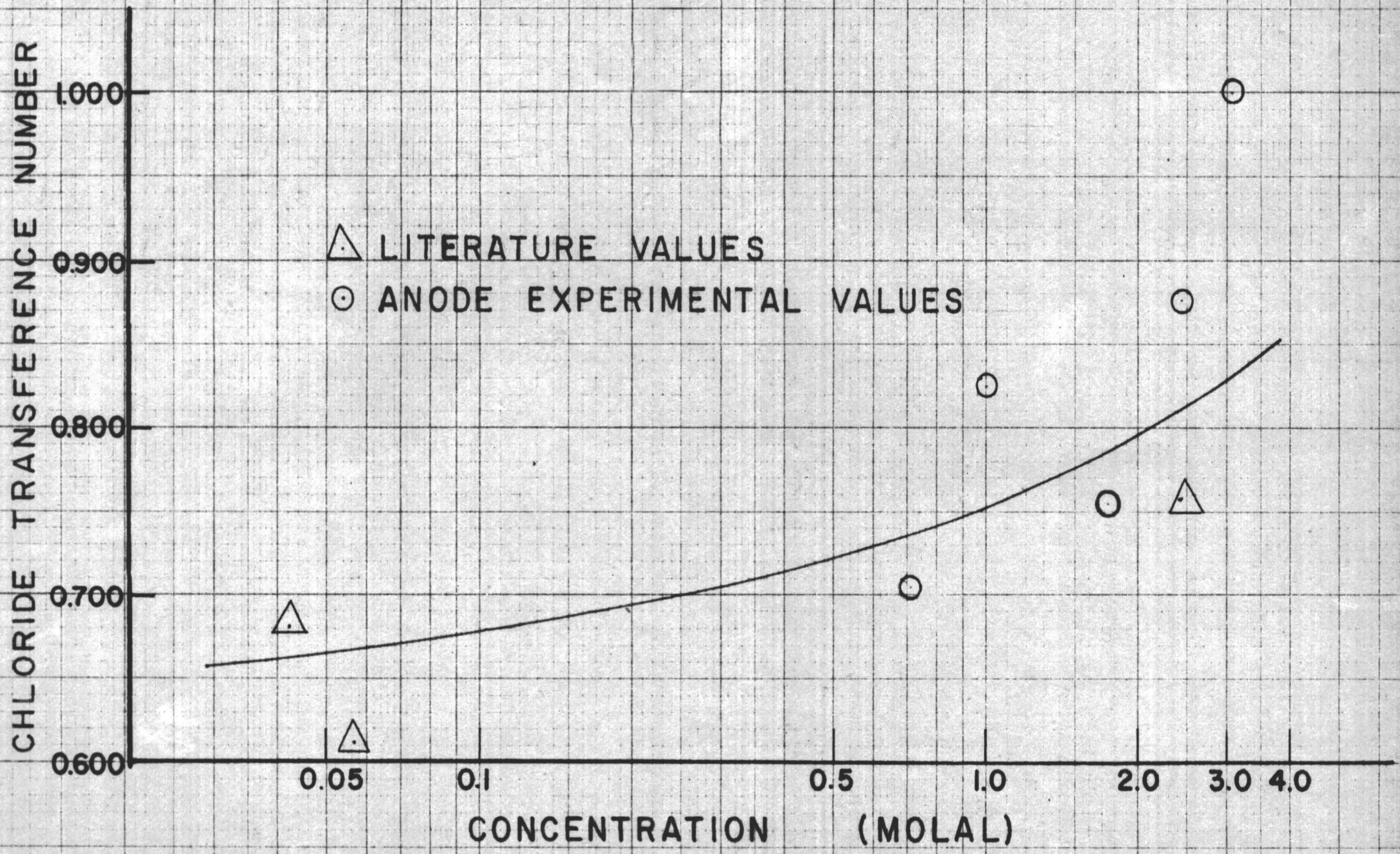

FIGURE 11 $MnCl_2$ TRANSFERENCE NUMBERS

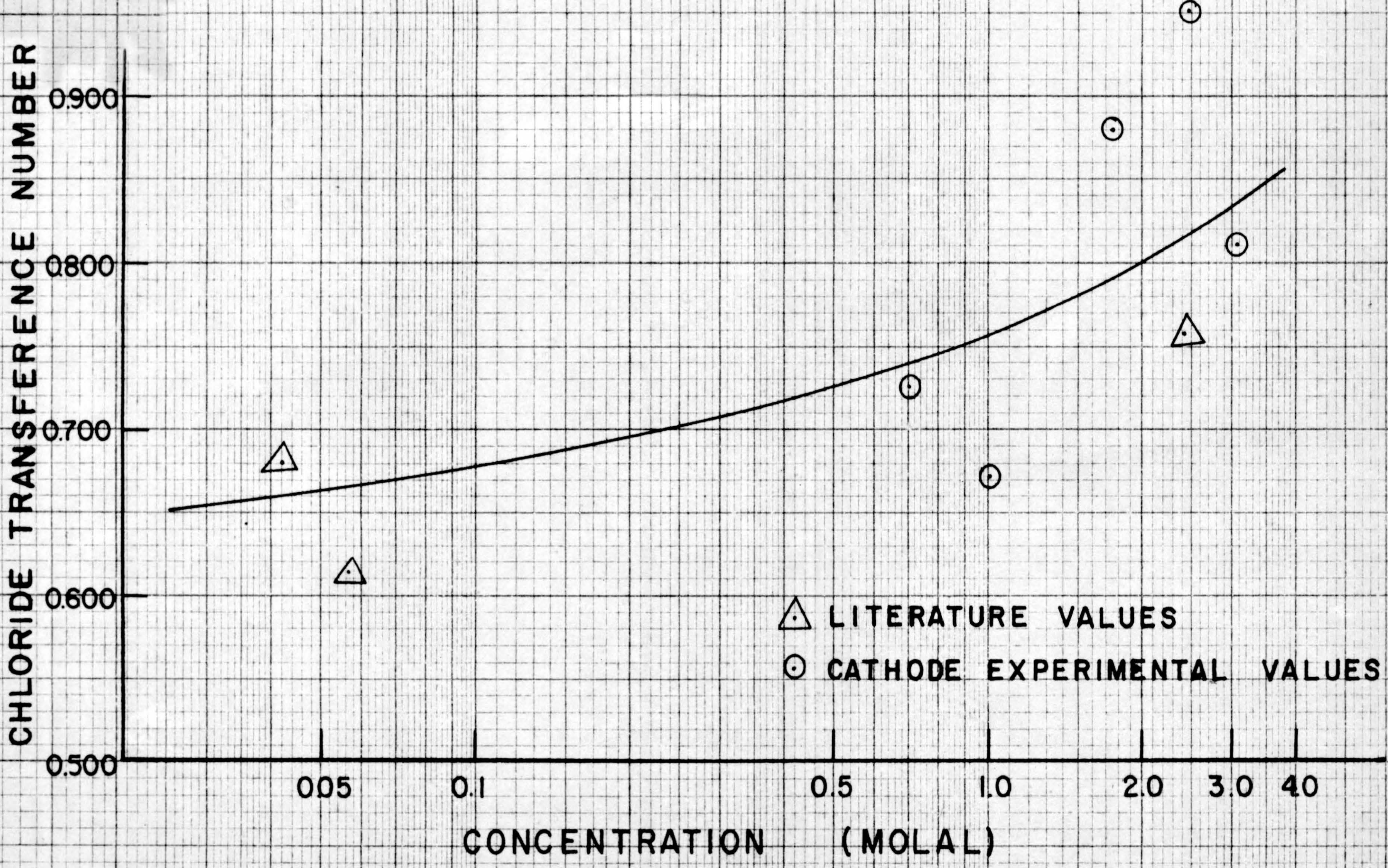

FIGURE 12 $MnCl_2$ TRANSFERENCE NUMBERS

<u>Sample Calculations</u>. The necessary data is listed below as a starting point for the nominal four molar determination.

