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A Study of the Heat Effects at Electrodes During Electrolysis

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To the Graduate Council:

I am submitting herewith a dissertation written by Howard Frank Holmes entitled "A Study of the Heat Effects at Electrodes During Electrolysis." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Michael J. Joncich, Major Professor

We have read this dissertation and recommend its acceptance:

William T. Smith, John A. Dean, William E. Brill, John W. Prados

Accepted for the Council:

Carolyn R. Hodges

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(Original signatures are on file with official student records.)

November 21, 1958

To the Graduate Council:

I am submitting herewith a dissertation written by Howard Frank Holmes entitled "A Study of the Heat Effects at Electrodes During Electrolysis." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

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Major Professor

We have read this dissertation
and recommend its acceptance:

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Accepted for the Council:

Dale Wantling
Dean of the Graduate School

A STUDY OF THE HEAT EFFECTS AT ELECTRODES DURING ELECTROLYSIS

A DISSERTATION

Submitted to
The Graduate Council
of
The University of Tennessee
in
Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

by

Howard Frank Holmes

December, 1958

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CHAPTER I

INTRODUCTION AND HISTORICAL

A. Classical Thermodynamics of Electrochemical Cells

The application of classical chemical thermodynamics to reversible electrochemical cells is well founded in both theory and experiments. The thermodynamics of Gibbs and Nernst provide one with the well known equations used in studying and describing reversible electrochemical systems. The study of such systems has provided a multitude of badly needed thermodynamic data as well as much useful information about the physical chemistry of solutions.

The usual method of conducting such a study is to measure the voltages of a reversible electrochemical cell as a function of concentration and temperature. From experiments such as these and by using the well known thermodynamic equations, one is able to obtain values for the enthalpy change, the free energy change, the entropy change, the standard potential of the cell, and activities of the solutions involved.

Studies such as these are limited in their application, however, as they are valid only for strictly reversible conditions. In actual practice, there are only a relatively few electrodes which are strictly reversible. As a further restriction, the condition of reversibility requires that the measurements be made under a state of zero current flow. Thus classical electrochemical thermodynamics is limited to those few electrodes which are reversible and then only under conditions of zero current flow.

The departure of the potential of an electrode from its reversible value under the influence of current flow is termed polarization, overvoltage, or overpotential. The total polarization is made up of three types of polarization, the relative magnitudes of which vary with the conditions and the electrode system. These are ohmic or resistance polarization, concentration polarization, and activation polarization. Ohmic polarization results from the potential drop associated with such things as oxide layers on the electrode, gas bubbles at the electrode-solution interface, and resistance of the solution in the immediate vicinity of the electrode. Concentration polarization results from the deficiency (in the case of cathodic reactions) or excess (in the case of anodic reactions) of electroactive ions* in the immediate vicinity of the electrode as compared to the bulk of the solution. Activation polarization, as the name implies, results from the activation energy associated with the rate controlling step in the postulated mechanism of the electrode reaction. Of the three types of polarization, activation polarization has received the most attention.

The usual method of studying polarization is to use a three electrode system. One of these, the working electrode, is the electrode of interest for which polarization values are desired. Another electrode

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*Electroactive ions are those ions which are directly involved in the electrode reactions.

is the reference electrode which is used in conjunction with the working electrode to obtain voltage values as a function of current strength. Essentially no current is passed between the reference electrode and the working electrode. Electrical connection between the working electrode and the reference electrode is accomplished by means of a capillary probe, the tip of which is placed very near the working electrode. The third electrode merely serves as a means of passing current through the working electrode. The difference between the potential (with respect to the reference electrode) of the working electrode during current flow and the potential under conditions of zero current is taken as equal to the polarization. One can see that, from the thermodynamic point of view, such polarization values are meaningless unless a satisfactory reversible value for the potential can be measured. Here again such values are thermodynamically significant only for those electrodes which are reversible. This leaves untouched vast numbers of practical irreversible electrodes and does not even suggest a method for measuring thermodynamic properties at electrodes where simultaneous reactions are occurring.

The preceding serves merely to emphasize the limitations of classical electrochemical thermodynamics and to stress the need for a new method for the study of electrochemical systems.

B. Previous Work

1. Heat Evolved by Electrochemical Cells

The earliest experiments appearing in the literature concerning the heat effects of a cell during electrolysis were those of Faure.[1] Faure used a mercury calorimeter of doubtful reliability to obtain his results. In addition the current density and temperature are not given. However, he does state that the current is so low that the irreversible Joule heat due to the ohmic resistance of the cell is negligible. Such a statement is highly questionable.

The phenomenon of a heat effect at a single electrode was first reported by Mills[2] in 1877. His findings were obtained by coating the bulb of a mercury thermometer with a metal which then served as the cathode in an electrolytic cell. Mills interpreted this heat effect as a result of the work of the electrode reaction "phenomena".

Two years later Bouty[3] began a research on a similar system. Like Mills, his results were obtained by using a metal plated thermometer bulb as an electrode. Bouty was the first to draw the analogy between the heat effect existing at a single electrode and the Peltier effect which occurs at the junction of two dissimilar metals.* Bouty studied copper, zinc, and cadmium electrodes and supplemented his work by making measurements on electrolytic thermocells.[4]

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*This explains why most of the earlier work appears in the literature under the title of the "electrolytic Peltier effect".

Jahn[5] used a Bunsen ice calorimeter to make his measurements on the work delivered by a battery. He used essentially the same experimental technique to make his measurements on heat effects localized at the electrodes in electrolytic cells. The metals studied by Jahn were copper, cadmium, zinc, and silver. It is in this article that Jahn states that the heat effect is equivalent to the current energy corresponding to polarization. Gill,[6] using a copper resistance thermometer, also made some measurements which were in direct disagreement with some of Jahn's earlier work.[7] Brauer[8] did some work on the so-called "electrolytic Peltier effect" using non-adiabatic calorimetry. He compared his results with measurements on the corresponding thermocells.

In 1913 J. W. Richards[9] carried out some experiments to show that overvoltage, or polarization, did no chemical work but was due to increased surface resistance of the electrodes. The reaction studied was the electrolysis of water. The question he wished to answer was whether the overvoltage increased the theoretical decomposition voltage or whether it appeared as an additional resistance voltage. To answer this, Richards treated an electrochemical cell containing dilute sulfuric acid as a calorimeter and measured the sensible heat given off during the electrolysis. Knowing the heat equivalent of the current passed, he subtracted the sensible heat measured and the difference was the heat disappearing in chemical work. From this, the decomposition voltage was calculated. Within experimental error, this was equal to the theoretical decomposition voltage in all cases, even when using different electrode materials. Using Richard's data, one can calculate the heat of formation of water.

This was done and values of -68.4, -67.8, and -70.0 kilocalories per mole of water were obtained. All three of the values are in fair agreement with the accepted value if one considers the accuracy of his experimental measurements. It is interesting to note that Richards never refers to an electrolytic Peltier effect.

Guglielmo[10] made some calorimetric measurements on heat effects occurring between zinc electrodes and a zinc sulfate solution. His calorimeter, however, was not suitable as it consisted of two beakers, one for each electrode, connected by a salt bridge, with a mercury thermometer immersed in each beaker.

Butler,[11] in discussing the seat of electromotive force in a galvanic cell, states that the latent heat in a cell is analogous to the Peltier effect. However, no statement is made concerning its magnitude or its definition in terms of other thermodynamic quantities.

In 1929 Bruzs[12] started making temperature measurements on working electrodes. His apparatus consisted of 240 thermocouples imbedded in a nickel electrode which served as an anode. The electrolyte was a mixture of nickel sulfate and ammonium sulfate with a little citric acid added. The only result recorded with this apparatus was that the surface temperature of the anode increased as the current density was increased up to the current density at which oxygen was evolved. At this point, there was a sudden rise in the anode surface temperature.

This apparatus was later modified by Bruzs[13] to enable him to measure the difference in temperature between the cathode and anode surfaces. It was found that during the electrolysis of water, there was a short period during which the cathode was at a higher temperature but the anode temperature eventually became greater in all cases. The difference in temperature of the two electrodes increased with an increase in current density. There was also a decided temperature rise at the cathode when silver was deposited from a silver nitrate solution. This effect was not nearly as great as in the case of evolution of oxygen or hydrogen. The temperature rise during the deposition of oxygen, hydrogen, and silver was found to be in the ratio of 7.3:4.9:0.6, respectively.

At no time in his first two articles did Bruzs mention a Peltier effect. However, in a later article[14] he stated that the temperature effect at a working electrode may be considered as a Peltier effect, or, as the latent heat of the electrode process. He reasoned, therefore, that these measurements could lead to a means of determining the entropy of ions. Accordingly, he measured the temperature effect on silver, lead, cadmium, bismuth, zinc, and copper electrodes. For molar solutions of silver, lead, and bismuth as nitrates and cadmium, zinc, and copper as sulfates, the following values for the absolute partial molal ionic entropies were obtained, respectively: 19, -1, -11, -26, -19, and -29 calories per mole per degree.

In 1930 Lange and his co-workers[15] began their series of measurements of the electrolytic Peltier effect. An adiabatic, differential calorimeter was employed to obtain measurements on the mercury-mercurous electrode. The heat values obtained during electrolysis increased in a positive direction with increasing metal ion concentration, in agreement with their theoretical prediction. Lange arrived at his theoretical interpretation by relating the heat effect at the electrode to the temperature coefficient of the electrode potential. Lange stated that this was possible only if one regards the heats of transfer* as being equal to zero.

Shortly thereafter Bruzs[16] completed his study of the mercury-mercurous electrode in both nitrate and perchlorate solutions. Studies were done at various concentrations and the results were applied to the calculation of the partial molal entropy of the mercurous ion. Bruzs' results are in general agreement with those of Lange and Monheim[15] both as to order of magnitude and in variation of the entropy with mercurous ion concentration. Bruzs reported the partial molal entropy of the mercurous ion in solutions of unit activity as 29 ± 1 calorie per mole per degree. He did not, however, explain how he arrived at the concentration of a solution in which the activity of the mercurous ion is unity.

In a later article Bruzs[17] gave a rather convincing argument that the heats of transfer of ions can affect the electrolytic Peltier heats only in the case of concentration polarization. He postulated that one may equate the Peltier heat and the latent heat of the electrode process in those cases where concentration polarization is not significant. In the same article he discussed some rather inconclusive measurements on the cadmium-cadmium amalgam electrode. Further, he gave an argument,

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*This quantity will be discussed in the section on thermocells.

which was rather vague, proposing the use of heat measurements to calculate absolute partial specific heats of individual ions.

In his last article in this series, Bruzs[18] described a dynamic calorimeter to make measurements on a copper electrode in a copper sulfate solution. His results were used to calculate the Peltier coefficient and partial molal entropy of the copper ion in the solutions used. For solutions of mole fraction 0.0180, 0.0040, and 0.0004, the partial molal entropy of the copper ion was found to be 27.8, 25.1, and 20.7 calories per mole per degree, respectively.

In 1932 Lange and Hesse[19] published an article on the electrolytic Peltier heat in the silver-aqueous silver nitrate system. Their discussion was based on the assumption that the Thompson relation cannot be regarded as valid for electrolytic systems because of its derivation for a circular process. However, they further assume that it may be applied to electrolytic systems if one adds a term involving the molecular heats of the substances moving under the influence of the current. Their investigation was started because of the possibility that errors may be present in previous measurements on the electrolytic Peltier heat. A comparison of their results with the corresponding electrolytic thermopower gave satisfactory results within the limits of experimental error. No attempt was made to correlate their results with partial molal ionic entropies of ions.

In their next article Lange and Hesse[20] described measurements made on the Peltier heats at a silver-silver chloride electrode. Here again Lange and Hesse introduced the concept of heats of transport.

They stated that these quantities are probably about 100-300 calories per mole, almost independent of concentration, but that they are related to transport numbers. Lange and Hesse[21] pursued this idea further by making measurements on the electrolytic heat effect in the systems silver-aqueous silver nitrate and silver-silver chloride in the presence of potassium, lithium, and hydrogen ions. Their results were interpreted as establishing the existence and necessity for considering heats of transport. However, their results might be interpreted just as well by considering the variation in activity of the chloride ion in aqueous solutions of potassium chloride, lithium chloride, and hydrogen chloride.

Chalmers,[22] without making reference to any of the earlier work, discussed the Peltier effect at metal-electrolyte junctions and at the liquid junction in concentration cells. This effect was given by him as being equal to the product of the absolute temperature and the entropy change occurring at the junction. He further stated that measurement of this effect would give a means of obtaining the absolute entropies of ions.

Tarasov[23] has measured the temperature changes at electrodes during the electrolysis of aqueous copper sulfate using copper electrodes. He made the rather astonishing statement that the Joule heat evolved has no effect on these temperature changes. The observation was made that the temperature change is positive throughout at the anode but that it is negative at the cathode at certain current densities. His results were expressed in terms of empirical equations and explained in terms of diffusion and rate of solution rather than on the basis of ionic entropies and heats of transport. Reasoning thusly, he arrived at the conclusion that curves of temperature change _versus_ current are more revealing in electrode processes than curves of current _versus_ voltage.

Nagaura[24] made a theoretical and experimental study of the heat balance in a cell for the electrolysis of water. He derived equations for the free energy and enthalpy changes in terms of temperature, the vapor pressure of water above the solution, and the heat of evaporation of water. These equations permitted the calculation of the free energy and enthalpy changes as a function of the temperature and the concentration of the sodium hydroxide solution used. To test this experimentally, he electrolyzed 20 per cent sodium hydroxide solutions and noted the final temperature. After this, the same cell was filled with an identical quantity of the sodium hydroxide solution and heated to the same final temperature with a measured quantity of electrical energy. Heats of formation for water from the three examples given were -68.9, -69.78, and -69.82 kilocalories per mole of water. Better agreement with the accepted value would have been obtained if a correction had been made for the water carried off by the gases evolved.

Antropov[25] has compared four different methods for calculating the heat evolved by an electrolytic cell. It is interesting to note that all four of the methods give different results. His opinion was that the correct result would be obtained by taking the difference between the energy equivalent of the current passed and the amount of energy necessary to bring about the chemical changes involved.

In 1954 two Russians, Gritsan and Bulgokova,[26,27,28,29,30] began a series of studies on the temperature difference between a cathode and the surrounding solution during electrodeposition of metal powders. They found that below a certain current density the temperature difference was practically zero but that above this current density, the temperature of the cathode was greater than the temperature of the surrounding solution. It was observed that this temperature difference became progressively larger as the concentration of the solution was decreased. The The effect of certain anions upon this temperature difference was studied and it was shown that there was a definite effect. Copper, cadmium, and zinc electrodes were studied and empirical equations were developed relating the temperature rise in terms of the concentration of the solution and the current density used. No theoretical basis was given for the equations but it was claimed that they were so exact that the concentration of an unknown metal solution could be determined merely by measuring the temperature difference between the cathode and the solution during electrolysis.

In 1954 Sherfey and Brenner[31] at the National Bureau of Standards started a program of study of the heat effects of dynamic electrochemical systems. This was undertaken to determine the feasibility and types of information available from simultaneous electrical and calorimetric measurements on the same system. From their studies they have obtained heats of reaction, polarization values, and entropy changes for a few electrolytic reactions. In cases in which comparison was possible, they have obtained fair agreement between their results and the existing data.

Throughout the literature, there seems to be no general agreement as to the quantities involved in the heat effects occurring at electrodes during electrolysis. Some of the quantities which have, at various times, been included in these heat effects are: heats of reaction, free energy changes, entropy changes, polarizations of all types, ohmic resistance, heats of transfer, and the Peltier effect.

2. Thermocells

a. Definition and types of thermocells. The electrolytic thermocouple, or "thermocell", is the electrolytic counterpart of the metallic thermocouple and many of the same relationships are valid for both systems. As is the case of metallic thermocouples, the electrical potential in a thermocell is caused by a temperature gradient in some portion of the cell and not by a difference in the potentials of two electrode reactions as is the case with a galvanic cell.

All of the thermocells which have been studied may be classified into one of five general types. These are:

I. $\mathrm{M} \underset{T_1}{\Big|} \mathrm{MX}\ (\text{Solid}) \underset{T_2}{\Big|} \mathrm{M}$

II. $\mathrm{M} \underset{T_1}{\Big|} \mathrm{MX}\ (\text{Fused}) \underset{T_2}{\Big|} \mathrm{M}$

III. $\text{Electrode} \underset{T_1}{\Big|} \text{Solution} \underset{T_1T_2}{\Big|} \text{Solution} \underset{T_2}{\Big|} \text{Electrode}$

IV. $\text{Electrode} \underset{T_1}{\Big|} \text{Solution A} \underset{T_1T_2}{\Big|} \text{Solution B} \underset{T_2T_1}{\Big|} \text{Solution A} \underset{T_1}{\Big|} \text{Electrode}$

V. $\text{Electrode} \underset{T_1}{\Big|} \text{Solution A} \underset{T_1T_1}{\Big|} \text{Solution B} \underset{T_2T_2}{\Big|} \text{Solution A} \underset{T_2}{\Big|} \text{Electrode}$

where M is a metal electrode, MX is a metal salt, and T refers to temperature.

Cells in which the electrodes are identical, such as those shown above, are often referred to as "pure" thermocells. Such need not be the case as an extension can easily be made to thermocells in which the electrodes are different. However, in this case the measured potential difference will contain a net electrode potential difference as well as a thermopotential. Eastman[32] has reserved the name "thermocell" for cells of Type III, but this distinction will not be maintained in this dissertation.

b. Relationship of thermocells to present work. The connection between thermocells and the heat evolved at electrodes lies in two quantities. These are the entropy change occurring in the electrode reaction, and the ionic heats of transfer. Thermocells such as Type III above have been used to calculate the temperature coefficient of single electrode reactions. From the temperature coefficient, it is possible to calculate the entropy change for the electrode reaction and absolute ionic entropies. Therefore, it is of interest to compare entropy values obtained from thermocells with those obtained from measurement of the heat effect at single electrodes during electrolysis.

The role of heat of transfer in thermocells is fairly well established, both in theory and experiment. However, as mentioned previously, the effect of ionic heats of transfer on the amount of heat liberated at a working electrode is still in dispute. Eastman[33] defined the heat of transfer of A as that "quantity of heat absorbed from the surroundings of the region (of infinite extent) from which one mole of constituent A is transferred." In his work[32] on the entropy of the chloride ion, Eastman stated that the entropy of transfer (the heat of transfer divided by the absolute temperature) is a result of a temperature difference between two points in the system. This concept is given further strength by Holtan's[34] work on thermocells in which the heat of transfer always appears multiplied by a temperature gradient. From this, it would appear that the heat of transfer would have no effect in an isothermal system.

3. Review of Work Done on Thermocells

Holtan's thesis[34] gives an extensive review of the earlier work which has been done on thermocells. In addition, Holtan did a thorough theoretical analysis of thermocells and supplemented this theoretical work with a few experiments. His theoretical treatment is by far the most complete and most general of any appearing in the literature. His experimental systems consisted of silver and thallium thermocells. He also did some interesting work on thermocells with colloidal solutions and on thermopotentials in nerve fibers. His results plus those of the earlier workers indicate that his equations are valid.

Previous to Holtan, Eastman[32,35,36] did considerable work on the theory of thermocells. However, Eastman's approach followed the line of classical thermodynamics. It was somewhat arbitrary in that some of the processes occurring in a thermocell are assumed to be irreversible and are therefore disregarded. The first and second laws of thermodynamics were then applied to the remaining processes, the supposedly reversible parts. Eastman arrived at a thermocell equation which was consistent with the experimental results but which did not give an accurate picture of the system. Eastman's students[37] have published some of their results from experiments on thermocells. In their paper the absolute partial molal entropy of the hydrogen ion was calculated to be -2.1 ± 0.4 calories per mole per degree from the Eastman thermocell equation.

Bonnemay[38] made a study of mercury, cadmium, and cadmium amalgam electrodes in thermocells from which he concluded that the enthalpy change of the electrode process is independent of temperature. Bonnemay and Fairbank[39] studied copper amalgam thermocells. From their results, they calculated the entropy change for the anodic dissolution of copper at unit activity and obtained a value of -37 calories per mole per degree. Bonnemay[40] also studied thermocells in which hydrogen, zinc, zinc amalgam, and copper electrodes were used. The basis for his calculation of single electrode reactions was his assumption[41] that the thermopotential for the non-isothermal liquid junction in his cells was equal to zero.

Hasse[42,43,44] has done considerable theoretical work on the subject of thermocells, paying particular attention to heats of transfer. Hasse's method was similar to that of Holtan[34] in that he employed the thermodynamics of irreversible processes. It is interesting to note that in one of Hasse's articles[42] he gave an explicit equation for the Peltier heat in a thermocell but that no mention was made of a Peltier heat in an isothermal cell.

The general consensus at the present time seems to be that measurements on thermocells cannot be used to determine absolute ionic entropies.

C. Statement of The Problem

There exists a recognized need for a new method for the study of electrochemical phenomena, particularly in the fields of polarization and in investigations of the thermodynamics of single electrode processes.

It was felt that a combination of simultaneous electrical and calorimetric measurements on the same system might supply this need. Such measurements would provide one with current, voltage, heat, and temperature values for the same system.

A theoretical investigation was undertaken to determine what quantities, if any, might be measured by such a combination of electrochemistry and calorimetry and to provide a basis for the experimental investigation. Recourse was taken to the thermodynamics of irreversible processes as applied to electrochemical process since classical thermodynamics is unable to treat irreversible electrochemical cells.

It was necessary that extensive instrumentation be used to make simultaneous measurements of both electrical and heat quantities. A preliminary determination of the magnitude of the temperature changes at electrodes during electrolysis provided the basis for the completion of the experimental apparatus.

The systems chosen for study were the well known copper-aqueous copper sulfate and silver-aqueous silver nitrate systems. It was hoped that these two systems would provide a check with each other and, in addition, also furnish a link with the quantities obtainable by classical thermodynamic methods.

It was desirable that the accuracy of the calorimetric techniques be checked by determining the enthalpy change involved for a reaction for which this quantity is well known. To prove this point, the enthalpy change involved in the decomposition of water was determined by the method described in this dissertation.

CHAPTER II

THEORETICAL DISCUSSION

A. Classical Thermodynamics as Applied to Electrochemical Cells

The limited discussion of classical electrochemical thermodynamics which is given here is covered thoroughly in most physical chemistry textbooks. This material is included to serve as a comparison to material which will be given in a later section and also to emphasize the limitations and restrictions which are imposed upon the classical thermodynamic methods. Historically speaking, the classical thermodynamics of electrochemical cells has its foundations in the brilliant work of such men as Nernst, Gibbs, and Helmholtz.

Before introducing electrode potentials as definite quantities, it would be well to indicate some of the well known relations between enthalpy, H, free energy,* F, and entropy, S. The total free energy has its basic definition in the equation:

$$F = H - TS, \qquad (1)$$

or, in terms of finite changes at constant temperature:

$$\Delta F = \Delta H - T\Delta S. \qquad (2)$$

Equation (2) is one of the most general relationships of classical thermodynamics and is valid for any isothermal process. This is a direct re-

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*"Free energy" as used in this dissertation denotes the Gibbs free energy as defined by equation (1).

sult of F, H, and S, all being thermodynamic quantities; that is, they are dependent only on the state of the system and changes in these quantities are entirely independent of the path taken between initial and final states.

The change in free energy for a process is related to the net useful work, $W_{net,rev.}$, at constant temperature and pressure by the following equation:

$$\Delta F = - W_{net,rev.} \quad (3)$$

Note that the work must be that obtainable under reversible conditions and at constant temperature and pressure. Another very useful equation is that for the temperature coefficient of the free energy. This equation is:

$$\left(\frac{\partial \Delta F}{\partial T}\right)_p = - \Delta S , \quad (4)$$

where T is the absolute temperature, and the subscript p indicates a constant pressure process. Here again equation (4) is valid only for a reversible transformation at constant pressure. Equations (2) and (4) may be combined to give one form of the Gibbs-Helmholtz equation:

$$\Delta F = \Delta H + T \left(\frac{\partial \Delta F}{\partial T}\right)_p . \quad (5)$$

Although this is a very useful equation, it is restricted to reversible processes occurring under conditions of constant pressure and temperature.

The relationships between electrochemical processes and thermodynamics stems from equation (3) which, when written in terms of electrical energy becomes:

$$\Delta F = - n \mathcal{F} \mathcal{E} \qquad (6)$$

where n is the number of electrons involved in the process, $\mathcal{F}$ is the Faraday, and $\mathcal{E}$ is the reversible electrode potential. It should be emphasized that the electrode potential as represented in equation (6) is that which would be obtained under strictly reversible conditions. Combining equation (6) with (5) gives the more familiar form of the Gibbs-Helmholtz equation:

$$\Delta H = - n \mathcal{F} \mathcal{E} + n \mathcal{F} T \left(\frac{\partial \mathcal{E}}{\partial T} \right)_p \qquad (7)$$

This also gives the relation between the entropy and the electrode potential as being:

$$\Delta S = n \mathcal{F} \left(\frac{\partial \mathcal{E}}{\partial T} \right)_p . \qquad (8)$$

One other very important equation in electrochemistry is the Nernst equation. This equation, which may be derived from either thermodynamics or kinetics, is:

$$\mathcal{E} = \mathcal{E}^{\circ} - \frac{RT}{n\mathcal{F}} \ln \frac{a_C^c a_D^d \cdot \cdot \cdot}{a_A^a a_B^b \cdot \cdot \cdot} \qquad (9)$$

for a reaction such as

$$aA + bB + . . . = cC + dD + . . . \quad . \qquad (10)$$

In equation (9) the superscript o refers to the standard state reversible potential, R is the gas constant, and a_A^a is the activity of A raised to the appropriate power a.

Thus it may be seen that measurement of electrical potential and its variation with temperature will yield values of ΔH, ΔF, and ΔS, all of which are very important thermodynamic quantities. It should also be pointed out that thermodynamic activities are readily available from equation (9).

The use of the above equations is limited by the conditions under which they are applicable. The conditions of constant temperature and pressure, although limiting, are not too stringent. All of the above equations, with the exception of (1) and (2), are limited to strictly reversible conditions. It is this restriction which imposes the most serious handicap on the use of classical thermodynamics to solve electrochemical problems.

It should be noted that no distinction has been made between cell potentials and single electrode potentials. This is because the given equations are applicable to both potentials provided suitable reversible potentials can be measured. This last provision explains why so many electrochemists have spent so much time in quest of the elusive absolute single electrode potential.

The preceding paragraphs are intended to stress not only the importance of classical thermodynamics as applied to electrochemical systems, but also some of the more serious shortcomings of the classical line of attack. In view of these shortcomings, several attempts at a new method for the study of electrochemical problems have appeared in the literature. These same shortcomings have led to the method of attack which is described in this dissertation.

B. Electrochemical Cells From an Energetic Viewpoint

A concept which attempts to be more general than traditional thermodynamics is that of energetics. The most important work in this field is Bronsted's monograph.[45] According to Bronsted's energetics, the first and second laws of thermodynamics may be replaced by two new principles; (a) the work principle and (b) the heat and equivalence principle. The work principle is restricted to reversible processes while the heat and equivalence principle may be used in considering irreversible processes. Entropy is introduced without defining it in terms of heat. All process are considered as having a "potential difference" as the motivating force. Another important concept of energetics involves relationships between entropy production, entropy change due to reversible processes, and entropy change due to irreversible processes.

In a consideration of electrochemical cells, energetics holds to the tenet that irreversible processes must always be present even though their extent may be small when compared to the cell process which is generally considered to be reversible. Electrode reactions are taken as analogous to Peltier heats in thermoelements. Peltier heats, however, are not identical with the reactions as thermoelements and galvanic cells have different energetic mechanisms. In the thermocell the electron is associated with a certain amount of entropy while in a galvanic cell the electron is associated with an electroactive substance. One of the main differences is that the classical method is based on electrical potentials while the energetic mechanism is based on the electrochemical potential.

Another striking difference between the classical and energetic viewpoint is in the location of the "seat" of the electromotive force. From the classical standpoint, the "seat" is taken as the metal-electrolyte boundary. The energetic mechanism holds that the "seat" is located at some region of "disequilibrium" in the electrolyte, *e. g.*, at the liquid junction in a concentration cell.

In spite of these widely different concepts, the equations derivable from the energetic mechanism are entirely equivalent to those obtained from the classical method of attack and therefore will not be repeated here.

C. Irreversible Thermodynamics of Electrochemical Cells

1. The Work of de Groot

The thermodynamics of irreversible thermodynamics as developed by de Groot in his book[46] is based on Onsager's reciprocal relations.[47] As a matter of fact, most of the work on irreversible thermodynamics is based on Onsager's relations. Onsager's theorem is essentially a statement that, provided a proper choice is made of the "fluxes" (or "flows") and "forces", the phenomenological coefficients of two mutually interferring irreversible processes are equal.

A fundamental tenet in de Groot's treatment of irreversible thermodynamics is the concept of entropy balance. In this entropy balance, the total entropy change of a system is considered as being made up of two parts. One part is due to the entropy exchange with the surroundings.

The second part is the internal entropy production due to the irreversible processes occurring inside the system. The calculation of the entropy production is based on two fundamental assumptions. The first of these is that the entropy production is positive. The other fundamental assumption is that Gibbs' relation is valid in systems not at thermodynamic equilibrium. This is equivalent to assuming that entropy depends only on energy, volume, and concentration.

Using these basic ideas, de Groot gives a brief description of electrochemical systems. In these derivations, he takes recourse to the concepts of electrochemical potential and electrochemical affinity, terms which are not unique to his method. By proper choice of "flux" and "force", de Groot arrives at the conclusion that the entropy production may be formulated in terms of the electrochemical affinity. At the conclusion of de Groot's treatment of electrochemical systems, he demonstrates that all of his generalizations reduce to the classical results for the special case of thermodynamic equilibrium.

2. The Work of Prigogine

Except for his rather elegant treatment of stationary non-equilibrium states as being states of minimum entropy production, Prigogine's treatment[48] of the thermodynamics of irreversible processes is identical to that of de Groot.[46] His results were identical also and, therefore, will not be considered further.

3. The Work of Van Rysselberghe

The work of Pierre Van Rysselberghe[49,50] is the most complete of the work on irreversible thermodynamics in relation to electrochemical cells. In his treatment, Van Rysselberghe considers not only galvanic and electrolytic cells, but also the phenomena occurring at single electrodes. The first law of thermodynamics is essentially the same as that obtained from the classical treatment. The second law for irreversible electrochemical cells is introduced on the basis of the uncompensated heat and the power of irreversibility. This treatment also has a strong basis in the concept of electrochemical affinity.

