

A CALORIMETRIC INVESTIGATION OF THE HYDRATION
OF COBALT (II) PERCHLORATE AND COBALT (II)
NITRATE IN ETHYL ALCOHOL

By

Glenn Dill Fielder

"

Bachelor of Arts

Oklahoma State University

Stillwater, Oklahoma

1963

Submitted to the faculty of the Graduate School of the
Oklahoma State University in partial fulfillment
of the requirements for the degree of
MASTER OF SCIENCE
May, 1965

OKLAHOMA
STATE UNIVERSITY
LIBRARY

SEP 20 1935

A CALORIMETRIC INVESTIGATION OF THE HYDRATION
OF COBALT (II) PERCHLORATE AND COBALT (II)
NITRATE IN ETHYL ALCOHOL

Thesis Approved:

John E. Moore

Thesis Advisor

Paul Arthur

J. H. Boyer

Dean of the Graduate School

ACKNOWLEDGMENT

I wish to express my appreciation to my wife, Carol, for her encouragement, and also to Dr. Tom E. Moore for his assistance and guidance.

I wish to thank my parents for their interest.

This study was supported in part by funds made available by the Atomic Energy Commission, Contract No. AT(11-1)-1175.

TABLE OF CONTENTS

| Chapter | Page |
|---|------|
| I. INTRODUCTION | 1 |
| Purpose and Scope of Investigation | 1 |
| Hydration of Transition Metal Salts in Organic Solvents | 5 |
| Titration Calorimetry | 10 |
| II. THE CALORIMETER | 14 |
| Components | 14 |
| Sensitivity | 19 |
| Performance Test | 22 |
| Heat of Mixing of Ethanol and Water | 25 |
| III. EXPERIMENTAL METHOD AND PROCEDURE | 28 |
| Preparation of Solutions and Analytical Procedures | 28 |
| Procedure for Operation of the Calorimeter | 29 |
| IV. TREATMENT OF THE DATA AND RESULTS | 32 |
| Determination and Calculation of the Heat of Reaction. | 33 |
| Calculation of the Heat of Mixing for Five Mole Percent Water in Ethanol | 37 |
| Corresponding Solutions | 40 |
| Results for Cobalt (II) Nitrate-Ethanol-Water System | 41 |
| Results for Cobalt (II) Perchlorate-Ethanol- Water System | 53 |
| Interpretation of Results. | 64 |
| V. SUMMARY AND SUGGESTIONS FOR FURTHER WORK. | 69 |
| BIBLIOGRAPHY | 71 |

TABLE OF CONTENTS (Continued)

| Chapter | Page |
|----------------------|------|
| APPENDIX A | 74 |
| APPENDIX B | 76 |
| APPENDIX C | 78 |
| GLOSSARY | 80 |

LIST OF TABLES

| Table | | Page |
|-------|--|------|
| I. | Experimental Measurement of the Heat of Formation of Water at 27.7°C | 23 |
| II. | Experimental Measurement of the Heat of Mixing of Water and Ethyl Alcohol. | 26 |
| III. | Calorimetrically Determined Heat of Mixing Data for Three Solutions of Water and Ethanol. | 38 |
| IV. | Calorimetrically Determined Heat of Reaction of Water Data for Three Solutions of Cobalt (II) Nitrate in Ethanol | 43 |
| V. | Experimental and Statistical Values of the Free Water and Average Ligand Number for Cobalt (II) Nitrate in Ethanol | 48 |
| VI. | Calorimetrically Determined Heat of Reaction of Water Data for Three Solutions of Cobalt (II) Perchlorate in Ethanol | 54 |

LIST OF FIGURES

| Figure | | Page |
|--------|---|------|
| 1. | Theoretical Complex Formation Curve | 3 |
| 2. | The Calorimeter | 15 |
| 3. | The Calorimeter Internal Heater Electrical Circuit . . . | 17 |
| 4. | Heat of Reaction of Water with Cobalt (II) Nitrate in Ethanol as a Function of the Total Water Concentration | 42 |
| 5. | Corresponding Solutions of Cobalt (II) Nitrate in Ethanol . | 46 |
| 6. | Experimental and Statistical Formation Curves for Aquo Complexes of Cobalt (II) Nitrate in Ethanol | 49 |
| 7. | Heat of Reaction of Water with Cobalt (II) Nitrate in Ethanol as a Function of the Water-Salt Mole Ratio . . | 51 |
| 8. | Slopes of the Curves Representing the Total Heat of Reaction of Water with Cobalt (II) Nitrate in Ethanol . . | 52 |
| 9. | Heat of Reaction of Water with Cobalt (II) Perchlorate in Ethanol as a Function of the Total Water Concentration | 56 |
| 10. | Slopes of the Curves Representing the Total Heat of Reaction of Water with Cobalt (II) Perchlorate in Ethanol | 57 |
| 11. | Corresponding Solutions of Cobalt (II) Perchlorate in Ethanol | 59 |
| 12. | Slope of the Curve Representing the Heat of Mixing of Water and Ethanol | 63 |

LIST OF FIGURES (Continued)

| Figure | | Page |
|--------|---|------|
| 13. | Heat of Reaction of Water with Cobalt (II) Perchlorate in Ethanol as a Function of the Water to Salt Mole Ratio | 65 |

CHAPTER I

INTRODUCTION

Purpose and Scope of Investigation. - This research is a part of a program concerned with the study of factors which influence the liquid-liquid extraction and separation of the transition metal salts. An adequate thermodynamic description of organic solvent-water-salt systems is important to valid conclusions or predictions about their behavior. One major objective of this research is to determine whether or not titration calorimetry can be used to study the thermodynamics of hydration. It is hoped that the information gained in this research with cobalt (II) perchlorate and cobalt (II) nitrate in ethyl alcohol can be applied to other, similar systems.

A knowledge of the formation constants and enthalpies of formation for aquo complexes in organic solvents is required in order to adequately describe and understand salt-water interactions at low water-salt ratios. Also, it is important to know to what degree hydration is involved in the extraction process; i. e. how much of the co-extracted water is hydrate or "bound" water and how much is second sphere or "free" water.

The system $\text{Co}(\text{ClO}_4)_2 - \text{EtOH} - \text{H}_2\text{O}$ was chosen because previous work by Yates et al. (34) seemed to indicate that cation-anion

association in hydrous alcohols was not very great, and therefore, a minimum of complications could be expected in studying the aquo complexes. The $\text{Co}(\text{NO}_3)_2 - \text{EtOH} - \text{H}_2\text{O}$ system was also selected for the calorimetric study of aquo complexes because Jorgensen (16) had previously determined an average formation constant for these spectrophotometrically. A direct comparison of the optical and calorimetric methods is therefore possible. Furthermore, comparatively simple behavior is to be expected of these salts in ethanol.

The calculation of successive formation constants depends on the determination of the average ligand number, \bar{n} , which, in the case of aquo complexes, is the average number of water molecules bound presumably to the cobalt (II) ions. The "free" or unbound water is then the water not complexed according to the following formulas:

$$(\text{H}_2\text{O}) = C_{\text{H}_2\text{O}} - \bar{n}C_{\text{M}}$$

$$C_{\text{M}} = \text{M} + \text{ML}_2 + \dots + \text{ML}_n$$

where

$$\begin{aligned} (\text{H}_2\text{O}) &= \text{free water concentration} \\ C_{\text{H}_2\text{O}} &= \text{total water concentration} \\ C_{\text{M}} &= \text{total metal concentration} \\ \text{M} &= \text{free "metal" concentration} = \text{Co (II)} \\ &\quad \text{concentration in non-complexed form} \\ \text{L} &= \text{free ligand concentration} = \text{uncombined} \\ &\quad \text{water concentration} \end{aligned}$$

The "corresponding solutions" treatment of Bjerrum (5) applied to enthalpy data is developed in Appendix A. This is shown there to offer

a direct method of obtaining \bar{n} . Then, if several values of \bar{n} are plotted versus the corresponding values of (H_2O) , a curve is obtained similar to Figure 1. The curve should become asymptotic to the line corresponding to the maximum coordination number of the particular metal ion at large "free" water concentrations.

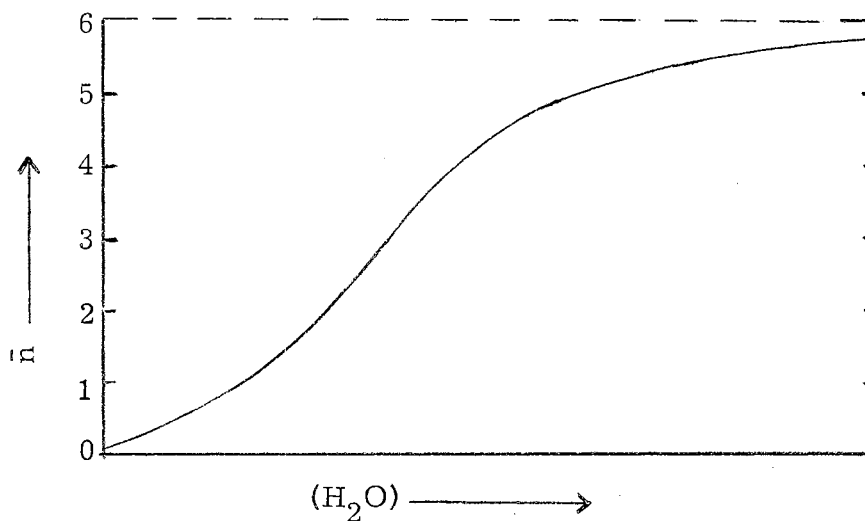


Figure 1. Theoretical Complex Formation Curve.

Now, in principle, if six \bar{n} values are chosen and the corresponding free water concentrations are taken from the graph of Figure 1 the six K values, or formation constant products, for the aquo complexes can be evaluated from the six equations analogous to those derived in Appendix A. There will be six equations and six unknown K values. The assumption is that the maximum number, N , of water molecules filling coordination positions in the octahedral environment of the cobalt (II) ion is six (6). In actual practice the maximum \bar{n} value is found; i. e. the \bar{n} value to which the curve in Figure 1 becomes asymptotic, and

this is taken as the maximum coordination number, N.

A comparison between the experimental aquo complex formation curve and a "statistical" formation curve (Appendix C) is of value in describing the formation of complexes. If the two curves, statistical and experimental, do not coincide within experimental error, then some explanation other than the statistical occupancy of coordination positions is required for the relative values of formation constants of the complexes of the system under investigation.

An essential part of the quantitative study of systems such as $\text{Co}(\text{ClO}_4)_2 - \text{EtOH} - \text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 - \text{EtOH} - \text{H}_2\text{O}$ is the preliminary qualitative description of them. As will be pointed out later, many questions are unanswered about these systems and it was hoped that through the use of titration calorimetry and proper interpretation of the experimental data both a better qualitative and quantitative understanding of the solvation in the systems would result.

The degree of association of the anion with the cation in an anhydrous organic solvent is important to know, for it is reasonable to expect that the difference in the extent of the hydration of cations surrounded by solvent molecules only and those coordinated with both solvent molecules and anions will effect the heat of hydration in solution and thus make interpretation of results more difficult.

As incoming water molecules replace anions and/or solvent molecules in the formation of aquo complexes, heat will be liberated because

of the greater base strength of water relative to either alcohol molecules or anions such as NO_3^- or ClO_4^- . The resulting hydration might even include more water molecules per metal ion than the six primarily coordinating ones, depending in part upon the salt concentration of the solution. One would expect that metal ions in a very dilute solution in an organic solvent could hydrate more fully because of the lower degree of interaction between the aquated metal ions and the anions.

A major objective of this research was, therefore, to obtain the formation constants for the aquo complexes of $\text{Co}(\text{NO}_3)_2$ and $\text{Co}(\text{ClO}_4)_2$ in ethanol and then to calculate the ligational enthalpies. From such a thermodynamic description of the solutions before and after the addition of water it should be possible to understand better the effect of coordinated and non-coordinated anions upon the exchange of ethanol for water about the cobalt (II) ion.

Hydration of Transition Metal Salts in Organic Solvents. - One of the earliest investigations of aquo complexes was made in 1909 when Jones and Anderson (13) discovered that the absorption spectra of many rare earth salts in alcoholic solution containing small amounts of water showed features of the spectra in pure water as well as in pure alcohol. It was reported that the phenomenon is largely independent of anion concentration, and therefore, must be caused by a change in solvation only.

No quantitative study of aquo complexes, that is, the evaluation of the formation constants was made apparently until after 1941 when Bjerrum (5) introduced his principle of corresponding solutions. This made possible the systematic study of the formation of aquo complexes when the concentration of free water could not be measured directly.

In 1950, Katzin and Gebert (17) explained qualitatively the marked color changes observed when water is added to $\text{Co}(\text{NO}_3)_2$ in alcohol as arising from the exchange of coordinately bound nitrate ions with solvating water molecules. At the same time a study of $\text{Co}(\text{ClO}_4)_2$ was carried out by Katzin and Gebert (17) and although there appeared to be evidence of some small degree of complex formation between the perchlorate anion and cations, it was clearly very much weaker than the nitrate. In a later study, Katzin (19) showed that the details of the anion spectrum of salts in organic solvents depends on both the cation and the ratio of anion to cation present in the solution. In particular, the nitrate anion has been shown to commonly occupy some of the coordination positions of transition metal cations.

During the 1950's there continued to be interest in the study of hydration of salts in non-aqueous solvents. Part of the interest was engendered by work on the extraction of electrolytes. Solvent extraction offers a method for obtaining information regarding the qualitative aspects of salt hydration in organic solvents through measurement of the increase in coextracted water with extracted salt. In 1953, Yates et al. (34) made

a study of hydration of divalent perchlorates and chlorides in octanol. The apparent degree of hydration of $\text{Co}(\text{ClO}_4)_2$ and $\text{Ni}(\text{ClO}_4)_2$ in 2-octanol was determined by solvent extraction and up to twelve moles of hydrate water per mole of each salt were found to be coextracted into 2-octanol. This seems to confirm the inability of the perchlorate anion to function effectively as a coordinating ion or to approach the cation closely. The cation is thus left free to exert its maximum influence on the solvent molecules. Such salts are probably best described as solvated ion associates. The chlorides, by contrast, seem to exist as molecular entities and chloro complexes in anhydrous octanol, the proportions of these changing as water is added (1).

The investigations mentioned above are very useful both quantitatively and qualitatively. As might be expected, the degree of anion and aquo-complexing is dependent on the mole ratio of ligand to metal ion. Depending on the type of association of anion and cation, the incoming water ligand exchanges for solvent molecules and/or anions.

In 1953 Bjerrum and Jorgensen (3) obtained the average formation constant for the aquo complexes of didymium chloride using the principle of corresponding solutions. They found that the maximum \bar{n} value (corresponding to the maximum coordination number) was six and further that the data (\bar{n} vs $\log \sqrt{[\text{H}_2\text{O}]}$) can be fitted by a statistical curve. However, in a discussion of the degree of ion-association of $\text{Co}(\text{NO}_3)_2$ in ethanol, the evidence for aquo complexes based upon spectral data

was challenged by Katzin and Gebert (18). Bjerrum and Jorgensen had contended that $\text{Co}(\text{NO}_3)_2$ in ethanol behaves as a medium dissociated electrolyte, and that the nitrate ion does not interfere with the exchange of ethanol for water molecules. Jorgensen (16) similarly determined what he regarded as the statistical average formation constants for the aquo complexes of the nitrates of Co(II), Ni(II) and Cu(II).

Jorgensen and Bjerrum (4) later agreed with Katzin and Gebert regarding the inner sphere coordination of nitrate but presented evidence that the spectral changes for $\text{Co}(\text{ClO}_4)_2$ in ethanol must be due to hydration and not to perchlorate coordination. It has been reported also that the absorption spectra of Co(II) and Ni(II) perchlorates in octanol does not change when the water-salt ratio exceeds six, which seems to indicate that only a small amount of free water is necessary to stabilize the hexaquo ion (16).

Larson and Iwamoto (22) in 1962 evaluated the step-wise formation constants for aquo complexes of Cu(II) in nitromethane by electrochemical methods and infrared spectral analysis. They also calculated the individual constants for the reactions in ethanol from the data of Minc and Libus (26). The average formation constant value differed only slightly from that given by Jorgensen (16). Larson and Iwamoto explained the rather large differences in the values of formation constants in ethanol and nitromethane as being due to a difference in the compatibility of water and the organic solvent. It would seem then that any comparison

of aquo-complexing of different cations should be made in the same solvent.

Friedman and Plane (10), in a spectrophotometric study of $\text{Cu}(\text{NO}_3)_2$ and $\text{Cu}(\text{ClO}_4)_2$ determined the degree of aquo-complexing by the displacement of water molecules by ethanol molecules in one case, acetone in another. Failure of either acetone or ethanol to occupy more than two sites in the first coordination sphere was interpreted to indicate a relatively strong, probably planer, 4:1 aquo complex over a wide range of solution compositions. In the case of $\text{Cu}(\text{ClO}_4)_2$, the effect of the anion-cation interaction was found to be essentially zero, but at water concentrations less than 0.5 mole fraction $\text{Cu}(\text{NO}_3)_2$ solutions were slightly more absorbing.

A correlation between the dielectric constant of the solvent and the degree of association of the anion and cation has been attempted (17). It was concluded that as the amount of organic solvent relative to water increases in a solution of $\text{Co}(\text{NO}_3)_2$ or $\text{Co}(\text{ClO}_4)_2$ the dielectric constant decreases, and the anion finally becomes strongly associated with the cation in the "dry" organic solvent. Competition between the water and a basic anion results in the anion finally becoming complexed.