Total weight of the solutions from the Findlay tubes:

Cathode	Anode	Middle
57.2334 grams	66.6203 grams	21.5046

Faradays passed through the system = 0.01792

Weight of sample analyzed:

Cathode	Anode	Middle	Original
13.1452 grams	19.3408 grams	6.6702 grams	18.5496 g

Diluted to:

500 ml	500 ml	250 ml	500 ml

Milliliters of silver nitrate required, 0.19578 normal.

30.22 ml	43.87 ml	30.38 ml	41.98ml

The grams of manganous chloride per gram of water must be found for the middle compartment and compared against a sample of the original solution. The difference should be negligible.

Middle Compartment

Weight of sample diluted to 250 milliliters is 6.6702 grams.

Chloride analysis shows:

(0.03038)(0.19578) = 0.005948 equivalents of silver nitrate which is the same as the equivalents of manganous chloride per 50 milliliter aliquot.

Then per 250 milliliters of solution there are 0.02974 equivalents or 1.872 grams of manganous chloride.

The total grams of salt in the middle compartment:

$$\frac{1.972}{6.\ 670} = \frac{\text{grams}}{21.51} \quad ; \quad \text{grams} = 6.073$$

which is also 0.09588 equivalents. Then there are (21.505) - (6.037) = 15.468 total grams of water in the middle compartment.

Original Solution

Weight of sample diluted to 500 milliliters is 18.5496 grams.

Chloride analysis shows:

(0.04198)(0.19578) = 0.008219 equivalents of silver nitrate which are the same as the equivalents of manganous chloride in a 50 milliliter aliquot.

Then per 500 milliliters of solution there are 0.08219 equivalents or 5.1730 grams of manganous chloride in the weighed sample.

Ratio for original solution $\frac{5.173}{13.38} = 0.390$

Ratio for middle solution $\frac{6.037}{15.47} = 0.387$

Difference = 0.8%

Cathode Compartment

Weight of sample diluted to 500 milliliters is 13.1452 grams.

Chloride analysis shows:

(0.03022)(0.19578) = 0.005917 equivalents of silver nitrate used in the titration which are the same as the number of equivalents of manganous chloride in a 50 milliliter aliquot.

In the 500 milliliter solution there are then 0.05917 equivalents or 3.724 grams of manganous chloride.

The total number of grams of salt in the cathode compartment is:

$$\frac{3.724}{13.1452} = \frac{\text{grams}}{57.2334} \quad ; \qquad \text{grams} = 16.213$$

which is 0.2576 equivalents. The number of grams of water in the compartment is:

$$(57.233)-(16.213) = 41.020$$

The original number of equivalents in the cathode compartment is calculated on the basis of grams of water in the middle compartment.

$$\frac{0.09588}{15.4700} = \frac{\text{equivalents}}{41.020} \quad ; \quad \text{equivalents} = 0.2542$$

The number of equivalents from the chemical analysis is too large by the number of faradays passed through the system. The manganese, instead of plating out of the solution, removes an equivalent amount of chloride from the silver chloride electrode.

Therefore, the corrected number of equivalents is (0.2576)-(0.0179) = 0.2397 equivalents remaining in the compartment after electrolysis.

The difference between the original number of equivalents and the corrected analyzed value is the number of equivalents transfered out during electrolysis.

$$(0.2542)-(0.2397) = 0.0145$$

The transference number is then defined as the change in equivalents per faraday of electricity:

$$\frac{0.0145}{0.0179} = 0.810$$

Anode Compartment. The anode compartment is calculated in the same manner as the cathode. The only difference is that the correction for the analyzed value of equivalents requires the number of faradays to be added because an equivalent amount of chlorine plated out on the silver electrode.