Van Rysselberghe considers the causes of irreversibility in an electrochemical cell as being due to the Joule effect and to polarization. Accordingly, he introduces equations which relate these two terms with the other quantities governing the behavior of electrochemical cells. This generalization is extended to the single electrode processes and the concept of anodic and cathodic currents. Simultaneous half-reaction reactions at the same electrode may be shown to follow the same laws as single reactions.

D. Irreversible Thermodynamics as Applied to Thermocells

1. The Work of Holtan[34]

The basic method of attack used by Holtan in his derivation of working equations applicable to thermocells is identical with that used by de Groot[46] and Prigogine.[48] Holtan's derivation will not be given here but the final results and some special cases are of importance and will be considered.

The general equation for the thermopotential, $\Delta\varphi_t$, of a thermocell is:

$$\mathcal{F}\Delta\varphi_t = -\sum_{k=1}^{n}\left(\frac{t_k}{Z_k}\right)\sum_{j=1}^{n-1}\frac{\partial u_k}{\partial C_j}\,\Delta C_j - \sum_{k=1}^{n}\frac{t_k}{Z_k}\,Q_k^*\,\frac{\Delta T}{T}$$

$$-\frac{Q_e^*}{T}\,\Delta T - \Delta S\Delta T \;. \qquad (11)$$

In this equation, t_k is the transference number of the kth component, Z_k is the charge on the kth component, u_k is the chemical potential of k, C_j is the concentration of j, Q_k^* is the molar heat of transport of k and Q_e^* is the molar heat of transport of the electron. The other symbols have their usual meaning. Thus it may be seen that the total thermopotential is made up of four separate terms. The first term on the right hand side of equation (11) is the thermal diffusion potential due to concentration gradients (the Soret effect). The second term is the contribution caused by the transport of heat by the charged species moving under the influence of the current. The influence of the electron is given by the third term. The last term gives the classical contribution to the thermopotential, i. e., the entropy change of the electrode reactions.

For the special case of a metallic thermocouple, equation (11) reduces to

$$\mathcal{F}\Delta\varphi_t = \left({}_AQ_e^*/T - {}_BQ_e^*/T\right)\Delta T + \left({}_AS_e - {}_BS_e\right)\,\Delta T \qquad (12)$$

where A and B refer to the two metals of which the thermocouple is made. Equation (12) is equivalent to the expression derived by de Groot.[46]

For thermocells with fused or solid electrolytes and with two charged components, the general equation reduces to

$$\mathcal{F}\Delta\varphi_t = -\sum_{k=1}^{2} \left(\frac{t_k}{Z_k}\right)\frac{Q_k^*}{T}\ \Delta T - \frac{Q_e^*}{T}\ \Delta T - \Delta S \Delta T \qquad (13)$$

For thermocells in which the Soret effect is present, the general equation (11) must be used. If the Soret effect is hindered and only two charged species are present, the general equation again reduces to (13). It is interesting to note in connection with heats of transfer that Lange and Hesse[20] had previously noted that these quantities are related to the transport number. That their conclusion was correct is obvious from Holtan's general thermocell equation (11).

In all cases in which the necessary experimental data are available, the above equations accurately describe the behavior of all types of thermocells.

2. The Work of Hasse[42,43,44]

The general method of attack used by Hasse is the same as that employed by Holtan. However, in Hasse's study much more emphasis was placed on heat and entropies of transport. Making allowance for the solvation of ions, Hasse shows that it may be possible to determine the entropy of transport from electromotive force measurements on thermocells.[44] His study still leaves the concentration and temperature dependence of heats of transport open to question.

E. Development of the Working Equation

The line of reasoning used to develop the working equation is essentially that given by Van Rysselberghe.[49,50] The first and second laws of thermodynamics for operating electrochemical cells are combined to give a final working equation. The system considered here is the same as that used by Van Rysselberghe and is shown in Figure 1. In this system α'' and α' are identical. As an alternative, the contact to the electrodes α and α' could have been made by two pieces of a third metal. The reason for this precaution is given later.

The potential differences considered here are differences in internal potentials or Galvani potential differences. These are related to the outer (or Volta) potentials, ψ, and the surface potentials, X, by

$$\varphi = \psi + X \tag{14}$$

where φ is the Galvani potential. This is in accordance with the definitions proposed by Lange[51] in his work on the different types of electrical potentials present in an electrochemical system.

The thermodynamic system dealt with here is $\alpha''\alpha\beta\beta'\alpha'$. This constitutes a closed system since the same number of electrons leave α'' as enter α'. The contact between α and β and between α' and β' constitutes what is usually termed the electrochemical double layer. In the absence of an electric current, the layer $\alpha'\beta'$ (or $\alpha\beta$) is only a few molecular diameters thick. The passage of an electric current results in an extension of the layer $\alpha'\beta'$ to a considerable distance (in comparison to

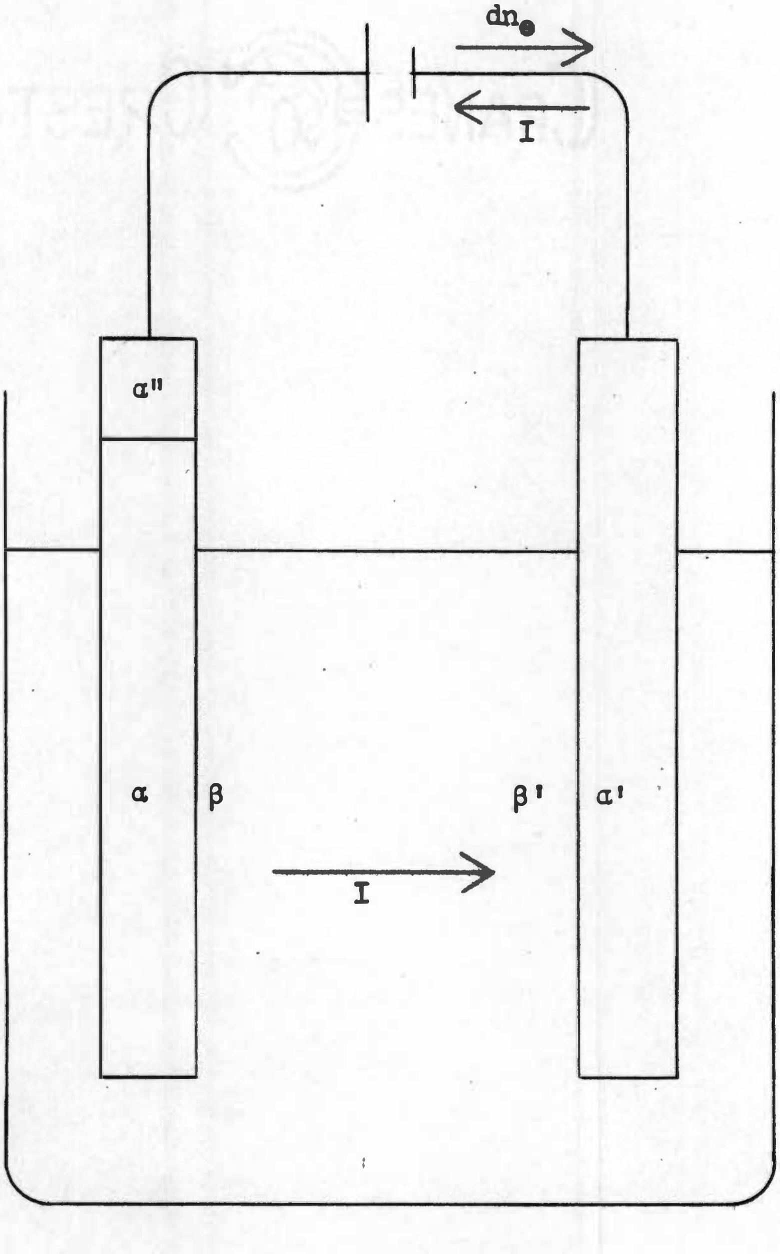

Figure 1. Model Used in Development of Working Equation.[49]

a few molecular diameters) from the electrode α'.

The electrodes are composed of a metal M. The electrolyte is an aqueous solution of the metal salt MX in which X is not electroactive. If the current is flowing in the direction indicated, the reaction

$$M = M^{+}_{(aq.)} + e_{(\alpha)} \tag{15}$$

is taking place at α and the reaction

$$M^{+}_{(aq.)} + e_{(\alpha')} = M \tag{16}$$

is occurring at α'. The electrode α is then functioning as an anode and α' is a cathode. It is not necessary to assume the electrode reaction (15) and (16) are the reverse of each other as the relationships given below are valid for any electrolytic reactions.

The positive current, I, is given by

$$I = \frac{\mathcal{F}\, dn_e}{dt} \tag{17}$$

where dn_e is the moles of electrons flowing from α'' to α' in time dt. Using modern conventions, the flow of electrons and the flow of positive current are in opposite directions.

During the time dt the internal energy of the system increases by an amount dE. In the same time interval, the system receives an amount of heat, dQ, from its surroundings and does a corresponding amount of work dW. The relation between these three quantities is

$$dE = dQ - dW \tag{18}$$

This is merely a statement of the first law of thermodynamics. The term dW may be broken up into several parts. The system does an amount of mechanical work, dW_m, against the surroundings. This is given by the equation

$$dW_m = pdV. \tag{19}$$

Equation (19) restricts the system to operation at constant pressure, which is the condition under which most electrochemical reactions are carried out. An amount of electrical work, dW_{el}, is done by the system. This work corresponds to the transfer of dn_e moles of electrons from α'' to α' and is given by

$$dW_{el} = \mathcal{F}(\varphi^{\alpha'} - \varphi^{\alpha''})\, dn_e\ . \tag{20}$$

If α'' and α' had not been identical, the system could also have done an amount of chemical work, dW_c, which is given by

$$dW_c = (\, u_e^{\alpha'} - u_e^{\alpha''})\, dn_e \tag{21}$$

in which $u_e^{\alpha'}$ and $u_e^{\alpha''}$ represent the molar chemical potentials of the electron in α' and α'', respectively. Since α'' and α' are identical, dW_c need not be considered. Insertion of (19) and (20) into (18) gives

$$dE = dQ - pdV - \mathcal{F}(\varphi^{\alpha'} - \varphi^{\alpha''})\, dn_e \tag{22}$$

as the statement of the first law.

From the second law of thermodynamics

$$dS = \frac{dQ}{T} \tag{23}$$

for any reversible process. However, this is not true for any real process. For a real isothermal process, one may introduce the uncompensated heat, dQ', as

$$dQ' = TdS - dQ \geqslant 0\ . \tag{24}$$

The uncompensated heat may be related to Prigogine's concept of entropy production.[48] The total entropy production, dS, may be regarded as the sum of two contributions: d_eS, due to heat exchange with the surroundings, and d_iS, resulting from irreversible phenomena within the system. Thus one has

$$dS = d_eS + d_iS \ . \tag{25}$$

By comparison with (24) one sees that

$$d_eS = \frac{dQ}{T} \tag{26}$$

and

$$d_iS = \frac{dQ'}{T} \geqslant 0 \ . \tag{27}$$

Following Prigogine, the entropy production is the rate of increase of entropy due to the internal irreversible phenomena. This gives

$$\frac{d_iS}{dt} = \frac{dQ'}{Tdt} \tag{28}$$

The ratio of dQ' to dt is known as the power of irreversibility,[49] P, and is related to the other quantities by

$$\frac{P}{T} = \frac{d_iS}{dt} = \frac{dQ'}{Tdt} \ . \tag{29}$$

By substitution of these quantities into (24), one obtains

$$dQ = TdS - Pdt \ . \tag{30}$$

This may then be inserted into (22) to give

$$dE = TdS - Pdt - pdV - \mathcal{F}(\varphi^{a'} - \varphi^{a''})\, dn_e \ . \tag{31}$$

Rearranging (31) yields

$$-\mathcal{F}(\varphi^{a'} - \varphi^{a''})\, dn_e = dE + pdV - TdS + Pdt \ . \tag{32}$$

From classical thermodynamics (for a constant pressure process)

$$dH = dE + pdV \; . \qquad (33)$$

Therefore equation (32) becomes

$$-\mathcal{F}(\varphi^{\alpha'} - \varphi^{\alpha''})\, dn_e = dH - TdS + Pdt \; . \qquad (34)$$

The term dn_e may be eliminated by rearranging (17) to give

$$dn_e = \frac{Idt}{\mathcal{F}} \; , \qquad (35)$$

which, when substituted into (34) gives

$$-(\varphi^{\alpha'} - \varphi^{\alpha''})\, Idt = dH - TdS + Pdt \; . \qquad (36)$$

However $(\varphi^{\alpha'} - \varphi^{\alpha''})$ is the measurable potential difference, $\mathcal{E}$, between α' and α''. This gives

$$-\mathcal{E}\, Idt = dH - TdS + Pdt \; . \qquad (37)$$

The power of irreversibility, P, may be divided into two terms, the irreversibility due to the Joule heat, and the irreversibility due to polarization. Therefore

$$P = RI^2 + P_p \qquad (38)$$

where R is the ohmic resistance of the system and P_p is the power of polarization. Since it is a power term, P_p may be set equal to the product of the polarization, η , and the current. This gives

$$-\mathcal{E}\, Idt = dH - TdS + RI^2dt + \eta\, Idt \qquad (38)$$

in place of (37). This equation may be integrated to give

$$-\mathcal{E}\, It = \Delta H - T\Delta S + RI^2t + \eta\, It \qquad (39)$$

for finite changes.

In the integration of (38), a few assumptions have been made which should be mentioned. The assumption of constant temperature and pressure has previously been made in the preliminary equations. It has also been assumed that $\mathcal{E}$, I, R, and η do not vary with time. Such is not necessarily the case. This may be circumvented by specifying that (39) is valid only under conditions of constant current. The value of $\mathcal{E}$ is then fixed by Ohm's law while η is also known to be constant at a constant current. η will vary with t for a short time after the current is turned on. This corresponds to the time necessary to build up the transition layers $\alpha'\beta'$ and $\alpha\beta$. However, such variations will be small in comparison to the total product of η It.

ΔH and ΔS are not necessarily molar quantities. The magnitude of these quantities will be governed by the product It, that is, the extent of the electrolytic reactions. The negative sign in the term $\mathcal{E}$ It appears because the equation refers to the ability of the system to do work. The heat, Q, given <u>off</u> by the system is given by

$$Q = -T\Delta S + RI^2t + \eta It . \qquad (40)$$

This arises because of the definition of the uncompensated heat given in equation (24).

The polarization, η, includes any and all types of polarization in the system regardless of whether they are ohmic, activation, or concentration. In this respect, it should be repeated that Richards[9] has definitely proven that polarization appears as a heat effect and does no chemical work. Bruzs[17] also noted in his experiments that concentration polarization had an effect on the Peltier heat at a working electrode.

From a classical thermodynamic point of view, equation (39) appears to be of the correct form. The corresponding equation for a completely reversible system is

$$-\mathcal{E}It = \Delta H - T\Delta S = \Delta F \ . \tag{41}$$

Now if the system is not reversible

$$-\mathcal{E}It \neq \Delta H - T\Delta S = \Delta F \ . \tag{42}$$

However, one can simply add terms to the equation to make it correct again. The logical choice would be to add a term corresponding to resistance and one corresponding to polarization to give the correct result. Such a treatment does not, however, bring out such facts as: (a) that the degree of irreversibility is related to the reaction rate and (b) that the entropy production due to internal irreversible processes is given by

$$\frac{d_iS}{dt} = \frac{RI^2 + \eta I}{T} \ . \tag{43}$$

It would be helpful now to look at some of the quantities which may be obtained by the experimental application of equation (39). Experimentally the two quantities to be measured would be the energy input, $-\mathcal{E}It$, and the heat given off by the system. The difference between these two quantities would give a value of ΔH directly. A knowledge of any two of the three terms involved in the sensible heat effect would give the remaining one. Thus it should be theoretically possible to obtain values of ΔH, ΔS, and η from combined electrical and thermal measurements on a working electrochemical system. A knowledge of ΔH and ΔS would allow one to obtain a value of ΔF. From this, one could calculate the reversible potential corresponding to the reaction taking place. It should be noted that values of η obtained by the above method would not be referred to a static potential as is the case with all of the values obtained by EMF studies of polarization.

If equation (39) is assumed to be valid for a single electrode system, some interesting results could be obtained. Thus measurements such as the above should lead to a value for the absolute potential of a single electrode reaction. The absolute electrode potential is a quantity which has been in dispute since the beginning of electrochemistry. Guggenheim[52,53] has taken the position that such potentials have no physical meaning and therefore cannot be measured. Recently, theoretical electrochemists have taken the viewpoint that such absolute electrode potentials could be calculated in principle. However, in his work on the electrochemical double layer, Grahame[54] has defended the older point of view as taken by Guggenheim.

Single electrode potentials are not necessary to describe a complete electrochemical cell from a thermodynamic viewpoint. However, in studies on electrode kinetics and in all cases where interfacial electrical fields are investigated, absolute single electrode potentials are important.[55]

F. The Relationship Between Thermocells and Isothermal Cells

The majority of the work which has been done on the correlations between thermocells and isothermal cells has been reported by Holtan.[34,56,57]

Consider the isothermal galvanic cell

$$M;\ MA_{(aq.)};\ A\ , \qquad (44)$$

in which MA is a univalent salt. The temperature coefficient of this cell is given by

$$\mathcal{F}\left(\frac{\partial \mathcal{E}}{\partial T}\right)_p = S_{A^-} + S_{M^+} - S_A - S_M . \quad (45)$$

The pure thermocells corresponding to (44) are:

$$\underset{T}{A};\ MA_{(aq.)};\ \underset{T+\Delta T}{A} \quad (46)$$

and

$$\underset{T}{M};\ MA_{(aq.)};\ \underset{T+\Delta T}{M} . \quad (47)$$

If the Soret effect is hindered and one neglects the transport of water by the ions, the thermopotentials of (46) and (47) are given by:

$$\mathcal{F}\left(\frac{\partial \mathcal{E}}{\partial T}\right)_p = - t^- S^*_{A^-} - t^+ S^*_{M^+} - {}_A S^*_e + S_{A^-} - S_A \quad (48)$$

for cell (46) and

$$\mathcal{F}\left(\frac{\partial \mathcal{E}}{\partial T}\right)_p = - t^- S^*_{A^-} - t^+ S^*_{M^+} - {}_M S^*_e + S_M - S_{M^+} \quad (49)$$

for cell (47). If one now subtracts (49) from (48) one obtains

$$\mathcal{F}\left(\frac{\partial \mathcal{E}}{\partial T}\right)_{p46} - \mathcal{F}\left(\frac{\partial \mathcal{E}}{\partial T}\right)_{p47} = S_{A^-} + S_{M^+} - S_A - S_M + {}_M S^*_e - {}_A S^*_e . \quad (50)$$

This result is identical with equation (45) except for the entropies of transfer of the electrons. However, according to Holtan, ${}_M S^*_e - {}_A S^*_e$ is simply the thermoelectric power of the thermocouple which would be formed from M and A. Relationships such as (50) have been tested experimentally by Holtan and Krogh-Moe[57] and found to be true within experimental error.

This indicates that the entropies of transfer of ions and electrons have no effect on the operation of isothermal cells.

CHAPTER III

EXPERIMENTAL

A. Materials

1. Copper Sulfate

All of the copper solutions used in this work were prepared from the pentahydrate of copper sulfate. Baker and Adamson reagent grade copper sulfate was used without further purification.

2. Potassium Sulfate

Baker and Adamson reagent grade anhydrous potassium sulfate was used for the preparation of all potassium solutions.

3. Sodium Sulfate

All sodium solutions were prepared from anhydrous Baker and Adamson reagent grade sodium sulfate.

4. Sulfuric Acid

Du Pont C. P. reagent grade sulfuric acid was used in the preparation of all solutions which contained sulfuric acid.

5. Silver Nitrate

Baker and Adamson reagent grade silver nitrate was used for preparing the necessary silver solutions.

6. Gelatin

Chemically pure gelatin (E. H. Sargent and Company) was used for the preparation of all gelatin solutions.

7. Solutions

Solutions of copper, potassium, sodium, and silver were prepared by weighing the required quantity of the appropriate salt, dissolving in distilled water, and diluting to volume in volumetric flask. Commercially available sulfuric acid was diluted to volume to obtain the necessary sulfuric acid solution. Gelatin solutions were prepared by weight from solid gelatin. The gelatin was dissolved in previously boiled distilled water and used within twenty-four hours to prevent contamination by bacteria.

B. Preliminary Experiments on the Temperature Rise at Electrodes During Electrolysis

1. Apparatus

Two copper electrodes, separated by plastic spacers, and contained in a 500 ml. cork-stoppered Dewar flask served as an electrolysis cell. A 110 volt A. C. power supply, equipped with transformer and rectifier, served as a source of electrolysis current. This supply had a maximum voltage output of 12 volts D. C. and the output current contained a large amount of ripple. This was subsequently replaced by a D. C. generator operated by a three phase 220 volt A. C. motor. This generator had a maximum output of 15 amperes at 75 volts D. C. and contained a smaller amount of ripple. This allowed electrolysis at a much higher current density than was possible with the previous power supply. In either case the D. C. voltage source was connected to the electrolysis cell through a 100 ohm variable resistance and a 0-1000 milliampere ammeter. This permitted manual control of the electrolysis current at a preselected value.

To detect the temperature change, a Beckmann thermometer was placed behind each electrode. These thermometers were held in place by the cork stopper of the Dewar flask. A stop watch was used to time the duration of the electrolysis runs.

2. Procedure

All of the preliminary experiments were carried out using copper electrodes and copper sulfate solutions. Two hundred milliliters of the copper sulfate solution was pipetted into the Dewar flask which contained the electrodes and thermometers. The system was then allowed to stand until thermal equilibrium had been attained, as evidenced by the constancy of the Beckmann thermometer readings. The current was switched on at time zero and quickly adjusted to the preselected value. Readings of the two Beckmann thermometers were taken at two minute intervals throughout the duration of the electrolysis. The period of electrolysis was usually thirty minutes.

Results from these experiments showed that a much more sensitive temperature sensing device was needed, preferably a differential arrangement with a short time lag. It was also recognized that a much more rigid and reproducible electrode arrangement was needed.

C. Temperature Difference Measurements on the Copper-Aqueous Copper Sulfate System

1. Apparatus

a. Thermistors. Thermistors were chosen as the temperature sensing devices in order to meet the requirements of stability, sensitivity, size, and small time lag. A matched set of Victory Engineering Corporation number 32A1 thermistors was chosen for the differential temperature measurements. These thermistors have the following characteristics:

Resistance at 25°	2000 ohms ± 20 per cent
Dissipation constant	1.0 milliwatts/°C.
Time constant	25 seconds

This thermistor is commercially available as a glass-enclosed probe which is 2 inches long and 0.100 inches in diameter. Electrical connection to the thermistor is accomplished by leads of 0.012 tinned Dumet.

Prior to incorporating these thermistors into the electrical circuit, they were aged for two weeks at 160°, then current of twice the amperage used in the actual experiments was passed through the thermistors for two to three days. This aging treatment completely stabilized the thermistors and prevented any drift during actual operation.

To protect the thermistors against mechanical shock, they were enclosed in a protective shield which consisted of a piece of glass tubing 9 cm. in length and 5 mm. diameter. The glass shield was sealed at both ends with deKotinsky cement in such a way that only the tip of the thermistor and the leads protruded. The seal served another useful purpose. It prevented the accidental shorting of the thermistor by moisture.

Two matched sets of these thermistors were prepared in the above manner as it was desired to make simultaneous measurements of two different temperature differences.

b. Power supply. It was desired that the thermistor be incorporated into a Wheatstone bridge circuit and the output voltage of the bridge be the quantity measured. Further, it was essential that the bridge output voltage be a function of temperature difference between the thermistors. To make these temperature difference measurements precise and accurate, it was mandatory that the voltage source to the bridge be a constant value.

The first attempt in this direction was the use of three 1.5 volt dry cells connected in parallel. Power was then applied to the bridge through a potential divider. This proved entirely unsatisfactory because of the lack of stability and the necessity of making frequent adjustments of the potential divider. A 2 volt lead storage cell was then connected to the bridge circuit through a Leeds and Northrup K potentiometer. This gave excellent stability but it was necessary to restandardize the potentiometer quite frequently. These two attempts showed that it was highly desirable to have a continuously regulated low voltage power supply of excellent stability.

To meet this demand, the low voltage power supply described by Greenough, Williams, and Taylor[58] was constructed.* This instrument proved to be ideally suited for the above application. It was found that

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*Constructed by Gerald Raine of this laboratory.

somewhat better voltage control could be obtained by shunting the output terminals with a 50 ohm resistance. The output voltage could be set at any preselected value from 0 to 8 volts and could be checked with a potentiometer. Output of this instrument had a ripple content of only 0.1 per cent and long term variations in the output voltage were less than 1 mv for a 1 volt output. The power supply was always allowed to warm up for a period of about thirty minutes before use.

c. Bridge circuits. Two separate bridge circuits were used for the temperature difference measurements. The thermistors were connected in opposite arms of Wheatstone bridge circuits as shown in Figure 2. One of these circuits (No. 1) was used to measure the temperature difference between the anode and the cathode. By moving the thermistor from the anode into the solution, it was also possible to measure the difference in temperature of the cathode and the bulk of the solution. The other bridge circuit (No. 2) was used to measure the temperature difference between the anode and the solution. R_2 and R_1 were 2200 ohm, 1/2 watt radio resistances, while R_1 and R_3 were Heathkit decade resistance boxes (0 to 99,999 ohms). R_3 was the 50 ohm, 2 watt radio resistance used to shunt the output terminals of the voltage supply. T_1, T_2, T_3, T_4 were the thermistors. T_1 and T_2 were one matched set while T_3 and T_4 were the other matched set.

R_1 and R_3 were used to adjust the initial unbalance potentials as close to zero as possible. This permitted the use of a lower range on the Leeds and Northrup K-3 potentiometer, thereby increasing the sensitivity of the circuits. This potentiometer was used to measure the un-

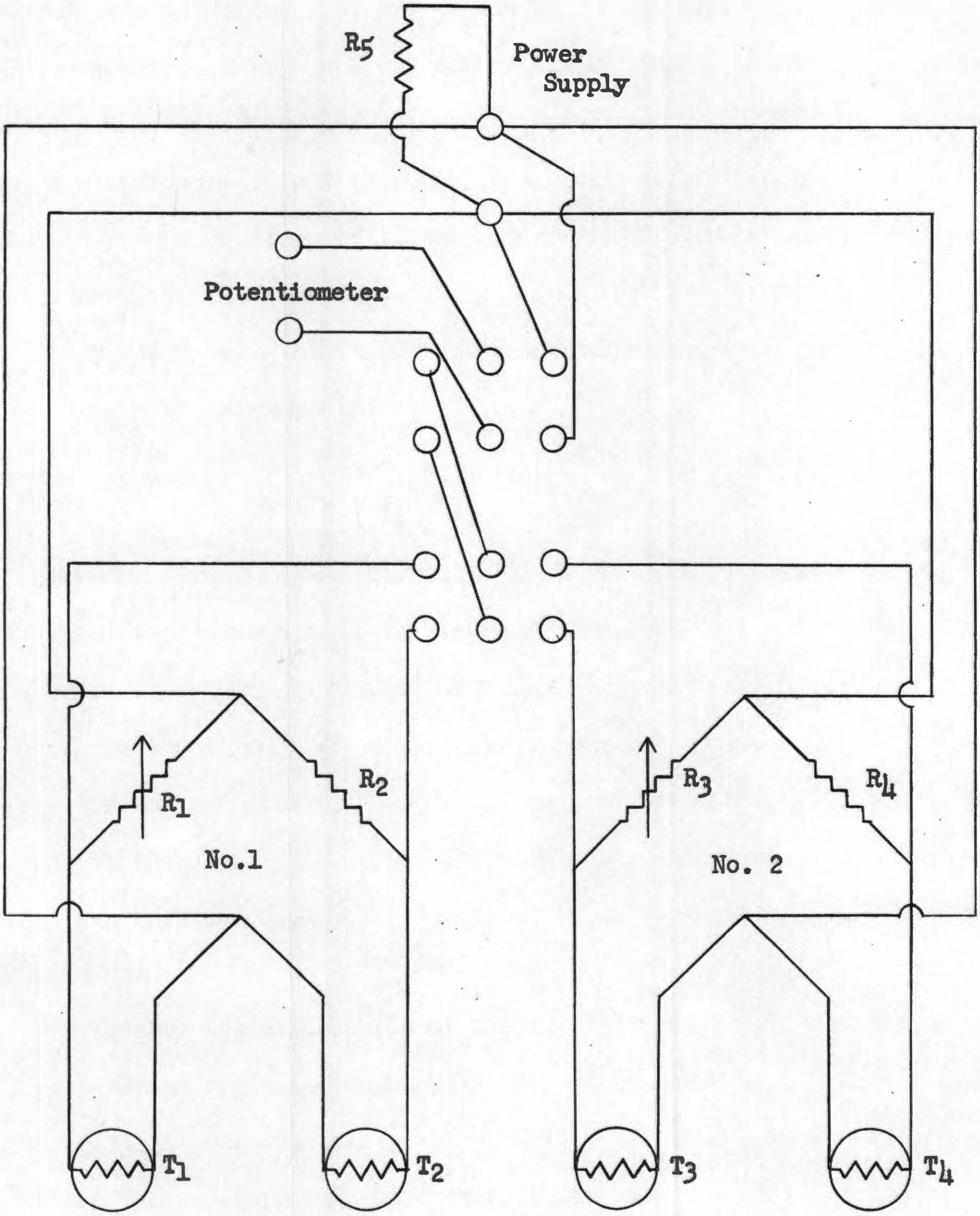

Figure 2. Bridge Circuits Used in Temperature Difference Measurements.

balance potentials to 0.001 mv. A Kin Tel Model 204A electronic galvanometer was used as a null detector. This instrument was ideally suited for this purpose because of its high sensitivity (2 x 10^{-11} amps. per scale division), fast response, and excellent stability. The same potentiometer was also used to set and check the output voltage of the power supply at 1.000 volts.

The unbalance potential of a Wheatstone bridge circuit may be represented by the equation,

$$E_o = E_i \left(\frac{T_1}{T_1 + T_2} - \frac{R_1}{R_1 + R_2} \right) \qquad (1)$$

where E_o is the unbalance potential, E_i is the bridge input voltage, and the other symbols refer to Figure 2. From (1) and the negative temperature coefficient of resistance of the thermistor (approximately 4 per cent per degree) the bridge circuits were calculated to have sensitivities of approximately 10 mv. per degree temperature difference between the thermistors. As the unbalance potentials were measured to 0.001 mv, this corresponded to temperature differences of approximately 0.0001°.