The thinking regarding nitrate complexing has changed through the years. Nitrates dissolved in organic solvents were once thought to be highly associated; then at a later time nitrates were regarded to be, at the most, ion-pair associated except in very dilute solutions, but recent work on the displacement of water by organic molecules has resulted in

a return to the original idea of nitrate to metal bonding in many solutions of nitrates. Perchlorates have always been held as dissociated (though possibly ion-paired) in solution with water and lower molecular weight oxygenated organic solvents.

Several methods have been employed in determining both the average and step-wise formation constants for aquo complexes. The most often used is, of course, spectrophotometry. There seems to have been very few attempts made to use calorimetry in the study of aquo-complexing (30). Such an approach to the problem would not only allow the study of enthalpies, but entropies and free energies also. This, as Marcus (25) has pointed out in his review of liquid-liquid extraction, is of the greatest importance, for much more information is needed on the hydration of ions, both with respect to hydration numbers and to the enthalpy and entropy of hydration in non-aqueous solvents.

Titration Calorimetry. - The principle of enthalpic titrimetry or titration calorimetry is not a new idea. The instrumentation has improved and new applications have been found, however.

In 1901, Steinwehr (32) and in 1926, Lange and Durr (20) used pipettes to add liquid reagent into a calorimeter. As early as 1921, Dutoit and Grobet (7) carried out a step by step thermal titration using a conventional buret introduced into a dewar. For detection of temperature changes, a thermometer with 0.01°C scale divisions was also placed in the dewar.

However, it remained until the 1940's, the time when much of today's laboratory instrumentation was under development for anyone to employ anything but a manually controlled apparatus. In 1948, Lingane (24) described a motor-driven buret and its use in an automatic potentiometric titration. This made possible the use of automatic recorders because the reagent could be added at a constant rate,

Another important phase in the development of titration calorimetry came in 1953 when Linde, Rogers and Hume (23) described the use of thermistors for enthalpy titrations. A thermistor, or thermally sensitive resistor, is a semi-conductor device which has a large negative temperature coefficient of resistance, usually of the order of 4 percent-deg. $^{-1}$ C at room temperature. The combination of high specific resistance, large temperature coefficient, small size, protection by a glass envelope from reagents, and rapid response to changes in temperature makes the thermistor a very useful device for enthalpy titrations. Thermistors are reliable and stable even when used under a variety of ambient temperatures, circuits and voltages (28). Up until the advent of the thermistor, thermocouples and thermopiles were in much use in temperature-sensing equipment. Benedict (2) gives an extensive comparison of the two devices which shows the thermistor to be more sensitive and dependable, especially in the temperature ranges encountered in titration calorimetry.

In 1957, Jordan and Alleman (14) described a calorimeter which

they had developed to use in enthalpy titrations. The buret was non-thermostated, was motor-driven for constant delivery, and dipped into a dewar flask. Temperature variations were measured by a thermistor in a Wheatstone-bridge arrangement and were recorded automatically as volume of titrant versus temperature. As the application of the instrument was to determine the end-point in neutralization reactions, the difference in temperature between the contents of the buret and dewar affected the shape of the curve but not the quantitative results. In 1959, Schlyter (31) described a precision calorimeter for enthalpy titrations in which the buret was maintained at a constant temperature by means of a water bath. The heat capacity of the calorimeter was measured one time and the calorimeter was adjusted to $25 \pm 0.10^{\circ}\text{C}$ after each addition of titrant.

The important features of good enthalpy titration equipment including the use of thermistors to detect temperature changes, and automatic recording of heat effects, is tied together in the American Instrument Co. Menisco-Matic Titra-Thermomat described by Jordan (15). The instrument has a 30 ml. capacity beaker which contains the solution to be titrated, a stirrer, a heater, a thermistor and the tip of a motor-driven buret. The buret is not thermostated; rather it is insulated to minimize heat gain or loss.

When work was first begun in this laboratory, measuring heats of hydration to study the complexing of inorganic salts in organic solvents,

a manually controlled semi-micro buret, 250 ml. dewar, thermistor, and recording potentiometer were used. The large volume of solution required and the poor protection against atmospheric moisture were serious drawbacks to this calorimeter, and it became necessary to redesign the equipment. Although a Titra-Thermomat was available, this instrument was not regarded as precise enough for the planned investigation.

A new calorimeter was built which is described in detail in the following chapter. The advantages of this calorimeter over the Titra-Thermomat are (1) increased volume of solution in a dewar flask (150 ml. compared with 30 ml.), (2) the entire system, buret and dewar, are more nearly adiabatic in operation and maintained much closer to the same temperature and (3) the sensitivity and precision are much improved.

CHAPTER II

THE CALORIMETER

Components. - A sketch of the calorimeter assembly is shown in Figure 2. The calorimeter vessel consisted of a 150 ml. capacity dewar flask suspended in an air bath whose temperature was closely regulated with a Yellow Springs Instrument Co. Thermistemp Temperature Controller. The outer jacket of the calorimeter was made of insulating bakelite material with a heater and fan mounted inside to insure a uniform environment for the dewar flask and its contents.

The dewar (D), which composed the bottom half, was coupled by a ground flange (G) to a glass solvent-tight lid (A). Through the lid was inserted the liquid reagent delivery needle (B), thermistors (C, I) for temperature detection and the large copper leads (H) from the internal heater (E). The heater itself was made from 40 gauge platinum wire, 30 ohms of which was wound on a cylindrical glass form. The platinum wire was connected to the copper leads through a mercury junction.

Two Veco (#32A30) 2000-ohm thermistors were calibrated and used together with a Rubicon Co. (catalog #3403HH) galvanometer ($0.0051 \mu\text{a-mm.}^{-1}$) in a shielded dc Wheatstone-bridge arrangement to monitor the temperature of the solution and also that of the buret. The

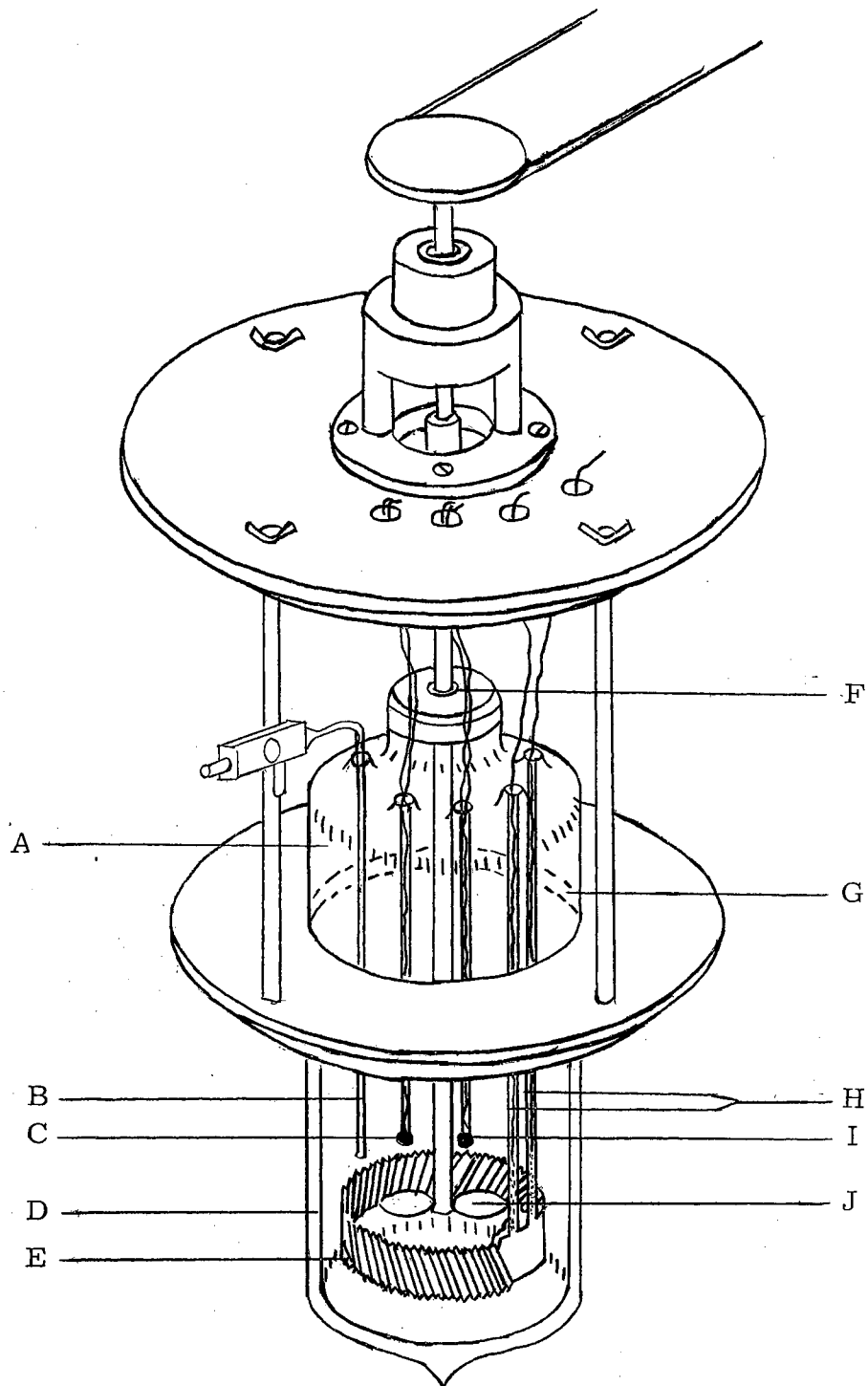


Figure 2. The Calorimeter

third thermistor was a Veco (#51A1) 10^5 -ohm probe constituting one arm of a shielded dc Wheatstone-bridge. The bridge voltage was provided by a Willard low-discharge 6-volt battery. It was found that the potential across this bridge held very constant. This circuit had as the detector of unbalanced current on the Wheatstone-bridge a Sargent Model SR recording potentiometer. The recorder, through interchangeable range-plugs, had several available sensitivity settings. A compromise could be reached whereby electrical noise caused by stirring could be minimized and at the same time the high sensitivity of the 10^5 -ohm thermistor fully utilized.

The stirrer blade and shaft (J) were made of Pyrex. The stirrer was connected through a plastic sleeve and ball bearing (F) to the shaft of the metal pulley on the outside of the calorimeter jacket by a latex sleeve joint. The latter greatly reduced any heat loss or gain by conduction to the calorimeter. The stirring rate was closely controlled with a Cole-Parmer, GT-21, thyatron controller.

A diagram of the circuit for the calibration heater is shown in Figure 3. The platinum heating element was entirely immersed and exposed to the solution in the dewar. By doing this thermal lags were made negligible. The mercury connection and copper leads from the calorimeter were made 12 gauge in order to make sure that any resistance in the leads outside the calorimeter would be very small compared to the resistance of the platinum heater. The heater circuit received

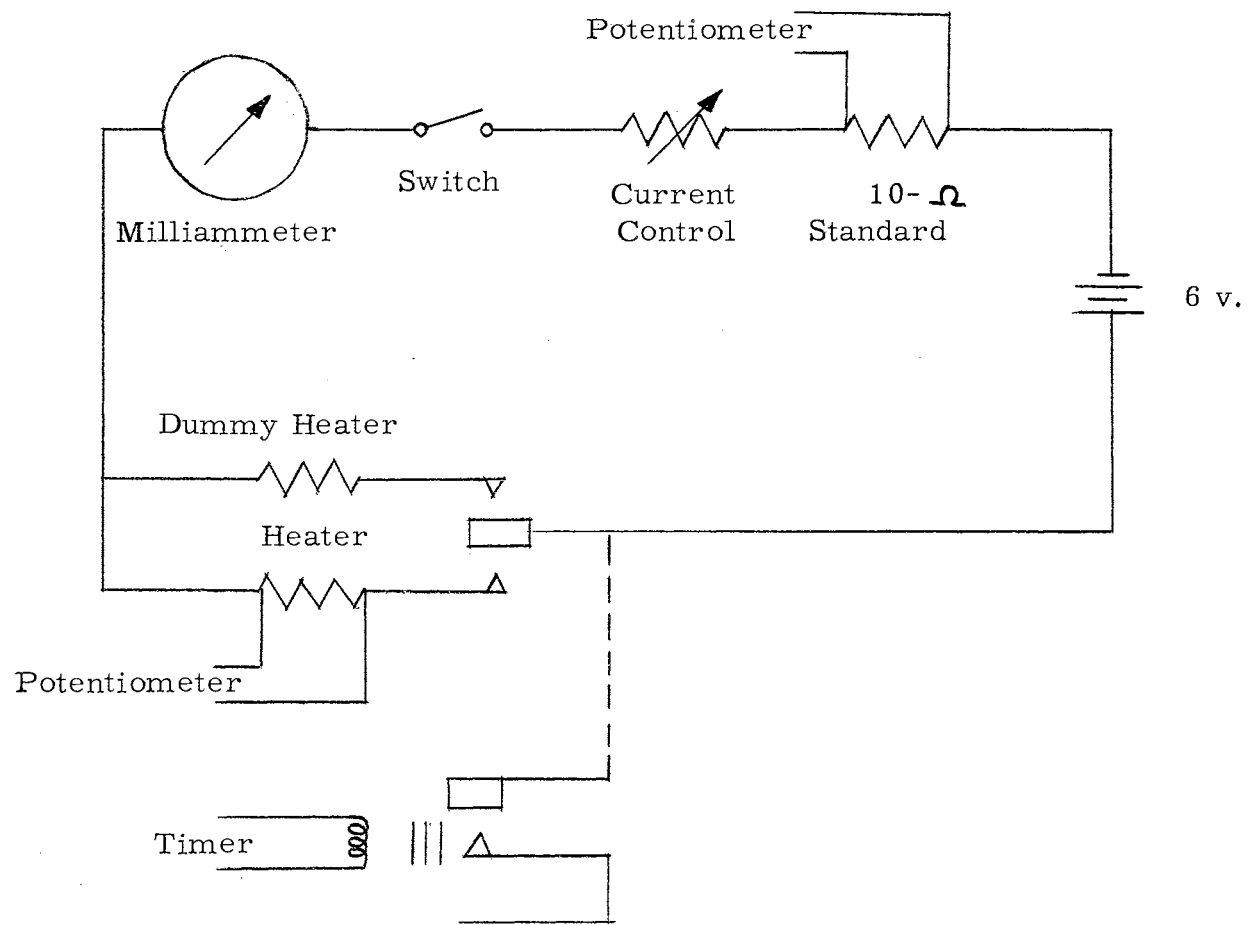


Figure 3. The Calorimeter Internal Heater Electrical Circuit

current from an isolated 6-volt storage battery; this was used because it was found that the voltage from the laboratory outlets was variable over the 90-second intervals used in measuring the heat capacity of the solution in the calorimeter.

The resistance of the internal heater was measured over a range of temperatures so that when the circuit to the internal heater was open, the same current could be caused to flow through a dummy heater of approximately the same resistance as the internal heater at the operating temperature of the calorimeter. The dummy heater was a decade resistance box.

When the circuit was closed to the internal heater by means of an X-ray timer switch, a Standard Time Co. (Model SI) timer was activated through a relay and then deactivated when the timer switch opened the circuit at the end of each preset time interval. The time was determined to the nearest 0.01 second.

The current used in the measurement of the heat capacity of the solution in the dewar was approximately 50 milliamperes. This value of the current was chosen in order that the same potentiometer (Rubicon Instrument Co., Model 2730) could be used by switching to measure both the voltage drop across the heater and across a General Radio (Series 500) secondary laboratory standard 10-ohm ($\pm 0.05\%$) resistor in series with the heater. This resistor had a resistance of 10.002 ohms when compared with a Leeds and Northrup Co. (Cat. #4025-B) standard

10.0000-ohm resistor.

Liquid reagent was added through a stainless steel needle; throughout the addition of reagent the end of the needle was kept beneath the level of liquid in the dewar. An American Instrument Co. Menisco-Matic buret delivered the reagent into the solution. This was a synchronous-motor-driven micro syringe having a digital readout of the volume delivered. The buret had a total capacity of approximately 3.2 ml., and the volume delivered could be read directly to 0.0001 ml. Any arbitrary increment of reagent could be added at a constant delivery rate.

A preliminary calibration of the buret was made. Weighed amounts of water delivered by the buret were converted to the corresponding volumes by density data and compared with the digital volume readings. It was found that the volume delivered was actually 0.983 of the volume shown on the digital dial. This correction was incorporated in all of the calculations.

When the rates required for the addition of reagent were less than that provided by the Menisco-Matic buret motor, a thyatron controlled motor of variable speed was used. This offered a much wider range of addition rates to coincide with the different systems encountered in the course of the research.

Sensitivity. - A calibration of the two 2000-ohm thermistors gave a linear $0.014 \text{ deg.} \cdot \text{-ohm}^{-1}$ relationship over the $25\text{-}27^{\circ}$ range. The individual runs made with the calorimeter were carried out within this

temperature span. A calculation of the quantity of heat added or subtracted from the solution in the dewar arising from the difference in temperature between the buret and the solution showed that no correction was necessary for temperature differences up to 0.1° because of the small increments added. Thus a 0.1 gm. water addition would change the temperature of the calorimeter contents by less than 0.0001° . The buret attained the temperature of the calorimeter jacket rapidly, and therefore the difference in temperature could be controlled easily within 0.1° . Usually, this difference in temperature was less than 0.05° . For this reason a thermometer with a $65-95^{\circ}\text{F}$ scale graduated in 0.05°F divisions was considered adequate for the comparison of the resistance of the two thermistors.