VI. DISCUSSION

The theory of the Hittorf method requires that the number of equivalents of a given ion that disappear from one electrode appear at the other. The transference number of the chloride ion as calculated from the anode and then from the cathode analysis should be the same. This condition was not met in the case of manganous chloride and only approximately in the case of potassium chloride for this work. The ultimate basis of the Hittorf method is that ions move from one compartment to another under a potential gradient producing no effect other than a change in concentration. The ideal case is where the anion and cation plate out on their respective electrodes. In most cases this ideality is denied and reactive electrodes must be prepared where quantitative reactions take place to effectively neutralize the presence of the migrated ion. In the case at hand, silver and silver chloride electrodes managed the chloride ion concentration in such a manner that metallic potassium or manganese were never formed.

Side Reactions. If hydrolysis, electrolysis of the water, or more than one reaction occurs at an electrode, the basis of the experiment is violated and the results rendered worthless.

Chemical Analysis. Standard methods of chemical analysis were used throughout this work. The arsenic-iodine titration and the Mohr method for chlorides are well written up in almost all quantitative analysis text books. Analytical precision was usually of the order of magnitude of one part in 1000 or better. Although much of the value of the results rests upon the technician type analytical abilities of the experimenter, there are other factore that influence the findings of the transference measurements.

Oxidation-Reduction. It is assumed that the chloride ion is the more stable of the ions and least likely to change in valence except for the quantitative reaction at the electrodes. The manganous ion is very easily oxidized to another valence state, and being in the presence of an oxidizing electrode brings it under suspicion. This ion is also capable of non quantitative cathodic reduction. If these effects occured quantitatively at either electrode, the result could be accounted for in the calculations. It was expected that the silver and silver chloride electrodes would prevent any change in valence. These electrodes are reported everywhere in the literature as being reversible. If, however, manganese were oxidized at the anode instead of chlorine plating out (as silver chloride) then the anode solution would have more chloride in it than supposed. The electrode correction by faradays, assuming an equivalent of chloride plated out per faraday, would have the chloride concentration too high. Subtraction of the original from the "corrected" analyzed value would have the change in equivalents too low and therefore a transference number would result. Conversely, if manganese plated out on the cathode, the difference between the original and "corrected" analyzed value of equivalents would be too large and the transference number would appear higher for the chloride ion. The anode values obtained are higher than the cathode values of the chloride ion corresponding to neither of the above arguments.

Another effect of oxidation is the possible hydrolysis of the highly positive manganese ion. This results in a mixed solution of ions and makes the results worthless.

The wide divergence between the calculations from the anode and cathode measurements suggests that unaccounted for side reactions are in fact taking place, at least to a limited extent.

Recommendations. In the opinion of the author the value of the transference numbers obtained in this work in themselves is small and there is no point in extending the present experiments further under the conditions at hand. The results speak rather clearly for themselves that more is involved than only the movement of ions, which is the basis of the method used. The excessive quantity of labor and time required to produce the results obtained lead to a strong recommendation to forsake the Hittorf method as presently employed. If a new analytical devise or method can be developed which has much greater speed and accuracy than the standard analytical techniques presently available, then perhaps a modified form of the Hittorf method can be developed to obtain useable results.

Limitations. The Hittorf method is recommended only for solutions less concentrated than 0.5 normal, and limited to ions with only one stable valence state in aqueous solutions. This method should only be attempted where reversible electrodes are available with only one chemical reaction which takes place quantitatively. Furthermore, due to the great precision required, only ions capable of such precise analysis should be studied. At best this method has an accuracy of about three to five per cent when compared to the moving boundary transference measurements.

V. CONCLUSIONS

Hittorf transference number measurements of the chloride ion in one molal potassium chloride and 0.7 to 3.0 molal manganous chloride in the Findlay apparatus have led to the following conclusions:

1. The ion which carries more than half of the current may be determined by this method.

2. Potassium chloride measurements may be relied upon for a precision of about three per cent.

3. Manganous chloride measurements may be relied upon to show that the chloride ion carries about 66 per cent of the current during electrolysis.