Ideally the calibration of the thermistors should be carried out using platinum resistance thermometers. Since these were not available, the sensitivity and linearity of the bridge circuits were checked using Beckmann thermometers. The two thermistors were placed in separate water-filled, cork-stoppered Dewar flasks. A Beckmann thermometer was then placed in each Dewar, and the unbalance potential of the bridge was measured as a function of the temperature difference as determined by the Beckmann thermometers. By this method the sensitivity of bridge No. 1 was found to be 9.65 mv per degree while the sensitivity of bridge No. 2 was 9.25 mv per degree as accurately as could be measured by the Beckmann thermometers. The change in bridge unbalance potential was found to be linear with temperature difference over the range of temperature differences measured in this work. The sensitivity and linearity are shown in Figure 3, in which the unbalance potentials of bridge No. 1 and bridge No. 2 are plotted as a function of temperature difference as determined by the Beckmann thermometers.

d. Cell and electrode. In order to obtain reproducible results, it was necessary that (a) the electrodes be maintained at a fixed position with respect to each other, and (b) that a definite reproducible electrode area be exposed to the solution. With this aim in mind, the electrolysis cell shown in Figure 4 was constructed. Lucite of 1/8 inch thickness was used for the construction. The cell was cemented together with a solution of lucite in acetic acid. The cell was constructed to fit snugly into a 500 ml. Dewar flask. The exposed area of each electrode was 19.35 sq. cm.

The copper electrodes were hollow, rectangular parallelopipeds (3 x 1-5/8 x 5/16 inches) and contained an aluminum well to position the thermistors. These aluminum wells provided for reproducible placing of the thermistor probes and afforded good thermal contact with the electrodes. This arrangement also made it a simple task to move a thermistor from the electrode into the solution whenever it was necessary to measure the difference of temperature between an electrode and the solution. The

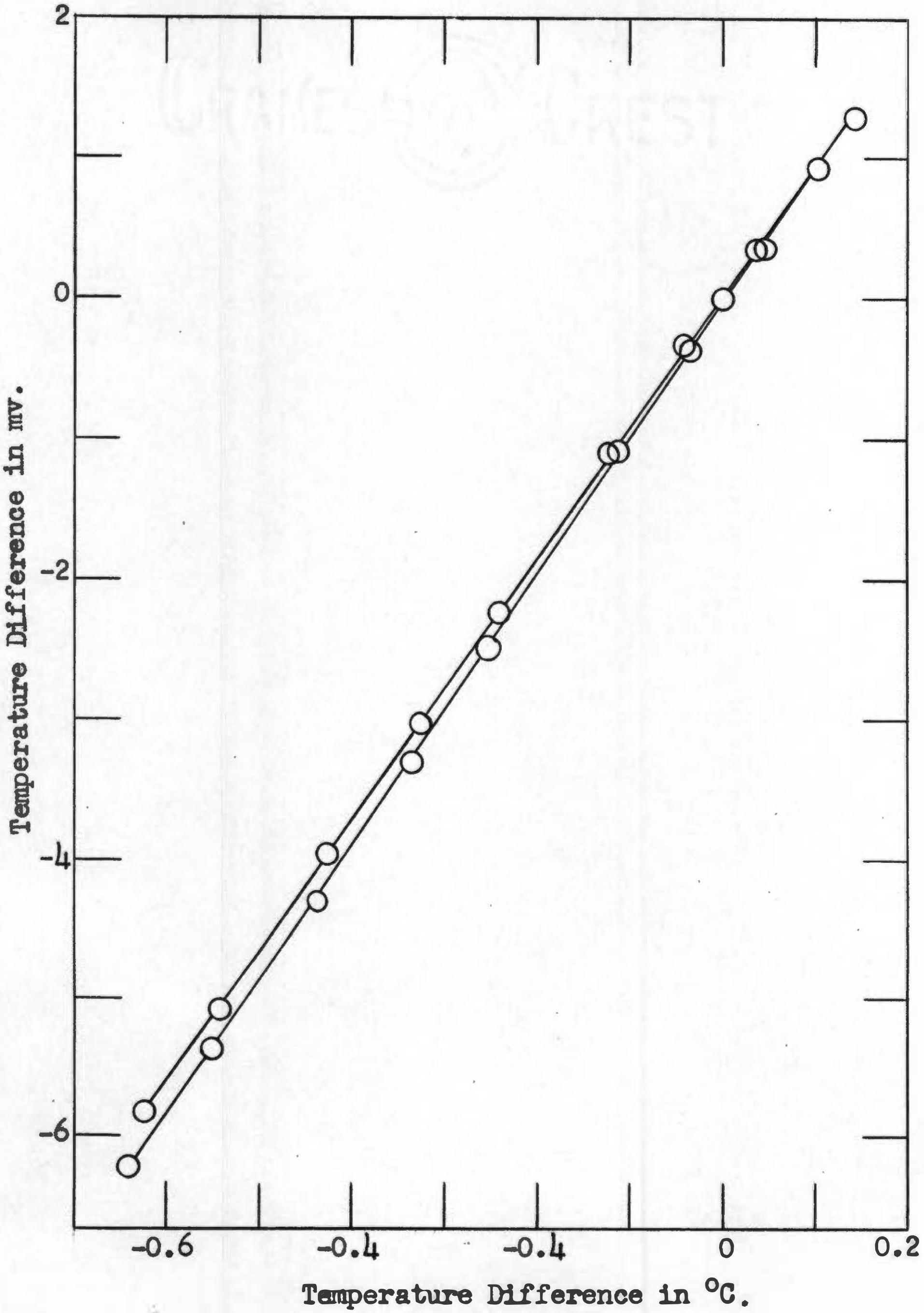

Figure 3. Sensitivity and Linearity of Bridge Circuits Shown in Figure 2.

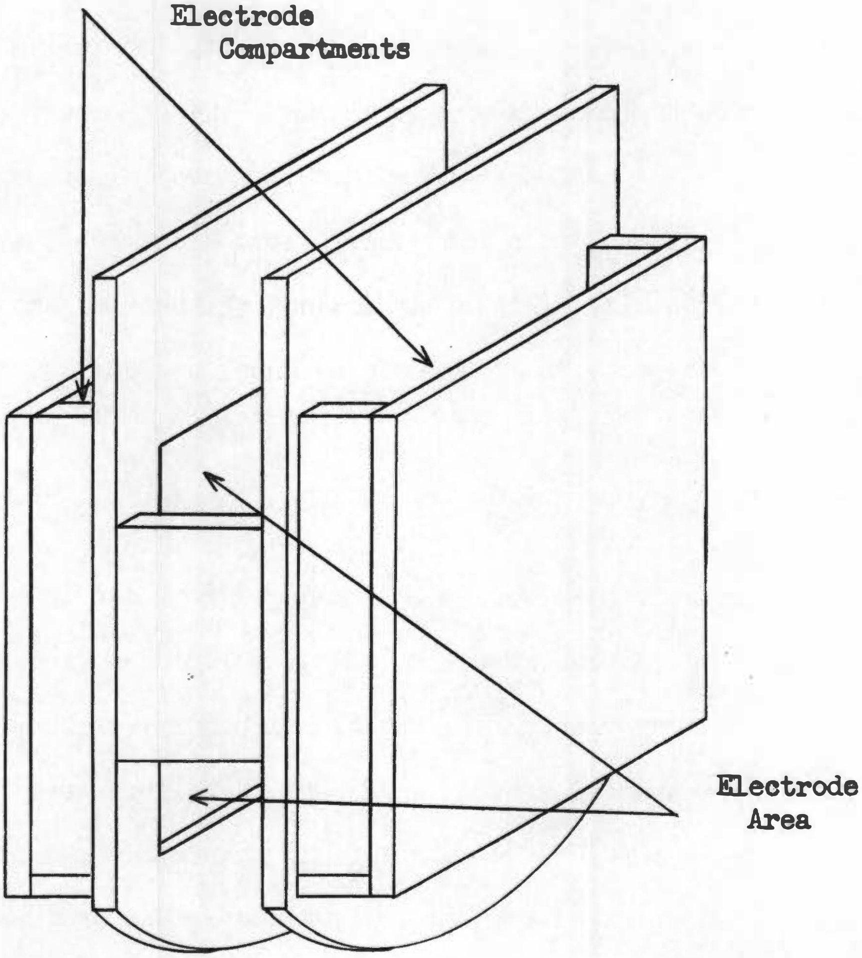

Figure 4. Electrolysis Cell.

same two electrodes were used for all of the temperature difference measurements.

e. Electrolysis circuit. A 32 volt battery pack (lead storage cells) was used as a source of direct current for most of the electrolyses. A few of the experiments required such a high current density that the D. C. generator used in the preliminary experiments was substituted for the battery pack. The current source was connected to the electrolysis cell through a 25 ohm potential divider and a 100 ohm variable resistance. This enabled one to manually control the electrolysis current at any selected value. This was found to be sufficiently constant to give reproducible results.

2. Procedure

For all of the measurements, 200 ml. of copper sulfate solution was used. A precisely constant volume of solution was not necessary to obtain reproducible results for determinations of temperature differences between the two electrodes as long as the entire electrode area was covered. However, when the temperature of the solution was involved in the measurements, it was necessary to use a constant volume of solution. Because of this, the same volume of solution was used in all of the experiments.

For measurements of the temperature differences between the electrodes and the solutions, the solutions must be brought to the same temperature before the start of electrolysis. This was also the case when measuring the temperature difference between the cathode and the anode whenever room temperature varied more than 2 or 3 degrees during the course of the experiment. For these measurements, the solutions were placed in a water bath (set at 30.0° ± 0.02°) before being pipetted into the Dewar flask (which was also contained in the water bath).

Before insertion into the solution, the cathode was cleaned by rubbing it with emery cloth and then dipping it into concentrated potassium cyanide solution for fifteen seconds. In cleaning the anode, it was found necessary to dip it into the cyanide solution for fifteen seconds. This procedure was necessary to obtain reproducible results on the temperature difference measurements.

After the solution was pipetted into the Dewar flask, the clean and dry electrode, cell, and thermistor assembly was inserted into the flask and the electrode and thermistor leads connected. The bridge voltage supply was connected at this point. The entire assembly was then allowed to stand for fifteen minutes after inserting the cell assembly before starting the electrolysis. This period was necessary for two reasons. One, thermal equilibrium must be attained in the solution. This was determined by the constancy of the unbalance potential. Two, polarization characteristic of the electrodes change with time and become constant after about ten minutes.[59]

After this initial waiting period, the electrolysis current was turned on and the current manually adjusted to the selected value (usually 300 ma). The current was manually controlled at this value for the entire electrolysis period. This period was ten minutes in nearly all cases. Readings of the unbalance potential of the bridge circuit were taken every thirty seconds for the first two minutes and then at two minute intervals for the remainder of the electrolysis period. The difference between these potentials and the steady unbalance potential before the start of electrolysis gives the temperature difference in mv. This value can be divided by the bridge sensitivity to obtain the temperature difference in degrees. Since the primary interest was in the relative values of the temperature differences, the temperature differences were recorded in mv.

D. Calorimetric Studies

1. Apparatus

The design and construction of the apparatus used in the calorimetric studies were governed by the quantities which were desired to be measured. These quantities were the heat liberated at each electrode, the heat capacity of the calorimeter, the voltage drops across the electrodes and probe, the electrolysis current, the heating current, and heating and electrolysis times. It was also necessary that both electrodes remain isothermal with respect to each other in order to avoid any effects due to temperature gradients.

a. Thermistors. The two thermistors used in the temperature control circuit were the same two used in bridge No. 1 in the preceding section and will not be discussed here.

The thermistor which functioned as a temperature sensing element was a Carboloy D503. This thermistor had a resistance of 500 ohms at 25° and a dissipation constant of 16.0 milliwatts per degree. The aging procedure carried out on this thermistor was the same as that described previously. As the thermistor was supplied with no protective coating, it was necessary to provide the thermistor with an inert covering. The purpose of this covering was to prevent shorting of the leads. This was done by applying four coats of glyptal resin to the thermistor, each coat being followed by baking in a 160° oven for twenty-four hours. The thermistor was then sealed in a 9 cm. length of 6 mm. (diameter) glass tubing with deKotinsky cement so that only the thermistor and the insulated leads were exposed. The result was a thermistor probe approximately 11 cm. in length which served as the temperature sensing element in all of the calorimetric experiments.

b. Standard resistances. Since the most convenient and precise method for determination of current strength is by measuring the potential drop across a resistance, it was necessary to have reliable and accurate resistances available. These were constructed from Advance resistance wire which had a resistance of 2.94 ohms per foot. Advance was selected because it has an extremely small temperature coefficient of resistance. The resistances were constructed by winding the appropriate length of Advance wire on buss fuses from which the conducting strips had been removed. Contact was made by soldering the ends of the Advance wire to the metal ends of the buss fuses. This afforded a convenient means of mounting the resistances by soldering them in fuse clips.

Each resistance was coated a number of times with glyptal resin, each coating being followed by baking in a 160° oven. After mounting, the resistance value of each was measured with a four decade Leeds and Northrup D. C. Wheatstone bridge. From observations of the extent of the galvanometer deflection, the fifth digit in the resistance values could be estimated. The resistance values were repeatedly checked throughout the course of this work and showed no deviation on aging or heating. Seven such resistances were prepared and their values will be given in the discussion of the various circuits.

c. Temperature control circuit. The temperature control circuit was the Wheatstone bridge No. 1 shown in Figure 2. The only difference between this bridge and the Wheatstone bridge previously described was that in this case the unbalance potential was measured by a Leeds and Northrup K-2 potentiometer using a Rubicon galvanometer as a null point detector. Using the 0.1 range on the potentiometer, the sensitivity of the galvanometer was such that a deflection of 1 mm. corresponded to a temperature difference of approximately 0.001°.

The term "heater control circuit" may be somewhat misleading. The deflection of the galvanometer only served to indicate whether the heater in the outer section of the calorimeter should be turned on or off. Thus the actual task of keeping the two sections of the calorimeter at the same temperature was accomplished by the manual operation of a switch controlling the heater.

d. Temperature measuring circuit. The temperature sensing circuit was designed for the purpose of obtaining an automatic record of the temperature of the calorimeter as a function of time. The final circuit design is shown in Figure 5. This circuit was used for all of the calorimetry experiments.

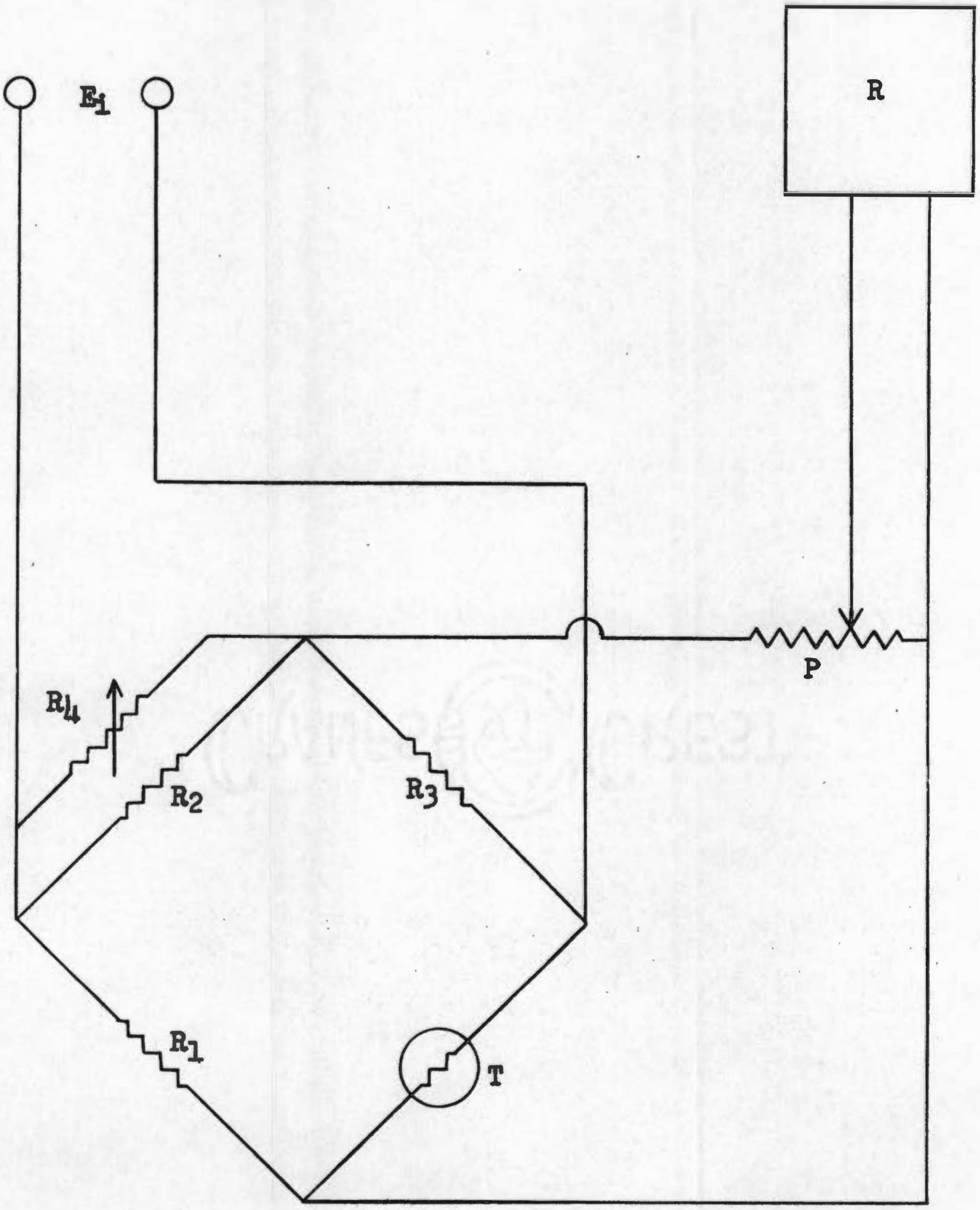

Figure 5. Temperature Measuring Circuit.

In this circuit R_1 and R_2 were 500 ohm, 1/2 watt radio resistances while R_3 was a 470 ohm, 1/2 watt radio resistance. A Heathkit decade resistance box, R_4, was used to adjust the unbalance potential of the bridge to approximately 14 mv at bath temperature (30°). This was accomplished by setting R_4 at 5300 ohms, a value which was not changed throughout the course of the experiments. T was the Carboloy D503 thermistor described previously. The input voltage, E_i, was from the regulated low voltage power supply which was set at 1.000 volts with the K-3 potentiometer.

The unbalance potential was fed to P, a Leeds and Northrup K potentiometer where a portion of the potential was bucked out and the remainder fed to R, a Leeds and Northrup Micromax recording potentiometer. This recorder originally had a range of 40 mv but this was altered so the recorder had an effective range of 0-10 mv full scale.

The range of the recorder and the output and linearity of the Wheatstone bridge circuit were tested extensively with the K-3 potentiometer and a Beckmann thermometer. These tests showed that recording errors were negligible. They also showed that the bridge had a sensitivity of approximately 10 mv per degree and that a plot of mv versus temperature was linear over a 4° range (29-33°). Thus the temperature measuring circuit provided an automatic record of the temperature of the calorimeter which could be read to approximately ± 0.001°. Temperatures were recorded in millivolts, however, as there was no advantage to be gained by converting them to degrees.

e. Heating circuits. Heating in the calorimeters was accomplished by the use of two essentially independent heating circuits (Figure 6). The definitions of the symbols used in Figure 6 are given in Table I.

The heaters and dummy heaters were constructed from the same Advance resistance wire used in the fabrication of the standard resistances. The heaters were constructed by winding the appropriate length of Advance wire on a 3 mm. diameter glass rod and seating with Sauereisen (a liquid porcelain cement). The heaters were provided with appropriate current carrying leads of copper magnet wire (B. and S. gauge 20). The heating coils were then inserted into 9 cm. (for inner compartment heater) and 14 cm. (for outer compartment heater) lengths of 8 mm. diameter Pyrex tubing which had been closed at one end with a test tube bottom. Light mineral oil was poured into these tubes until the heating coils were covered. This completed construction of the two calorimeter heaters. The resistance values of the heaters were measured with the same D. C. Wheatstone bridge used for measuring the resistances of the standard resistors. These values were checked periodically during the course of this work. It was found that the resistances did not deviate from their original values.

The dummy heaters were made by winding the necessary lengths of Advance on porcelain cores and seating with Sauereisen. This was followed by four coatings of glyptal resin. Each coating was baked in a 160° oven before applying the next coat. With the exception of the calorimeter heaters, all resistances and the dummy heaters were mounted on

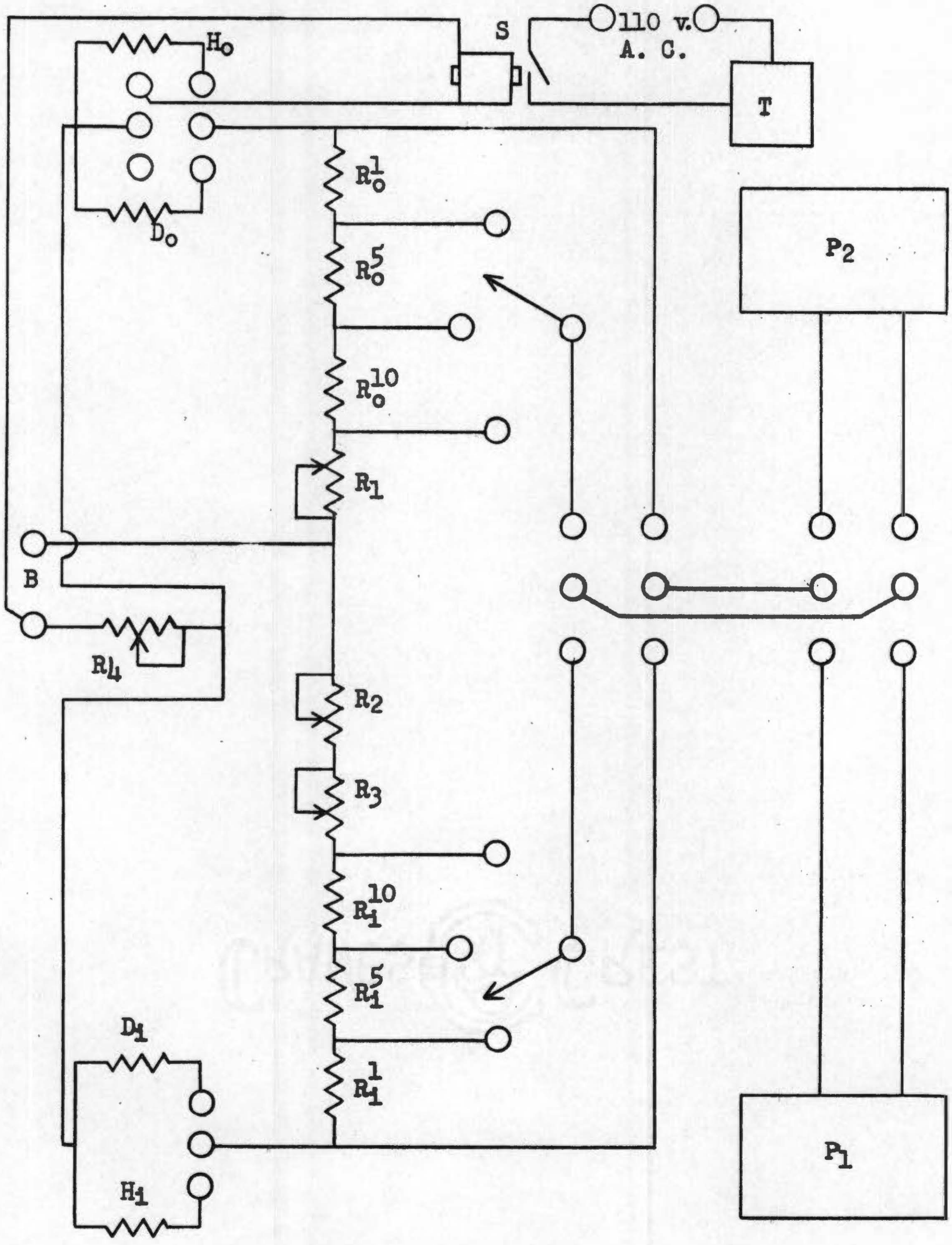

Figure 6. Heating Circuit.

TABLE I

DEFINITION OF SYMBOLS USED IN FIGURE 6

Symbol	Definition
R_1, R_3	25 ohm, 4.5 amp. Rheostats
R_2	65 ohm, 3.2 amp. Rheostat
R_4	100 ohm, 25 watt Variable Resistance
R_o^1	1.0394 ± 0.0002 ohm Standard Resistance
R_o^5	4.7442 ± 0.0004 ohm Standard Resistance
R_o^{10}	8.3474 ± 0.0006 ohm Standard Resistance
R_i^1	1.0623 ± 0.0002 ohm Standard Resistance
R_i^5	4.7907 ± 0.0004 ohm Standard Resistance
R_i^{10}	8.3610 ± 0.0006 ohm Standard Resistance
D_i	15 ohm Dummy Heater
H_i	5.0388 ± 0.0005 ohm Heater
D_o	30 ohm Dummy Heater
H_o	10.168 ± 0.002 ohm Heater
S	30 volt D. C. Relay
B	32 volt Battery Pack
T	Timer
P_1	Leeds and Northrup K-2 Potentiometer
P_2	Leeds and Northrup K-3 Potentiometer

Note: Subscript i refers to inner section of calorimeter while o refers to outer section.

the same panel to provide compactness and easy accessibility of these components.

The two heaters were designed to operate in the following manner: the inner compartment heater would be left on continuously during a heat capacity run while the outer compartment heater would be operated intermittently to provide just enough heat to keep the outer compartment at the same temperature as the inner compartment. Whether the two compartments were at the same temperature would be indicated by the temperature control circuit. The inner compartment heater could easily be timed with an ordinary stop watch while the outer calorimeter heater required a timer which would measure the total time during which the outer calorimeter heater was on. This requirement was met by obtaining a 110 volt 60 cycle electric timer. The time was actuated by a 30 volt D. C. relay which in turn was activated by the outer compartment heater switch as shown in Figure 6. This was done to prevent the possibility of inducing stray emf's in the heater circuit. The electric timer was checked against a stop watch and no significant difference was found.

The switching arrangement between the various potentials made it possible to use the K-3 potentiometer for heat capacity calibrations and the K-2 for calorimetric runs as the K-3 was then being used for other purposes.

f. Electrolysis circuit. The working equation (39) in Chapter II was derived for the condition of constant current. This condition could be satisfied by (a) manual control of the current or (b) having an electronic device which would deliver a constant current irrespective of the load. Because of the practical limitation on the number of functions which one operator can satisfactorily perform, the latter course was chosen.

To meet these requirements, the automatic coulometric titration device described by Wise, Gille, and Reynolds[60] was constructed.* Under the conditions used in this work, this instrument furnished a constant current with a maximum deviation of 0.004 per cent and an average deviation of 0.002 per cent.

The electrolysis circuit is shown in Figure 7. The reistance R_s was a standard resistance prepared as previously described and having a value of 5.1274 ± 0.0005 ohms. The switching arrangement made it possible to measure the potential drop between the probe and either electrode or the potential drop across R_s to obtain a value for the current. The electrodes and probes will be discussed in a later section.

g. The calorimeter. As it was desired to measure the amount of heat liberated or absorbed for a single electrode reaction, it was necessary to have the calorimeter divided into two sections. Thus the two sections should be thermally insulated from each other as well as possible but should offer no appreciable barrier to the passage of current between the electrodes. It was also necessary that the two sections of the calorimeter be isothermal with respect to each other. This was necessary to prevent such effects as the thermal diffusion potential, the Soret effect, heats of transfer, and other thermocell phenomena.

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*Constructed by Gerald Raine of this laboratory.

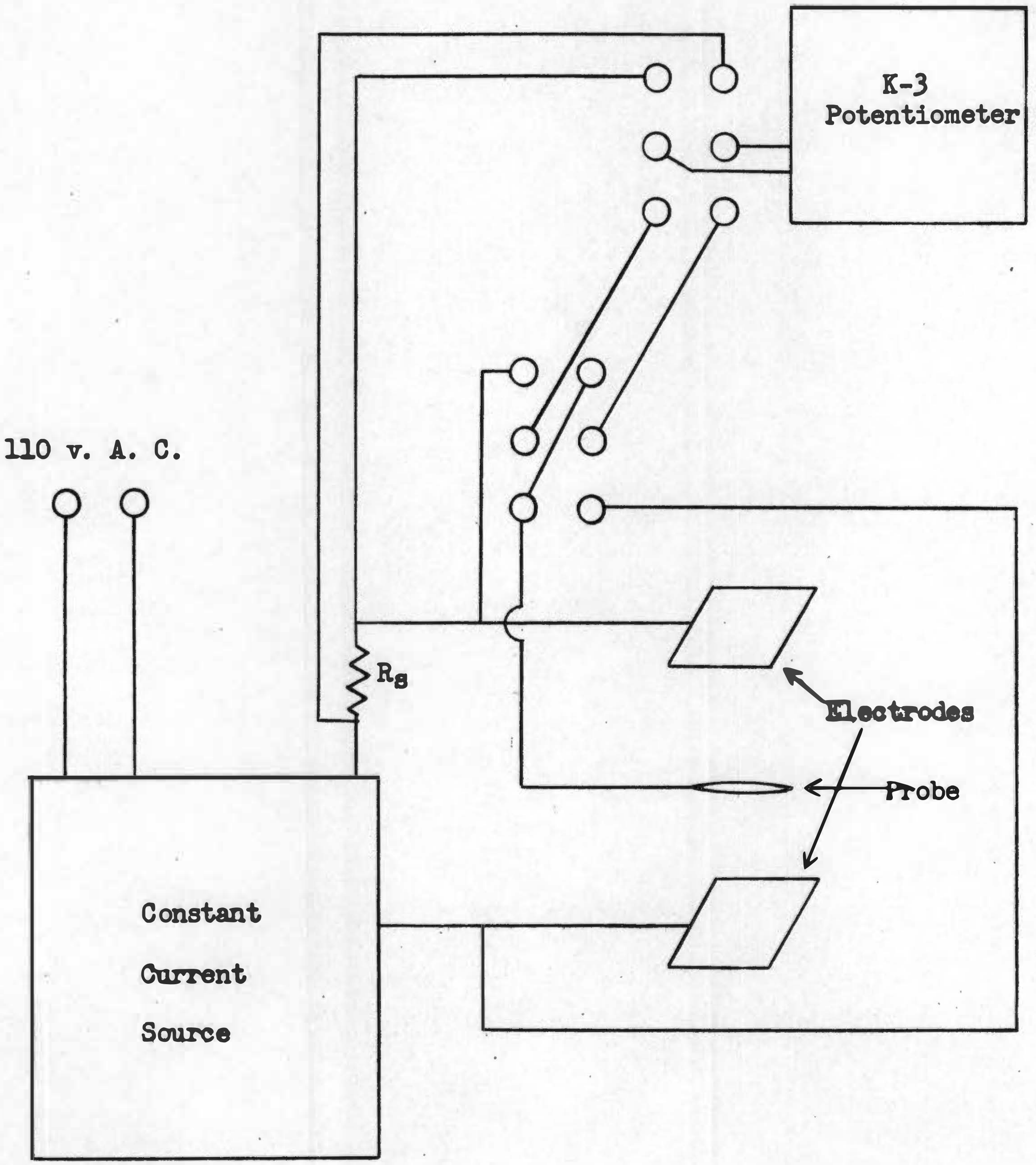

Figure 7. Electrolysis Circuit.