The 10^5 -ohm thermistor used to measure the heats of reaction had a temperature coefficient of resistance of $4.6\% \text{ deg.}^{-1}$. This is equivalent to $-4600 \text{ ohm-deg.}^{-1}$ at 25° . When aqueous solutions were in the dewar and the one millivolt range-plug was used in the recorder, the full sensitivity of the system was utilized corresponding to 65 ohms for full scale deflection of the recorder pen. This is equivalent to about $0.08 - 0.09 \text{ calories-cm.}^{-1}$ depending on the weight and temperature of the solution. However, when ethyl alcohol solutions were in the dewar, the 2.5 mv. range-plug was used in the recorder since there was considerable stirring noise introduced; presumably this was due to the lower density and heat capacity of the alcohol. The 2.5 mv. plug gave a

sensitivity of 0.10 - 0.12 calories-cm.⁻¹, corresponding to 170 ohms for full scale deflection.

A 6-volt potential was impressed across the thermistors at all times to assure stability and uniformity of response (28).

The values of current, resistance of the heater, and time were measured to four significant figures. The timer had 0.01 second divisions and the heating runs were about 90 seconds duration. The method used in calculating the heat capacity of the calorimeter was to find the values of h from

$$h = i^2Rt/4.186d$$

where

- i = current, amps
- R = heater resistance, ohms
- t = time, seconds
- d = recorder deflection, cm.
- 4.186 = Joules/calorie.

This gave a value of h in calories-cm.⁻¹ at a given temperature. Any single measurement of the heat capacity raised the temperature of the solution less than 0.014°, and usually 2 or 3 successive measurements could be made without increasing the temperature more than this. When corresponding calibrations were compared, the results were always within about 1% of each other. This deviation possibly occurred because the calibration times, chosen to give a quantity of heat corresponding to approximately the amount of heat produced when an increment of solution or water from the buret was added, were long enough that significant

fluctuations or drifts arising from the instability of the battery may have occurred. Also, any differences in the time required for the heater resistance to reach a constant value when the current was switched on would contribute to the 1% variation observed. Current and resistance measurements were taken midway through a given run in an attempt to obtain average values.

Performance Test. - The overall performance of the calorimeter and associated components was tested by a measurement of formation of water by the reaction in solution:



Listed in Table I are the results from a typical series of determinations.

Approximately 0.15N hydrochloric acid was prepared by diluting reagent grade (Fisher Scientific Co.) acid with carbonate-free distilled water. Reagent grade (Fisher Scientific Co.) sodium hydroxide was first dissolved in distilled water, and then barium chlorate was added to precipitate the carbonate. The solution was filtered very quickly and then stored in a polyethylene bottle. The base was standardized against potassium acid phthalate (Merck and Co., primary standard) and the acid against tris-hydroxymethylamino-methane (Fisher Scientific Co., primary standard). A weighed amount of the acid, about 4 gm., was added to approximately 125 gm. of water which had been weighed into the calorimeter dewar. The number of milliequivalents of base per gram of acid

TABLE I
 EXPERIMENTAL MEASUREMENT OF THE HEAT OF
 FORMATION OF WATER AT 27.7°C

| Solution Temperature | Buret Temperature | Volume NaOH | Millimoles NaOH | Total Calories | ΔH_f |
|----------------------|-------------------|-------------|-----------------|----------------|--------------|
| 27.67 | 27.62 | 0.2044 | 0.0689 | 0.903 | 13.11 |
| 27.67 | 27.62 | 0.1945 | 0.0655 | 0.863 | 13.18 |
| 27.69 | 27.62 | 0.1995 | 0.0672 | 0.891 | 13.26 |
| 27.69 | 27.64 | 0.1969 | 0.0664 | 0.870 | 13.10 |
| 27.69 | 27.64 | 0.1966 | 0.0663 | 0.877 | 13.23 |
| 27.72 | 27.67 | 0.2425 | 0.0817 | 1.079 | 13.21 |
| 27.72 | 27.67 | 0.2477 | 0.0835 | 1.100 | 13.17 |
| 27.73 | 27.67 | 0.2194 | 0.0739 | 0.979 | 13.25 |
| Average: 13.19±0.05 | | | | | |

had been determined, so the endpoint of the neutralization could be calculated with accuracy as a further check on the performance of the calorimeter. The concentrations chosen for the acid and base were such as to allow approximately 0.2 ml. increments of the sodium hydroxide to be added to the acid in the dewar. The heat liberated was then sufficient to give a full scale deflection of the recorder using the 1 mv. range-plug.

The method used in calculating the heat of formation, ΔH_T , of water at temperature T was as follows:

$$Q_T(\text{cal.}) = h \cdot d$$

where h is the number of calories required to produce one cm. of deflection and d is the number of cm. of deflection. The heat added or subtracted as a correction because of a difference in the temperatures of the buret and solution in the dewar was calculated by

$$Q'_T(\text{cal.}) = C_p \cdot \Delta T \cdot W.$$

Here C_p is the heat capacity of water, ΔT is the difference in temperature between the buret and solution in the dewar, and W is the weight of NaOH solution delivered by the buret in a particular increment. Then adding Q_T and Q'_T and dividing by the number of milliequivalents of base added, the number of kilocalories of heat produced per mole of water formed, ΔH_T , was found. Calculation of the correction for the heats of dilution of HCl, NaOH, and NaCl showed that this correction was negligible.

The heat of formation of water has been found to decrease by 0.248 kcal-mole⁻¹ in going from 25° to 30° (29). By linear interpolation, the correction to the most recent literature value of -13.34 kcal. for the heat of formation per mole is -0.13 kcal. (11). This gives -13.21 kcal-mole⁻¹ compared with -13.19±0.05 kcal-mole⁻¹ found experimentally.

The degree of agreement (±0.4%) is within the desired precision of the calorimeter (1%). The performance of the calorimeter for the measurement of quite small heat increments is thus good. In comparing the results of measurements of the heat of neutralization with the recent literature values, it should be emphasized that the actual number of calories measured in the calorimeter was only approximately 0.01 that measured, for example, by Hale, Izatt and Christensen (11). The calorimeter was designed to measure heats of reaction of the order of one calorie with an accuracy of 1% or better. This seems to have been achieved. Furthermore, the calorimeter was designed to permit successive metered additions of reagent, and the overall accuracy includes any errors in the volumetric addition of reagent.

Heat of Mixing of Ethanol and Water. - A higher degree of precision was obtained in the measurement of the heat of mixing of water and ethyl alcohol. In these measurements the water was added in increments of about 0.03 ml., releasing about two calories per increment. Each series covered a relatively large temperature range (0.6°) and required repeated measurement of the heat capacity because of the progressive increase in

temperature and change in the composition of the solution.

The values tabulated in Table II for the heat of formation of a 1.0 molal solution of water in ethanol show about a 0.3% variation for three determinations.

TABLE II
EXPERIMENTAL MEASUREMENT OF THE HEAT OF
MIXING OF WATER AND ETHYL ALCOHOL

| ΔH_{mix} (1 molal) | ΔH_{mix} (1.142 molal) | Average Temperature |
|-----------------------------------|---------------------------------------|---------------------|
| 0.404 | 0.021 | 25.0 |
| 0.402 | 0.021 | 26.7 |
| 0.403 | 0.021 | 27.0 |

As a further check on the accuracy of the calorimeter the values for the heat of formation of a 0.05 mole fraction solution (1.142m) of water in ethanol solution was calculated from experimental data. This was done in order to make a comparison with the meager data in the literature. The literature value of 7 cal.-mole⁻¹ ethanol does not compare favorably with the value of 21 cal.-mole⁻¹ obtained in this work (33). This difference in values may have been due in part to the manner in which they were obtained. Whereas the ethanol solutions employed in this research were relatively "dry" (0.04% water) and required very

little extrapolation back to a completely dry solution, the methods used in previous work necessitated a long extrapolation from heat of dilution of ethanol in water data (29). In other words, the shape of the mixing curve at very low water concentrations was directly measured during the course of this research.

CHAPTER III

EXPERIMENTAL METHOD AND PROCEDURE

Preparation of Solutions and Analytical Procedures. - Ethanolic solutions of partially dehydrated cobalt (II) nitrate hydrate were prepared by dissolving oven dried (50°) reagent grade (Fisher Scientific Co.) cobalt (II) nitrate hexahydrate in U. S. P. - N. F. absolute alcohol (U. S. Industrial Chemicals Co.). The hydrous cobalt (II) perchlorate solutions in ethanol were prepared in the same manner using reagent grade cobalt (II) perchlorate hexahydrate (G. F. Smith Chemical Co.) which had been oven dried at 135° . Aqueous solutions of both the nitrate and perchlorate were found to have a pH very close to 7 after the drying procedure.

The alcoholic solutions were passed through a column of molecular sieve material (Type 3A, Linde Division, Union Carbide Corporation) for further drying. All solutions were tested for and found to contain no sodium or chloride.

Cobalt concentration was determined by EDTA titration using murexide as the indicator (9).

The water content of the solutions was determined by the Karl Fischer method using standard procedures (27). The solutions in the calorimeter initially had water-salt mole ratios in the range of from 0.1 to 0.3.

Solution densities were determined using standard pycnometric techniques. A density versus total metal concentration plot was made for each of the two systems under investigation so that weight concentrations could be converted to volume concentrations as needed.

Procedure for Operation of the Calorimeter. - The calorimeter dewar was first filled with approximately 150 ml. of solution and clamped tightly to the flanged top, which held in place the heater, thermistors, stirrer, and liquid reagent delivery needle. The calorimeter dewar was next placed inside the insulating jacket. The buret and delivery needle were then connected, both having first been filled completely with distilled water. A three-way connecting valve was opened between the buret and a water reservoir, and the buret was activated for a few seconds to drive out any air that might be trapped. The valve was then opened between the buret and needle; however, no water flowed from the buret except when the buret was activated. The calorimeter jacket port was then closed, and the stirrer started.

By means of the internal and external heaters the calorimeter temperature was raised about 2° above that of the room ($24-25^{\circ}$). This was done in order to better control the heat gain or loss by the solution in the dewar. At the elevated temperature it was much easier to obtain a temperature-time curve whose slope approached zero.

Before any water was added to the solution from the buret, several heat capacity calibrations were made to insure that the calorimeter was

functioning properly. Measured quantities of water were then added, time being allowed before and after each increment to attain, again, a constant slope in the temperature-time curve. The temperatures of both the solution and buret, and the volume of water delivered by the buret were recorded. Since each run covered a span of about 1° in temperature, the heat capacity was checked by two or three calibrations at intervals of about 0.2° .

When the water in the buret had been expended and the final heat capacity calibrations made, the apparatus was turned off. The valve between the buret and needle was closed to make certain that no more water could flow into the solution. The buret was then uncoupled, and the dewar was removed from the calorimeter and weighed immediately. The parts of the calorimeter which had been in contact with the solution were now washed and submerged in distilled water.

Solutions were weighed at the end of a run rather than at the start in order to minimize both evaporation and the amount of moisture absorbed from the air. The weight of the added water was subtracted from the total weight. It was determined in preliminary experiments that the weight of a solution after being placed in the calorimeter and allowed to reach equilibrium was not significantly different from the weight of the solution initially present. This meant that the small amount of solution which clung to the heater, etc. was negligible. The solutions, which were about 125 gms., were weighed to the nearest ten milligrams. The

solutions were found to absorb a small amount of water during the transfer from storage bottle to dewar and presumably also from the glass of the dewar and lid. Therefore, determination of the water content of the solutions was made on samples withdrawn just prior to the first heat capacity measurement.

CHAPTER IV

TREATMENT OF THE DATA AND RESULTS

It was shown in Appendix B, that the molar heat of reaction, $\Delta \bar{H}_r$, is given by

$$\Delta \bar{H}_r = \sum_{1}^N a_n x_n \quad (1)$$

where a_n is the fraction of metal in the n th complex and x_n is the enthalpy of formation of the n th complex in solution. In order to use the principle of corresponding solutions in treatment of the data to obtain the average ligand number, and the free or unbound water, $\Delta \bar{H}_r$ must be experimentally evaluated.

The experimental value of Q , the heat liberated in the calorimeter, may be thought of as consisting of two parts. One is the heat of mixing of ethanol and water. The other part is simply the heat of exchange of water molecules for solvating molecules and/or coordinated anions. The latter corresponds to eq. (1) above. As pointed out in Chapter I, there is evidence that $\text{Co}(\text{ClO}_4)_2$ in ethanol solution probably exists as $[\text{Co}(\text{EtOH})_6^{++}] (\text{ClO}_4)^-$ with the anions outside the first coordination sphere. These may be partly associated as ion pairs, however. On the other hand, $\text{Co}(\text{NO}_3)_2$ in ethanol apparently involves some slight

degree of cation-anion coordination. Therefore, the species which might exist in equilibrium in solution are $\left[\text{Co}(\text{EtOH})_6^{++} \right] (\text{NO}_3)_2$, $\left[\text{Co}(\text{EtOH})_5 \text{NO}_3^+ \right] \text{NO}_3^-$ and $\text{Co}(\text{EtOH})_4 (\text{NO}_3)_2$.

In order to obtain $\Delta \bar{H}_r$, the heat of mixing of ethanol and water, $\Delta \bar{H}_{\text{Mix}}$, must be subtracted from the total heat of reaction per mole of salt, $\Delta \bar{H}_T$ (35).

$$\Delta \bar{H}_r = \Delta \bar{H}_T - \Delta \bar{H}_{\text{Mix}}. \quad (2)$$

In this chapter there are described possible methods of calculating $\Delta \bar{H}_T$, $\Delta \bar{H}_{\text{Mix}}$ and $\Delta \bar{H}_r$ which will permit the treatment of data by corresponding solutions. The results obtained by these methods for the systems under investigation are presented.

Determination and Calculation of the Heat of Reaction. - The value of Q , the number of calories liberated in the calorimeter, was calculated in the same manner for the salt-ethanol-water reactions as for the heat of formation of water described in Chapter II. Thus,

$$Q = h \times d + (T_S - T_B) \cdot C_P \cdot W \quad (3)$$

where

| | | |
|-------|---|--|
| Q | = | total calories |
| h | = | heat capacity of solution, cal.-cm. ⁻¹ |
| d | = | recorder deflection, cm. |
| T_S | = | temperature of solution, °C |
| T_B | = | temperature of buret, °C |
| C_P | = | heat capacity of water, cal.-gm. ⁻¹ -deg. ⁻¹ |
| W | = | weight of water, gm. |

Following each increment of water added to the dewar, the

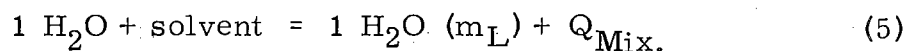
following experimental quantities were determined:

- (1) Total calories evolved, Q
- (2) Total moles of H_2O , y
- (3) Total moles of salt, z
- (4) Volume of solution, V

The total increase in enthalpy per mole of salt was then calculated from

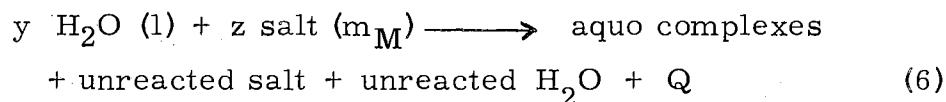
$$Q/z = \bar{\Delta H}_T \quad (4)$$

In order to obtain $Q_{\text{Mix.}}$ and therefore, $\bar{\Delta H}_{\text{Mix.}}$ water was added in small increments to ethanol in the dewar, and the number of calories per mole of water was calculated for the reaction

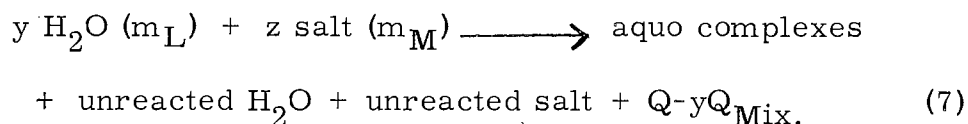


A plot of $Q_{\text{Mix.}}$ versus the molality of the water was then constructed and used to find the partial molal heat of mixing of water with ethanol.

Consider the following process in the calorimeter. To z moles of salt M at molal concentration m_M there is added y moles of water, liberating Q calories of heat. The latter may be partitioned into the differential heat of solution of y moles of water in a m_L solution of water in ethanol and the heat of reaction of y moles of water at concentration m_L with z moles of salt at concentration m_M to form a series of aquo complexes. For the process, therefore, one has the overall reaction equation



The heat of mixing, $Q_{\text{Mix.}}$, is given by eq. (5) above so that one has after combining,



The reference solutions of water and salt in ethanol are solutions of concentrations m_L and m_M respectively, and since these are arbitrary, consideration must be given to their choice. Ideally, all thermal properties should be referred to the infinitely dilute state, but this necessitates knowledge of the heats of dilution of both reactants and products. While it is possible to make measurements of the heats of dilution of the reactants, clearly this is not possible for the aquo complexes. The alternatives are (1) to study the reaction at high dilutions or (2) to assume that the nature of the reacting substances and products are such that their partial molal enthalpies at experimental concentrations are essentially constant. The latter approach was adopted and the consequences of this assumption will be discussed.

From the plot of $Q_{\text{Mix.}}$ versus m_L , the heat of forming a 1.0 molal solution of water in ethanol was found to be $0.403 \text{ kcal-mole}^{-1} \text{H}_2\text{O}$ (Table II, Chapter II).

It is obvious that $0.403 \text{ kcal-mole}^{-1} \text{H}_2\text{O}$ is the apparent molal heat of mixing of water with pure solvent to give a 1.0 molal solution of water in ethanol assuming the enthalpy of liquid water is zero. It is

also the average of the partial molal values over the range of water concentrations from 0-1.0 molal.