4. As the concentration of the manganous chloride is increased the chloride ion transference number increases.

5. This is not a precision method of determining relative ionic mobilities.

6. A method of analysis that is superior to the standard methods at hand is required to find the small changes in concentration of the pure salt solutions.

VI. SUMMARY

The chloride ion transference number was determined analytically in a one molal solution of potassium chloride with an agreement to within three per cent of the values found in the literature. Three per cent is about the accuracy accepted in other literature reports. The mobility of the chloride ion in potassium chloride does not change with concentration up to one molal. In manganous chloride solutions stronger than 0.7 molal the chloride ion becomes more mobile as the concentration is increased. Dilute solutions of manganous chloride were not examined, and only three manganous chloride transference numbers could be found in the literature. It was recommended that a different method be developed to find ionic mobilities in order to avoid the complicating side reactions found in the Hittorf method.

VII. BIBLIOGRAPHY

1. Allgood, R.W. and D.J. LeRoy and A.R. Gordon: The Variation of the Transference Numbers of Potassium Chloride in Aqueous Solution with Temperature, J. Chem. Phys., 8, 418, (1940)

2. _____________ and A.R. Gordon: The variation of the Transference Numbers of Sodium Chloride in Aqueous Solution with Temperature II, J. Chem. Phys., 10, 126 (1942)

3. Bein, W.: Zur Bestimmung dir Uberfuhrung Bei der Electrolyse verdunnter wasseriger Saltzlosungen, Zeit fur phys Chem., 27, 1 (1898)

4. Benson, C.G. and A.R. Gordon: The Conductance of Aqueous Solutions of Calcium Chloride at Various Temperatures from 15 °C to 45 °C., J. Chem. Phys., 13, 470 (1945)

5. _____________________________: A Reinvestigation of the Conductance of Aqueous Solutions of Potassium Chloride, Sodium Chloride, and Potassium Bromide at Temperatures from 15 °C to 45 °C., J. Chem. Phys., 13, 473 (1945)

6. Brand, G.E.: The Effect of a Magnetic Field on the EMF of a Galvanic Cell, (Unpublished PhD Dissertation) Department of Chemistry, State College of Washington (1955).

7. __________: Personal Communication, Sept. 1955, Rolla, Missouri.

8. Daniels, F. et al: "Experimental Physical Chemistry," p. 332-340, McGraw Hill Book Co., Inc. New York, N.Y., 1941, 3rd ed.

9. Davies, C.W.: "The Conductivity of Solutions," John Wiley & Sons, Inc., New York, N.Y., 1930, 2nd ed.

10. Dole, M.: The Limiting Law for Transference Numbers, J. Phys. Chem., 35, 3647 (1931)

11. Dye, J.L. and F.H. Spedding: The Application of Onsager's Theory of Conductances and Transference Numbers of Unsymetrical Electrolytes, J. Am. Chem. Soc., 76, 888 (1954)

12. Falk, G.K.: Transference Experiments with Thallous Sulfate and Lead Nitrate, J. Am. Chem. Soc., 32, 1555 (1910)

13. Faulk, C.W. and A.T. Bawden: A New Type of End Point in Electrometric Titrations and its Application to Iodometry, J. Am. Chem. Soc., 48, 2044 (1926)

14. Findlay, A.: "Introduction to Physical Chemistry" p. 212-249, Longmans, Green & Co., New York, N.Y., 1946, 7th ed.

15. ___________: "Practical Physical Chemistry," p. 188-193, Longmans, Green & Co., New York, N.Y., 1941, 2nd ed.