The above were the basic requirements kept in mind while designing the calorimeter.

The basic part of the calorimeter was a 500 ml. Dewar flask. Although Dewar flasks are not very precise calorimeters, the restriction of having no metal parts, other than the electrodes, exposed to the solution automatically limited the choice to a glass apparatus. In order to provide the best possible thermal insulation, a silvered, vacuum jacketed glass cylinder was chosen for the innermost compartment of the calorimeter. This cylinder was 10 cm. long, had an inside diameter of 2.7 cm., and was open at both ends.

In order to isolate the two compartments of the calorimeter, one end of the inner cylinder had to be closed with some material which would afford free passage of an electrolytic current and still maintain a fair degree of thermal insulation. The first material tried for this was porous Vycor glass. However, for some unknown reason, this material invariably cracked on extended contact with the solution. This effect had been noted previously by other workers.[31] The next material tried proved to be very suitable for the partition. This was a Watman's filtering pad. Not only did this material provide a reasonable amount of thermal insulation, it also offered negligible resistance to the passage of current. The filtering pad was fastened to one end of the cylinder with glyptal resin. This proved to be a suitable cement in that the partition remained intact during a series of runs. The partition was changed only when a different electrolyte was used.

It was necessary that the calorimeter be provided with a cover, support for the inner compartment, and entry for the electrical leads and stirrers. This was effected by three machined brass plates, each of which was 1/8 inch thick. The bottom plate was machined to fit snugly over the top of the 500 ml. Dewar flask and was cemented to the flask with "3M" cement* as shown in Figure 8. The middle plate was designed to provide support for the inner compartment while not blocking entry into the outer compartment. The plate was cemented to the inner compartment with "3M" cement and had the shape shown in Figure 9. The top plate provided a cover for, and ports for entry into, the calorimeter. The ports for entry into the calorimeter were made by soldering 4 in. lengths of 3/8 inch copper tubing to the top plate. These tubes provided openings for the electrical leads and the stirrers. The bottom and top plates were grooved to provide seats for the "O" rings. The "O" rings served to seal the calorimeter against leakage of water from the water bath into the calorimeter. The three plates were fastened together with four bolts. This is illustrated in Figure 10.

Stirring for the calorimeter was provided by two stirrers fashioned from 6 mm. diameter glass rod. The blade of the inner compartment stirrer was 1 cm. in diameter while the blade of the outer compartment stirrer was 2 cm. in diameter. Both stirrers were driven by the same Sargent stirring motor at a constant speed of approximately 150 rpm. While providing a fairly uniform temperature, this rate of stirring was not enough to add a measurable quantity of heat to the calorimeter during an

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*Weatherstripping adhesive manufactured by Minneapolis and Minnesota Mining Co.

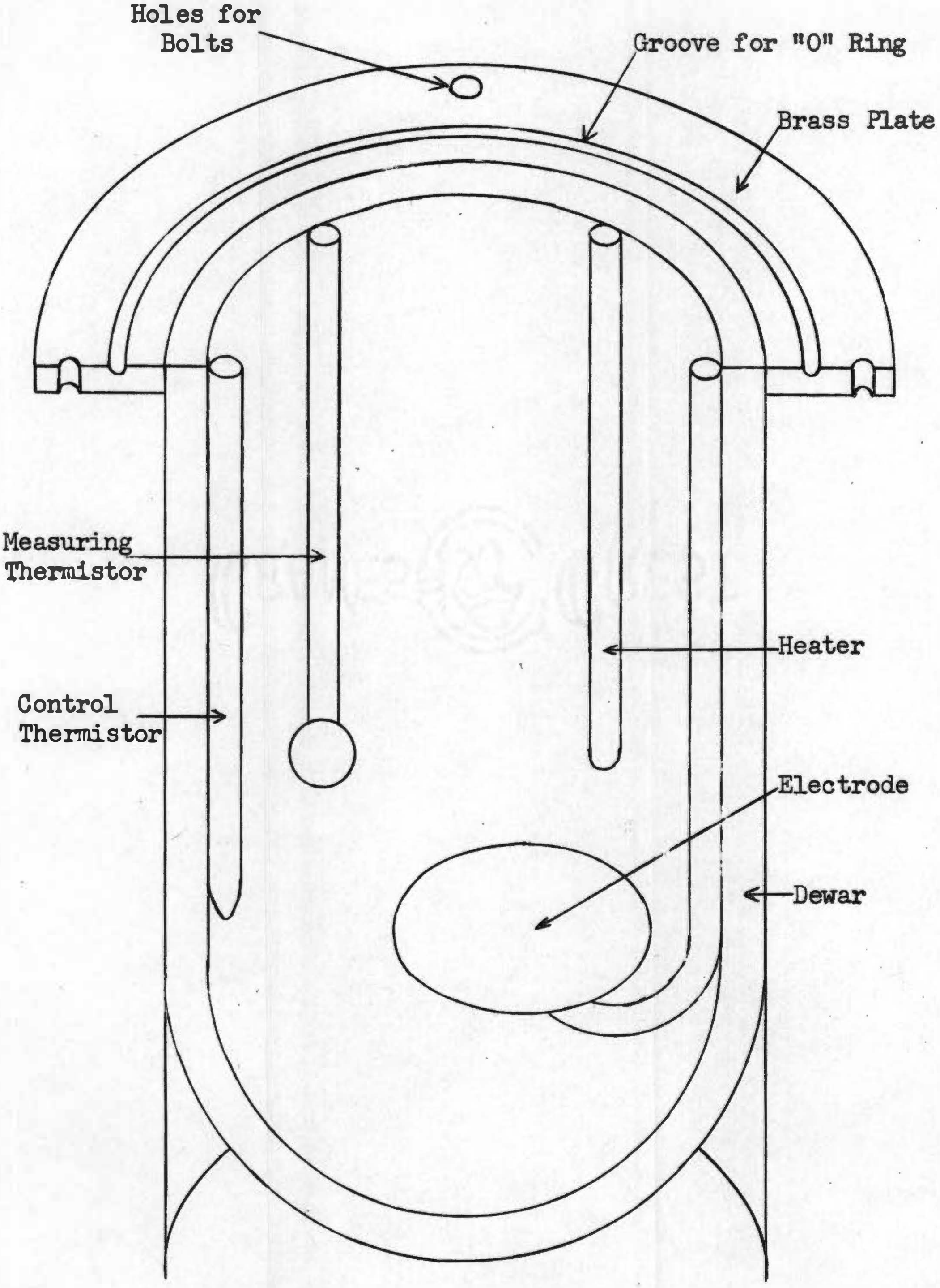


Figure 8. Section View of Calorimeter (Outer Compartment).

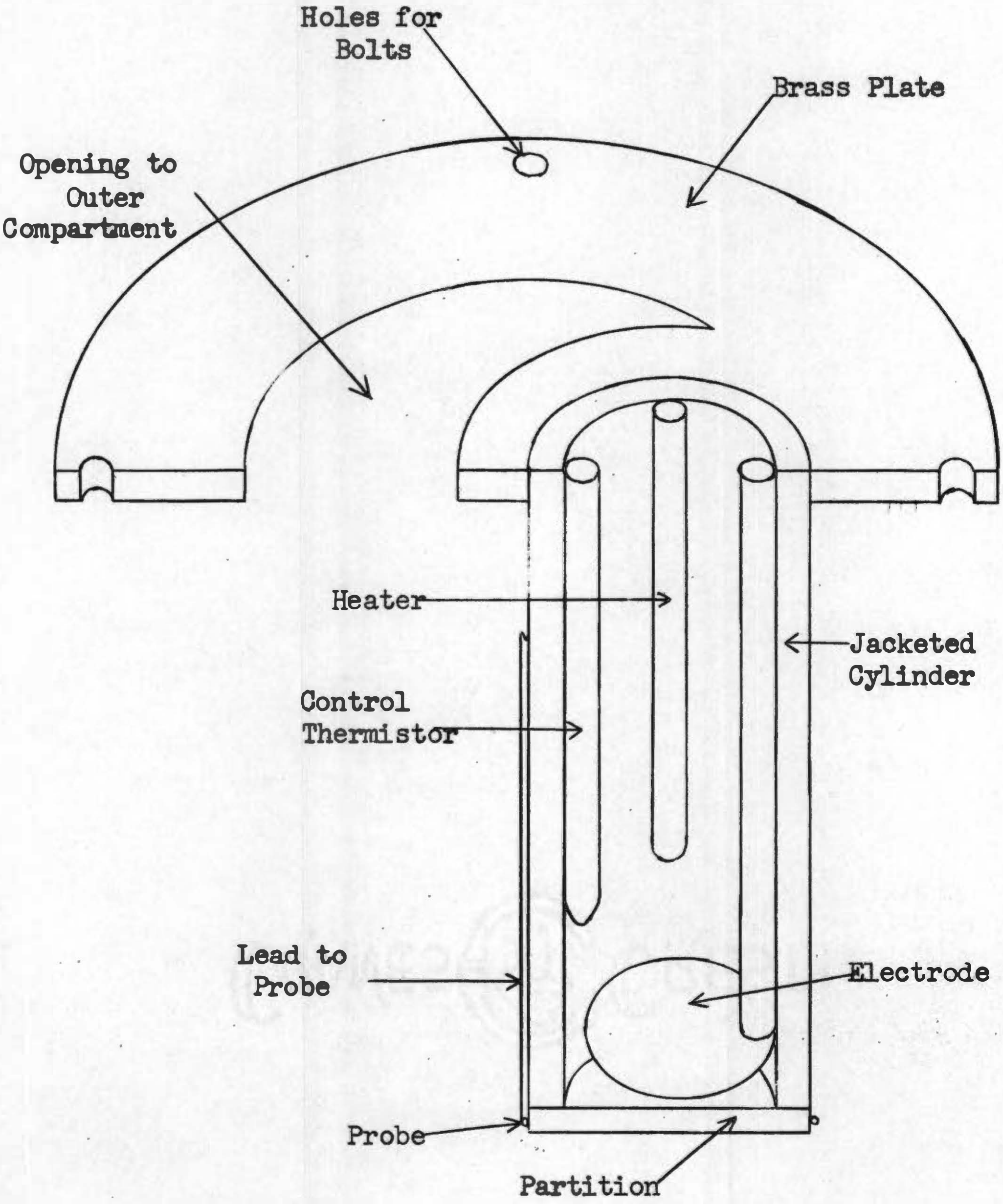
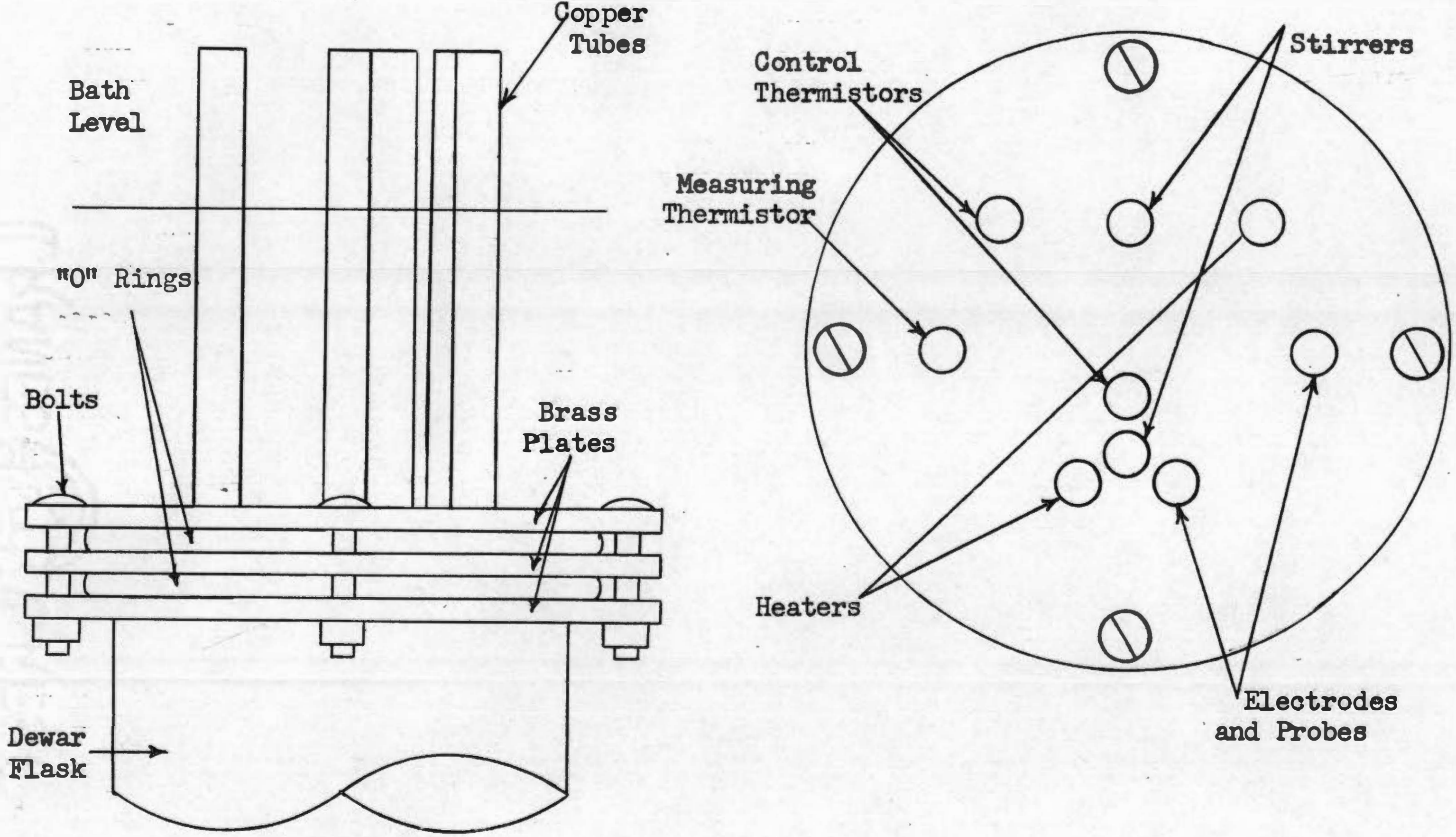


Figure 9. Section View of Calorimeter (Inner Compartment).


Side View

Top View

Figure 10. Assembled Calorimeter.

experiment. This was demonstrated by the fact that the calorimeter reached the same steady state regardless of whether it was stirred or not. This is in agreement with the experiment of White[61] which showed that a stirrer with a 4 cm. diameter propeller operated at 500 rpm. causes a temperature rise of only 0.00006° per minute.

The arrangement and positions of the components of the calorimeter are illustrated in Figures 8, 9, and 10. The heaters, thermistors, and electrodes were fastened to the sides of the calorimeter with "3M" cement. This was necessary to insure a rigid position of these components throughout an experiment.

A water bath was used as the constant temperature jacket for the calorimeter. This bath was set at 30.0° and had fluctuations of no more than 0.001° during the course of a series of experiments. This water bath was a commercial unit obtained from E. H. Sargent and Co. Some alterations were carried out to obtain the desired performance. A quartz infrared heater was substituted for the off-on control heater in the commercial unit. This quartz heater was ideal in that the time lag was very small. The mercury thermoregulator was placed downstream from the control heater to reduce overshoot of the bath temperature. The thermoregulator was mounted off center from the stirring motor in order to impart a vertical vibration to the thermoregulator. This had the effect of being more like a continuous control instead of a simple off-on switch. Ten per cent of the 200 ohm heater in the commercial unit was left on continuously. This provided enough heat to keep the bath to within 1 to 2° of the desired bath temperature. The bath was also provided with a leveling device by means of which water was constantly added to compensate for evaporation. All of the above factors are known to greatly improve the performance of constant temperature baths.[62] The water level of the constant temperature bath with respect to the calorimeter is indicated in Figure 10.

h. Electrodes and probes. The copper and silver electrodes were made from electrolytic sheet metal. All electrodes used were circular discs. All of the anodes had an area of 3.93 cm.^{2}. The area of each cathode was 15.53 cm.^{2} with the exception of the platinum and a few of the copper cathodes. These had an area of 3.93 cm.^{2}. The back sides of the electrodes were always coated with glyptal and baked.

The center probes were fashioned from small wires of the same material as the electrodes. These probes were attached to the filtering pad partition as shown in Figure 9. The potential difference between the probes and the electrodes was zero in all cases under condition of zero current flow.

i. Complete apparatus. The relationship of all the components to each other is shown in the block diagram of the complete apparatus (Figure 11). All leads and switches were mounted on a central control board to provide for compactness and ease of operation.

2. Procedure for Calorimetry Experiments

Prior to the assembling of the calorimeter, all of the components were checked for shorts and breakage of seals. The electrodes were cleaned as described previously. The various components were then assem-

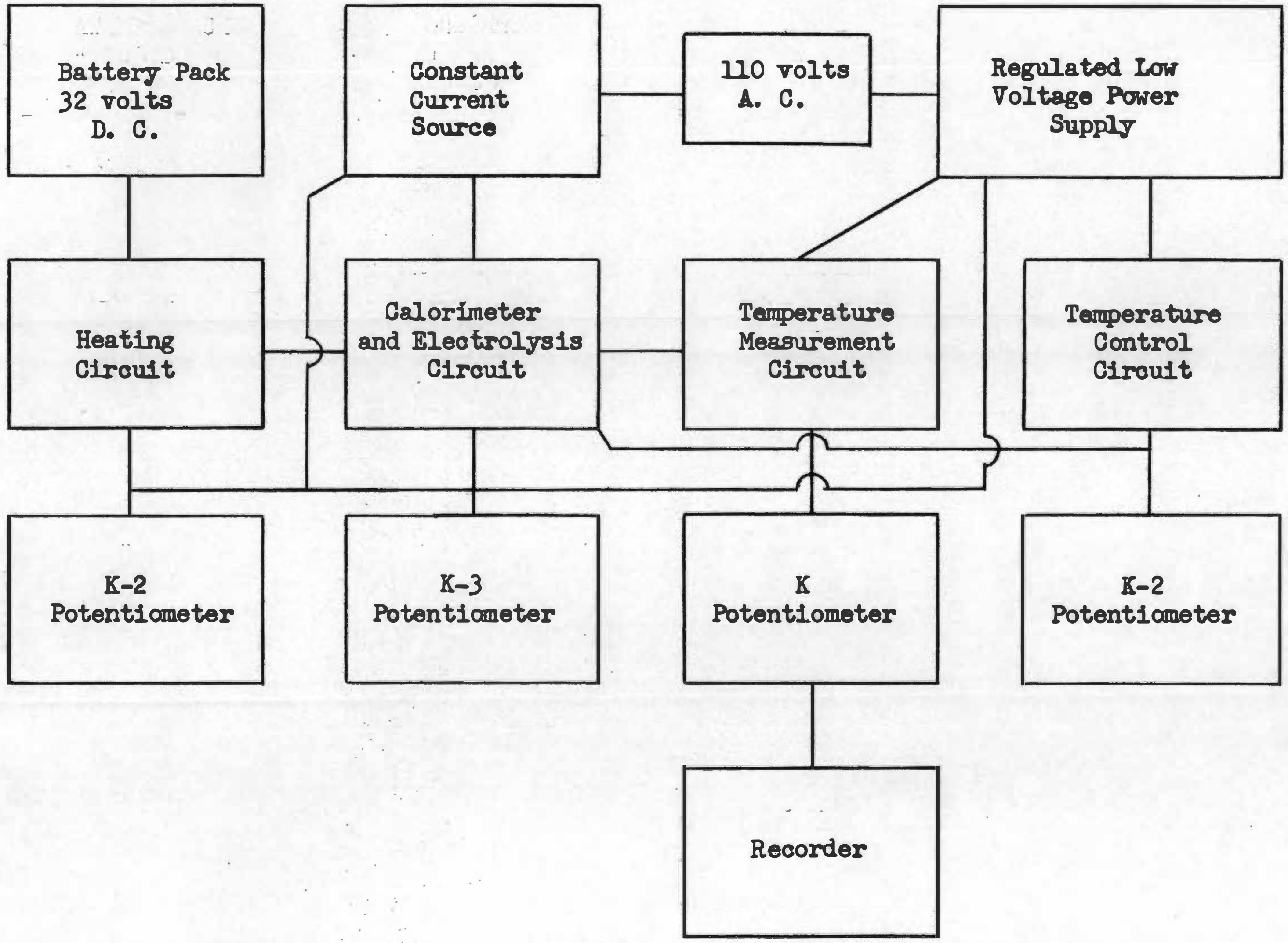


Figure 11. Block Diagram of Complete Apparatus.

bled as shown in Figures 8 and 9. The calorimeter was filled with enough solution (approximately 350 ml.) to submerge the components. Stirrers were inserted and top bolted on to give the completely assembled calorimeter as shown in Figure 10. The calorimeter was then placed in the constant temperature bath and the electrical leads and the stirring motor connected.

The calorimeter was brought to within approximately 0.3° of bath temperature with the heaters. With a few exceptions, the bath temperature was approximately halfway between the initial and final temperatures of the calorimeter for all of the experiments. At this point, final adjustment was made of the power supply, current source, and all of the potentiometers were standardized. At the beginning of the fore rating period, which was approximately thirty minutes in all cases, it was necessary to make sure that the inner and outer compartments were at the same temperature. This was done by noting the deflection of the galvanometer associated with the potentiometer in the temperature control circuit and manually regulating the heater in the outer compartment. Up to this point, the procedure was the same for both heat capacity and electrolysis runs.

To initiate the heat capacity measurements, the inner compartment heater was turned on. Simultaneously, the stopwatch was started. Values of the potential drop across a standard resistance in the inner compartment heating circuit were measured. When the temperature of the inner compartment rose to 0.003 to 0.005° higher than the temperature of the outer compartment, the outer compartment heater was turned on. Since there was a small amount of lag in the heater, the outer compartment heater was turned off when the galvanometer indicated that the two compartments were at the same temperature. By this procedure, it was possible to keep the two compartments at the same temperature within approximately 0.005°. Large deviations were seldom greater than 0.01° and never greater than 0.02°. Turning on the outer compartment heater automatically activated the electric timer in the outer compartment heating circuit and this timer recorded the total time that the outer compartment heater had been on. During the time that the outer compartment heater was on the potential drop across standard resistances in both heater circuits were measured and recorded. This process was repeated as often as possible during a heat capacity run.

When the desired temperature rise had been attained (usually 0.4 to 0.7°), the electrical heating was terminated. This was accomplished by turning off the inner compartment heater with the outer compartment approximately 0.003° warmer than the inner compartment. The heat left in the inner compartment heating coil would then bring the two compartments to very nearly the same temperature (usually less than 0.001° difference). Heating times were recorded from the stop watch and the electric timer. A thirty minute rating period completed the data necessary for a heat capacity determination.*

In the electrolysis experiments, the only source of heat supplied to the inner compartment was the heat effects caused by the passage of

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*Treatment of both the heat capacity and electrolysis data will be given in the Appendix.

current through the solution. In addition to the heat effect of the electrolysis current through the solution, it was necessary to add heat from the heater in the outer compartment to maintain all parts of the calorimeter at the same temperature. The outer compartment heater was manipulated in the manner described above in order to keep the two compartments at the same temperature.

The electrolysis experiments were initiated by turning on the electrolysis current, the constant current source having previously been set at the desired current strength. Throughout the course of the electrolysis, the potential difference between the cathode and the probe, and between the anode and the probe were measured and recorded. Each time the outer compartment heater was turned on, the potential drop across a standard resistance in the outer compartment heating circuit was measured and recorded. At some convenient time during the electrolysis, usually about half-way through the electrolysis, the current strength was measured by measuring the potential drop across the standard resistance in the electrolysis circuit (Figure 7). When the desired temperature rise had been achieved, the electrolysis was terminated. In this case, the electrolysis current was turned off only at a time at which both compartments of the calorimeter were at the same temperature. Electrolysis and heating times were recorded and a thirty minute rating period completed the data for an electrolysis experiment. This is, of course, in addition to the preliminary rating period.

In nearly all cases, the above two runs were followed by a heat capacity run, an electrolysis run, and another heat capacity run before removing and tearing down the calorimeter.

3. Current Efficiency Studies

It was essential that the current efficiency be 100 per cent in all cases for the working equation to apply to a single reaction. In view of this, it was decided to ascertain if the electrode reactions were proceeding in a quantitative manner.

To test this by experiment, copper and silver electrodes were prepared in the same manner as previously described. These were then weighed and immersed in the same solutions as used in the calorimetric experiments, *i. e.*, copper electrodes in copper sulfate and silver electrodes in silver nitrate. The two electrolysis cells were equipped with the same stirrers used in the calorimetric experiments and connected in series in the electrolysis circuit in place of the calorimeter. The electrolysis current was then turned on and timed with the stop watch. The current was continuously monitored by measuring the potential drop across the standard resistance in the electrolysis circuit. This care proved entirely unnecessary as all detectable deviations in the current were much less than the error in weighing the electrodes. At the end of about a thirty minute electrolysis period, the electrodes were removed, rinsed, dried, and weighed. Knowing the current strength, time of electrolysis, and loss or gain of weight in the electrodes, the current efficiency was easily calculated.

CHAPTER IV

RESULTS

A. Preliminary Experiments

The preliminary experiments served merely to indicate some of the important concepts to be kept in mind for the design of the apparatus which was to be used eventually for the calorimetric measurements. Attempts to repeat the results of Gritsan and Bulgokova[30] on the temperature differences between electrodes and solution during electrolysis were entirely unsuccessful. As expected, it was found that the temperature rise at an electrode during electrolysis increased with decreasing concentration and increasing current density. These temperature effects were also highly dependent on the geometry of the electrolysis cell.

Results from a typical experiment with the preliminary apparatus described in Chapter III are given in Figure 12. In this figure, the temperature rise in each electrode compartment as indicated by Beckmann thermometers is plotted as a function of time. The interesting part of the figure is the time lag of the anode temperature as compared to cathode temperature during the first part of the electrolysis. It was felt, however, that the Beckmann thermometers were not accurate enough and did not respond rapidly enough to give accurate measurements of the heat effects.

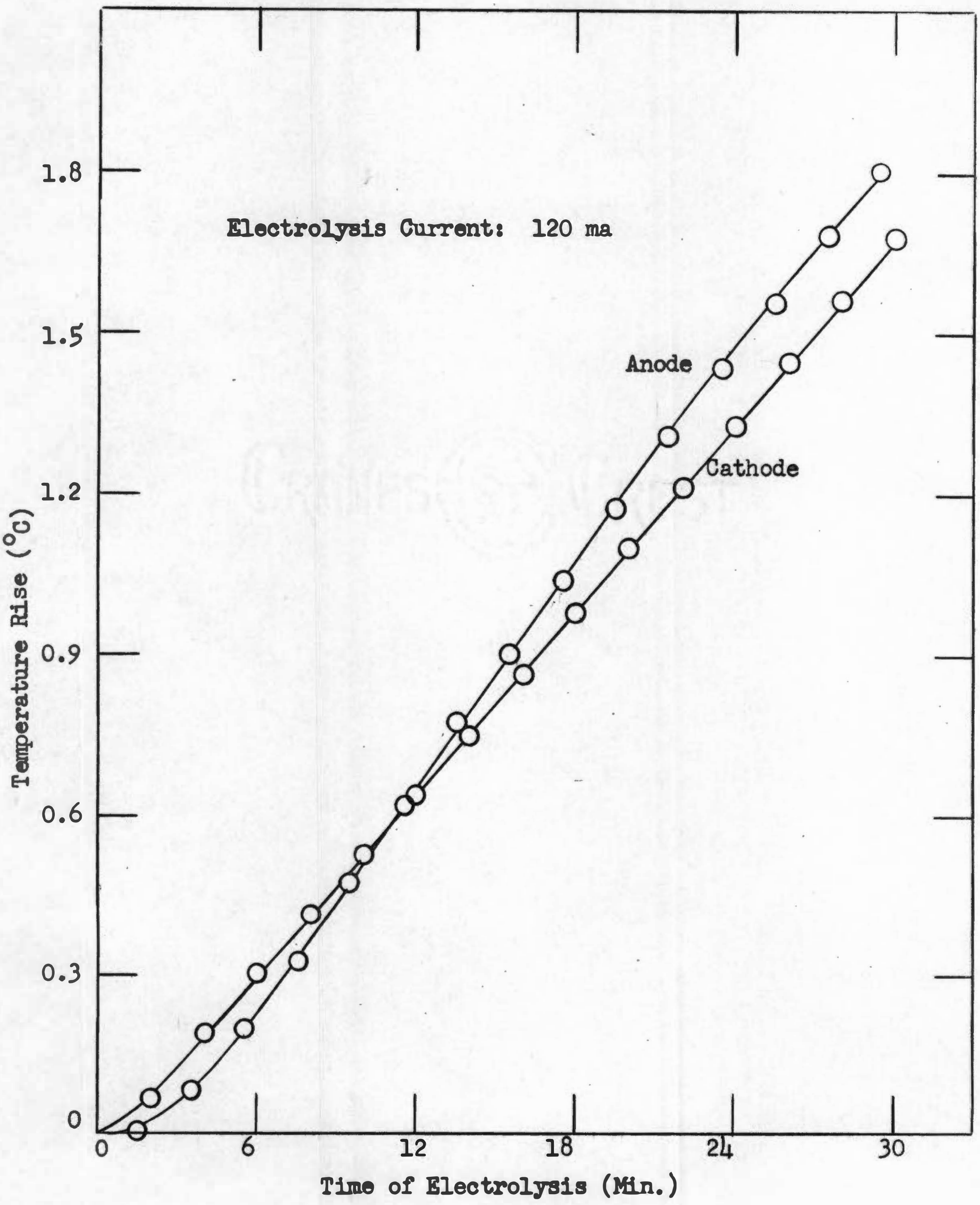

Figure 12. Temperature Rise at the Electrodes for the Electrolysis of 0.0125 M Copper Sulfate.