From the definition for the heat of mixing,

$$d Q_{\text{Mix.}} / d N_L = \bar{H}_L - \bar{H}_L^{\circ} \quad (8)$$

where $Q_{\text{Mix.}}$ is the heat obtained experimentally, N_L is the moles of water, \bar{H}_L is the partial molal enthalpy of water in the mixture, and \bar{H}_L° is the molal enthalpy of pure water, the partial molal heat of mixing for a one molal solution would be the slope at that point, or 0.338 kcal-mole⁻¹ H₂O. The manner in which the water was added, i. e. incrementally, permitted an experimental approximation to $d Q/d N_L$. The slope at various water concentrations, obtained from the experimental values of $\Delta Q/\Delta N_L$, varied from 0.511 to 0.338 kcal-mole⁻¹ H₂O at concentrations of 0.009 and 1.000 molal water in ethanol respectively.

Because of the variation in $\Delta Q/\Delta N_L$ over the range of water concentrations employed, the average value of 0.403 kcal-mole⁻¹ H₂O was thought to be the best approximation to the true heat of mixing values when calculating the heat of reaction; this will be discussed later, however.

It should be noted that a direct measure of the heat evolved for the reaction of the water initially present in the solutions was not possible. A value for Q was obtained from a short extrapolation to zero water concentration on a Q versus total water concentration plot.

Corrections for the contraction of ethanol when water was added were not considered necessary in the calculations. For ten weight-percent of water, they are about one percent (12). Never more than three weight-percent of water was encountered in the research.

Calculation of the Heat of Mixing for Five Mole Per Cent Water in Ethanol. - As a preliminary check upon the accuracy of the calorimeter, the heat of forming a 0.05 mole fraction water solution was calculated for comparison with literature values. The values of the heat liberated are shown in Table II, Chapter II for 0.05 mole fraction water in ethanol (1.142 molal). For a given solution in the calorimeter, the number of moles of ethanol, s , was, of course, constant. Therefore if y represents the moles of water added to form a 0.05 mole fraction solution,

$$y/(y + s) = 0.05 \quad (9)$$

$$y = s/19 \quad (10)$$

The number of calories, Q , liberated when $s/19$ moles of water had been added was divided by the moles of ethanol in the solution. The resulting values averaged 21 kcal-mole⁻¹ of ethanol, which can be compared directly with data in the literature. The comparison was made in Chapter II, and possible reasons given there for the disagreement between the two sets of values.

In Table III, is listed the experimental data for the three determinations of the heat of mixing of water and ethanol.

TABLE III

CALORIMETRICALLY DETERMINED HEAT OF MIXING DATA
FOR THREE SOLUTIONS OF WATER AND ETHANOL

| 1 | | 2 | | 3 | |
|----------------------|-------------------|----------------------|-------------------|----------------------|-------------------|
| 125.19 Grams Ethanol | | 122.49 Grams Ethanol | | 117.50 Grams Ethanol | |
| 24.8 - 25.2° C | | 26.7 - 27.3° C | | 26.6 - 26.9° C | |
| Millimoles Water | Total Calories | Millimoles Water | Total Calories | Millimoles Water | Total Calories |
| 3.61 | 1.30 | 2.51 | 1.10 | 2.15 | 1.10 |
| 7.49 | 3.06 | 6.42 | 2.93 | 6.93 | 3.49 |
| 11.74 | 4.90 | 10.35 | 4.74 | 10.82 | 5.39 |
| 15.85 | 6.76 | 14.76 | 6.64 | 15.97 | 7.72 |
| 20.13 | 8.78 | 19.28 | 8.75 | 21.01 | 10.07 |
| 24.36 | 10.72 | 24.35 | 11.05 | 26.56 | 12.60 |
| 28.84 | 12.76 | 29.39 | 13.30 | 33.02 | 15.41 |
| 33.19 | 14.70 | 34.12 | 15.35 | 35.72 | 16.57 |
| 37.60 | 16.65 | 37.98 | 17.03 | 40.38 | 18.58 |
| 42.12 | 18.57 | 42.09 | 18.76 | 46.84 | 21.27 |
| 46.86 | 20.56 | 46.87 | 20.83 | 53.48 | 23.97 |
| 51.76 | 22.66 | 52.01 | 22.99 | 59.80 | 26.55 |
| 56.71 | 24.75 | 57.44 | 25.24 | 66.84 | 28.97 |
| 61.94 | 26.76 | 62.68 | 27.44 | 74.02 | 31.75 |
| 67.00 | 29.01 | 68.17 | 29.57 | 81.44 | 34.52 |

TABLE III (Continued)

| | | | | | |
|--------|-------|--------|-------|--------|-------|
| 71.88 | 30.96 | 74.36 | 31.94 | 89.08 | 37.40 |
| 77.07 | 33.04 | 80.03 | 34.13 | 97.02 | 40.20 |
| 82.73 | 35.27 | 85.75 | 36.27 | 104.69 | 42.88 |
| 88.18 | 37.33 | 91.58 | 38.38 | 112.96 | 45.77 |
| 93.59 | 39.38 | 97.77 | 40.56 | 120.74 | 48.40 |
| 99.41 | 41.55 | 104.48 | 42.93 | 128.98 | 51.12 |
| 105.00 | 43.59 | 110.97 | 45.14 | 137.74 | 53.90 |
| 110.87 | 45.67 | 117.68 | 47.40 | 146.69 | 56.70 |
| 116.97 | 47.80 | 124.26 | 49.55 | | |
| 123.07 | 49.90 | 131.26 | 51.77 | | |
| 129.11 | 52.02 | 138.14 | 53.99 | | |
| 135.26 | 54.10 | | | | |
| 141.11 | 56.03 | | | | |
| 147.52 | 58.11 | | | | |

Corresponding Solutions. - In the following discussion $\Delta\bar{H}_r$, the increase in the enthalpy per mole of salt attending the reaction of water at molality m_L with the salt solutions, will be referred to as $\Delta\bar{H}$ for simplicity. The total volume concentration of water present in a solution is C_L , the total salt concentration is C_M , and the concentration of unbound water is (H_2O) . All concentrations are given in moles-liter⁻¹. A general discussion of the relationships between $\Delta\bar{H}$, C_L , C_M , (H_2O) , and \bar{n} will be presented in this section. Actual results obtained for the particular systems investigated will be presented in the sections following.

Values of $\Delta\bar{H}$ and C_L were determined after each increment of water, and curves of $\Delta\bar{H}$ versus C_L for several solutions of the same system (e. g., $Co(ClO_4)_2 - EtOH - H_2O$) were plotted on the same graph (Figures 4 and 9).

According to the corresponding solutions principle, if for, say, three concentrations of C_M , $\Delta\bar{H} = \Delta\bar{H}' = \Delta\bar{H}''$, the solutions have the same \bar{n} and the same (H_2O) . Therefore, in accordance with the defining equation for \bar{n} ,

$$(H_2O) = C_L - \bar{n} C_M, \quad (11)$$

a plot of C_L versus C_M for solutions having the same $\Delta\bar{H}$ values gave lines of slope \bar{n} , and intercepts of (H_2O) (Figure 5 and 11).

The statistical \bar{n} versus $\log (H_2O)$ curves were calculated by the method of Bjerrum (5) described in Appendix B and compared to the

experimental aquo complex formation curves (Figure 6).

The differential heat of reaction, $\Delta Q/\Delta N_L$, curve was also calculated for each increment and plotted versus the C_L/C_M ratio to determine when the hydration reaction was complete (Figures 8 and 10).

The values of $\Delta\bar{H}$ were plotted versus the C_L/C_M ratio for further comparison of the degree of hydration of the different concentrations of metal ions (Figures 7 and 13).

Results for Cobalt (II) Nitrate-Ethanol-Water System. - Figure 4 represents the integrated curves of $\Delta\bar{H}$ versus the total water concentration for three $\text{Co}(\text{NO}_3)_2$ solutions. The curves were obtained from the data listed in Table IV. The curves were very smooth as would be expected from the small increments of water added. The limited buret volume (ca. 3.2 ml.) restricted the water concentrations for any one titration to values less than one molar, but still sufficient to allow application of the corresponding solutions method.

The corresponding solutions plot is represented by Figure 5 for $\Delta\bar{H}$ values ranging from $0.2 \text{ kcal-mole}^{-1}$ to $3.0 \text{ kcal-mole}^{-1}$. It can be seen that there is a small deviation from linearity for the five uppermost lines. The method of least squares was applied to the three points in each case to obtain the equation of the best straight line. The values of $\Delta\bar{H}$ for which the non-linearity occurred were in the region where a small error in $\Delta\bar{H}$ resulted in a relatively larger error in C_L .

Theoretically, the limiting value of the slopes obtained from such

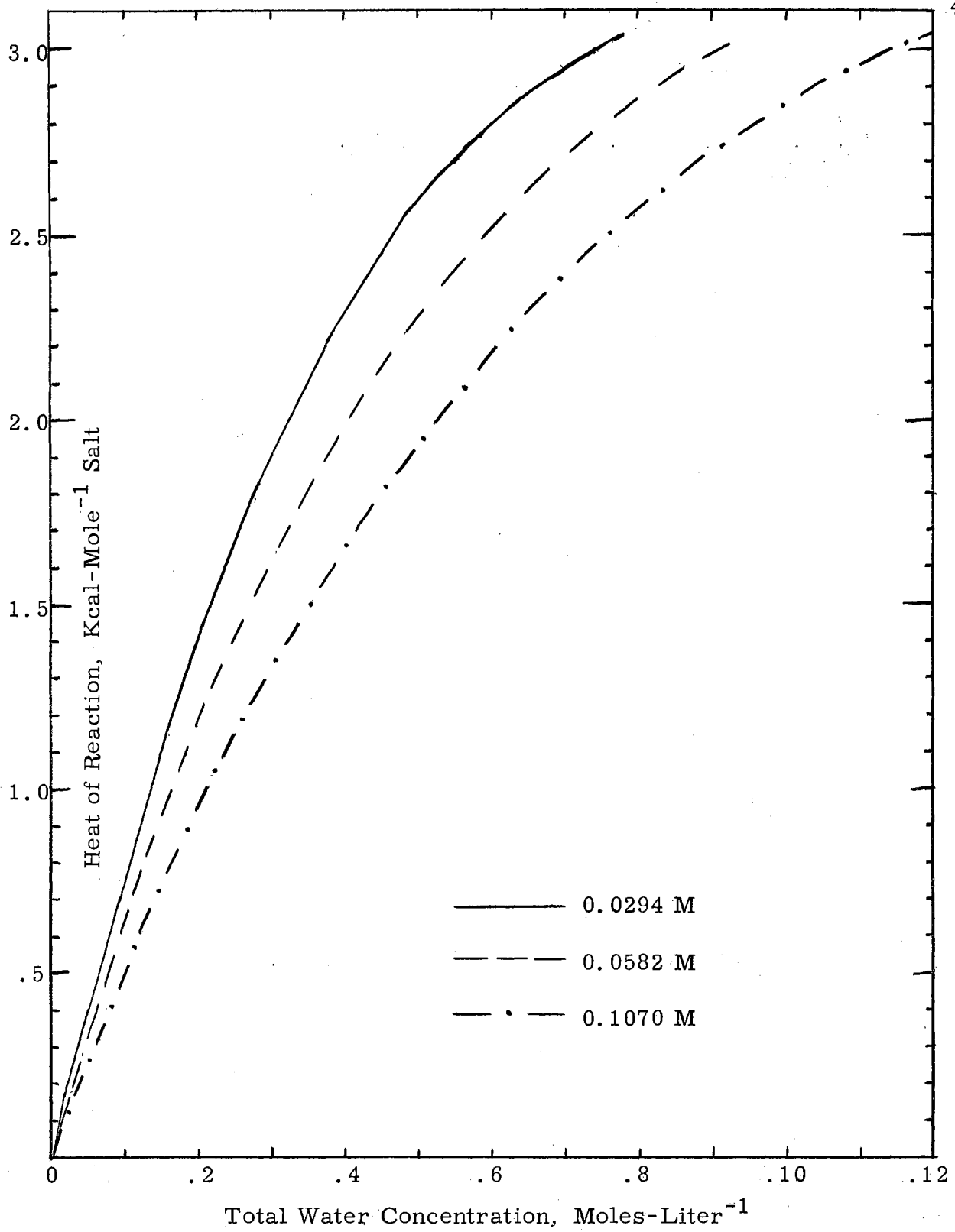


Figure 4. Heat of Reaction of Water with Cobalt (II) Nitrate in Ethanol as a Function of the Total Water Concentration.

TABLE IV

CALORIMETRICALLY DETERMINED HEAT OF REACTION OF
WATER DATA FOR THREE SOLUTIONS OF COBALT (II)
NITRATE IN ETHANOL

| 1 | | 2 | | 3 | |
|----------------------|-------------------|----------------------|-------------------|---------------------|-------------------|
| 0.0294 M (150.4 ML.) | | 0.0582 M (159.8 ML.) | | 0.107 M (151.1 ML.) | |
| 26.2 - 26.8° C | | 26.2 - 27.5° C | | 27.6 - 28.6° C | |
| Millimoles Water | Total Calories | Millimoles Water | Total Calories | Millimoles Water | Total Calories |
| 1.58 | 1.00 | 2.70 | 2.40 | 2.20 | 2.10 |
| 4.64 | 2.82 | 6.18 | 4.78 | 5.22 | 4.97 |
| 8.12 | 5.02 | 8.90 | 6.90 | 8.32 | 7.90 |
| 11.56 | 7.16 | 11.02 | 8.51 | 10.38 | 9.87 |
| 14.67 | 9.08 | 13.78 | 10.58 | 12.61 | 11.95 |
| 18.09 | 11.22 | 16.59 | 12.69 | 15.04 | 14.20 |
| 21.48 | 13.23 | 19.22 | 14.62 | 17.55 | 16.48 |
| 24.56 | 15.05 | 21.87 | 16.50 | 20.20 | 18.84 |
| 28.40 | 17.27 | 25.25 | 18.89 | 22.55 | 20.89 |
| 31.65 | 19.16 | 28.21 | 20.98 | 24.81 | 22.85 |
| 35.17 | 21.10 | 31.65 | 23.36 | 27.58 | 25.22 |
| 38.80 | 23.09 | 35.43 | 25.90 | 29.96 | 27.25 |
| 42.32 | 25.00 | 38.66 | 28.05 | 32.43 | 29.30 |
| 46.14 | 27.06 | 42.12 | 30.35 | 34.70 | 31.21 |
| 49.72 | 28.92 | 45.83 | 32.70 | 37.31 | 33.37 |

TABLE IV (Continued)

| | | | | | |
|-------|-------|--------|-------|--------|-------|
| 53.73 | 31.06 | 49.32 | 34.91 | 39.84 | 35.45 |
| 57.44 | 32.95 | 52.59 | 36.98 | 42.48 | 37.50 |
| 60.96 | 34.73 | 56.11 | 39.20 | 45.07 | 39.53 |
| 65.40 | 36.96 | 59.46 | 41.23 | 48.03 | 41.83 |
| 69.53 | 38.99 | 63.06 | 43.42 | 50.98 | 44.06 |
| 73.66 | 40.98 | 66.78 | 45.67 | 53.93 | 46.22 |
| 77.93 | 43.04 | 70.68 | 47.92 | 56.84 | 48.38 |
| 82.45 | 45.17 | 74.57 | 50.19 | 60.06 | 50.75 |
| 86.88 | 47.24 | 78.42 | 52.32 | 63.20 | 53.04 |
| 90.78 | 49.01 | 82.10 | 54.37 | 66.33 | 55.31 |
| 95.48 | 51.13 | 86.23 | 56.66 | 69.92 | 57.82 |
| | | 90.45 | 58.92 | 73.26 | 60.11 |
| | | 94.50 | 61.10 | 76.78 | 62.51 |
| | | 98.68 | 63.30 | 80.57 | 65.09 |
| | | 103.41 | 65.78 | 84.51 | 67.68 |
| | | 107.96 | 68.12 | 88.22 | 70.16 |
| | | 112.29 | 70.26 | 92.24 | 72.75 |
| | | 116.66 | 72.41 | 96.40 | 75.46 |
| | | 121.45 | 74.76 | 100.76 | 78.16 |
| | | 125.47 | 76.71 | 104.97 | 80.83 |
| | | | | 109.42 | 83.51 |

TABLE IV (Continued)

| | | |
|--|--------|--------|
| | 113.60 | 85.98 |
| | 118.16 | 88.68 |
| | 122.69 | 91.29 |
| | 127.73 | 94.20 |
| | 132.52 | 96.93 |
| | 137.41 | 99.66 |
| | 142.30 | 102.33 |
| | 147.21 | 104.96 |
| | 152.20 | 107.57 |
| | 157.23 | 110.21 |
| | 162.47 | 112.88 |
| | 167.29 | 115.31 |