16. Forbes, G.F.: The Solubility of Silver Chloride in Chloride Solutions and the Existence of Complex Argentichloride Ions, J. Am. Chem. Soc., 33, 1937 (1911)

17. Glasstone, S.: "Introduction to Electrochemistry," p. 29-130, D. VanNostrand Co., Inc., Lancaster, Pa., 1942

18. Goode, K.H.: A Continuous Reading Electrotitration Apparatus, J. Am. Chem. Soc., 44, 26 (1922)

19. Gunning, H.E. and A.R. Gordon: The Conductance and Ionic Mobilities for Aqueous Solutions of Potassium and Sodium Chloride at Temperatures from 15°C to 45°C., J. Chem. Phys., 10, 126 (1942)

20. Hallam, H.E.: A Student Transference Apparatus, J. Chem. Ed., 31, 306 (1954)

21. Hamer, W.J.: Temperature Variation in Transference Numbers of Concentrated Sulfuric Acid Solutions as Determined by the Galvanic Cell Method, J. Am. Chem. Soc., 57, 662 (1935)

22. Harned, H.S. and E.C. Dreby: Properties of Electrolytes in Mixtures of Water and Organic Solvents, IV Transference Number of Hydrochloric Acid in Water and Dioxane Mixtures from 0 °C to 50°C., J. Am. Chem. Soc., 61, 3113 (1939)

23. ___________ and W.J. Hamer: The Thermodynamics of Aqueous Sulfuric Acid Solutions from EMF Measurements, J. Am. Chem. Soc., 57, 27 (1935)

24. ___________ and B.B. Owen: "Electrolytic Solutions," pp. 75-94, 135-178, Reinhold Publ. Corp., New York, N.Y., 1950, 2nd ed.

25. Hartley, G.S.: A New Method of the Determination of Transference Numbers, Trans. Faraday Soc., 30, 648 (1934)

26. Hoyt, C.S.: Factors Affecting the Accuracy of Transference Number Determinations, J. Chem. Ed., 14, 472 (1937)

27. International Critical Tables, VI, p. 309

28. Jahn, H.: Uber die Wanderungsgeschwindigkeit der Ionen in verdunnten Losungen, Zeit fur phys Chem., 37, 691 (1901)

29. Jones, G. and B.C. Bradshaw: The Transference number of Lithium Chloride as a Function of Concentration, J. Am. Chem. Soc., 54, 138 (1932)

30. Keenan, A.G. and H.G. McLoed and A.R. Gordon: The Variation of Transference Numbers for Calcium Chloride in Aqueous Solutions with Temperature III, J. Chem. Phys., 13, 466 (1945)

31. Lang, A.E. and C.V. Ing: Transference Numbers in Aqueous Zinc and Cadmium Sulfates, J. Am. Chem. Soc., 76, 4716 (1954)

32. LeRoy, D.J.: Transference Numbers of Electrolytes: A Bibliography, University of Toronto Studies, Papers from the Chemical Laboratories Number 156 (1939)

33. Levy, A.L.: Difficulties in the Hittorf Method of Determining Transference Numbers, J. Chem. Ed., 29, 384 (1952)

34. Longsworth, L.G.: Transference Numbers of Aqueous Solutions of Potassium Chloride, Sodium Chloride Lithium Chloride, and Hydrochloric Acid at 25 °C by the Moving Boundary Method, J. Am. Chem. Soc., 54, 2740 (1932)

35. ________________: Transference Numbers of Aqueous Solutions of Some Electrolytes at 25 °C by the Moving Boundary Method, J. Am. Chem. Soc., 57, 1185 (1935)

36. MacInnes, D.A.: "The Principles of Electrochemistry," p. 59-95 Reinhold Publ. Corp., New York, N.Y., 1939

37. ________________: The Ionization of Some Typical Strong Electrolytes, Trans. Faraday Soc., 23, 400 (1927)

38. ________________ and J.A. Beattie: The Free Energy of Dilution and the Transference Numbers of Lithium Chloride Solutions, J. Am. Chem. Soc., 42, 1117 (1920)

39. ________________ and M. Dole: Differential Potentiometric Titrations III An Improved Apparatus and its Application to Precision Measurements, J. Am. Chem. Soc., 51, 1119 (1929)