B. Temperature Difference Measurements on the Copper-Aqueous Copper Sulfate System (Thermal Electroanalysis)

The results reported here were obtained using the apparatus which is described in Chapter III. Data for the pure copper sulfate solutions were obtained for the concentration range from 0.02 to 0.20 molar. In addition to this, results are reported for 0.08 molar copper sulfate to which potassium, sodium, or hydrogen sulfate had been added at a concentration of 0.02 molar. The effect of gelatin (40 mg./liter) was also studied.

The results given here are expressed in terms of three temperature variables; T_C; T_A, and T_S, where T_C is the temperature of the cathode, T_A is the temperature of the anode, and T_S is the temperature of the solution. Some typical plots of T_C-T_A versus time of electrolysis at a current of 300 ma* are shown in Figure 13. This is the type of curve expected in all cases, with the steady state temperature of the anode higher than the steady state temperature of the cathode. The specific shape of the curves, however, did vary with the current and, as can be noted from Figure 13, the concentration of the solution being electrolyzed. After an electrolysis time of approximately two minutes, T_C-T_A becomes more negative at a faster rate in the case of the less concentrated solutions than with the more concentrated solutions. The curve for 0.20 M copper sulfate is completely smooth and no maximum appears in this curve. A maximum in each curve was observed in solutions contain-

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*Total current is given rather than current density as T_C-T_A depends on many other factors in addition to current density.

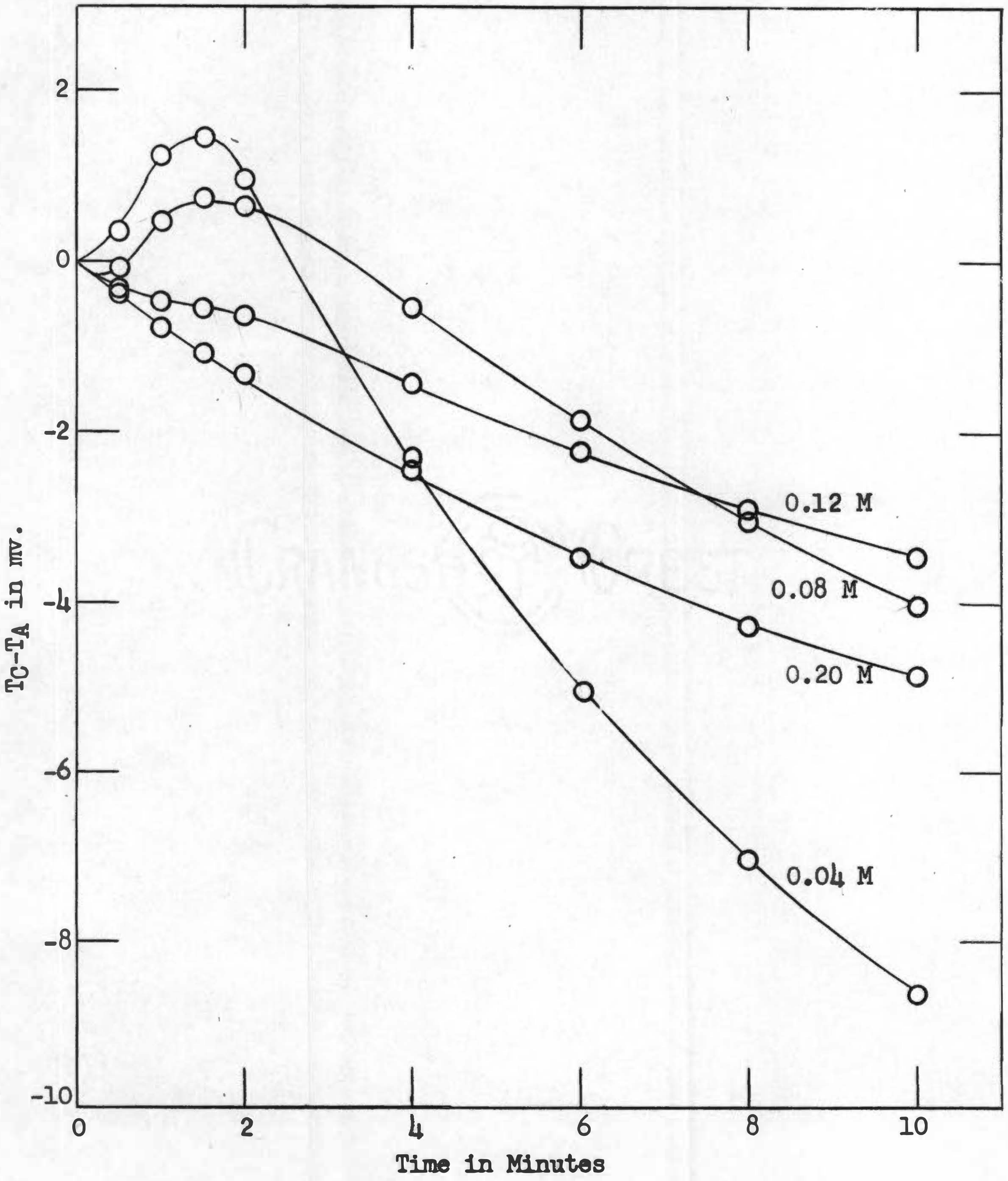

Figure 13. T_C-T_A versus Time of Electrolysis for the Electrolysis of Copper Sulfate at 300 ma.

ing 0.04, 0.08, and 0.12 M copper sulfate. It was found, in general, that with concentrations above 0.12 M, the curves were smooth, the slopes were negative over the entire time period, and there was little variation of T_C-T_A with concentration. With solutions of concentrations below 0.12 M, the curves always exhibited a portion with a positive slope and showed wide variation with concentration.

In Figure 14 the value of T_C-T_A at the end of ten minutes of electrolysis is plotted versus the molar concentration of copper sulfate. All values were obtained at a constant current of 300 ma. The maximum in this curve at approximately 0.10 M copper sulfate corresponds to the point above which a portion of the copper plated on the cathode is darker in appearance than the base metal. From 0.16 to 0.20 M, the horizontal portion of the curve, the copper plated over the entire cathode was dark, indicating a high degree of subdivision of the deposit. Up to a concentration of 0.10 M, no plating was evident since the copper was deposited in the form of a finely divided metal powder.

The values of T_C-T_A at the end of one minute of electrolysis at a current of 300 ma are shown in Figure 15. The effect of concentration appears to be opposite to that observed for the ten minute values. The slope in this case is opposite in sign. The one minute values of T_C-T_A were not as reproducible as the ten minute values and are probably more closely associated with polarization effects.

The T_C-T_S and T_A-T_S versus time plots are shown in Figure 16. T_S is in both cases the temperature of the solution. These curves were obtained to check the T_C-T_A values obtained previously. The difference

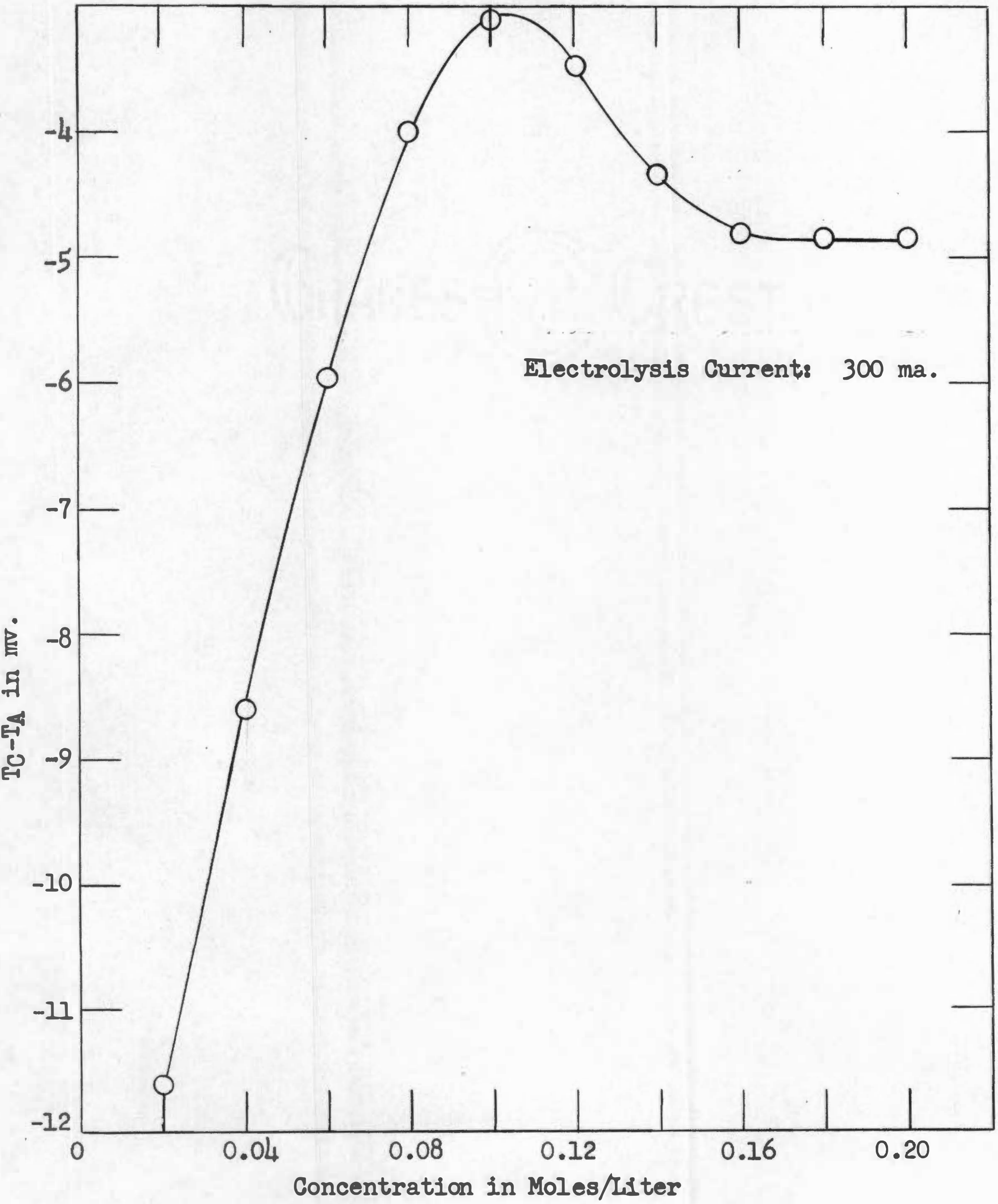

Figure 14. Ten Minute Values of T_C-T_A *versus* Molar Concentration of Copper Sulfate.

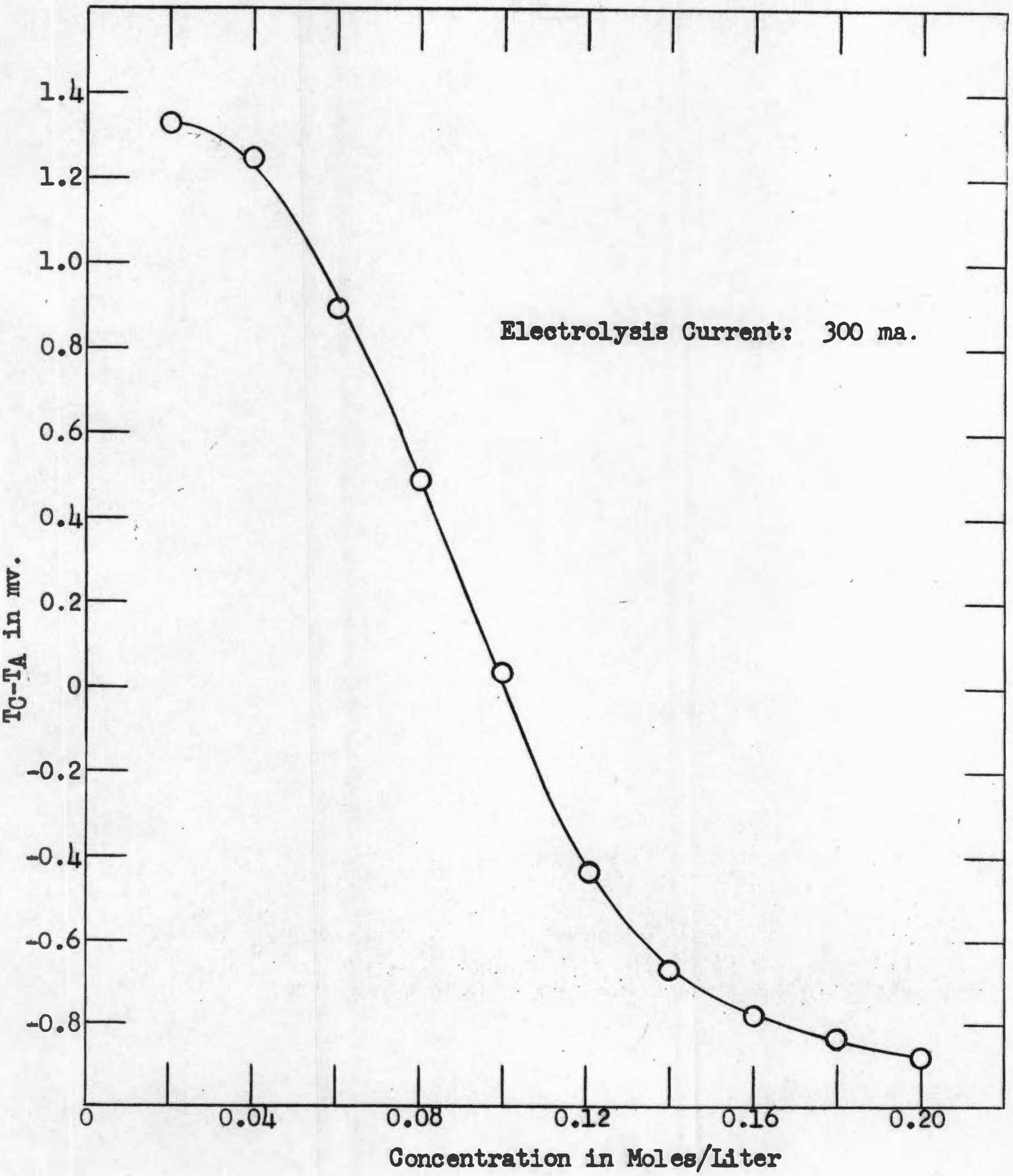

Figure 15. One Minute Values of T_C-T_A <u>versus</u> Concentration of Copper Sulfate.

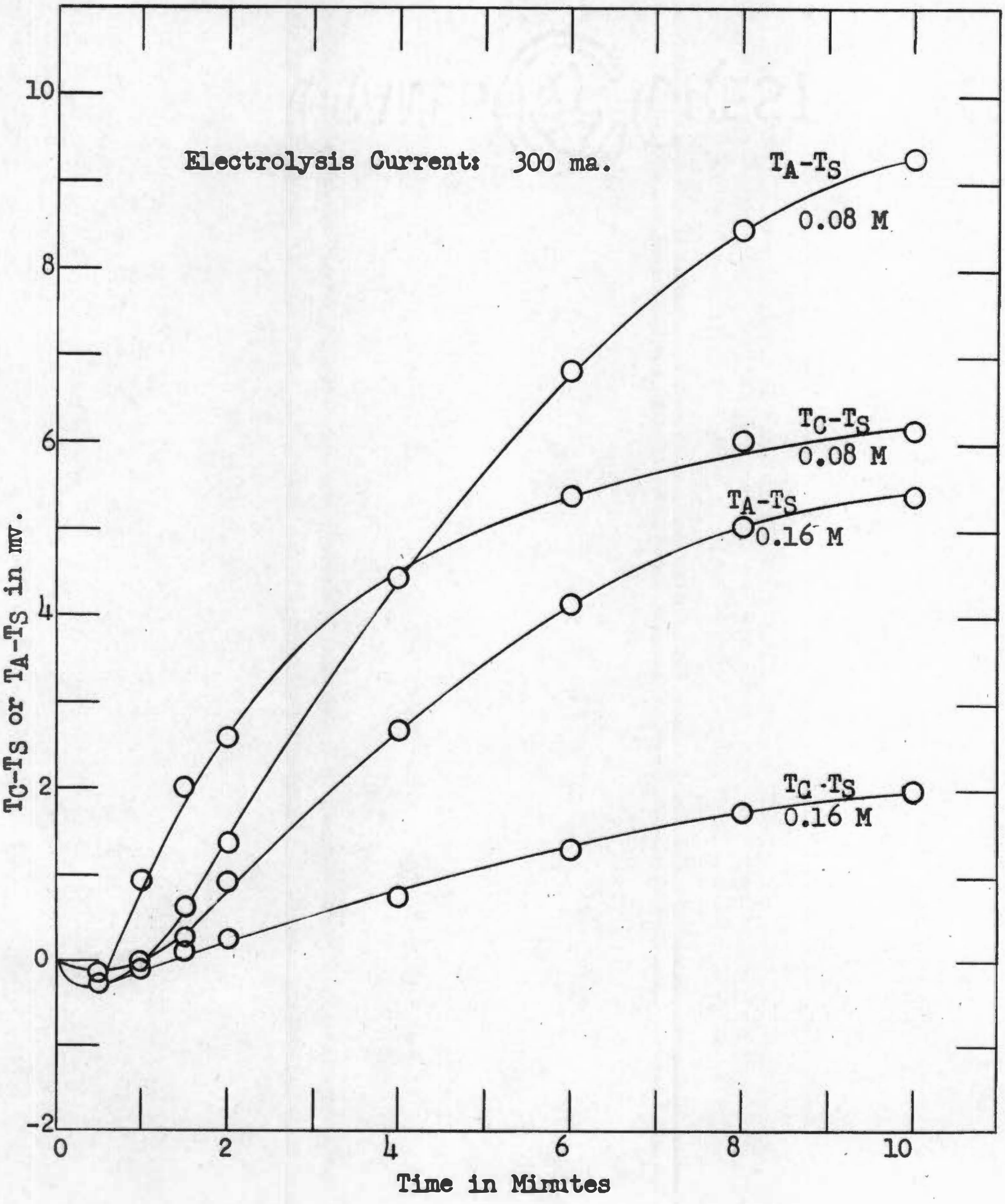

Figure 16. T_C-T_S and T_A-T_S versus Time for the Electrolysis of Copper Sulfate.

between the two curves, T_C-T_S and T_A-T_S, should reproduce the experimentally obtained T_C-T_A curve. Within experimental error, this was true in all cases. The check, therefore, was exceedingly good, particularly in view of the fact that two different bridge circuits were used. In no case was a negative value of T_A-T_S or T_C-T_S observed after about one minute of electrolysis.

In Figure 17 the ten minute values of T_C-T_S and T_A-T_S are plotted versus the molar concentration of copper sulfate for electrolysis at 300 ma. Although both of these curves show the same general trend with concentration, their difference reproduces quite well the variation of T_C-T_A with molar concentration as shown in Figure 14. Figure 17 also demonstrates conclusively that both the cathode and the anode are warmer than the surrounding solution.

Figure 18 illustrates the effect of current variation on the shapes and magnitudes of the T_C-T_A values when plotted as a function of time. These curves were obtained using the same concentration of copper sulfate (0.08 M) for all of the experiments. This set of curves shows a striking resemblance to the family of curves shown in Figure 13 in which the current was held constant and the copper concentration was varied. From these two sets of curves it appears that decreasing the current has the same effect on the T_C-T_A versus time curves as does increasing the concentration. In Figure 19 the ten minute values of T_C-T_A for the electrolysis of 0.08 M copper sulfate are shown plotted as a function of the electrolysis current. This curve shows the great need for maintaining a constant electrolysis current if one wishes to obtain reproducible and accurate values of T_C-T_A.

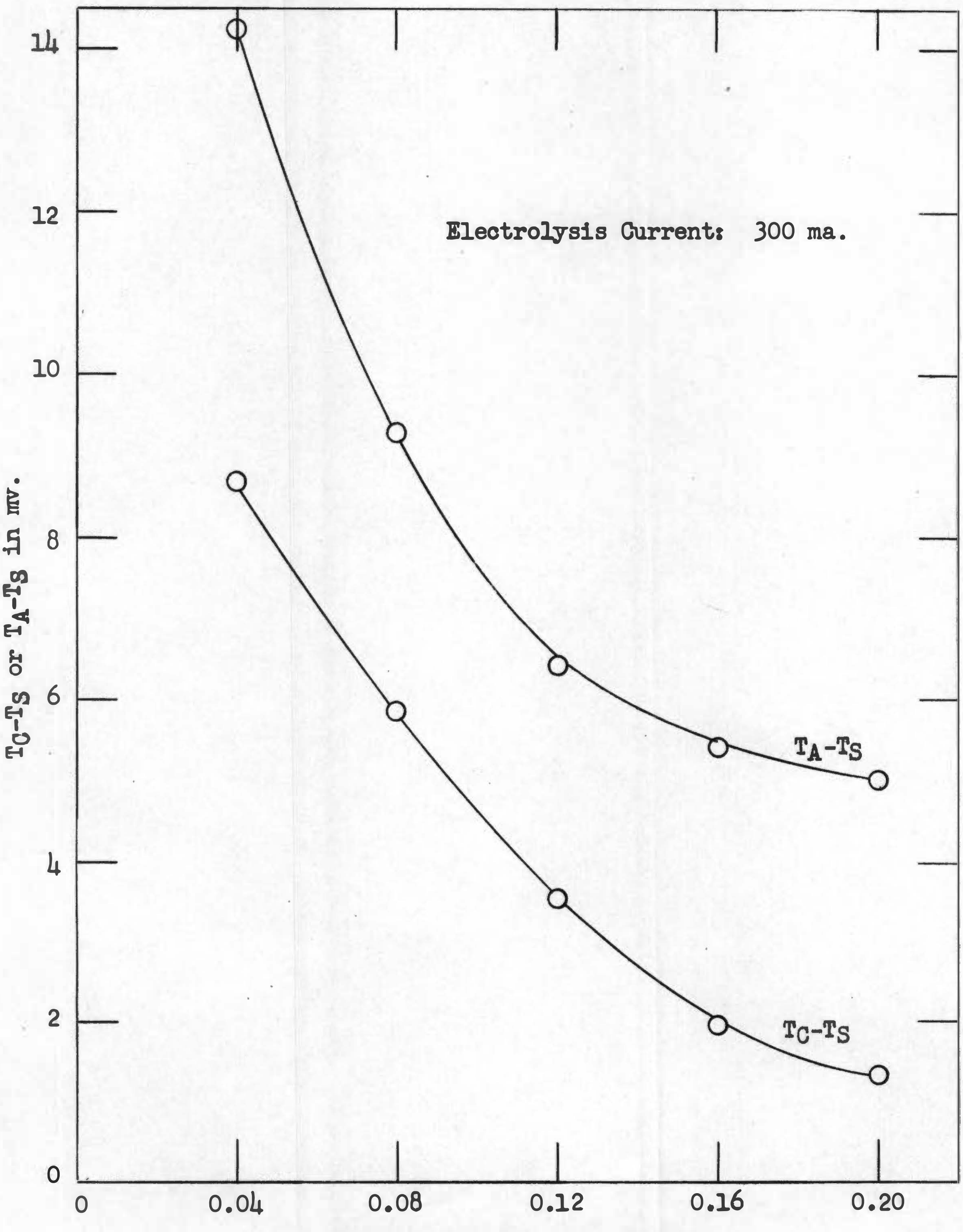

Figure 17. Ten Minute Values of T_C-T_S and T_A-T_S versus Concentration of Copper Sulfate.

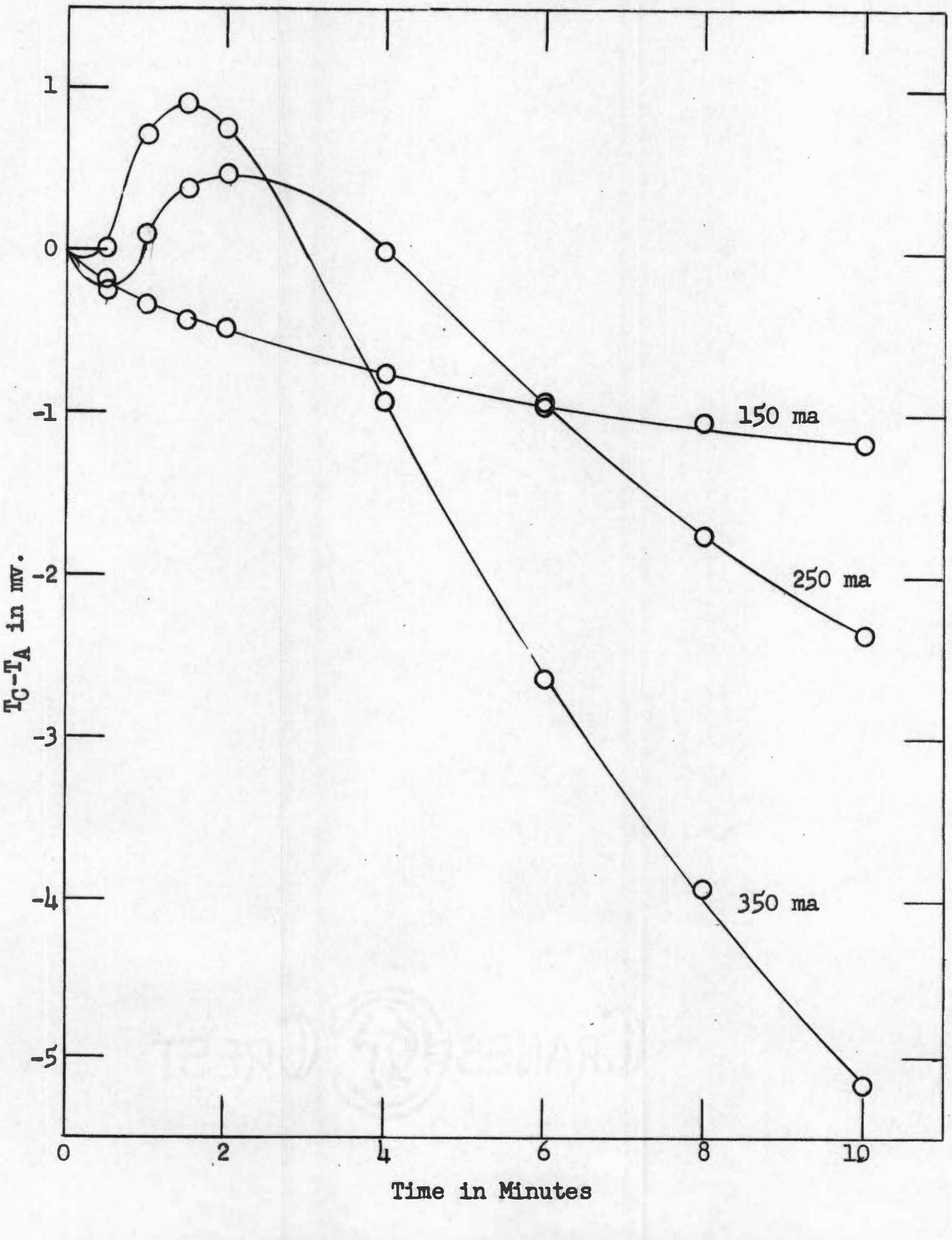

Figure 18. T_C-T_A versus Time for the Electrolysis of 0.08 M Copper Sulfate at Various Currents.

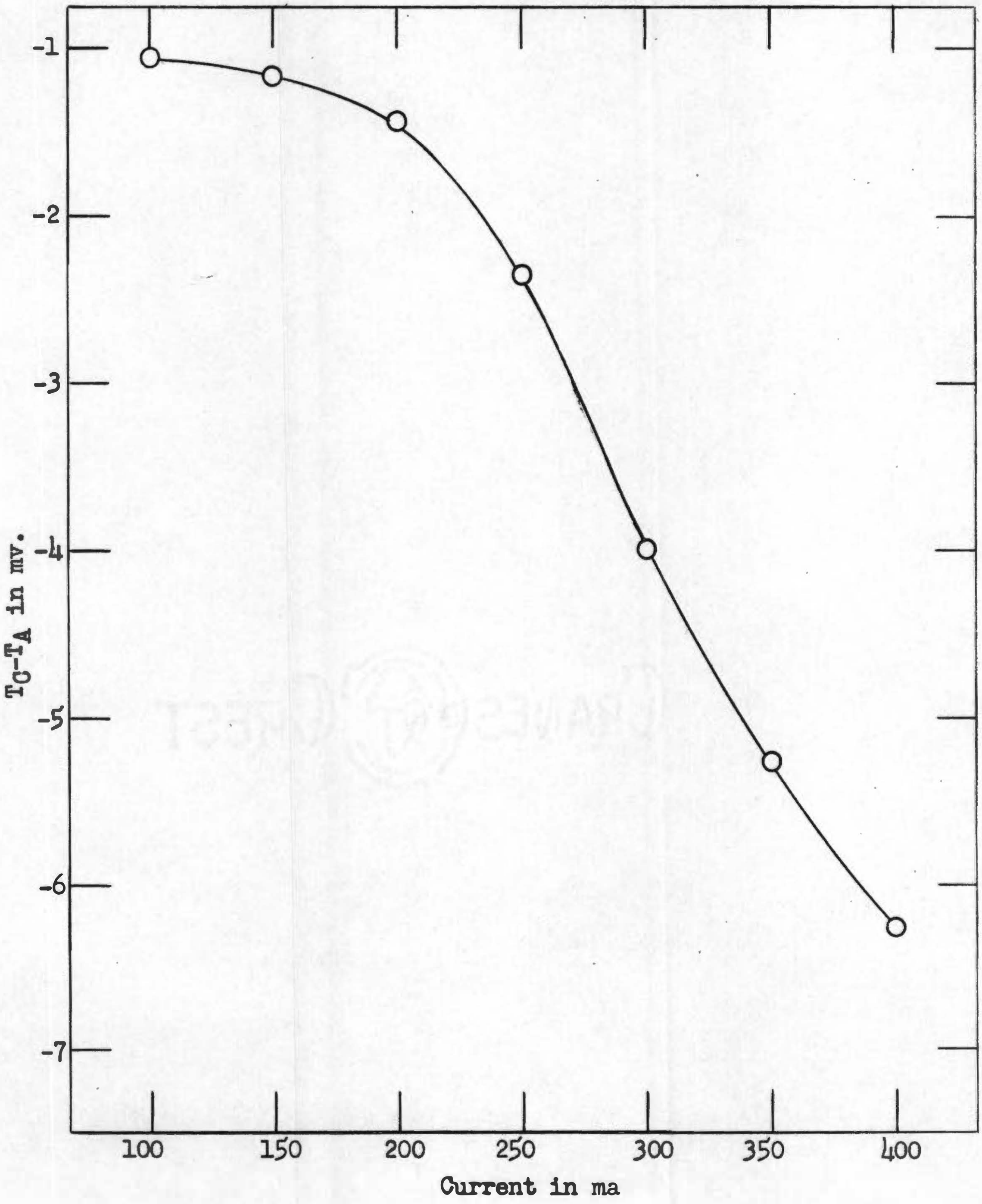

Figure 19. Ten Minute Values of T_C-T_A *versus* Current at Which 0.08 M Copper Sulfate Was Electrolyzed.