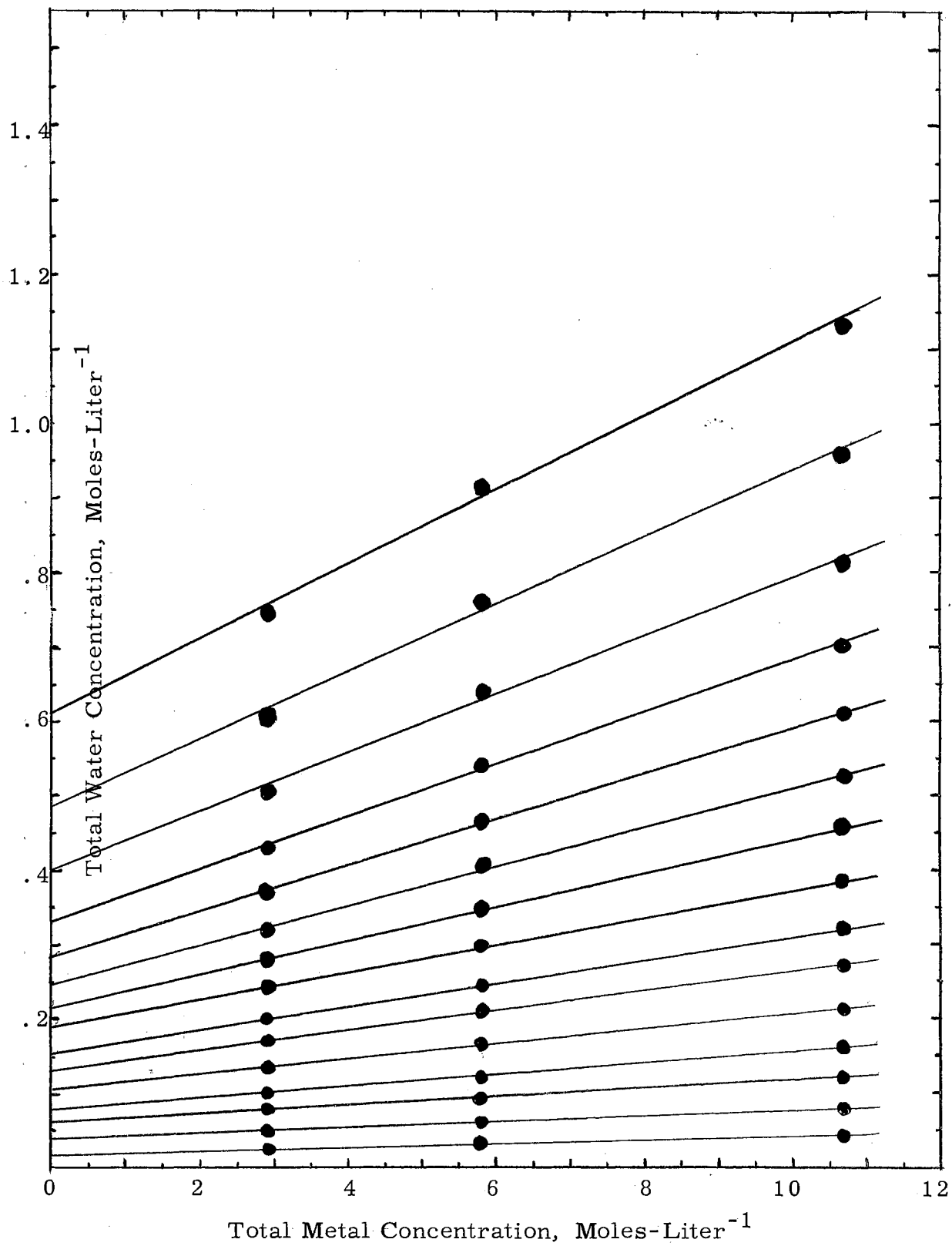


Figure 5. Corresponding Solutions of Cobalt (II) Nitrate in Ethanol.

a plot as Figure 5 should equal the maximum coordination number of the metal ion under investigation. Thus, for solutions containing excess ligand there should be parallel lines with the maximum slope; for these lines the larger the values of $\Delta\bar{H}$, the larger the intercept, (H_2O) .

Listed in Table V are the experimentally obtained values of \bar{n} and (H_2O) . The $\Delta\bar{H}$ values from which they were taken are also included. Figure 6 shows the shape of the formation curve for aquo complexes of $Co(NO_3)_2$ in ethanol using the data from Table V with \bar{n} plotted versus $\log (H_2O)$. The upper portion of the curve at \bar{n} about five appears to be bending over and may become asymptotic to the line representing \bar{n} equal to six.

A value for K_{av} (Appendix C) can be determined for the statistical case when the formation of the aquo complexes is half completed, or assuming a maximum coordination of six, when \bar{n} equals three.

Then

$$K_{av} = 1/(H_2O) = 3.57 \text{ liter-mole}^{-1} \quad (12)$$

from Figure 6.

The stepwise formation constants evaluated from

$$k_n = \left[\frac{(N - n + 1)}{n} \right] K_{av} \quad (13)$$

are: $k_1 = 21.4$, $k_2 = 8.92$, $k_3 = 4.76$, $k_4 = 2.68$, $k_5 = 1.43$, and $k_6 = 0.60 \text{ liter-mole}^{-1}$. The dashed curve, shown in Figure 6, was

TABLE V

EXPERIMENTAL AND STATISTICAL VALUES OF THE FREE
WATER AND AVERAGE LIGAND NUMBER FOR
COBALT (II) NITRATE IN ETHANOL

| Experimental Case | | | Statistical Case for N = 6 and $K_{av} = 3.57$ | |
|-------------------|-----------|--------------------|---|--------------------|
| $\Delta\bar{H}$ | \bar{n} | (H ₂ O) | \bar{n} | (H ₂ O) |
| 0.2 | 0.2 | 0.02 | 0.9 | 0.05 |
| 0.4 | 0.4 | 0.04 | 1.6 | 0.10 |
| 0.6 | 0.6 | 0.06 | 2.1 | 0.15 |
| 0.75 | 0.8 | 0.08 | 2.5 | 0.20 |
| 0.9 | 0.9 | 0.09 | 3.1 | 0.30 |
| 1.2 | 1.3 | 0.13 | 3.5 | 0.40 |
| 1.5 | 1.8 | 0.17 | 3.8 | 0.50 |
| 1.8 | 2.3 | 0.22 | 4.1 | 0.60 |
| 2.0 | 2.7 | 0.25 | 4.3 | 0.70 |
| 2.2 | 3.1 | 0.28 | 4.4 | 0.80 |
| 2.4 | 3.5 | 0.33 | | |
| 2.5 | 3.8 | 0.36 | | |
| 2.6 | 4.0 | 0.38 | | |
| 2.7 | 4.3 | 0.43 | | |
| 2.8 | 4.6 | 0.46 | | |
| 2.9 | 4.8 | 0.50 | | |
| 3.0 | 5.0 | 0.56 | | |

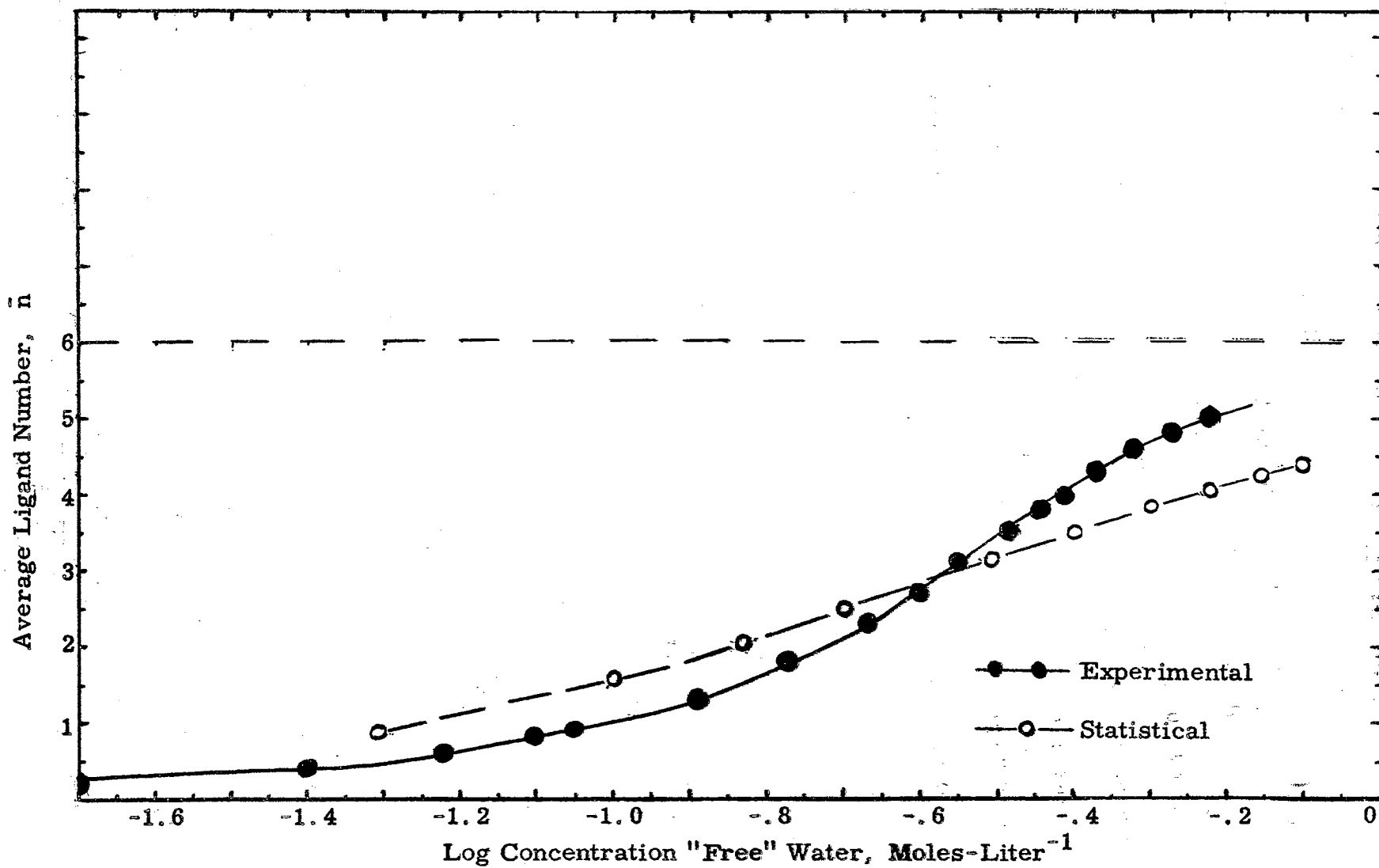


Figure 6. Experimental and Statistical Formation Curves for Aquo Complexes of Cobalt (II) Nitrate in Ethanol.

plotted from the data in Table V for the statistical case. The two curves are much closer together below \bar{n} equal to three than above that value. Apparently the formation of aquo complexes in the $\text{Co}(\text{NO}_3)_2$ system is not adequately described by the statistical approach.

When the correction for the heat of mixing, $0.403 \text{ kcal-mole}^{-1} \text{ H}_2\text{O}$, is subtracted from the total heat evolved for the hydration of cobalt (II) ions in $\text{Co}(\text{NO}_3)_2$, plots of $\Delta\bar{H}$ versus the water-salt mole ratio give the curves of Figure 7. Theoretically, if proper allowance is made for $\Delta\bar{H}_{\text{Mix}}$, the curves of Figure 7 should have zero slope when hydration is complete, for presumably when this occurs, the only interaction is the mixing of water and ethanol. Therefore, if this is subtracted out, the resulting change in $\Delta\bar{H}$ would be zero.

Figure 8 presents the same information in a different manner. The incremental slopes, $\Delta Q/\Delta N_L$, in $\text{kcal-mole}^{-1} \text{ H}_2\text{O}$ are considered in terms of moles of water per mole of salt. The hydration reaction would be expected to be complete whenever the slope of a particular curve became constant and equal to the Q_{Mix} value if this were constant. For larger water-salt mole ratios,

$$\Delta Q/\Delta N_L - Q_{\text{Mix}} = \text{a constant} \quad (14)$$

At the highest water-salt mole ratios obtained, the curves of both Figure 7 and Figure 8 show that the hydration reaction was probably not complete for any of the solutions. The curve representing the most

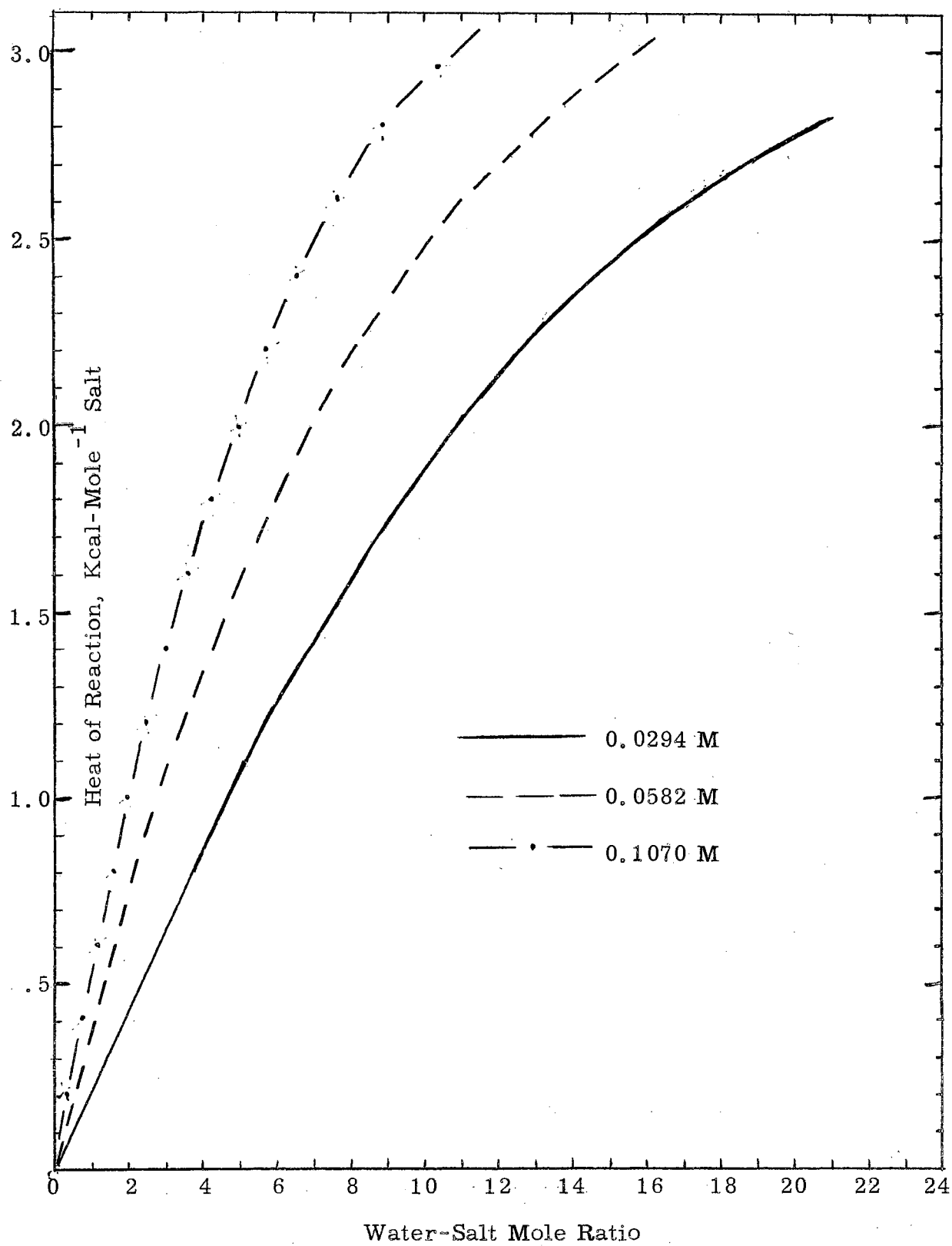


Figure 7. Heat of Reaction of Water with Cobalt (II) Nitrate in Ethanol as a Function of the Water to Salt Mole Ratio.