40. ____________________________: The Transference Number of Potassium Chloride. New Determinations by the Hittorf Method and a Comparison with Results Obtained by the Moving Boundary Method, J. Am. Chem. Soc., 53, 1357 (1931)

41. ________________ and L.G. Longsworth: Transference Numbers by the Method of Moving Boundaries, Chem. Rev., 11, 171 (1932)

42. Mason, C.M. and E.F. Mellon: An Experiment for the Determination of Transference Numbers by the EMF Method, J. Chem. Ed., 16, 512 (1939)

43. McBain, J.W.: The Experimental Data of the Quantitative Measurements of the Electrolytic Migration, Proceedings Wash. Acad. Sci., 9, 1, (1907)

44. Moore, W.J.: "Physical Chemistry," p. 435-497, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1955, 2nd ed.

45. Murphy, G.W.: Equivalent Circuit Model of the Transference Cell, J. Electrochem. Soc., 101, 44 (1954)

46. Noyes, A.A. and K.G. Falk: The Properties of Salt Solutions in Relation to the Ionic Theory of Electrical Transference Numbers, J. Am. Chem. Soc., 33, 1436 (1911)

47. ___________ and M.S. Sherrill: "A Course of Study in Chemical Principles," p. 297-362, The MacMillan Co., New York, N.Y., 1954, 2nd ed.

48. ___________ and G.V. Sammet: The Equivalent Conductivity of the Hydrogen Ion from Transference Number Experiments with Hydrochloric Acid, J. Am. Chem. Soc., 24, 946 (1902)

49. ___________________________: Die aquivalent Leitgahigkeit des Wasserstoffions abgeleitet aus Uberfuhrungsversuchen mit Salzsaure, Zeit fur Phys Chem., 58, 641 (1907)

50. Pierce, W.C. and E.L. Haenisch: "Quantitative Analysis," p. 293, John Wiley & Sons, Inc., New York, N.Y., 1948, 3rd ed.

51. Reilley, J. and W.N. Rae: "Physico-Chemical Methods," p. 577-587, 2, Methuen & Co., Ltd., London, 1954, 5th ed.

52. Roemer, T.J. and Cooley: An Inexpensive Transference Apparatus, J. Chem. Ed., 28, 37 (1951)

53. Robinson, R.A. and R.H. Stokes: "Electrolyte Solutions," p. 48-172, Butterworths Scientific Publications, London (1955).

54. Smith, C.J.: "Electricity and Magnetism," p. 636-696, Edward Arnold Publishers, Ltd., London (1954).

55. Stokes, R.H.: The Variation of Transference Numbers with Concentration, J. Am. Chem. Soc., 76, 1988 (1954).

56. VanName, R.G. and F.Fenwick: The Behavior of Electrodes of Platinum and Platinum Alloys in Electrometric Analysis II Polarized Electrodes, J. Am. Chem. Soc., 47, 19 (1925).

57. Washburn, E.W.: The Iodine Coulometer, J. Am. Chem. Soc., 30, 31 (1908).

58. ____________: The Hydration of Ions Determined by Transference Experiments in the Presence of a non Electrolyte, J. Am. Chem. Soc., 31, 322 (1909).

59. ____________ and S.J. Bates: The Iodine Coulometer and the Value of the Faraday, J. Am. Chem. Soc., 34, 1341 (1912).

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The author was born May 18, 1930 at East Chicago, Indiana. He was educated in the public schools of East Chicago, and Hammond, Indiana. In August 1952 he graduated from Indiana University with a B.S. degree in chemistry, and was employed as a chemist by the Socony Vacuum Oil Company. The three summers previous he worked for Inland Steel Company in the open hearth department and in the electrolytic tinplate department. In January 1953 he was inducted into the Army Corps of Engineers at Fort Leonard Wood, Missouri, and was released from active duty as a sergeant in January 1955. The author entered the graduate school at Missouri School of Mines and Metallurgy the Spring semester of 1955, and was appointed a graduate assistant. In September 1956 he was appointed an Instructor of Chemistry.