Figure 20 shows the effect of the addition of potassium sulfate to copper sulfate on the T_C-T_A, T_C-T_S, and T_A-T_S curves. From a comparison of Figures 20 and 16, it can be seen that the major effect of the addition of potassium sulfate to the system is a reduction of the heat evolved at the anode. This gives rise to a more positive T_C-T_A curve while the T_C-T_S curve remains relatively unchanged.

Figures 21 and 22 show the effect of the addition of sodium sulfate and sulfuric acid, respectively, on the T_C-T_A, T_A-T_S, and T_C-T_S values obtained during the electrolysis of 0.08 M copper sulfate at a current of 300 ma. As is the case with potassium sulfate, the major effect is at the anode. A comparison of Figures 16, 20, 21, and 22 shows that the effect of sodium, potassium, and hydrogen sulfates on the T_A-T_S *versus* time curves is in the increasing order of sodium, potassium, and hydrogen.

In Figure 23, results are shown for 0.08 M copper sulfate solution to which gelatin (40 mg./liter) has been added. In this case, however, the evolution of heat at the anode is increased. This results in a slightly more negative T_C-T_A curve than in the case of pure copper sulfate solutions.

Figure 24 shows the effect of increased potassium sulfate concentration on the ten minute values of T_C-T_A obtained from the electrolysis of 0.08 copper sulfate at 300 ma. This plot indicates that further addition of potassium sulfate has no effect on either T_C-T_A, T_A-T_S, or T_C-T_S after a certain limiting concentration of potassium sulfate has been attained.

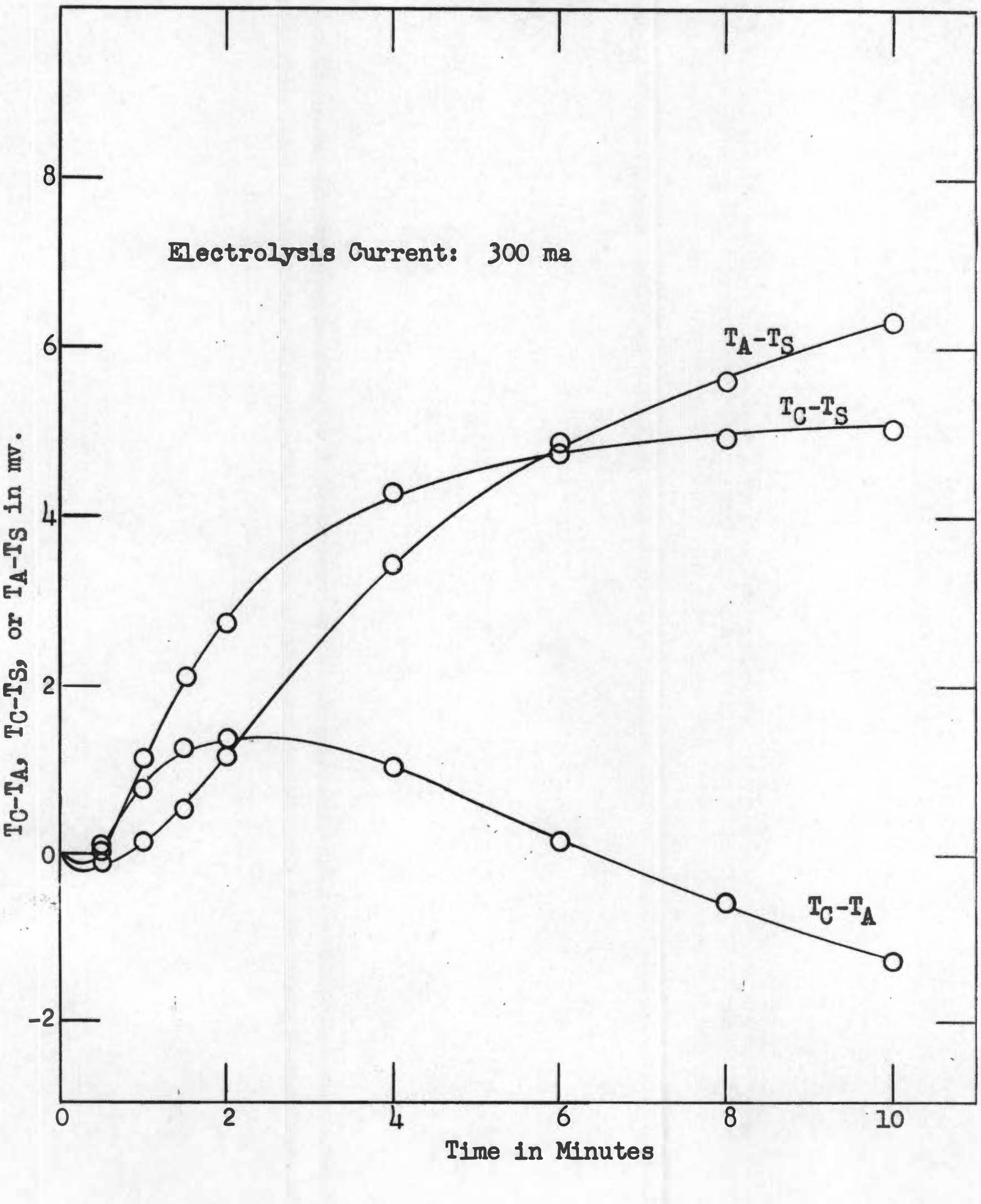

Figure 20. T_C-T_S, T_A-T_S, and T_C-T_A versus Time for the Electrolysis of 0.08 M Copper Sulfate (0.02 M in Potassium Sulfate).

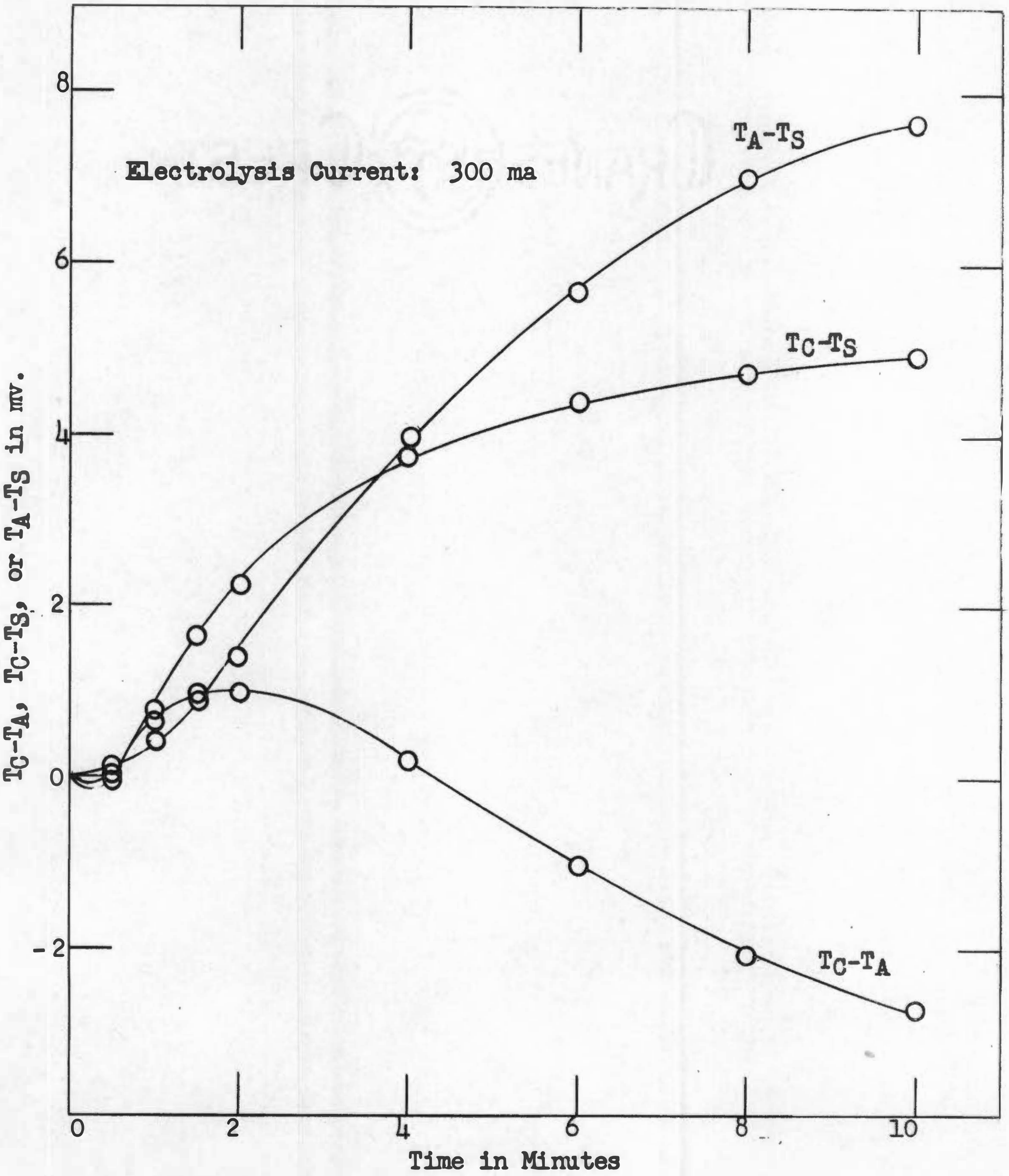

Figure 21. T_C-T_S, T_A-T_S, and T_C-T_A versus Time for the Electrolysis of 0.08 M Copper Sulfate (0.02 M in Sodium Sulfate).

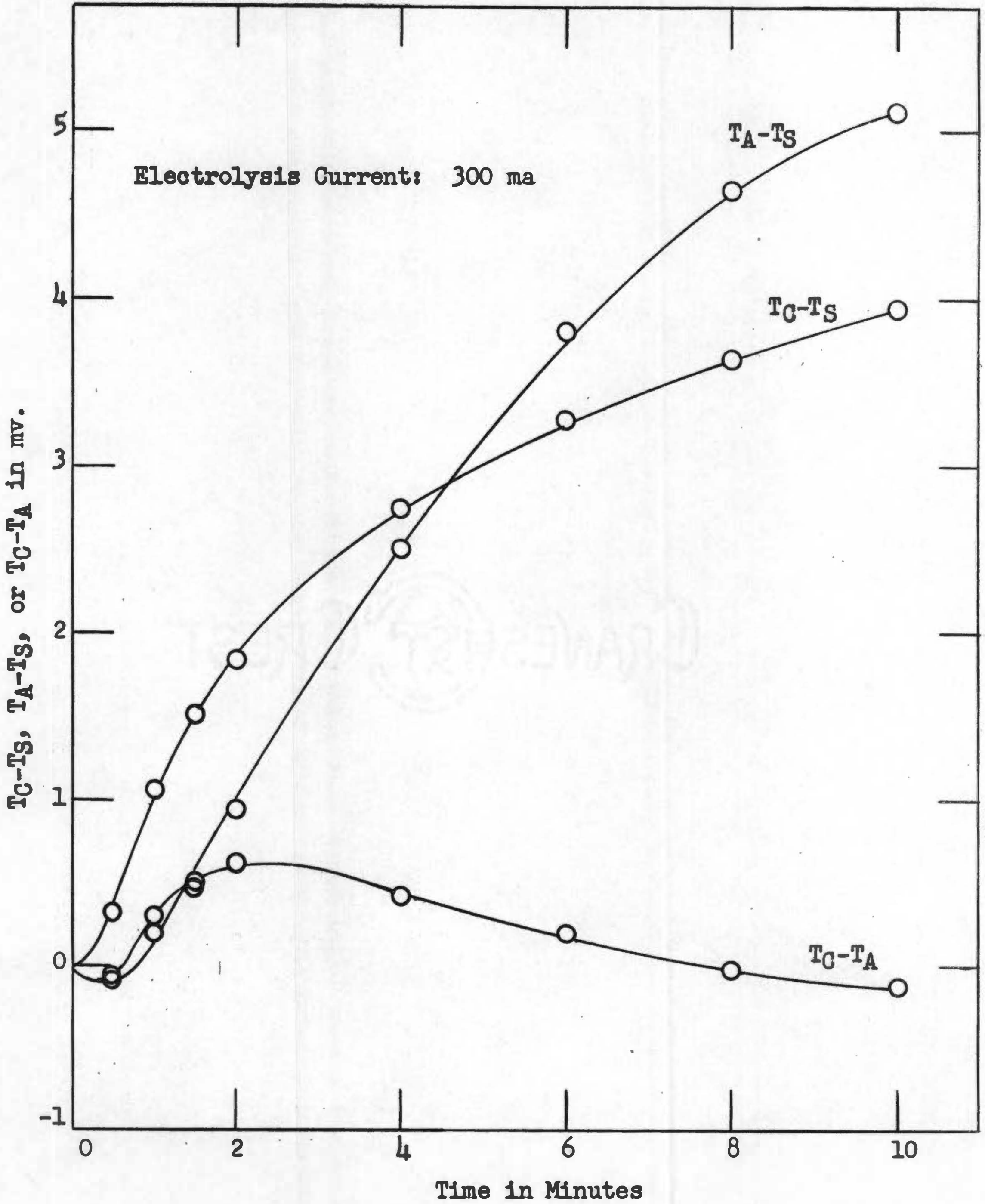

Figure 22. T_C-T_S, T_A-T_S, and T_C-T_A versus Time for the Electrolysis of 0.08 M Copper Sulfate (0.02 M in Sulfuric Acid).

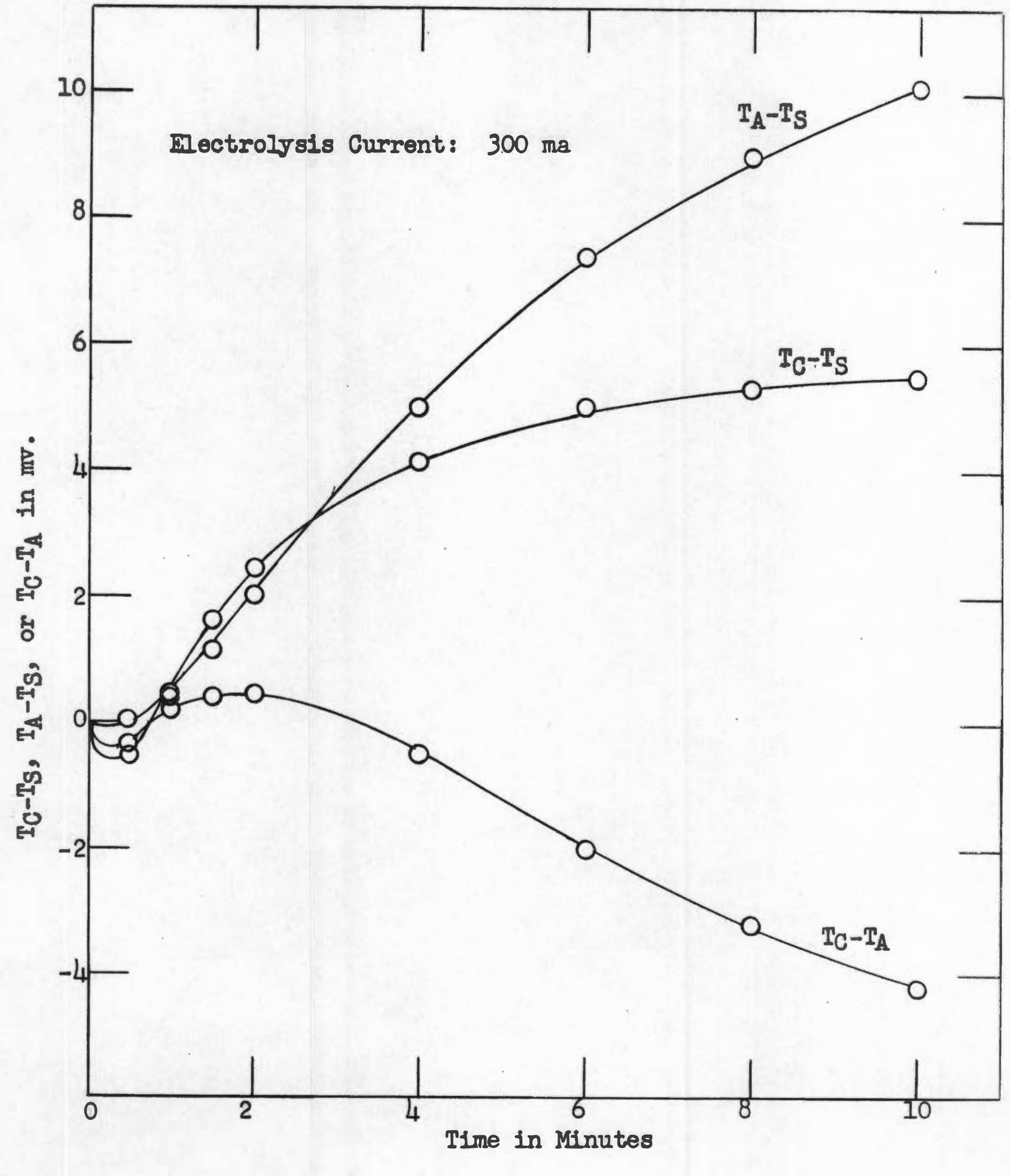

Figure 23. T_C-T_S, T_A-T_S, and T_C-T_A *versus* Time for the Electrolysis of 0.08 M Copper Sulfate to Which Gelatin (40 mg./l.) Has Been Added.

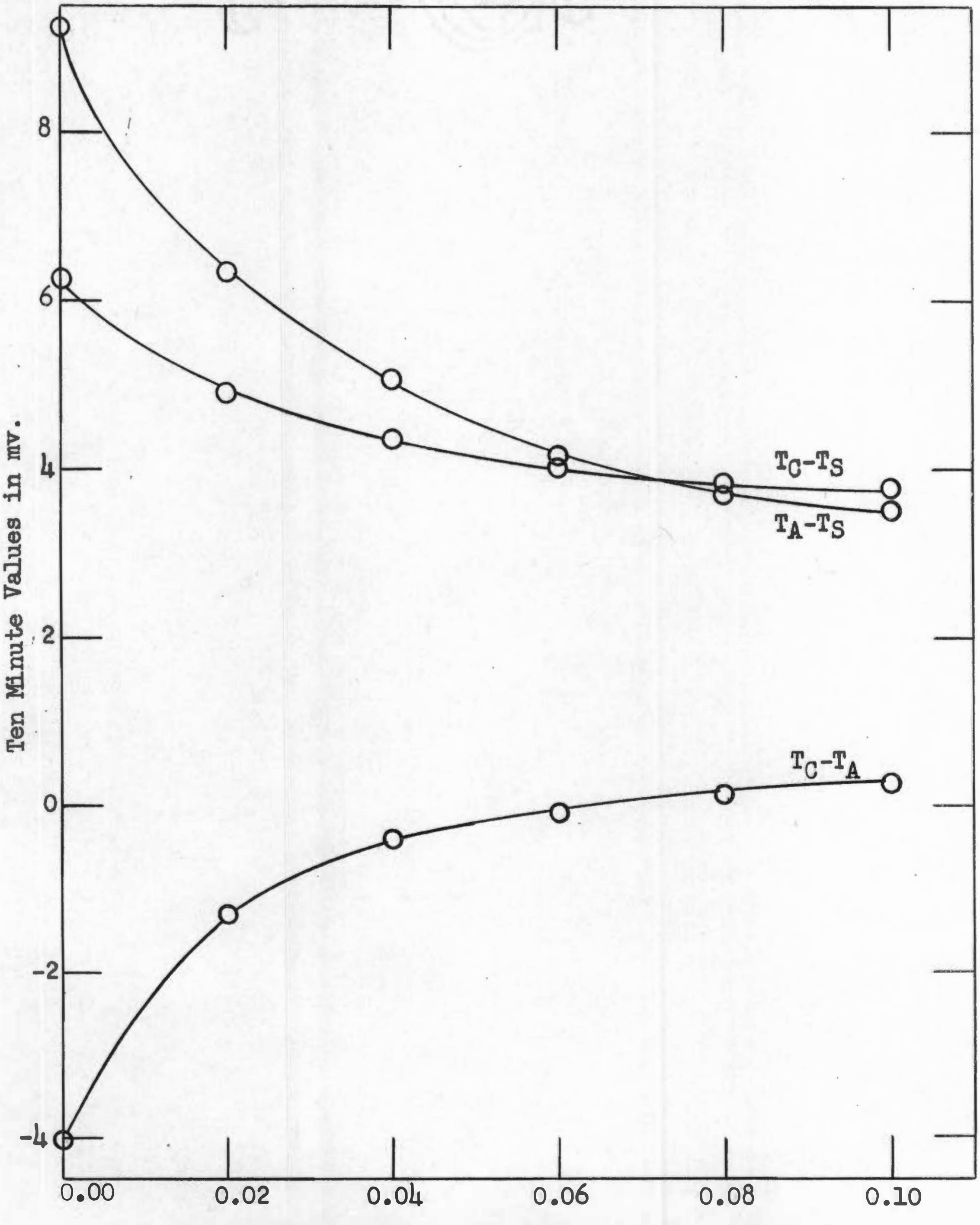

Figure 24. Effect of Potassium Sulfate on the Electrolysis of 0.08 M Copper Sulfate at 300 ma.

Repeats of runs on 0.08 M copper sulfate solutions over several weeks showed the average deviation of the ten minute values of T_C-T_A to be ± 0.025 mv. This corresponds to an uncertainty of ± 0.0005 in the molarity of the copper sulfate solution for the curve shown in Figure 14.

C. Calorimetric Measurement of the Heat Effects at Single Electrodes During Electrolysis

The equipment and procedure used for obtaining the results reported here are fully described in the section on calorimetric experiments in Chapter III. Three different systems were studied in the calorimetric part of this work. They were: copper | aqueous copper sulfate | copper, silver | aqueous silver nitrate | silver, and platinum | aqueous sulfuric acid | platinum. Thus for each of the two metal salt systems, the anodic and cathodic reactions were the exact reverse of each other. For the aqueous sulfuric acid system, the electrode reactions were not the reverse of each other and the cell reaction was the electrolytic decomposition of water.

Three different concentrations were used in the studies on each of the metal salt systems while two different concentrations were used for the aqueous sulfuric acid study. These concentrations are given with the results.

1. Copper-Aqueous Copper Sulfate System

All of the data taken in the calorimetric experiments were treated as outlined in the Appendix. From this treatment, values were calculated for the enthalpy change for the total cell reaction and also for the entropy change for each electrode reaction.

Pertinent calorimetric data obtained by the electrolysis of the copper-aqueous copper sulfate system are summarized in Table II. The meaning of the various symbols used in Table II are given below. $Q^{i}_{R+\eta}$ and $Q^{o}_{R+\eta}$ were the heat equivalents of resistance and polarization in the inner and outer compartments of the calorimeter, respectively. Q^{o}_{a} was the heat added to the outer compartment with the electric heater in order to maintain isothermal conditions. Q^{i}_{m}, Q^{o}_{m}, and Q^{t}_{m} refer to the heat equivalent to the temperature rise in the inner and outer compartments and the total heat, respectively. It should be mentioned here that the anode was always contained in the inner compartment and the cathode was always in the outer compartment. The values in Table II are tabulated in joules as this was the unit for the electrical calibration of the calorimeter. In most cases, more significant figures than necessary are given as they were not rounded off until the conversion to thermodynamic quantities.

A few remarks about the quantities listed in Table II would serve to clarify the data. The sum of $Q^{i}_{R+\eta}$ and $Q^{o}_{R+\eta}$ was, in all cases, equal to the electrical energy input to the cell. This, of course, was a necessity as the potential difference between the cathode and the anode was equal to the sum of the potential differences between the cathode and the probe and between the probe and the anode. The sum of Q^{o}_{m} and Q^{i}_{m} was always equal to Q^{t}_{m} as the total heat capacity of the calorimeter was the sum of the heat capacities of the two compartments. It is interest-

TABLE II

CALORIMETRIC DATA OBTAINED ON THE ELECTROLYSIS OF THE $Cu_{(s)} \mid CuSO_{4(aq.)} \mid Cu_{(s)}$ SYSTEM AT 30°C

Run No.	Moles of Cu Reacting	Electrical Energy Input to Cell (Joules)	$Q^{i}_{R+\eta}$ (Joules)	$Q^{o}_{R+\eta}$ (Joules)	Q^{o}_{a} (Joules)	Q^{i}_{m} (Joules)	Q^{o}_{m} (Joules)	Q^{t}_{m} (Joules)
1	4.9204×10^{-4}	103.41	60.77	42.64	431.45	68.92	466.14	535.06
2	5.4670×10^{-4}	109.44	79.77	29.67	585.69	89.56	605.73	695.29
3	7.0570×10^{-4}	136.73	52.45	84.28	456.16	71.29	521.90	593.19
4	7.7190×10^{-4}	146.15	52.64	93.51	452.53	72.02	527.21	599.23
5	5.0905×10^{-4}	94.57	66.73	27.84	583.54	79.96	598.18	678.14
6	1.0784×10^{-3}	41.21	17.71	23.50	267.98	41.13	255.00	296.13
7	1.2240×10^{-3}	54.63	21.38	33.25	399.76	63.18	391.70	454.88

ing to note that the sum of Q_a^o and the electrical energy input to the cell is very nearly equal to Q_m^t (except for Run No. 6). This is a direct consequence of the enthalpy change for the cell reaction being equal to zero and would not be true if the enthalpy change were different from zero. Details of the calorimetric calculations are given in the Appendix.

The enthalpy and entropy values obtained, together with the current densities and the concentrations of copper sulfate solutions used are given in Table III. The ΔH value given for the total cell reaction may be taken as equal to zero within experimental error. Theoretically the enthalpy change for the total cell reaction should be exactly zero since the anodic reaction is the opposite of the cathodic reaction. Deviation from zero is due to experimental error. The entropy changes are tabulated in terms of the anodic value for each concentration as the cathodic and anodic reaction are the exact reverse of each other. These values decrease (become more negative) by approximately 6.8 cal./mole/degree for each doubling of the concentration. Variation of the current density seemed to have no effect on the entropy values. This is a good indication that the electrode reaction proceeded at 100 per cent current efficiency at all of the current densities employed in the experiments. The values obtained by the electrolysis of 0.40 M copper sulfate which had been made 1.00 M in sulfuric acid indicates that the sulfuric acid had little or no effect on the entropy values which would have been obtained had a pure 0.40 M copper sulfate solution been used. This is supported by the fact that approximately the same decrease in entropy was observed between the

TABLE III

RESULTS OF CALORIMETRIC MEASUREMENTS ON THE ELECTROLYSIS OF THE $Cu_{(s)} \mid CuSO_{4(aq.)} \mid Cu_{(s)}$ SYSTEM AT 30°C

Run No.	Current Density ma/cm.^{2}	Conc. $CuSO_4$ Moles/Liter	Conc. H_2SO_4 Moles/Liter	ΔH_{total} Cal./Mole	ΔS_{anodic} Cal./Mole/Deg.	$\Delta S_{cathodic}$ Cal./Mole/Deg.
1	2.30	0.10	0	-97	-13.1	+12.7
2	2.29	0.10	0	+66	-14.1	+14.0
3	17.8	0.20	0	-7	-20.6	+20.7
4	18.1	0.20	0	-24	-20.0	+19.2
5	3.55	0.20	0	+14	-20.5	+20.4
6	28.1	0.40	1.00	-3,374*	-19.9*	+27.7
7	28.8	0.40	1.00	+88	-26.9	+27.6

For $Cu_{(s)} = Cu_{(s)}$ $\Delta H = +7$ cal./mole (Average value).

Reaction	ΔS
$Cu_{(s)} = Cu^{++}_{(aq.,\ 0.10\ M)} + 2e^-_{(Cu)}$	-13.5 ± 0.6 cal./mole/deg.
$Cu_{(s)} = Cu^{++}_{(aq.,\ 0.20\ M)} + 2e^-_{(Cu)}$	-20.2 ± 0.4 cal./mole/deg.
$Cu_{(s)} = Cu^{++}_{(aq.,\ 0.40\ M)} + 2e^-_{(Cu)}$	-27.4 ± 0.3 cal./mole/deg.

*Not included in averages.

0.20 M and the 0.40 M solution as was observed between the 0.10 M and 0.20 M solutions. The average deviation of the entropy values is approximately correct. The expected deviation (± 0.5 cal./mole/deg.) was calculated from the known uncertainty in the calorimetric data.

2. Silver-Aqueous Silver Nitrate System

The data obtained from the electrolysis of the silver-aqueous silver nitrate system are summarized in Table IV in the same manner as was done with the copper system. The same statements made in regard to Table II are equally applicable to Table IV and will not be repeated here.

The data for the silver system were treated in the same manner as the data for the copper system. Results of these calculations are summarized in Table V.

Here again the enthalpy change for the total cell reaction may be taken as equal to zero within experimental error since the reaction at the anode is opposite to that at the cathode. The entropy changes are tabulated, as was done with the copper system, in terms of the anodic reaction. However, the decrease in entropy in the silver system is approximately 5 cal./mole/degree each time that the concentration was doubled instead of the 6.8 cal./mole/degree decrease observed with the copper system. The tabulated deviation of ± 0.1 cal./mole/degree for the 0.80 M silver nitrate appears to be too low in view of estimated uncertainty of ± 0.5 cal./mole/degree. This may be fortuitous.