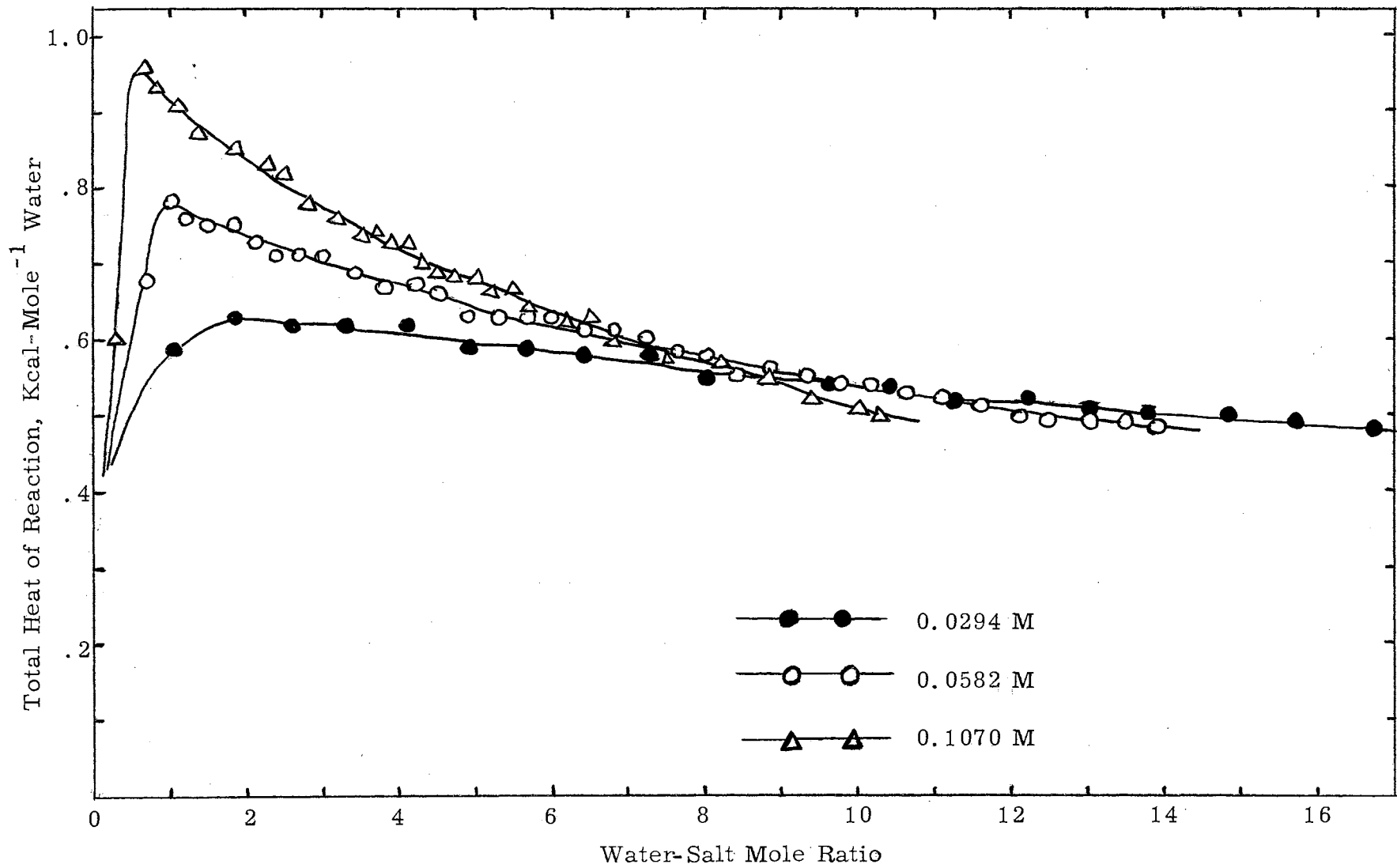


Figure 8. Slopes of the Curves Representing the Total Heat of Reaction of Water with Cobalt (II) Nitrate in Ethanol.

concentrated solution, 0.107 M, approached the (arbitrary) 0.403 kcal-mole⁻¹ value for the heat of mixing most rapidly, however.

It should be noted also that initially the curves in Figure 8 increase and then decrease. Several factors probably contribute to this behavior, and these will be discussed.

Results for Cobalt (II) Perchlorate-Ethanol-Water System. - In general, the data for the perchlorate solutions were treated in the same manner as for the nitrate solutions. Some important differences between the two systems became apparent, however, and these will be discussed.

The data in Table VI, obtained experimentally, were used to construct the integral heat of reaction curves of Figure 9. Although the same average value for Q_{Mix} was used to correct for the heat of mixing of water and ethanol it is obvious that in contrast to the cobalt (II) nitrate results, the curves for cobalt (II) perchlorate reach a maximum and then decrease. This occurs within the same range of total water concentration as that for the nitrate solutions.

Figure 10 shows that for the differential heat of reaction curves, $\Delta Q/\Delta N_L$ for the three solutions falls below the average heat of mixing value of 0.403 kcal-mole⁻¹ H₂O; although the curves all attain constant slopes. The solutions act "normal" only in the sense that the least concentrated one, 0.0444 M, approaches the heat of mixing value most slowly.

The values of C_L and C_M obtained from Figure 9 are presented

TABLE VI

CALORIMETRICALLY DETERMINED HEAT OF REACTION OF
WATER DATA FOR THREE SOLUTIONS OF COBALT (II)
PERCHLORATE IN ETHANOL

| 1 | | 2 | | 3 | |
|----------------------|-------------------|----------------------|-------------------|----------------------|-------------------|
| 0.0444 M (142.6 Ml.) | | 0.0617 M (143.6 Ml.) | | 0.0842 M (138.6 Ml.) | |
| 26.4 - 27.0° C | | 26.1 - 26.8° C | | 26.4 - 27.3° C | |
| Millimoles Water | Total Calories | Millimoles Water | Total Calories | Millimoles Water | Total Calories |
| 2.53 | 2.60 | 1.14 | 1.20 | 3.49 | 4.50 |
| 4.77 | 4.71 | 3.00 | 3.06 | 5.29 | 6.51 |
| 6.52 | 6.30 | 4.63 | 4.90 | 6.96 | 8.28 |
| 8.67 | 8.16 | 6.42 | 6.66 | 9.03 | 10.28 |
| 10.98 | 10.07 | 8.45 | 8.63 | 11.31 | 12.40 |
| 13.59 | 12.03 | 10.69 | 10.64 | 13.46 | 14.32 |
| 16.24 | 13.84 | 13.16 | 12.64 | 15.76 | 16.21 |
| 19.12 | 15.71 | 15.69 | 14.67 | 18.16 | 18.14 |
| 21.97 | 17.45 | 18.25 | 16.58 | 20.82 | 20.11 |
| 25.12 | 19.28 | 21.11 | 18.61 | 23.66 | 22.10 |
| 28.63 | 21.26 | 24.02 | 20.52 | 26.66 | 24.07 |
| 32.32 | 23.21 | 26.99 | 22.40 | 29.65 | 25.99 |
| 36.35 | 25.24 | 30.51 | 24.48 | 32.75 | 27.89 |
| 40.39 | 27.20 | 34.19 | 26.62 | 36.16 | 29.83 |
| 44.26 | 29.08 | 38.12 | 28.75 | 39.73 | 31.80 |

TABLE VI (Continued)

| | | | | | |
|--------|-------|--------|-------|--------|-------|
| 48.56 | 31.08 | 42.07 | 30.86 | 43.34 | 33.76 |
| 53.08 | 33.14 | 46.43 | 33.03 | 47.36 | 35.80 |
| 57.63 | 35.16 | 50.73 | 35.15 | 51.34 | 37.77 |
| 62.36 | 37.21 | 55.28 | 37.25 | 55.56 | 39.77 |
| 66.85 | 39.09 | 60.04 | 39.44 | 59.91 | 41.77 |
| 71.35 | 40.96 | 65.22 | 41.74 | 64.57 | 43.82 |
| 76.11 | 42.91 | 70.57 | 44.05 | 69.06 | 45.73 |
| 81.32 | 44.97 | 75.85 | 46.27 | 73.71 | 47.66 |
| 86.60 | 47.00 | 81.26 | 48.51 | 78.72 | 49.68 |
| 91.95 | 49.02 | 86.95 | 50.78 | 83.78 | 51.64 |
| 97.82 | 51.22 | 92.45 | 52.92 | 89.15 | 53.69 |
| 103.92 | 53.43 | 98.31 | 55.16 | 94.34 | 55.61 |
| 110.80 | 55.86 | 104.39 | 57.47 | 99.95 | 57.62 |
| | | 110.46 | 59.68 | 106.05 | 59.77 |
| | | 116.84 | 61.95 | 111.97 | 61.80 |
| | | 123.56 | 64.28 | 118.04 | 63.86 |
| | | 130.48 | 66.61 | 123.97 | 65.78 |
| | | 137.27 | 68.89 | 129.79 | 67.60 |

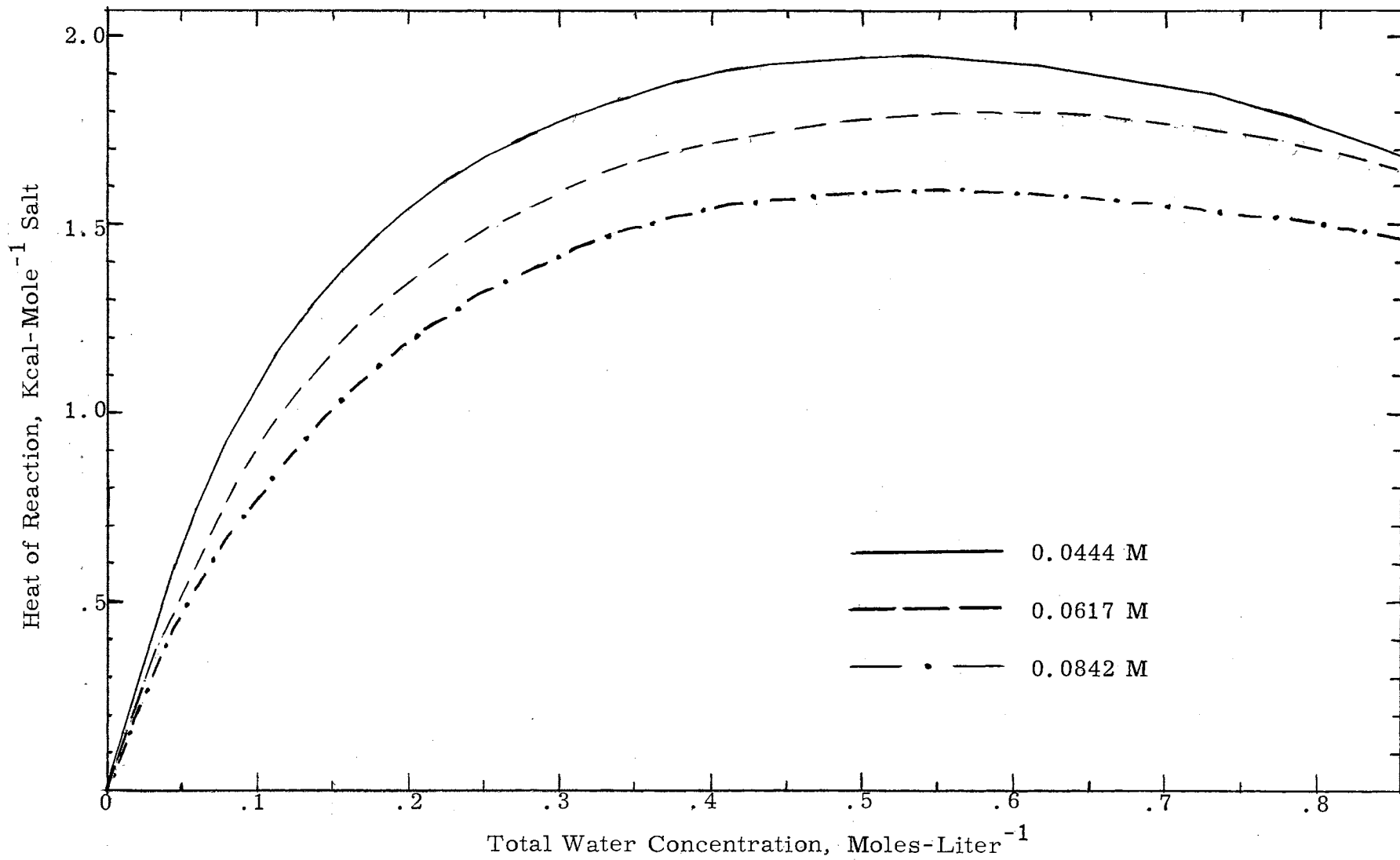


Figure 9. Heat of Reaction of Water with Cobalt (II) Perchlorate in Ethanol as a Function of the Total Water Concentration.

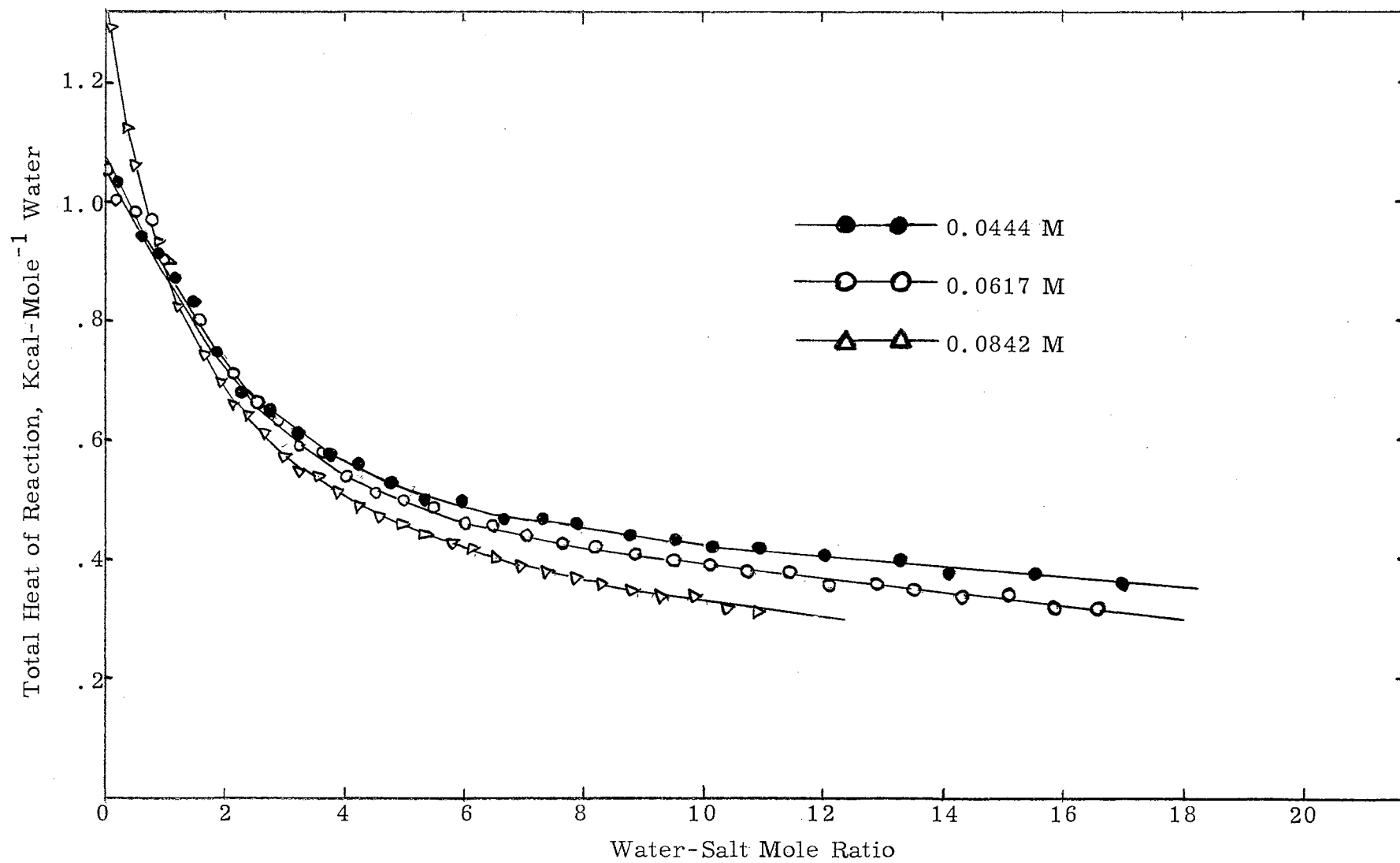


Figure 10. Slopes of the Curves Representing the Total Heat of Reaction of Water with Cobalt (II) Perchlorate in Ethanol.

in Figure 11 as a corresponding solutions plot. At \bar{n} values greater than about three it is seen that the lines begin to intersect. Also, the maximum value of \bar{n} obtainable from the data is only about four. The intersection of the lines indicates that the solutions are not corresponding and suggests that the heat of mixing correction as well as the basic theory of the method needs to be reexamined for the $\text{Co}(\text{ClO}_4)_2$ -ethanol- H_2O system.

A first attempt was made to correct for the linear portion of the curves which fall below the $0.403 \text{ kcal-mole}^{-1} \text{ H}_2\text{O}$ limit in Figure 10. For all three solutions, it is apparent that the linear portion begins at about that value. This suggests that the partial molal heat of mixing of excess water with the aquo complexes of $\text{Co}(\text{ClO}_4)_2$ in ethanol is different for each salt concentration and cannot be represented by an average value.

The total heat evolved in the calorimeter is the result of four thermochemical quantities.

$$\sum_1^N X_n (\bar{H}_n - \bar{H}_M^\circ - n \bar{H}_L^\circ) + (1 - \sum_1^N X_n) (\bar{H}_M - \bar{H}_M^\circ) + (R - \sum_1^N n X_n) (\bar{H}_L - \bar{H}_L^\circ) - R Q_{\text{Mix.}} = - \Delta \bar{H}_T \quad (15)$$

where X_n is the fraction of the n th complex, R is the water-salt mole ratio, \bar{H} and \bar{H}° are the partial molal enthalpies of the reacting species in the equilibrium mixture and in a reference state respectively. The reference states were chosen as the anhydrous salt and

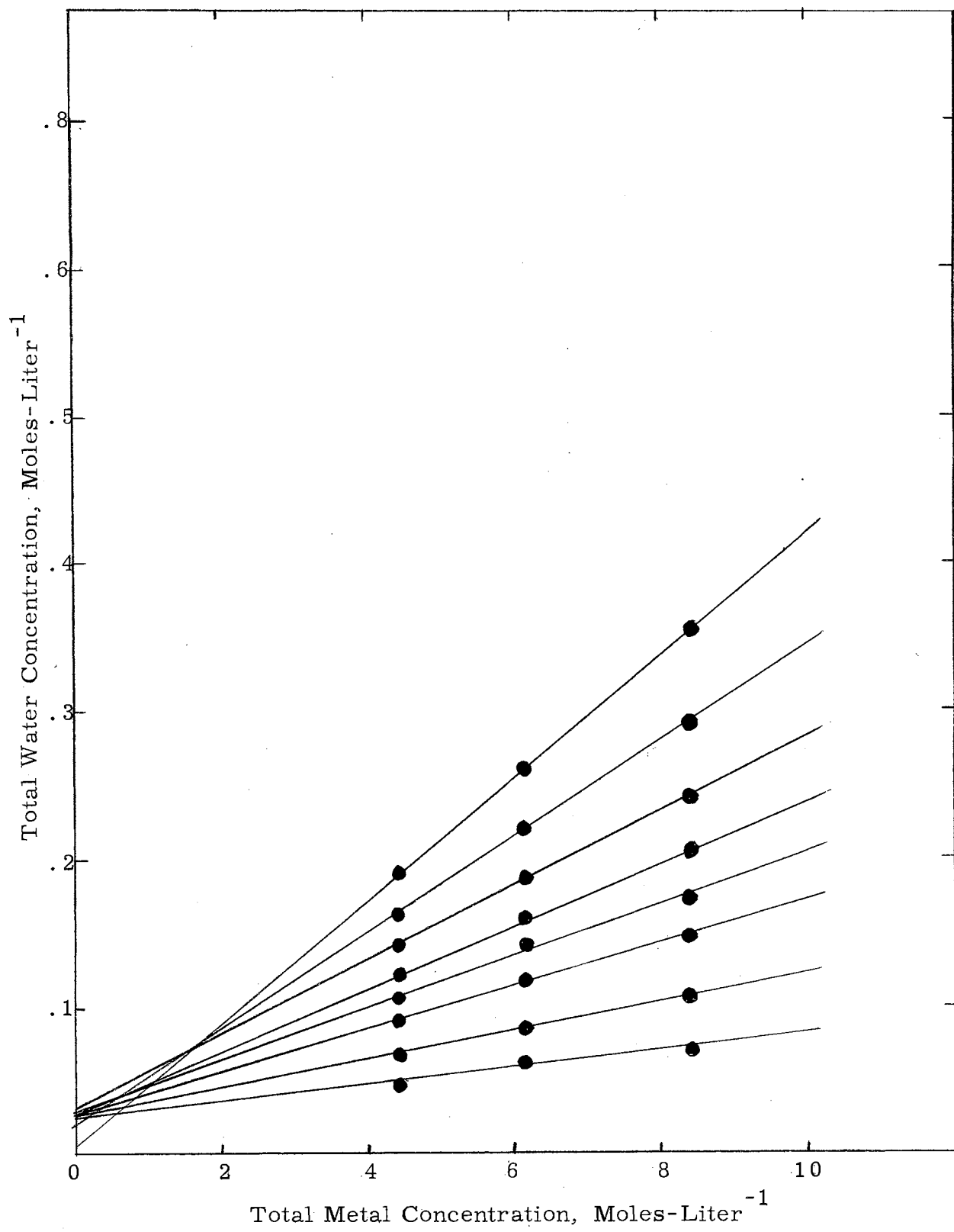


Figure 11. Corresponding Solutions of Cobalt (II) Perchlorate in Ethanol.

water in their respective binary mixtures with ethanol. The concentration of salt in the reference state was, of course, different in each series, but since the heat of dilution was found to be negligibly small, \bar{H}_M^0 was assumed to be the same in each. It was assumed that the second and third quantities were essentially zero. This assumption seems justified from the fact that as more and more water is added and more complexes are formed, $(1 - \sum_1^N X_n)$ approaches zero, or the non-complexed metal concentration is small; furthermore, it is reasonable that $(\bar{H}_M - \bar{H}_M^0)$ is also small. At low water-salt ratios, $(R - \sum_1^N n X_n)$ which is really $(R - \bar{n})$, the free water concentration, is assumed small. The term $(R - \bar{n})(\bar{H}_L - \bar{H}_L^0)$ describes the unbound water contribution to $\Delta \bar{H}_T$, and since the difference between the partial molal enthalpy of the free water and that of the water in the reference state is probably small the contribution of this term was considered negligible. Only the interaction of water and ethanol is included in $(\bar{H}_L - \bar{H}_L^0)$, since other interactions leading to complex formation are already included in the first term of eq. (15).

However, if the heat effect represented by $(\bar{H}_L - \bar{H}_L^0)$ is not sufficiently small, then $(R - \bar{n})(\bar{H}_L - \bar{H}_L^0)$ may not be negligible for large R and may be a function of R .

When the hydration reaction is essentially complete, and \bar{n} approaches N , then eq. (15) becomes

$$(\bar{H}_N - \bar{H}_M^0 - N\bar{H}_L^0) + (R - N)(\bar{H}_L - \bar{H}_L^0) = -\Delta \bar{H}_T + RQ_{\text{Mix}}. \quad (16)$$

If $(\bar{H}_L - \bar{H}_L^0)$ is a function of R , differentiation gives

$$f(R) + (R-N) df(R) = d(\bar{\Delta H}_T)/dR + Q_{\text{Mix.}} \quad (17)$$

The portion of the curve below $0.403 \text{ kcal-mole}^{-1} \text{ H}_2\text{O}$ in Figure 10 suggested a linear correction of the form

$$(\bar{H}_L - \bar{H}_L^0) = f(R) = mR + b \quad (18)$$

whence

$$df(R) = m \quad (19)$$

Substitution into the previous eq. (17) gives

$$d(\bar{\Delta H}_T)/dR = Q_{\text{Mix.}} - 2mR + (mN-b) \quad (20)$$

Integration gives

$$\bar{\Delta H}_T - RQ_{\text{Mix.}} = -mR^2 + (mN-b)R + C \quad (21)$$

The constant of integration, C , was evaluated for each salt solution at the point where the curves of Figure 9 become linear. This is equivalent to assuming that reaction is complete when this occurs. When the correction was calculated, however, for other water-salt ratios, the resulting corrected $\bar{\Delta H}_T$ values were inconsistent with the curves of Figure 9. That is, the points calculated from eq. (21) for a particular salt concentration were scattered and discontinuous with the existing heat-of-reaction curve in Figure 9.

The failure of the above to properly correct the $\Delta\bar{H}_r$ values for the apparent dependence of $(\bar{H}_L - \bar{H}_L^0)$ upon the water-salt ratio may be due in part to the factor $(R-\bar{n})$ in eq. (15) which contains \bar{n} as an unknown variable. Thus the $\Delta\bar{H}_r$ values should be corrected over the entire range of water-salt ratios.

Arbitrarily choosing Q_{Mix} as the $\Delta Q/\Delta N_L$ value (0.338 kcal-mole⁻¹ H₂O) for a 1.0 molal water in ethanol solution raised the heat-of-reaction curves, but gave \bar{n} lines with slopes greater than nine. The lines were found to still intersect, also. Although there is some spectrophotometric evidence that \bar{n} values in cobalt (II) perchlorate are greater than six, without additional information no significance can be attached to this fact (8).

Figure 12 shows how the slope of the heat of mixing curve varies with the total concentration of water. At each concentration of water in a given salt-ethanol-water system, the water-salt ratio can be multiplied by the slope of the curve in Figure 12 at the particular total water concentration and this used as $\Delta\bar{H}_{\text{Mix}}$.

$$R(\Delta Q/\Delta N_L) = \Delta\bar{H}_{\text{Mix}} \quad \text{at some } C_L \quad (22)$$

When this was done and the $\Delta\bar{H}_r$ values then plotted, again \bar{n} values greater than six were obtained. Also, values for C_L and C_M for the three solutions were no longer linearly related at constant values of $\Delta\bar{H}_r$. Furthermore, there is no theoretical justification for this

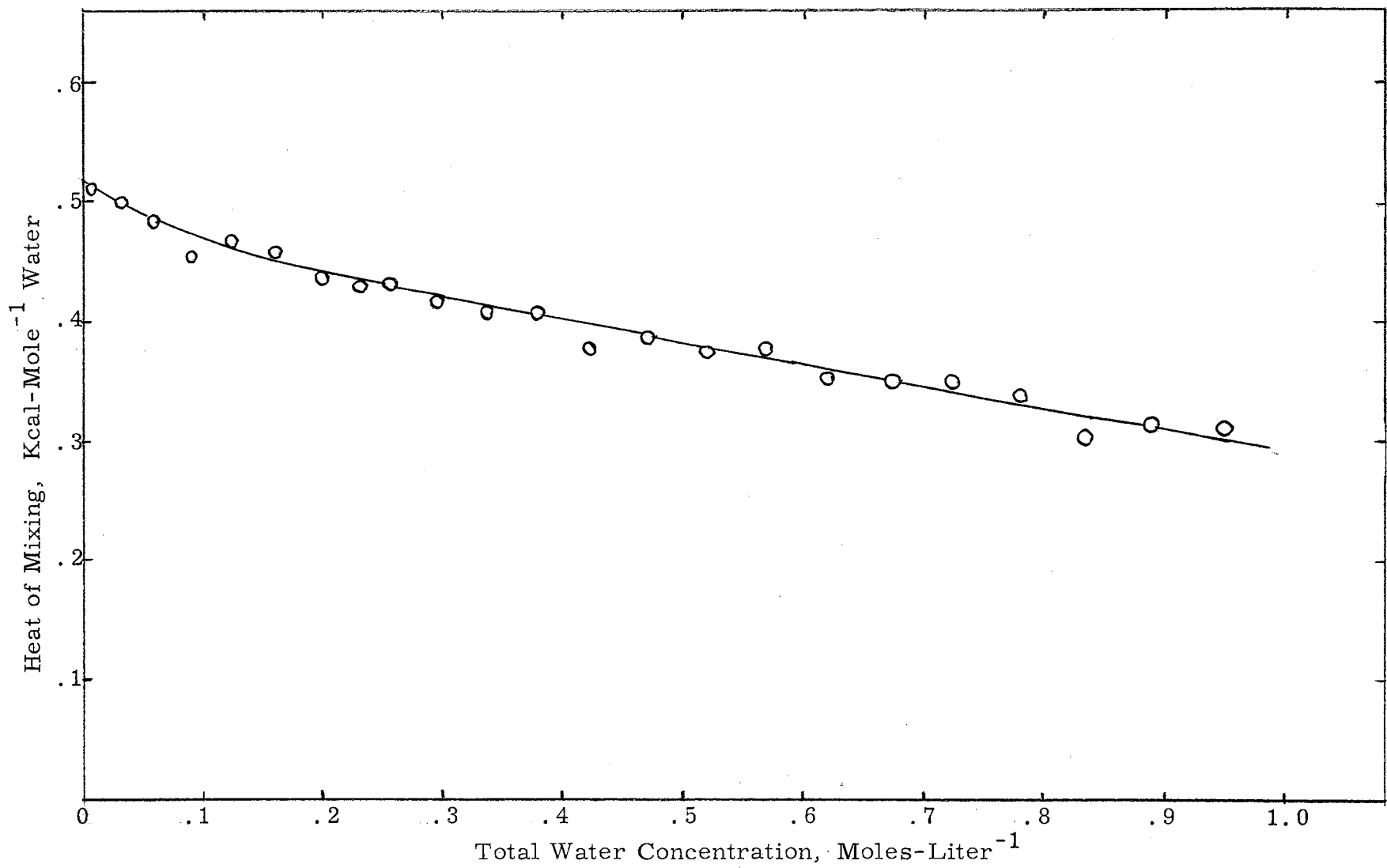


Figure 12. Slope of the Curve Representing the Heat of Mixing of Water and Ethanol.

kind of correction since it is equivalent to assuming a variable reference state for water in the solution.

The corresponding solutions plot (Figure 11), although probably unreliable in its present form for \bar{n} values greater than about four, shows that very little free water is present in the solutions for \bar{n} values of four or less. This indicates that the aquo complexes formed are relatively strong in the case of $\text{Co}(\text{ClO}_4)_2$. The corresponding solutions treatment cannot be carried out accurately when complexes are either too strong or too weak, and the first seems to be true here.

Still another interesting feature is noticeable when the heat of reaction is plotted versus the water-salt ratio as in Figure 13. The curves for the three solutions lie almost on a common curve up to a water-salt ratio of about four; at larger ratios they begin to separate. For strong complexes C_L/C_M is a good approximation to \bar{n} and hence the curves of this figure show that $\Delta\bar{H}_r$ is a function of \bar{n} only, in the range 0-4. This fact suggests strongly that the maximum coordination number may be no greater than four for the reaction of water with $\text{Co}(\text{ClO}_4)_2$.

Interpretation of Results. - The experimental formation curve of Figure 6 clearly indicates that hydration of $\text{Co}(\text{NO}_3)_2$ in ethanol solutions cannot be explained by the statistical formation of aquo complexes.

Since for the replacement of one neutral ligand by another the step-wise enthalpy changes have been found to be nearly equal in most aqueous

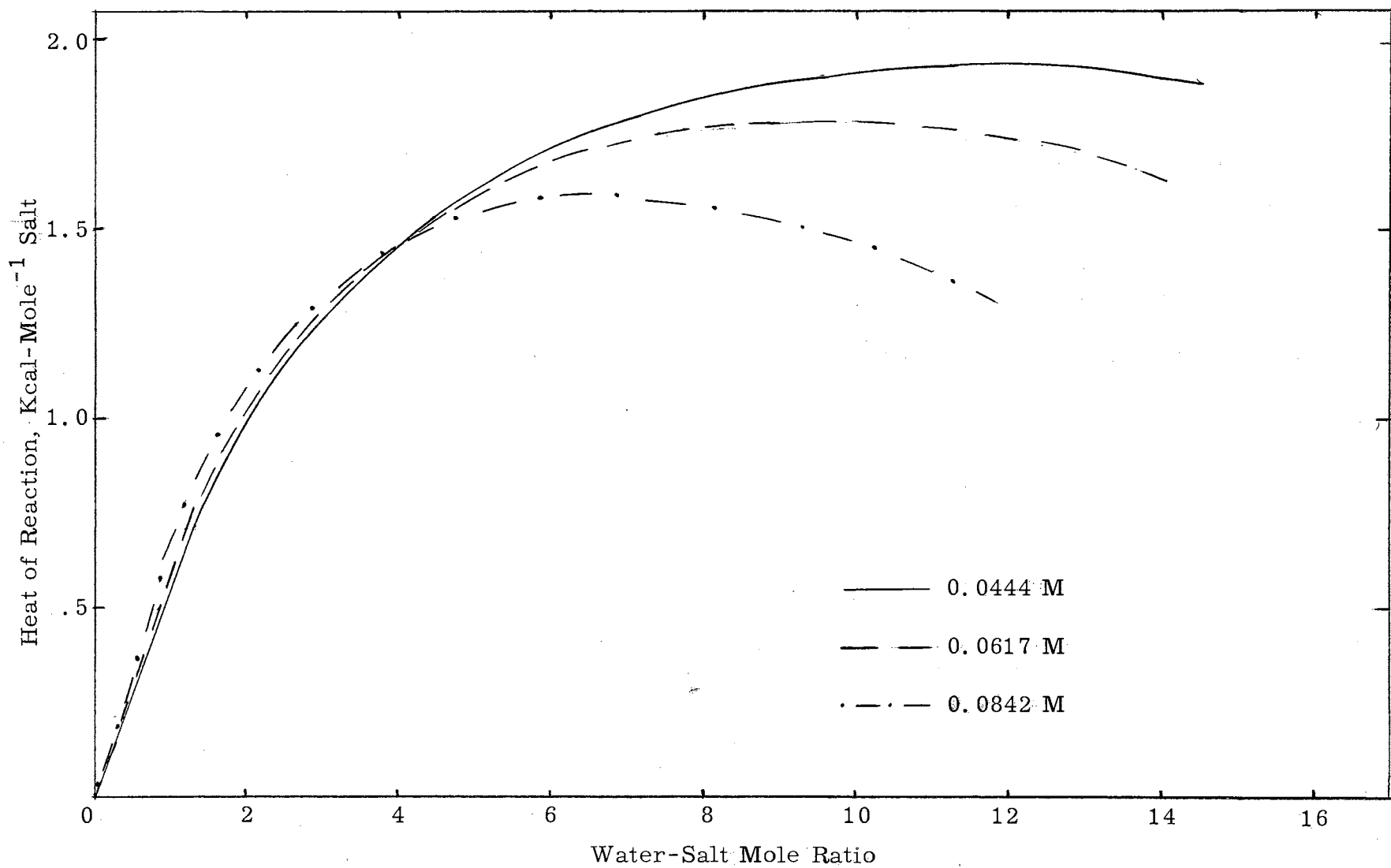


Figure 13. Heat of Reaction of Water with Cobalt (II) Perchlorate in Ethanol as a Function of the Water to Salt Mole Ratio.

systems, the ratio of successive formation constants must be determined largely by statistical considerations in such cases. It is reasonable that the same would be true of the systems under investigation. Thus, the deviation from statistical behavior may be due in part to a difference in the type of ligands involved; i. e., uncharged species such as water molecules replacing charged ions rather than only neutral solvent molecules. This would be the case, as Katzin argues, when there are nitrate ions in the inner coordination sphere.

The formation curve for aquo cobalt (II) ions in $\text{Co}(\text{NO}_3)_2$ solutions found from this research does not compare favorably with that of Jorgensen (16), although the K_{av} obtained from Figure 6 is only about three, whereas Jorgensen reports about one. The total water concentrations employed were much less than those investigated by Jorgensen. This results, as pointed out earlier, in an incomplete heat-of-reaction curve and a formation curve which does not approach closely a limiting value.

The curves of Figure 8, $\Delta Q/\Delta N_L$ versus the water-salt ratio, have a peculiar shape. In contrast to what one might expect, there is a maximum in the slope at a low water-salt ratio. There are at least two possible explanations for the existence of such a maximum. First, some particular combination of K_n values and $\Delta\bar{H}_n$ (the heat of formation of the nth aquo complex) values could lead to a maximum, or alternatively, an endothermic process, such as electrolytic dissociation of

cation-anion associates by the incoming water molecules would offset the initial heat of the solvent replacement reaction. It can be seen that the maximum $\Delta Q/\Delta N_L$ value occurs at very low water-salt ratios, and therefore, smaller increments of water need to be added to more nearly anhydrous salt-ethanol solutions in order to study the matter further. However, the results obtained in this work seem in qualitative agreement with observations of Katzin and Gebert (17) who reported that the greatest spectral change occurs upon the addition of the first few per cent of water to ethanol solutions of $\text{Co}(\text{NO}_3)_2$. Probably both sets of observations are to be associated with the displacement of nitrate ions from coordination positions about the cobalt (II) ions.