TABLE IV

CALORIMETRIC DATA OBTAINED ON THE ELECTROLYSIS OF THE $Ag_{(s)} | AgNO_{3(aq.)} | Ag_{(s)}$ SYSTEM AT 30°C

Run No.	Moles of Ag Reacting	Electrical Energy Input To Cell (Joules)	$Q^i_{R+\eta}$ (Joules)	$Q^o_{R+\eta}$ (Joules)	Q^o_a (Joules)	Q^i_m (Joules)	Q^o_m (Joules)	Q^t_m (Joules)
1	7.3488×10^{-4}	59.60	51.69	7.91	99.23	17.99	140.54	158.53
2	7.6547×10^{-4}	59.38	51.82	7.56	77.83	15.50	121.06	136.56
3	1.9294×10^{-3}	145.16	113.74	31.42	131.63	35.22	241.10	276.32
4	1.8335×10^{-3}	186.54	166.36	20.18	550.65	93.99	643.40	737.39
5	3.3557×10^{-3}	192.02	163.52	28.50	192.83	49.64	335.48	385.12
6	2.1202×10^{-3}	124.09	112.31	11.78	260.71	40.22	345.24	385.46

TABLE V

RESULTS OF CALORIMETRIC MEASUREMENTS ON THE ELECTROLYSIS OF THE $Ag_{(s)} \mid AgNO_{3(aq.)} \mid Ag_{(s)}$ SYSTEM AT 30°C

Run No.	Current Density ma/cm.^{2}	Conc. $AgNO_3$ Moles/Liter	ΔH_{total} Cal./Mole	ΔS_{anodic} Cal./Mole/Deg.	$\Delta S_{cathodic}$ Cal./Mole/Deg.
1	3.30	0.20	+98	+36.1	-35.8
2	3.29	0.20	+203	+37.4	-36.7
3	7.72	0.40	+56	+32.1	-31.9
4	9.43	0.40	-27	+31.1	-31.2
5	9.48	0.80	-19	+26.8	-26.8
6	9.50	0.80	-74	+26.8	-27.1

For $Ag_{(s)} = Ag_{(s)}$ $\Delta H = +40$ cal./mole (average value)

Reaction	ΔS
$Ag_{(s)} = Ag^{+}_{(aq.,\ 0.2\ M)} + e^{-}_{(Ag)}$	+36.5 ± 0.5 cal./mole/deg.
$Ag_{(s)} = Ag^{+}_{(aq.,\ 0.4\ M)} + e^{-}_{(Ag)}$	+31.6 ± 0.4 cal./mole/deg.
$Ag_{(s)} = Ag^{+}_{(aq.,\ 0.8\ M)} + e^{-}_{(Ag)}$	+26.9 ± 0.1 cal./mole/deg.

3. Platinum-Aqueous Sulfuric Acid System

Table VI summarizes the data and the results obtained by calorimetric measurements on the electrolysis of the platinum-aqueous sulfuric acid system. The same general remarks under Table II are applicable to the data portion of Table VI except for one instance. In this case, Q_m^t is not equal to the sum of the electrical energy input to the cell and Q_a^o. As mentioned before, this is because the enthalpy change for the cell reaction is not equal to zero. The enthalpy value obtained for the total cell reaction is in very good agreement with the accepted value of -68.3174 kcal./mole for the heat of formation of water at 25°.[63] The average deviation listed in Table IV for ΔH for the cell reaction is probably too low. Estimates from the calorimetric data places the uncertainty in this value at about 200 cal./mole.

The listed values for the entropy changes occurring at the cathode and anode appear to be in error.* There are two reasons for making this statement; (a) the magnitudes of these entropy changes are not correct as compared to the copper and silver systems and (b) the sum of the entropy changes at the cathode and at the anode does not give a reasonable entropy change for the cell reaction.

D. Current Efficiencies of the Copper and Silver Systems

As stated in Chapter II, it is necessary that the electrode reactions proceed with 100 per cent current efficiency if the calculated

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*Reasons for this will be explained in Chapter V.

TABLE VI

CALORIMETRIC DATA AND RESULTS OBTAINED BY THE ELECTROLYSIS OF THE $Pt_{(s)} | H_2SO_4(aq.) | Pt_{(s)}$ SYSTEM AT 30°C

Calorimetric Data								
Run No.	Moles of H_2 Liberated	Electrical Energy Input To Cell (Joules)	$Q^i_{R+\eta}$ (Joules)	$Q^o_{R+\eta}$ (Joules)	Q^o_a (Joules)	Q^i_m (Joules)	Q^o_m (Joules)	Q^t_m (Joules)
1	3.4603×10^{-4}	118.98	78.52	40.46	418.45	50.62	387.96	438.58
2	2.2024×10^{-4}	88.19	44.13	44.06	200.03	26.02	199.40	225.42
3	8.882×10^{-5}	41.03	26.82	14.21	117.31	17.53	115.38	132.91

Results					
Run No.	Current Density ma/cm.^{2}	Conc. H_2SO_4 Moles/Liter	ΔH_{total} Cal./Mole	ΔS_{anodic} Cal./Mole/Deg.	$\Delta S_{cathodic}$ Cal./Mole/Deg.
1	13.01	0.50	+68,280	+63.6	+161.6
2	12.80	0.50	+68,150	+64.8	+160.1
3	3.28	4.0	+68,430	+82.4	+144.2

For $H_2O(l) = H_2(g) + \frac{1}{2}O_2(g)$ $\Delta H = +68,300 \pm 60$ cal./mole of H_2O

quantities are to have a meaningful reference to a single reaction. This appeared to be true but it was necessary to be absolutely sure of 100 per cent current efficiency by making an experimental determination of current efficiencies on the copper and silver systems.

The current density, 15.6 ma/cm.^{2}, used in these experiments were comparable to, or higher than, the current densities used in the calorimetric experiments. The results of these experiments are given below.

Reaction	Current Efficiency (Per Cent)
$Ag(s) = Ag^+(aq.) + e^-_{(Ag)}$	100.00
$Ag^+_{(aq.)} + e^-_{(aq.)} = Ag(s)$	99.68
$Cu(s) = Cu^{++}_{(aq.)} + 2e^-_{(Cu)}$	100.27
$Cu^{++}_{(aq.)} + 2e^-_{(Cu)} = Cu(s)$	99.46

Within experimental error* the current efficiencies are all 100 per cent. It can be safely concluded that no error in the calorimetric results were introduced because of side reaction at the electrodes.

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*A weighing error of 0.2 mg. would account for all of the deviations from 100 per cent.

CHAPTER V

DISCUSSION

A. Preliminary Experiments

The preliminary experiments gave no reliable quantitative data. They did serve to point out some important factors to bear in mind during the planning of the later experiments. One of the important points indicated by the preliminary experiments was the lag in the anode temperature as compared to the cathode temperature in the initial part of the electrolysis. Further, it was demonstrated that, at some time during the electrolysis, the anode temperature invariably rose above that of the cathode (see Figure 12).

The Beckmann thermometers used in these first experiments were not sensitive enough to give a sufficiently accurate value for the temperature difference between the anode and the cathode. The second undesirable feature of the Beckmann thermometers was their slow response time. This is due to the high heat capacity of the thermometers and rather slow heat transfer. These two objections were quite satisfactorily circumvented by the use of thermistors as the temperature sensing elements.

Another very important point which the preliminary experiments seemed to stress was that the position and area of the electrode must be fixed and reproducible from experiment to experiment. This was a necessity for the procedure of obtaining reproducible, accurate results.

This fact had a direct bearing on the design of the electrolysis cell for the subsequent sets of experiments.

Attempts to correlate the preliminary results with those of Gritsan and Bulgakova[30] were entirely unsuccessful. The only conclusive relationship between the results reported here and those of Gritsan and Bulgakova was that there was a definite temperature rise at each electrode.

B. Temperature Difference Measurements on the Copper-Aqueous Copper Sulfate System (Thermal Electroanalysis)

1. Pure Copper Sulfate Solutions

In Chapter II (Equation 39) it was shown that the heat effect of an electrochemical reaction is made up of three terms. Thus the heat, Q, given off by an electrochemical reaction is given by:

$$Q = -T\Delta S + RI^2t + \eta It \tag{1}$$

where the symbols are defined as in Chapter II. Since each of the three terms involved in the heat effect varies with the concentration of the solutions being electrolyzed, it was expected that the heat effect should also show a variation with concentration. Gritsan and Bulgakova[30] have stated that this variation of the heat effect with concentration is so exact that one may determine the concentration of the solution being electrolyzed merely by measuring the temperature difference between an electrode and the electrolyte during electrolysis.

In view of this, it was decided to direct the experiments in such a manner as to furnish design data for the calorimetric experiments and, at the same time, attempt to work out an analytical method based on thermal electrochemical measurements. With this in mind, it was thought that measurement of the temperature difference between the cathode and the anode would be the most worthwhile. By measuring the temperature differences of the electrodes rather than a measurement involving the temperature of the solution, it was thought that the effect of inert ions on the resistance of the solution could be minimized. It was later found that such inert ions do have an effect on the temperature rise at a working electrode. However, the effect does not lie in an alteration of the resistance of the solution but is due to factors which will be discussed in a later section.

As can be noted from the plots of T_C-T_A versus time (Figure 13) the anodic electrode reaction is more exothermic. This is true in every case and is due to a difference in sign of the entropy change at the anode as compared to the entropy change at the cathode. Since the electrode reactions are equal but opposite in direction, the entropy change at the electrodes will be equal in magnitude but opposite in sign. This was verified by the calorimetric results given in Chapter IV (a negative entropy change for the anodic dissolution of copper which corresponds to an evolution of heat and a positive entropy change for the cathodic deposition of copper which corresponds to the absorption of heat).

The positive portion of the plot of T_C-T_A as a function of time is caused by concentration polarization at the cathode. This is indicated by three experimental observations. First, there is a short time lag before the temperature of the cathode rises above that of the anode. This corresponds to the time necessary to deplete the copper ions in the vicinity of the cathode. When the copper ions are depleted by the plating reaction, a concentration gradient will be set up, resulting in a concentration polarization effect, and a heat effect due to this concentration polarization. The second bit of experimental evidence for the above statement is obtained by observing the effect of concentration on the shape of the T_C-T_A versus time curve. The portion of the curve at which T_C-T_A is positive is decreased by increasing the concentration and finally no positive values of T_C-T_A are observed at the higher concentrations (Figures 13 and 15). This is in line with the fact that concentration polarization will be minimized in concentrated solutions. The third effect observed which is consistent with the above reasoning deals with experimental results obtained by holding the concentration constant and decreasing the current (Figure 18). In this case, the concentration polarization effect will not be present if the current is sufficiently low to allow the copper ions to migrate to the cathode as fast as they are plated out. These last two observations are consistent with experimental observations of other workers dealing with concentration polarization.[64]

In order to use temperature difference measurements as an analytical method, some relationship must be established between T_C-T_A and the concentration of the solution being electrolyzed. No attempt was made in this phase of the work to obtain a rigid theoretical relationship between these two quantities. Instead, an empirical calibration curve was obtained. This curve is shown in Figure 14, and is a plot of the ten minute values of T_C-T_A versus concentration. The uncertainty in that portion of the curve up to about 0.09 M is equivalent to an uncertainty of

±0.0005 M in the concentration. That portion of the curve above 0.10 M is, of course, entirely unsuitable for use as a calibration curve to determine concentrations. This can easily be avoided by the construction of another calibration curve at a higher current.

Theoretically the one minute values of T_C-T_A could also be used as a basis for an analytical method. This would be based on a calibration curve such as shown in Figure 15. However, since the one minute values of T_C-T_A are much smaller than the corresponding ten minute values, the accuracy would be smaller than that obtained by the use of the ten minute values. Also, as pointed out in Chapter IV, the one minute values of T_C-T_A are not as reproducible as the ten minute values of T_C-T_A.

Figure 16 shows T_C-T_S and T_A-T_S as a function of time of electrolysis for two different concentrations of copper sulfate. These curves lend additional experimental proof to the T_C-T_A curves which were obtained in a direct manner. Again it may be seen from these curves that, in the early part of the electrolysis, the temperature of the cathode is higher than the temperature of the anode.

Figure 17 is an example of a type of plot which might also be used as a calibration curve for an analytical determination. However, this is not to be recommended as this type of plot involves the temperature of the solution and is therefore not as reproducible as the T_C-T_A determinations.

The effect of the magnitude of the electrolysis current on the ten minute values of T_C-T_A is clearly illustrated in Figure 19. At the lower current values plating was observed on the cathode. The appearance of the plate was very similar to those obtained during the electrolysis using higher concentrations of copper sulfate when the current was maintained constant. It thus appears that the horizontal portions of Figures 14 and 19 are quite analogous to each other.

This type of measurement is interesting in that, as a method of analysis, it could lend itself quite well to instrumentation. The unbalance signal of the bridge could easily be amplified or recorded for either automatic or control operations. It should be emphasized that the magnitude of the temperature differences, but not the shape of the curves, will be changed if the equipment is changed. That is, there will be a difference in the values of T_C-T_A if the electrodes, bridge circuits, thermistors, or geometry of the cell is changed.

2. Copper Sulfate Solutions to Which Potassium Sulfate, Sodium Sulfate, or Sulfuric Acid Has Been Added

The effect of the addition of the above electrolytes to the copper sulfate solutions as shown in Figures 20, 21, and 22 is interpreted as follows. The chief effect of these electrolytes is to alter the heat effect at the anode. This is supported by a comparison of the T_A-T_S *versus* time curves shown in Figures 16, 20, 21, and 22. A comparison of the T_C-T_S *versus* time curves in these same figures shows little effect due to the addition of these electrolytes whereas the effect at the anode is considerable.

Two explanations have been devised to interpret the effect of inert electrolytes such as potassium sulfate. One explanation proposes that the potassium sulfate decreases the anodic polarization of copper in a copper sulfate solution. This would have to be tested by experiment as no literature was found on this subject.

The other explanation lies in the theory of irreversible thermodynamics as applied to thermocells[34,42] since this is a non-isothermal system. This interpretation involves ionic heats of transfer and transport numbers of the current-carrying species as shown in Equation (11) in Chapter II. In this equation the ionic heats of transfer, Q_i^*, is multiplied by the transport number, t_i, of the species to which it refers. This is independent of the electrode reaction. A comparison of the effect of hydrogen, potassium, and sodium sulfate on the heat effect at the anode shows that it is in the order $H^+ > K^+ > Na^+$. This is the exact order of the transference numbers of these three ions. A simple physical picture of the above interpretation is that the faster moving cation carries more heat away from the anode.

Another piece of experimental evidence in line with the above reasoning comes from the work of Lange and Hesse.[21] They measured the "Peltier heats" of the systems $Ag|AgNO_3$ and $Ag|AgCl|Cl^-$ in the presence of potassium, hydrogen, and lithium ions. Here again the values were in the same order as the transference numbers of the three ions.

Gritsan, Bulgakova, and Zolotareva[27] have studied the effect of certain anions on the temperature rise at zinc, copper, and cadmium cathodes. Their results showed that the temperature rise at the cathode varied if the anion of the metal salt were changed. A comparison of their results with existing transference number data indicates that the effect is directly proportional to the transference number of the anion. All of the above results indicate that the temperature rise at an electrode definitely depends on the ionic heats of transport and the transference numbers of all of the ions in solution.

It is obvious that from the above discussion that one cannot use a calibration curve such as Figure 14 for the determination of the copper concentration of a solution which contains extraneous ions. Figure 24 shows the effect of potassium sulfate on the measured temperature differences as a function of the concentration of added potassium sulfate. It may be seen from this figure that the effect of potassium sulfate on the temperature differences approaches a constant value if the potassium sulfate concentration is large enough. This points the way to a possible method to avoid the interference of inert electrolytes such as potassium sulfate. That is, enough of the inert electrolyte could be added to the standards and the unknowns to "swamp" the solution and produce a constant effect. This constant effect would be expected if the inert electrolyte were carrying practically all of the current. These ideas are based, of course, on the interpretation that the effect due to the inert electrolytes are based on the ionic heats of transport and the transference numbers.

3. Copper Sulfate Solutions to Which Gelatin Has Been Added

The effect of gelatin as shown in Figure 23 is smaller than that of the inert electrolytes discussed in the previous section. It is somewhat surprising that the effect of gelatin on the heat production at the anode is opposite to that of the electrolytes. Although the increase in the evolution of heat at the anode may be due wholly to an increase in anodic polarization, it is quite possible that a large part of the effect may be caused by a decrease in the mobility of the cation. This would have the effect of decreasing the amount of heat carried away from the anode.

Although no quantitative comparison is possible, the results obtained here are consistent with those obtained by Parsons and Winkler[59] for the cathodic polarization of copper in the presence of gelatin.

4. Suggestions for Further Work

It would be interesting and informative to extend this type of study to another system. A particularly good system for this work would be the silver-aqueous silver nitrate system. This system is somewhat different from the copper system in that the cathodic reaction is more exothermic as shown by the calorimetric measurements.

More work needs to be done on the measurements in the presence of inert electrolytes. This would do much toward putting the analytical aspects on a firmer foundation and also aid in correlating these results with existing thermocell data.

Examination of Figure 24 shows that the ten minute value of T_C-T_A approaches zero as the potassium sulfate concentration is increased. These data are for 0.08 M copper sulfate only, however. In view of this, ten minute values for T_C-T_A need to be measured for solutions of different copper sulfate concentration with each having a large concentration of potassium sulfate. Although it is thought that the ten minute values of T_C-T_A would still show a variation with concentration of copper sulfate, this needs to be proven experimentally. If the ten minute values of T_C-T_A were zero in all cases, recourse could still be taken to the one minute values of T_C-T_A as a basis for an analytical technique.

C. Calorimetric Measurements of Heat Effects at Single Electrodes During Electrolysis

The discussion given here is based on the assumption that Equation (39) in Chapter II is valid for a single electrode system. Preliminary work has indicated that the equation is valid for a single electrode system although no rigorous theoretical derivation has been worked out. At present, there seems to be no obvious reason for the equation not being valid for a single electrode system.

1. The Copper-Aqueous Copper Sulfate System

The most striking feature of the results presented in Table III is their rather wide variation of entropy change during electrolysis with the concentration of the solution. As shown below, this variation is much more than would be expected if ideal behavior were observed. Ideal behavior, as used here, means that the thermodynamic activity of a single ionic species is equal to its concentration.

The entropy of an ion (or any substance), S_1, in a solution of activity, a_1, may be represented as

$$S_1 = S^o - R \ln a_1 , \qquad (2)$$

where S^o is the entropy at unity activity and R is the gas constant. In a like manner, the entropy in a solution in which the ionic activity is

a_2 is given by

$$S_2 = S^o - R \ln a_2 \ . \tag{3}$$

If (2) is subtracted from (3), one obtains

$$\Delta S = S_2 - S_1 = R \ln \frac{a_1}{a_2} \ . \tag{4}$$

Equation (4) gives the entropy change accompanying the transfer of one mole of the ions from a solution in which the activity is a_1 to a solution where the activity is a_2. If one now assumes that a_1 is twice as large as a_2, the entropy change would be

$$\Delta S = (1.987)(\ln 2) = 1.377 \text{ cal./mole/degree} \ . \tag{5}$$

If one assumes that activities are equal to concentration* then this is the entropy change which should be observed on passing from one solution to another which is only half as concentrated.

One can obtain an experimental value for this from Table III. For the 0.1 M copper sulfate, the reaction is

$$Cu_{(s)} = Cu^{++}{}_{(0.1\ M)} + 2e^-{}_{(Cu)} \tag{6}$$

for which

$$\Delta\ S = -13.5 \text{ cal./mole/degree} \ . \tag{7}$$

The corresponding reaction for the 0.2 M copper sulfate is

$$Cu_{(s)} = Cu^{++}{}_{(0.2\ M)} + 2e^-{}_{(Cu)} \tag{8}$$

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*This, of course, is not correct, particularly at the concentrations worked with here. In this connection it is interesting to look at the mean activity coefficients for aqueous copper sulfate. These are 0.150, 0.104, and 0.071 for solutions in which the concentrations are 0.1, 0.2, and 0.4 molal respectively.[65] Although these are mean activity coefficients, it is still obvious that it is incorrect to assume that the ionic activity is equal to the concentration.

for which

$$\Delta S = -20.2 \text{ cal./mole/degree} . \tag{9}$$

If one now subtracts (8) from (6), the reaction

$$Cu^{++}_{(0.2\ M)} = Cu^{++}_{(0.1\ M)} \tag{10}$$

is obtained. The entropy change for (10) is obtained by subtracting (9) from (7) which gives

$$\Delta S = 6.7 \text{ cal./deg./mole} , \tag{11}$$

a value which is very much larger than the 1.377 cal./mole/degree calculated for the ideal case. Although the experimental value obtained does not seem to be compatible with the ideal case, the experimental values cannot be ruled invalid on this basis alone as nothing is known about the activity of a single ionic species. In fact, a considerable portion of the present day chemists hold that the activity of a single ionic species cannot even be defined, much less measured.

In this connection it would be of interest to calculate the absolute entropy of the copper ion for comparison with values which have been obtained by other investigators. The absolute entropy of solid copper is given by Stull and Sinke[66] as 8.01 cal./mole/degree at 300° K. This value may be subtracted from the tabulated values in Table III to give the absolute entropy of the copper ion plus two electrons. If one disregards the entropy of the two electrons*, the resulting value may be taken as equal to the absolute entropy of the copper ion. The values obtained are tabulated in Table VII together with some values obtained

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*This is probably not valid. A discussion of this point is given later.

TABLE VII

ENTROPY OF THE COPPER ION

Electrolyte	Conc. Copper Moles/Liter	Temperature °K	$S_{Cu^{++}}$ Cal./Mole/Degree	Reference
$CuSO_4$	0.10	303.2	-5.5	This Work
$CuSO_4$	0.20	303.2	-12.2	This Work
$CuSO_4 + H_2SO_4$ (1 M)	0.40	303.2	-19.4	This Work
$CuSO_4$	a=1 (?)	Thermocell	-37	Bonnemay[39]
$CuSO_4$	0.018*	Not Given	+27.8	Bruzs[18]
$CuSO_4$	0.004*	Not Given	+25.1	Bruzs[18]
$CuSO_4$	0.0004*	Not Given	+20.7	Bruzs[18]
$CuSO_4$	1	290-297	-29	Bruzs[14]
$CuSO_4 + H_2SO_4$ (1 M)	0.75	298	-24.9	Sherfey and Brenner[31]
- - -	a=1	298.16	-26.5	Latimer[67]
$Cu(NO_3)_2$	1.8	~285	-26.0	Bouty[3]
$CuSO_4$	0.625	~298	-19.5	Gill[6]
$CuSO_4$	0.55	273	+2.8	Jahn[7]
$CuSO_4$	0.55 (?)	273	-26.3	Jahn[5]
$CuSO_4 + H_2SO_4$ (0.005 M)	0.5	297-298	-22	Brauer[8]

*Mole fraction.

by other investigators.

Table VII indicates some of the wide variations found in the literature in an attempt to arrive at a value for the absolute entropy of a single ionic species. Latimer's value[67] has been included only for comparison as it is a relative value based on the assumption that the absolute entropy of the hydrogen ion is zero at unit activity. Bonnemay's value is based on thermocells and thus is probably not valid for the reasons indicated by Holtan.[34]

Since there is such a wide variation in the values given in Table VII, the easiest manner of comparison would be to plot all of the values as a function of the concentration of the copper ion. This is done in Figure 25.

The normal procedure in constructing a graph of this type is to plot these values as a function of the square root of the ionic strength. This has its basis in the theory of Debye and Huckel. However, the Debye-Huckel theory is good only as a limiting law and then only with solutions of ionic strength below 0.1. A plot of this type did not provide a satisfactory means for testing the agreement of the values given in Table VII.

It was found that a plot of the entropy values <u>versus</u> the logarithm of the molarity gave a satisfactory straight line. No theoretical explanation was attempted for Figure 25. The equation for the straight line in Figure 25 is

$$S_{Cu^{++}} = -28.51 - 23.07 \log M \qquad (12)$$

as calculated by the method of least squares from the data obtained in

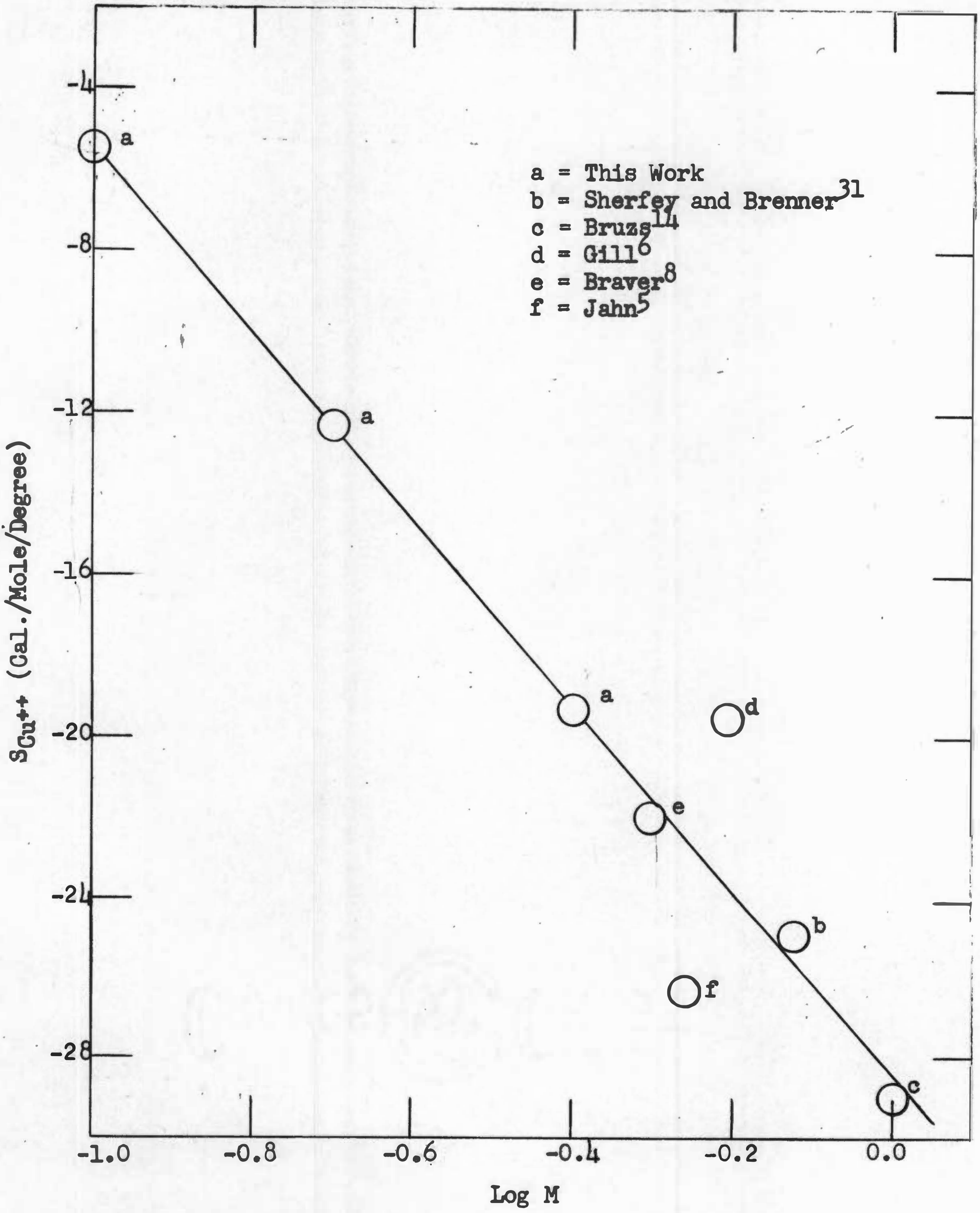

Figure 25. Entropy of the Copper Ion as a Function of the Concentration of Copper.

this work.

It can be seen that the results of this work and those obtained by Sherfey and Brenner,[31] Bruzs,[14] and Brauer[8] agree quite well according to this correlation. Some of the earlier results are in fair agreement with the results obtained here while some of the values in Table VII disagreed so badly that they were omitted from Figure 25.

At the beginning of this research it was hoped that this type of attack would provide a value of the absolute electrode potential. The method by which this quantity was to have been obtained is outlined below. The general working equation may be written as

$$-\mathcal{E}It = \Delta H + Q \tag{13}$$

where the terms are defined as before. Measuring Q and $\mathcal{E}It$ will permit the calculation of ΔH. As ΔS may be obtained from Q, it would be an easy matter to obtain ΔF from the relation

$$\Delta F = \Delta H - T\Delta S \ . \tag{14}$$

Knowing ΔH, the electrode potential may easily be obtained as

$$\mathcal{E} = -\frac{\Delta F}{n\mathcal{F}} \ . \tag{15}$$

This may easily be done for the total cell reaction. However, when one attempts to apply the same procedure to a single electrode, he finds that the data are not sufficient. Although the heat given off a single electrode may easily be measured, this is not the case with the energy input, $\mathcal{E}It$. Attempts to get around this by dividing the total energy input into two parts by a trial and error method met with failure. This was because the necessary number of independent equations are not available from the data.

2. The Silver-Aqueous Silver Nitrate System

The same general remarks made for the copper system are also applicable to the silver system and will not be repeated here.

The data in Table V may be used to calculate an entropy change accompanying a concentration change in the same manner as was done with copper.

$$Ag_{(s)} = Ag^{+}{}_{(0.2\ M)} + e^{-}{}_{(Ag)} \qquad (16)$$

$$\Delta S = +36.5 \text{ cal./mole/deg.} \qquad (17)$$

$$Ag_{(s)} = Ag^{+}{}_{(0.4\ M)} + e^{-}{}_{(Ag)} \qquad (18)$$

$$\Delta S = +31.6 \text{ cal./mole/deg.} \qquad (19)$$

Subtracting (18) from (16) gives

$$Ag^{+}{}_{(0.4\ M)} = Ag^{+}{}_{(0.2\ M)} \ . \qquad (20)$$

ΔS for this reaction is obtained by subtracting (19) from (17) and is equal to +4.9 cal./mole/degree. Again this value is much greater than would be expected for the ideal case (1.377 cal./mole/degree) but is somewhat less than the corresponding value for copper. Once again this value depends on the activity of a single ionic species which has not been evaluated.

As was the case with the copper system, one can calucate the entropy associated with a silver ion and one electron for each of the three concentrations studied. The necessary piece of datum is the entropy of solid silver. This is given by Stull and Sinke[68] as 10.24 cal./mole/degree at 300° K. This value, along with some previous values for the entropy of the aqueous silver ion, are tabulated in Table VIII. It may be noted that, for the purpose of comparison, the entropy of the electron has been neglected.

TABLE VIII

ENTROPY OF THE SILVER ION

Electrolyte	Conc. Silver Moles/Liter	Temperature °K	S_{Ag^+} Cal./Mole/Degree	Reference
$AgNO_3$	0.20	303.2	46.7	This Work
$AgNO_3$	0.40	303.2	41.8	This Work
$AgNO_3$	0.80	303.2	37.1	This Work
$AgNO_3$	1	290-297	19	Bruzs[14]
$AgNO_3$	1.6	290-297	19.2	Bruzs[14]
$AgNO_3$	0.8	290-297	19.5	Bruzs[14]
$AgNO_3$	0.1	290-297	30.3	Bruzs[14]
$AgNO_3$	0.55	273	37.6	Jahn[7]
$AgNO_3$	0.17	~298	20.8	Gill[6]
- - -	a=1	298.1	17.54	Latimer[67]

Figure 26 shows the various values given in Table VIII plotted as a function of the concentration. This plot was constructed in the same manner as Figure 25 for the copper system. The equation for this line, as obtained by the method of least squares, is

$$S_{Ag^+} = 35.51 - 16.04 \log M \; . \qquad (21)$$

Again the values obtained in this work fall on a very satisfactory straight line. Very little agreement was obtained with any of the previous results except for the fair agreement with the early result of Jahn.[7]

3. The Electrolysis of Water

The only significant datum obtained by calorimetric measurements on the electrolysis of aqueous sulfuric acid using platinum electrode was the enthalpy change accompanying the decomposition of water. This value was compared with the accepted value and found to be in very good agreement. The validity of all of the calorimetric measurements was enhanced by this agreement. In addition, this demonstrates that the method employed in this work is a very convenient way to determine the enthalpy change for any reaction which may be carried out in a quantitative manner by an electrochemical method.