As mentioned previously, results indicate that the aquo complexes of $\text{Co}(\text{ClO}_4)_2$ are too strong for the successful application of the corresponding solutions treatment. The free water concentration is thus too small for a reliable determination of its value from the plots of Figure 11, and it is, therefore, not possible to construct a complex formation curve. It is reasonable to presume that the degree of cation-anion association would be much less in the perchlorate solutions than it is in the nitrate solutions, and direct coordination of perchlorate ions would not occur. This is contradicted by the apparent maximum \bar{n} value of about four for the reaction with water, however.

Failure of the slopes of the total heat of reaction curves to show a maximum similar to the case of $\text{Co}(\text{NO}_3)_2$ might indicate that a

corresponding initial dissociation process does not occur for $\text{Co}(\text{ClO}_4)_2$.

The heat of reaction for the binding of the same average number of water molecules (\bar{n}) is less for $\text{Co}(\text{ClO}_4)_2$ than for $\text{Co}(\text{NO}_3)_2$. This is in agreement with the spectral evidence of Katzin and Gebert (18). The order of ligand field strengths for the three species involved, assuming the cobalt to be free for ligand substitution in ethanol solution, is thought to be $\text{H}_2\text{O} > \text{NO}_3^- > \text{EtOH}$ (4). If this is the case, then more heat per mole of metal would be evolved in the exchange of water molecules for nitrate ions, than for water molecules replacing ethanol molecules. Qualitatively, it seems reasonable, also, that a greater change in entropy would be involved in the replacement of a charged ion for a neutral molecule.

One final point seems of sufficient importance to deserve repetition. In all of the studies reported in the literature of replacement of organic solvent by water, it has been necessary to assume that the degree of electrolytic dissociation is without affect upon the formation constants for the aquo complexes. Alternatively, either completely dissociated salts must be assumed or complete ion-pairing must be assumed. For small water-salt ratios this seems a reasonable assumption, but its correctness has not been demonstrated, and the linear decrease of the slope of the $\Delta Q/\Delta N_L$ versus R curve at larger R values (Figure 10) may be due in part to the endothermic electrolytic dissociation of $\text{Co}(\text{ClO}_4)_2$ superimposed upon the exothermic mixing of excess water with ethanol.

CHAPTER V

SUMMARY AND SUGGESTIONS FOR FURTHER WORK

The purpose of the investigation was to study the feasibility of titration calorimetry as a method for obtaining thermodynamic information about aquo complex formation in organic solutions of salts. A micro calorimeter was constructed for the measurement of heats of reaction, in solution, of one calorie or less with a precision and accuracy of one per cent or better. The calorimeter was shown to have the desired capability by study of the neutralization of sodium hydroxide by hydrochloric acid at 27°.

Two systems were studied in anhydrous ethanol. These were (1) $\text{Co}(\text{NO}_3)_2$ at concentrations from 0.03M to 0.1M; (2) $\text{Co}(\text{ClO}_4)_2$ at concentrations from 0.04M to 0.08M. The reaction of water with solutions of each salt at several different concentrations was investigated by measurement of the differential heat of reaction. The results obtained for $\text{Co}(\text{NO}_3)_2$ indicate that although this salt is probably to some degree nitrate complexed in ethanol solution, the strength of the aquo complexes formed upon the addition of water are of the correct magnitude to permit determination of the formation curve by Bjerrum's method of corresponding solutions. Values for the individual formation

constants were not calculated, however, in view of the uncertainty in the nature of the anhydrous solutions.

Cobalt (II) perchlorate is apparently not a perchlorate complex and appears to form stronger aquo complexes than $\text{Co}(\text{NO}_3)_2$. From the data, it is evident that a correction needs to be made for the amount of free water present in the solutions, particularly at large values of the water-salt ratios. The correction needed appears to be dependent upon the concentrations employed, becoming less as the concentration decreases. Therefore, lower metal concentrations should be studied, probably at least by a factor of ten, if the correction is to become negligible. At the same time, the lower metal concentrations should make possible the extension of the measurements to higher water-salt ratios.

The questions that have been raised by the results obtained for the $\text{Co}(\text{ClO}_4)_2$ -EtOH- H_2O system lead one to reconsider the $\text{Co}(\text{NO}_3)_2$ -EtOH- H_2O system. It seems clear from the results of the investigation that calorimetric titrations can be used to determine step-wise formation constants and thermodynamic quantities for aquo complexes, if measurements are carried out in sufficiently dilute solutions. The results obtained with $\text{Co}(\text{NO}_3)_2$ and $\text{Co}(\text{ClO}_4)_2$ are such that one should probably investigate these systems at much lower metal concentration and at much higher water concentrations in order to convincingly demonstrate the usefulness of the technique, however.

A SELECTED BIBLIOGRAPHY

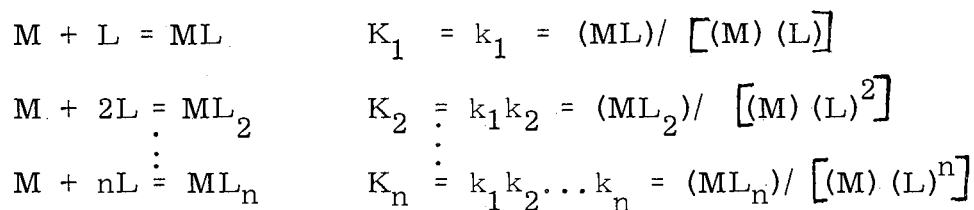
1. Beaver, W. D., L. E. Treverrow, W. E. Estill, P. C. Yates, and T. E. Moore, *J. Am. Chem. Soc.*, 75, 4556 (1953).
2. Benedict, R. P., *Elec. Manuf.*, 54, (2), 120 (1954).
3. Bjerrum, J. and C. K. Jorgensen, *Acta. Chem. Scand.*, 7, 951 (1953):
4. Bjerrum, J. and C. K. Jorgensen, *Nature*, 175, 426 (1955).
5. Bjerrum, J., "Metal Ammine Formation etc.", Thesis, Copenhagen, 1941.
6. Brintzinger, H. and C. Ratanarat, *Z. anorg. allgem. Chem.*, 222, 113-25 (1935).
7. Dutoit, P. and E. Grobet, *J. Chim. Phys.*, 19, 324 (1921).
8. Fetzer, P., M. S. Thesis, Oklahoma State University, 1962.
9. Flaschka, H. A., EDTA Titrations, Pergamon Press, New York, 1959, p. 79.
10. Friedman, N. J. and R. A. Plane, *Inorg. Chem.*, 2, 11 (1963).
11. Hale, J. D., R. M. Izatt, and J. J. Christensen, *J. Phys. Chem.*, 67, (12), 2605-8 (1963).
12. Hodgeman, C. D., (Ed.), Handbook of Chemistry and Physics, 32nd ed., p. 1768.
13. Jones, H. C. and J. A. Anderson, "The absorption spectra of solutions...", Publ. 110, Carnegie Inst. of Wash., 1909.
14. Jordan, J. and T. G. Alleman, *Anal. Chem.*, 29, 9 (1957).
15. Jordan, J., *J. Chem. Ed.*, 40, A5 (1963).
16. Jorgensen, C. K., *Acta. Chem. Scand.*, 8, 175 (1954).

17. Katzin, L. I. and E. J. Gebert, *J. Am. Chem. Soc.*, 72, 5457 (1950).
18. Katzin, L. I. and E. J. Gebert, *Nature*, 175, 425 (1955).
19. Katzin, L. I., *J. Chem. Phys.*, 20, 1165 (1952).
20. Lange, E. and F. Durr, *Z. Phys. Chem.*, 121, 361 (1926).
21. Lange, J. and J. Berga, *Monatsh. für Chem.*, 81, 933 (1950).
22. Larson, R. C. and R. T. Iwamoto, *Inorg. Chem.*, 1, 316 (1962).
23. Linde, H. W., L. B. Rogers, and D. N. Hume, *Anal. Chem.*, 25, 404 (1953).
24. Lingane, J. J., *Anal. Chem.*, 20, 285 (1948).
25. Marcus, Y., *Chem. Rev.*, 63, 139 (1963).
26. Minc S. and W. Libis, *Roczniki Chem.*, 29, 1073 (1955).
27. Mitchell, J., Jr. and D. M. Smith, *Aquametry*, Interscience Publishers, Inc., New York, 1948.
28. Müller, R. H. and H. J. Stolten, *Anal. Chem.*, 25, 1103 (1953).
29. Rossini, F. D. et al., *Selected Values of Chemical Thermodynamic Properties*, Washington, D. C.: Circular 500 of the National Bureau of Standards, U. S. Government Printing Office, 1952.
30. Rossotti, F. J. C. and H. Rossotti, *The Determination of Stability Constants and Other Equilibrium Constants in Solution*, McGraw-Hill Book Co., New York, 1961.
31. Schlyter, K., "A Precision Calorimeter for Enthalpy Titrations," *Trans. Royal Inst. of Tech.*, Stockholm, Sweden, No. 132 (1959).
32. Steinwehr, H. von, *Z. Phys. Chem.*, 38, 185 (1901).
33. Timmermans, J., *The Physico-Chemical Constants of Binary Systems in Concentrated Solutions*, Vol. 4, Interscience Publishers, Inc., New York, 1960, p. 206.

34. Yates, P. C., R. J. Laran, R. E. Williams and T. E. Moore, J. Am. Chem. Soc., 75, 2212 (1953).
35. Yatsimirskii, K. B. and V. P. Vasilev, Instability Constants of Complex Compounds, Tranl. Ed. R. H. Prince, Pergamon Press, New York, 1960.

APPENDIX A

The equations for the step-wise formation of ligand complexes, ML_n , and the respective formation constants are:



Bjerrum (5) has shown that since $\bar{n} = \frac{C_L - (L)}{C_M}$, and

$$C_M = M + ML + ML_2 + \dots + ML_n, \text{ and}$$

$$C_L = L + ML + 2ML_2 + \dots + nML_n,$$

$$\text{then } \bar{n} = \frac{ML + 2ML_2 + \dots + nML_n}{M + ML + ML_2 + \dots + ML_n}$$

Substituting the formation constants and dividing both numerator and denominator by (M)

$$\bar{n} = \frac{K_1(L) + 2K_2L^2 + \dots + nK_n(L)^n}{1 + K_1(L) + K_2(L)^2 + \dots + K_n(L)^n} = \frac{\sum_1^N n K_n(L)^n}{1 + \sum_1^N K_n(L)^n}$$

In order to obtain an equation in useful form,

$$\bar{n} \left[1 + \sum_1^N K_n (L)^n \right] - \sum_1^N n K_n (L)^n = 0$$

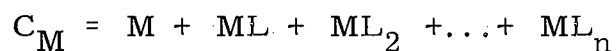
$$\text{or } \bar{n} + (\bar{n} - 1) K_1(L) + (\bar{n} - 2) K_2(L)^2 + \dots + (\bar{n} - n) K_n(L)^n = 0$$

If at some \bar{n} value, the corresponding (L) is used an equation is obtained:

$a + bK_1 + cK_2 + \dots + dK_n = 0$, where a , b , c , and d are constants. If $n = 6$ and six equations are used, evaluated at the six different half integral \bar{n} values, the equations are the six normal equations to the \bar{n} versus (L) curve. A computer solution is readily available for these six K values.

APPENDIX B

Let the following equation represent all of the metal ions in a solution of solvent and complexing ligand;



where C_M is the total metal concentration, M is the metal and L is the ligand.

If x_n represents the heat of formation of the n th complex, and a_n is the fraction of metal complexed in the n th complex, then

$$\Delta H/C_M = a_1 x_1 + a_2 x_2 + \dots + a_n x_n = Q, \text{ or}$$

the amount of heat evolved per mole of metal is equal to the sum of the heats evolved by the complexes. At another concentration of metal, C_M' ,

$$Q' = a_1' x_1 + a_2' x_2 + \dots + a_n' x_n.$$

When $Q = Q'$,

$$x_1 (a_1 - a_1') + x_2 (a_2 - a_2') + \dots + x_n (a_n - a_n') = 0,$$

and $a_1 = a_1'$, $a_2 = a_2'$, \dots $a_n = a_n'$. Therefore, since

$$a_n = \frac{K_n (M) (L)_n}{(M) \left[1 + \sum_1^N K_n (L)^n \right]}, \quad a_{n'} = \frac{K_n (M)' (L)'^n}{(M)' \left[1 + \sum_1^N K_n (L)'^n \right]},$$

$$\text{and } \bar{n} = \frac{\sum_1^N n K_n (L)^n}{1 + \sum_1^N K_n (L)^n} \quad (\text{See Appendix A}),$$

then $(L) = (L)'$ and $\bar{n} = \bar{n}'$. The solutions are "corresponding" since for the same value of $\Delta \bar{H}_r$, they have the same percentage distributions of the solvated ions and the same ligand number, \bar{n} , i. e., average number of ligand molecules bound per metal ion and consequently the same concentration of free ligand, (L) .

$$(L) = C_L - \bar{n} C_M \quad \text{and} \quad (L)' = C_L' - \bar{n}' C_M'$$

Since $\bar{n} = \bar{n}'$,

$$0 = \bar{n} (C_M' - C_M) + (C_L' - C_L)$$

If a plot of C_M versus C_L is made, \bar{n} can be found as the slope,

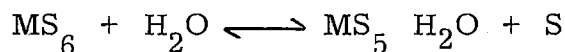
$$(C_L' - C_L) / (C_M' - C_M).$$

APPENDIX C

The calculation of a statistical \bar{n} versus free water or log free water curve requires that a statistical "factor" be defined for each step of the aquo complex formation. The value of the factor is simply the maximum number of replaceable coordination sites for the forward reaction divided by the maximum number for the reverse process, or

$$f_n = \frac{N - n + 1}{n}$$

It is assumed that each consecutive step is as likely as any other and that related ligands are exchanged. Thus, for the first aquo complex formation reaction, with one incoming water molecule encountering a solvated metal ion with a maximum coordination number of six:



The statistical factor, f_1 , would be 6/1, or 6. The values for the six factors would be:

$$f_1 = 6/1$$

$$f_2 = 5/2$$

$$f_3 = 4/3$$

$$f_4 = 3/4$$

$$f_5 = 2/5$$

$$f_6 = 1/6$$

If an average formation constant, K_{av} , is defined as

$$K_{av} = (k_1 \cdot k_2 \cdot \dots \cdot k_N)^{1/N} = \frac{1}{(H_2O)} \cdot \left[\frac{M(H_2O)_6}{(M)} \right]^{1/6}$$

and

$$k_n = f_n \cdot K_{av}$$

and

$$K_n = k_1 \cdot k_2 \cdot \dots \cdot k_n$$

then for a particular value of the free water concentration, an \bar{n} value can be found using the equation

$$\bar{n} = \frac{\sum_1^N n K_n (H_2O)^M}{1 + \sum_1^N K_n (H_2O)^n} \quad (\text{See Appendix A}).$$

Using several values for the free water concentration within the experimental concentration range a statistical curve can be obtained. The average formation constant is evaluated:

$$K_{av} = 1/(H_2O)$$

when $\bar{n} = N/2$, or the midpoint of the formation of the complexes (5).

GLOSSARY

Q = heat liberated in the calorimeter for reaction of $H_2O(l)$ + solution

Q_r = heat liberated in the calorimeter for reaction of $H_2O(m_L)$ + salt (m_M)

Q = $Q_r + Q_{\text{Mix.}}$

$\bar{\Delta H}_T$ = enthalpy increase per mole of salt for reaction of $H_2O(l)$ + solution

$\bar{\Delta H}_r$ = enthalpy increase per mole of salt for reaction of $H_2O(m_L)$ + salt (m_M)

$\bar{\Delta H}_T$ = $\bar{\Delta H}_r + \bar{\Delta H}_{\text{Mix.}}$

$\bar{\Delta H}_{\text{Mix.}}$ = $H_{H_2O(m_L)} - H_{H_2O(l)}$

VITA

Glenn Dill Fielder

Candidate for the Degree of

Master of Science

Thesis: A CALORIMETRIC INVESTIGATION OF THE HYDRATION OF
COBALT (II) PERCHLORATE AND COBALT (II) NITRATE IN
ETHYL ALCOHOL

Major Field: Chemistry

Biographical:

Personal Data: Born in Ada, Oklahoma, February 6, 1941, son
of Armer Glenn and Roxie Althus Fielder.

Education: Attended grade school in McAlester, Oklahoma, and
Billings, Montana; graduated from Dawson County High
School, Glendive, Montana, in 1959; received the Bachelor
of Arts degree from the Oklahoma State University, with
a major in Chemistry, in August, 1963; completed require-
ments for the Master of Science degree, with a major in
Chemistry, in May, 1965.

Professional Experience: Held membership in the Student
Affiliates of the American Chemical Society while an under-
graduate; employed by Fansteel Metallurgical Corporation
the summer of 1962; obtained a teaching assistantship from
the Chemistry Department of the Oklahoma State University
from September, 1962, through May, 1964; obtained a grad-
uate research assistantship from the Research Foundation
of the Oklahoma State University made available with funds
from the Atomic Energy Commission from May, 1964,
through February, 1965.