It was stated in Chapter IV that the entropy values obtained for this system were invalid. This is particularly true in view of the fact that the sum of the calculated entropy changes for the electrode reactions is very much is disagreement with the accepted value for the entropy change for the cell reaction. If one refers to the method used to calculate these

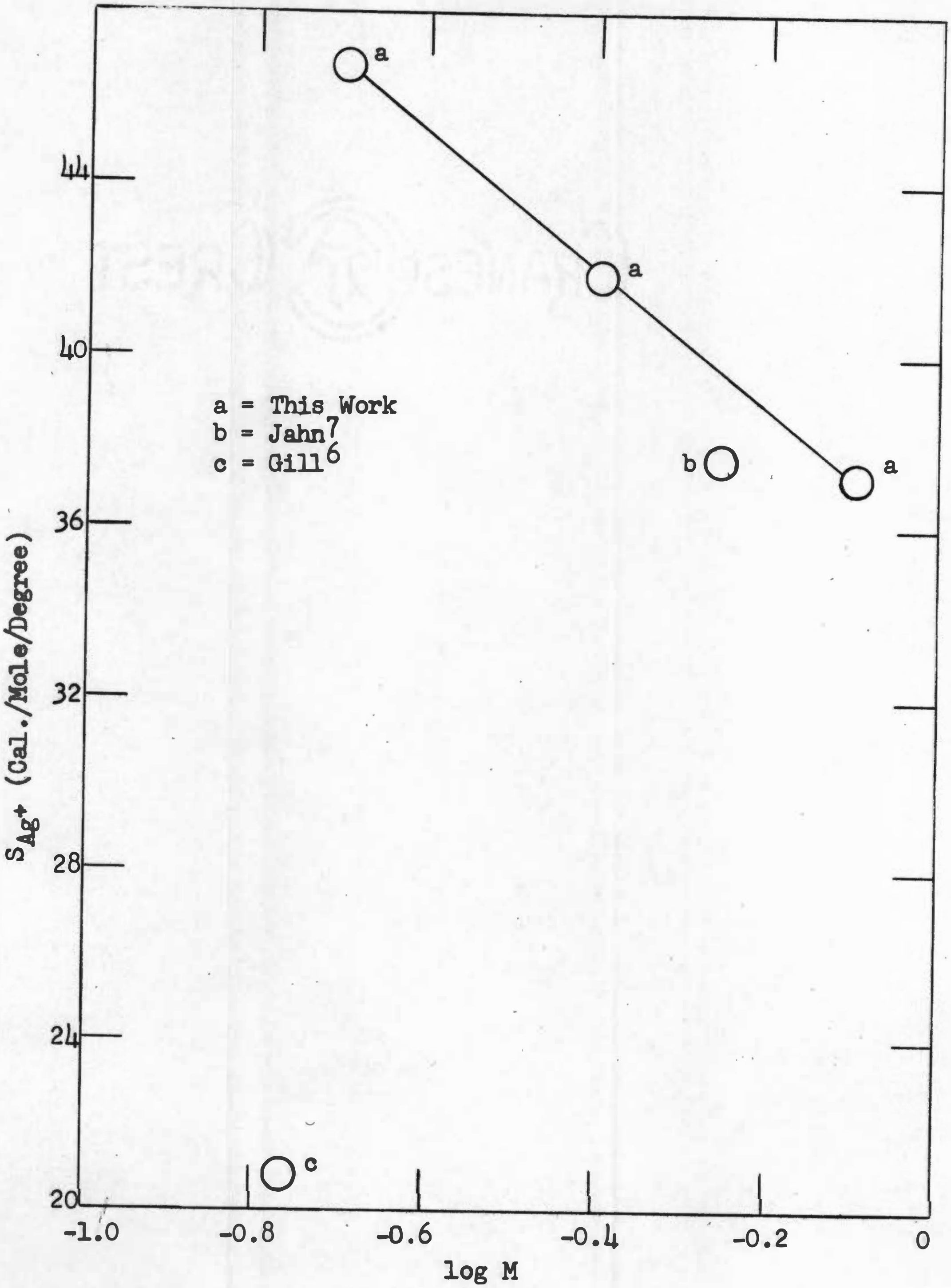

Figure 26. Entropy of the Silver Ion as a Function of the Concentration of Silver.

entropy values, it is not difficult to see why the results do not correspond to the entropy changes occurring at the electrode. The method of calculation is based on the assumption that the static potentials of the probe *versus* the electrodes are equal to the reversible potential of the cell reaction. For the copper and silver systems, this was true and the static potential of the probe *versus* either electrode was zero in all cases. The static potential of the probe *versus* either electrode was also zero for the platinum-aqueous sulfuric acid system. This had to be true as the probe and both electrodes were constructed of platinum and were dipping into the same solution. However, this is not the reversible potential corresponding to the decomposition of water. In view of this, the entropy values calculated as in the appendix cannot be taken as corresponding to the entropy changes occurring at the electrode. This difficulty could be avoided by using reversible electrodes.

This situation is quite analogous to the direct current method for measuring electrolytic conductance. Conductance data of the highest order of accuracy are obtainable by this method but only if strictly reversible electrodes are used as potential measuring probes.[69]

The above statements have nothing to do with the enthalpy values obtained by this method since they are not dependent upon the reversibility of the electrodes. These values may be obtained for any quantitative electrochemical reaction regardless of whether the reversible potential corresponding to the reaction can be measured or not.

4. Comparison of the Copper and Silver Systems

It is possible to calculate the value of the entropy change for the reaction

$$Cu_{(s)} + 2Ag^{+}_{(aq.)} = Cu^{++}_{(aq.)} + 2Ag_{(s)}. \qquad (22)$$

The necessary data are readily available in the literature.[66,67,68] The ionic values are based on the standard state entropy of the hydrogen ion being equal to zero. In the subtraction of relative entropies, an absolute entropy change is obtained.

The entropy values for each ion is given below:

$$\begin{array}{cccc} Cu_{(s)} + & 2Ag^{+}_{(a=1)} = & Cu^{++}_{(a=1)} & + 2Ag_{(s)} \\ S=7.97 & S=17.54 & S=26.5 & S=10.20 \end{array} \qquad (23)$$

The entropy values are written beneath the species to which they refer and are given in cal./deg./mole. The entropy change for this reaction is then

$$\Delta S = -26.5 + 2 \times 10.20 - 7.97 - 2 \times 17.54 \qquad (24)$$

$$\Delta S = -49.15 \text{ cal./deg./mole of Cu at } 298.16^{\circ} \text{ K.}$$

One can also calculate the entropy change for a like reaction from Table III and V. This may be done in the following manner.

$$Cu(s) = Cu^{++}_{(0.2\ M)} + 2e^{-}_{(Cu)} \qquad \Delta S = -20.2 \text{ cal./mole/deg.} \qquad (25)$$

$$Ag(s) = Ag^{+}_{(0.2\ M)} + e^{-}_{(Ag)} \qquad \Delta S = +36.5 \text{ cal./mole/deg.} \qquad (26)$$

Multiplying (26) by 2 and subtracting from (25) one obtains

$$Cu_{(s)} + 2Ag^{+}_{(0.2\ M)} + 2e^{-}_{(Ag)} = Cu^{++}_{(0.2\ M)} + 2Ag_{(s)} + 2e^{-}_{(Cu)}$$

$$\Delta S = -93.2 \text{ cal./deg./mole.} \qquad (27)$$

Using the data for the 0.4 M solution in exactly the same manner, one obtains

$$Cu_{(s)} + 2Ag^{+}_{(0.4\ M)} + 2e^{-}_{(Ag)} = Cu^{++}_{(0.4\ M)} + 2Ag_{(s)} + 2e^{-}_{(Cu)}$$

$$\Delta S = -90.6 \text{ cal./deg./mole} \qquad (28)$$

Except for two reasons, the ΔS for reactions (27) and (28) should be exactly the same* as the ΔS for reaction (23).

One of these reasons for the large difference between (28) and (23) or (27) and (23) is that the entropy changes for reactions (27) and (28) involve the activity of the copper and silver ions while the ΔS for reaction (23) is under the strict conditions of unit activity. It is unfortunate that, at the present time, these ionic activities cannot be evaluated. In this respect, mention should be made of the mean ionic activity coefficients for aqueous silver nitrate in order that they may be compared with the values given previously for copper sulfate. For solutions of 0.2, 0.4, and 0.8 molal silver nitrate, the mean activity coefficients are 0.657, 0.567, and 0.464, respectively.[70] It can be seen that these values are much larger than the corresponding values for copper sulfate. In fact, a 6.0 molal solution of silver nitrate has a larger mean ionic activity coefficient than does a 0.1 molal solution of copper sulfate. However, this cannot explain the differences in entropy values listed above as these are mean ionic activity coefficients. It does, however, emphasize that fact that there is a vast difference between copper sulfate and silver nitrate.

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*There is also a small temperature difference between the reactions but this would have a very small effect.

The second reason is that, as one may note, the electrons appearing in reactions (27) and (28) are in two different metals. The subject of the entropy of an electron in a metal is far from settled. One group holds that the entropy of an electron in any metal may be taken as equal to zero.[37] However, this is vigorously opposed by the second group who believe that this entropy is not zero but is variable from metal to metal and is responsible for a number of thermoelectric phenomena.[34,71]

Latimer[71] has shown that the thermopotential of a metallic thermocouple may be represented as a function of the difference in entropy of the electrons in the two different metals. His treatment gives fair agreement with the data in existence at that time. Bronsted[45] also attributes the thermopotential of a thermocouple to the entropy associated with the electrons in the metal. Other authors who also consider the entropy of electrons in metals are Holtan[34] and Van Rysselberghe.[49,50]

It should be pointed out, however, that all of the above treatments are for conditions of zero current flow. It may be that the magnitude of the current flow could have a considerable effect on the amount of entropy associated with an electron in any given metal.*

The results given here are not in definite disagreement with values which may be obtained from literature data. However, in view of the above reasons, no definite statement can be made concerning the degree of agree-

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*This would seem to be in disagreement with the modern theories of electrical conduction in metals in that it would involve a change in the energy level of the electron. However, there does not seem to be sufficient experimental evidence available to definitely prove that a change in the energy level of an electron does not occur when a flow of electrons exist.

ment. While Latimer[71] has suggested that the difference between the entropy of an electron in copper and the entropy of an electron in silver is probably very small, one still has the problem of activities of single ionic species to contend with. In view of the above statements, the absolute acceptance of the values given in this dissertation must, of necessity, await further research along this same line.

5. Suggestions for Further Work

In view of the statement made in the preceding section concerning further research, it is only fitting that a few remarks be made concerning the direction of such research.

Experience has shown that the most desirable, if not actually necessary, improvement to acquire before continuing this type of research would be a much more sensitive calorimeter. Several suggestions for attaining this increased sensitivity are enumerated below.

1. The reasons for choosing a Dewar flask for the calorimeter are given in the Experimental section. However, a metal calorimeter, which is more desirable, could be made by having the walls of the calorimeter serve as the electrodes. The electrodes could be separated and insulated by the partition used to isolate the anode and cathode compartments. A metal calorimeter, in addition to allowing the use of larger electrodes, would give a measurable, reproducible heat leak.

2. Increasing the electrode area would give a greater ratio of reversible to irreversible heat which would result in more accurate values.

3. A more sensitive temperature sensing system would be extremely advantageous. Use of a thermistor with a higher resistance and an electronic recorder with a one mv. range would give an automatic recording system accurate to 0.0001°.

4. Automatic control of the temperature difference between the two electrode compartments would be necessary if the first three improvements were made. Further, it would be desirable to record the amount of heat added to the cooler compartment. The instrumentation involved would be extensive but not prohibitive in cost.

Once the above improvements had been made and the system was operative, there are a number of highly desirable experiments to perform. Perhaps one of the most promising routes would be to continue working with the copper and silver system except at much lower concentrations than used in the present work. This would permit the extrapolation of the data to zero concentration. It is probable that this technique would give the absolute standard state entropy of an ion as well as information about the activity of a single ionic species.

It would also be very worthwhile to use the techniques of electrochemical calorimetry to determine ΔH values for a number of reactions. In some cases, it is very difficult to obtain these ΔH values by other methods.

Finally, it would be highly desirable to make some measurements on a system which consisted of two different reversible electrodes plus a reversible probe.

CHAPTER VI

SUMMARY

Temperature difference measurements were made during the electrolysis of aqueous copper sulfate between copper electrodes. The temperature differences measured were those between the cathode and the anode, the cathode and the solution, and the anode and the solution. These values were obtained as a function of the time of the electrolysis. The variation of these differences with time and their magnitudes were explained in terms of the entropy changes occurring at the electrodes, resistance, and polarization.

The effect of some inert electrolytes on these temperature differences was determined as was the effect of gelatin. Explanations for these effects were given in terms of polarization and the thermodynamics of irreversible processes as applied to thermocells.

It was found that these temperature differences were extremely dependent on, and had a definite relationship to, the concentration of the copper sulfate solutions. Accordingly, a method was proposed whereby such temperature differences could be used as an analytical method. This method was given the name, "Thermal Electroanalysis."

A theoretical analysis was made of the quantity of heat evolved by an electrochemical reaction during electrolysis. This analysis was made from the standpoint of the thermodynamics of irreversible processes and its relationship to classical thermodynamics was indicated.

A calorimetric method was developed which made it possible to measure the amount of heat liberated at a single electrode during an electrochemical reaction. It was also possible to measure the total amount of heat liberated by the same electrochemical reaction. These data, coupled with the theoretical analysis, made it possible to calculate the enthalpy change for the total reaction as well as the entropy change occurring at each electrode. This was done for the copper-aqueous copper sulfate-copper and silver-aqueous silver nitrate-silver systems at three different concentrations of electrolyte for each system.

The values obtained for these systems were compared with the existing literature data where possible. Certain differences were pointed out in the case of the entropy values, especially their variation with concentration. Explanations were postulated for these differences and further work was proposed to clarify these points.

In order to test the calorimetric technique and to prove the validity of the method, the enthalpy change for the decomposition of water was measured by this combination of calorimetric and electrochemical techniques. The values obtained were in very good agreement with the accepted value for this quantity. This was considered to be sufficient proof that this technique is a valuable tool for obtaining thermodynamic data which is extremely difficult to obtain by other means.

APPENDIX

TREATMENT OF CALORIMETRIC DATA

A. Time-Temperature Curve and the Method for Evaluating ΔT

A typical time-temperature curve obtained from either heat capacity or electrolysis runs is shown in Figure 27. The variation of temperature with time during the rating periods has been exaggerated to show the method for evaluating ΔT. In an actual run, the temperature of the calorimeter remained nearly constant during the rating periods. The irregularities in the curve during the reaction period were periods when the heater in the outer compartment was off. During a run there were a number of these irregularities but they were usually not as pronounced as indicated in Figure 27.

A time-temperature curve from a calorimetric experiment usually approximates an exponential curve quite closely. Because of this, the most precise method of treating a time-temperature curve is to integrate the area under the curve and evaluate the thermal leak constant of the calorimeter. However, heat leakage through glass, such as the Dewar flask used in this work, is not reproducible. This automatically prevents one from obtaining highly precise data. Because of this a much simpler method was used to evaluate the temperature use. This method is illustrated graphically in Figure 27. The time on the experimental time-temperature curve corresponding to 63 per cent of the distance between the extrapolated lines from the rating periods was found. This distance was then taken as equal to ΔT as shown in Figure 27. This

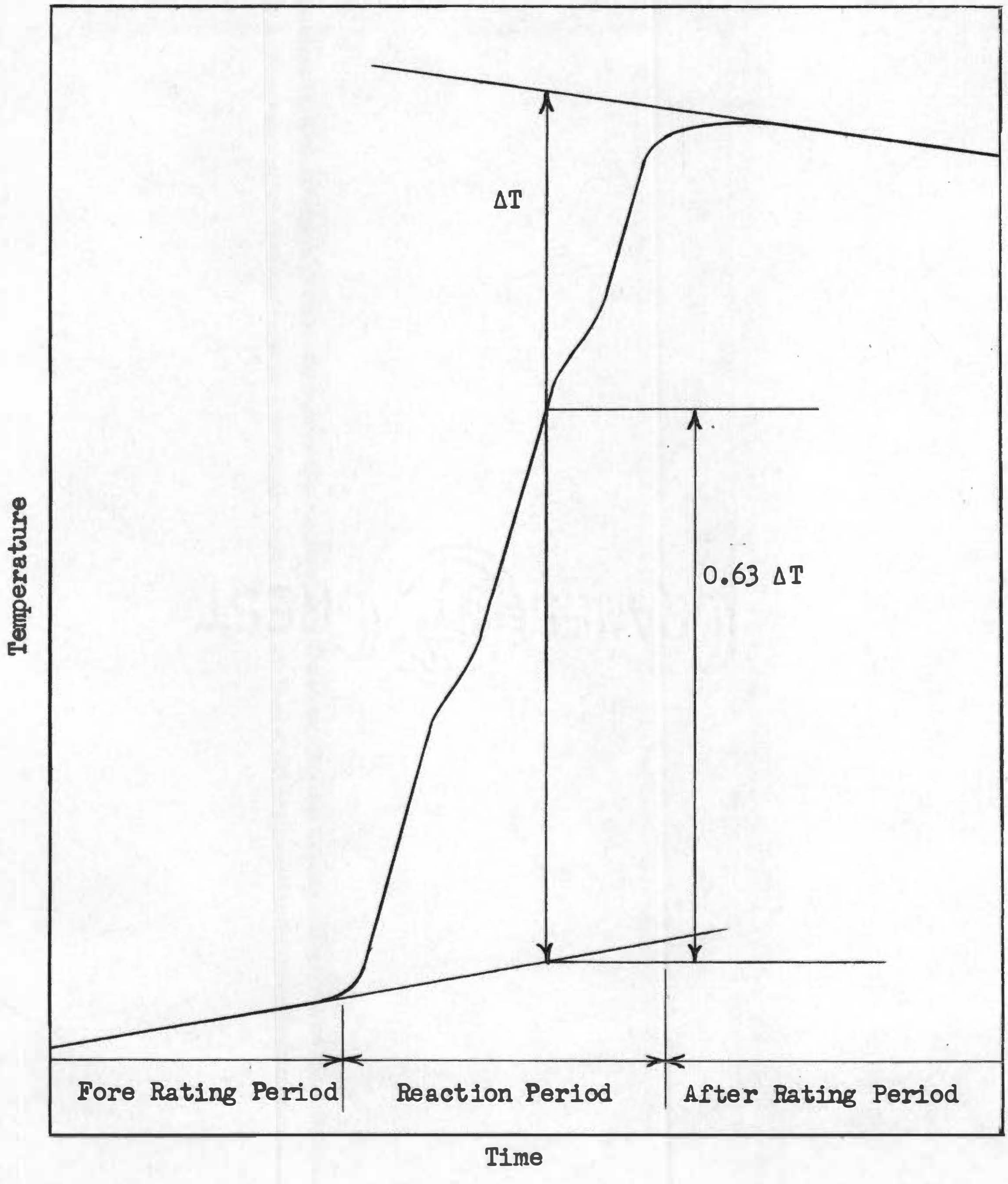

Figure 27. Typical Time-Temperature Curve and Method of Evaluating ΔT.

method presupposes an exponential temperature rise and is capable of a precision of 1 part in 1000.[72]

B. Heat Capacity of the Calorimeter

The calculation of the heat capacity of the calorimeter is best explained by reproducing an actual calculation performed during this work. This is done here for a heat capacity run on the calorimeter containing aqueous silver nitrate. Unless otherwise specified, the symbols used correspond to those defined previously.

In this particular run, H_i was on for a total of 721.3 seconds while H_o was on for a total of 258.6 seconds. Thus H_i was on alone for 462.7 seconds. It was necessary to separate the time that H_i was on alone because the voltage drop across R_i^1 with both heaters on was considerably different from the voltage drop across R_i^1 when only one heater was on. Several readings of the voltage drops across R_i^1 and R_o^1 were taken during the course of the run. These voltage drops were averaged to give the value used in the calculations. Theoretically, these values should have been integrated as a function of time but deviation from the average were less than 0.05 per cent. This was much less than the temperature measurement errors. The average voltage drop across R_i^1 while only H_i was on was 0.18371 volts. The average voltage drop across R_i^1 while both H_i and H_o was on was 0.14735 volts. The corresponding value for R_o^1 was 0.51818 volts. These values, coupled with the values for the resistances of R_i^1 and R_o^1, were then used to calculate a value for the heating current, I^h, from Ohm's law.

$$I_i^h \text{ (only } H_i \text{ on)}^* = \frac{0.18371}{1.0623} \tag{1}$$

$$I_i^h \text{ (} H_i \text{ and } H_o \text{ on)} = \frac{0.14735}{1.0623} \tag{2}$$

$$I_o^h = \frac{0.51818}{1.0394} \tag{3}$$

These values for the heating current were used to calculate the heat added, Q (in Joules) from

$$Q = RI^2t \ , \tag{4}$$

where R is the resistance of the heater in ohms, I is the current in amperes, and t is the heating time in seconds. Thus:

$$Q_i \text{ (only } H_i \text{ on)} = 5.0388\left(\frac{0.18371}{1.0623}\right)^2 (462.7) = 69.73 \text{ Joules}, \tag{5}$$

$$Q_i \text{ (} H_i \text{ and } H_o \text{ on)} = 5.0388\left(\frac{0.14735}{1.0623}\right)^2 (258.6) = 25.07 \text{ Joules}, \tag{6}$$

$$Q_o = 10.168\left(\frac{0.51818}{1.0394}\right)^2 (258.6) = 653.52 \text{ Joules}, \tag{7}$$

and $$Q_i \text{ (total)} = 69.73 + 25.07 = 94.80 \text{ Joules}. \tag{8}$$

The remaining datum necessary to calculate the heat capacity is the temperature rise. The temperature rise for this run, evaluated as shown in Figure 27 and expressed as the unbalance potential of the Wheatstone bridge, was 4.58 mv. The heat capacities, C^h, were then calculated by dividing the energy input by the temperature rise.

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*The subscripts i and o refer to the inner and outer compartments of the calorimeter, respectively.

$$C_i^h = \frac{94.80}{4.58} = 20.70 \text{ Joules/mv.} \tag{9}$$

$$C_o^h = \frac{653.52}{4.58} = 142.69 \text{ Joules/mv.} \tag{10}$$

The total heat capacity of the calorimeter, C_t^h, was taken as the sum of C_i^h and C_o^h. The average of three heat capacity runs for this system gave the results:

$$C_i^h = 20.84 \pm 0.15 \text{ Joules/mv.} \tag{11}$$

$$C_o^h = 142.66 \pm 0.25 \text{ Joules/mv.} \tag{12}$$

$$C_t^h = 163.50 \pm 0.25 \text{ Joules/mv.} \tag{13}$$

These are the heat capacity values which are used for the calculations in the next section.

C. Calorimetric Data From Electrolysis Runs

The calculations given here are for calorimetric measurements on the electrolysis of 0.40 M silver nitrate using silver electrodes (Run No. 4 in Tables IV and V). The necessary data for making the calculations are tabulated below.

Average voltage drop between cathode and probe = 0.11409 volts.

Average voltage drop between anode and probe = 0.94024 volts.

Voltage drop across R_s (the standard resistance in the electrolysis circuit) = 0.75030 volts.

Average voltage drop across R_o^1 = 0.52935 volts.

Duration of electrolysis = 1209.1 seconds.

Total time H_o on = 208.8 seconds.

Here again average voltage drops have been used instead of integrated values. Any error due to the use of an average value is small in comparison with the error associated with the calorimetric measurements.

It was shown in Chapter II that the heat, Q, given off by an electrolytic reaction is given by

$$Q = -T\Delta S + RI^2t + \eta It \qquad (14)$$

in which the symbols have the definitions given in Chapter II. Instead of treating R and η as separate terms, they were combined into a single term. Since the electrodes and probe were constructed of the same metal (silver in this case) any deviation from zero potential between the probe and either electrode was due to resistance and polarization. Therefore the total heat effect due to resistance and polarization can be calculated directly from the average voltage drop between the probe and the electrode, the electrolysis current, I, and the time.

The electrolysis current was calculated from Ohm's law by

$$I = \frac{\text{voltage drop across } R_s}{R_s} = \frac{0.75030}{5.1274} = 0.14633 \text{ amperes.} \qquad (15)$$

The extent of the reaction was easily calculated from Faraday's law.

$$\text{Equivalents} = \frac{It}{\mathcal{F}} = \frac{(0.14633)\ (1209.1)}{96,496} = 1.8335 \times 10^{-3} \text{ moles of Ag.} \qquad (16)$$

The heating current for the outer compartment was calculated from Ohm's law and is given by

$$I_o^h = \frac{0.52935}{1.0394}\ . \qquad (17)$$

The heat added to the outer compartment, Q_a^o, to maintain isothermal condition is then

$$Q_a^o = 10.168\left(\frac{0.52935}{1.0394}\right)^2 (208.8) = 550.65 \text{ Joules.} \qquad (18)$$

Heat produced in the inner compartment by resistance and polarization is equal to the product of the voltage drop between the anode and the probe, the electrolysis current, and the time of electrolysis.

$$Q^i_{R+\eta} = (0.94029)\ (0.14633)\ (120.91) = 166.36 \text{ Joules.} \qquad (19)$$

In like manner

$$Q^o_{R+\eta} = (0.11409)\ (0.14633)\ (120.91) = 20.18 \text{ Joules.} \qquad (20)$$

The electrical energy input is, of course, the sum of $Q^i_{R+\eta}$ and $Q^o_{R+\eta}$ since the voltage applied to the cell is equal to the sum of the voltage drops between the probe and the electrodes and is equal to 186.54 Joules. The total energy input to the calorimeter is then equal to the sum of 186.54 and Q_a^o or 737.19 Joules.

The temperature rise for this run, evaluated as shown in Figure 27, was 4.51 mv. The heat evolved in each compartment is then equal to the product of the heat capacity of the compartment and the temperature rise.

$$Q_m^i = (20.84)\ (4.51) = 93.99 \text{ Joules} \qquad (21)$$

$$Q_m^o = (142.66)\ (4.51) = 643.40 \text{ Joules} \qquad (22)$$

$$Q_m^t = (163.50)\ (4.51) = 737.39 \text{ Joules} \qquad (23)$$

From the working equation developed in Chapter II,

$$\Delta H = -\mathcal{E}It - Q\ . \qquad (24)$$

$$\Delta H = 737.19 - 737.39 = -0.20 \text{ Joules} \qquad (25)$$

This can be converted to calories per mole.

$$\Delta H = \frac{0.20}{(4.1840)\ (1.833 \times 10^{-3})} = -26 \text{ cal./mole.} \qquad (26)$$

$\mathcal{E}$It has been inserted as a positive quantity in (25) because the negative sign in (24) refers to work done by the system.

The heat evolved in each compartment is given by

$$Q = -T\Delta S + RI^2t + \eta It\ . \qquad (27)$$

Rearranging (27) gives

$$T\Delta S = RI^2t + \eta It - Q\ , \qquad (28)$$

or, in terms of the heat due to resistance and polarization

$$T\Delta S = Q_{R+\eta} - Q\ . \qquad (29)$$

Thus, for the inner compartment (the anode reaction)

$$(T\Delta S)_i = 166.36 - 93.99 = +72.37 \text{ Joules.} \qquad (30)$$

This can be converted into the conventional units for ΔS by dividing the absolute temperature, the moles of silver reacting, and the conversion factor for Joules to calories.

$$\Delta S = \frac{+72.37}{(303.2)\ (4.1840)\ (1.8333 \times 10^{-3})} = +31.11 \text{ cal./mole/deg.} \qquad (31)$$

This entropy value is for the reaction

$$Ag_{(s)} = Ag^{+}{}_{(aq.,\ 0.40\ M)} + e^{-}{}_{(Ag)}\ . \qquad (32)$$

The entropy change for the cathodic reaction may be calculated in exactly the same manner except that the energy added from the heater must be included.

$$(T\Delta S)_o = Q^o_{R+\eta} + Q^o_a - Q^o_m \qquad (33)$$

$$(T\Delta S)_o = 20.18 + 550.65 - 643.40 = -72.57 \text{ Joules} \qquad (34)$$

$$\Delta S = \frac{-72.57}{(303.2)\ (4.1840)\ (1.8335 \times 10^{-5})} = -31.20 \text{ cal./mole/deg.} \qquad (35)$$

This ΔS value is for the reaction,

$$Ag^{+}_{(aq.,\ 0.40\ M)} + e^{-}_{(Ag)} = Ag_{(s)}\ . \qquad (36)$$

Within experimental error, the entropy values calculated in (31) and (35) are equal but opposite in sign. This is the correct relationship since reactions (32) and (36) are the reverse of each other.

The uncertainty in the entropy value is approximately ± 0.5 cal./mole/deg. as estimated from the deviation in the heat capacity data and the uncertainty in the temperature rise.

Finally it would be helpful to indicate the calculation for the enthalpy change for the electrolysis of water. This is in contrast to the ΔH value calculated in equation (26).

The data and calculation below are for Run No. 1 in Table VI. The total energy input to the cell is given by the sum of the electrical energy added and the heat added by the outer compartment heat. This is equal to

$$418.45 + 118.98 = 537.43 \text{ Joules.} \qquad (36)$$

The measured heat given off in the calorimeter was 438.58 Joules. Thus, from (24) ΔH is given by

$$\Delta H = 537.43 - 438.58 = +98.85 \text{ Joules.} \qquad (37)$$

The extent of the reaction was such that 3.4603×10^{-4} moles of hydrogen were liberated. This corresponds to the decomposition of 3.4603×10^{-4} moles of water. The ΔH per mole of water is then

$$\Delta H = + \frac{98.85}{(3.4603 \times 10^{-4})\ (4.1840)} = +68{,}280 \text{ cal./mole of } H_2O \ . \tag{38}$$

This calculation was included in order to show the difference between reactions in which there is a net ΔH (decomposition of water in this case) and those reactions in which the net ΔH is zero (such as silver in the preceding calculation).

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