A THERMODYNAMIC STUDY OF THE AQUOCOMPLEX FORMATION OF COBALT(II) AND NICKEL(II) PERCHLORATE IN 1-BUTANOL

By

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Continued)

CHAPTER I

INTRODUCTION

Background to the Problem - The bulk of the scientific research concerned with solution chemistry has been done with aqueous media. However, nonaqueous solvent systems often are available which provide better physical and chemical properties than does water for particular investigations. In analytical chemistry, for example, very weak acids or bases are often titrated in a nonaqueous solvent. Much nonaqueous polarography is now done, and nonaqueous solvents are vitally important to spectroscopy. The technique of solvent extraction would be impossible without the use of at least one nonaqueous solvent.

The present research has been undertaken in an attempt to learn more of the solution behavior of transition metal salts in a nonaqueous medium containing small amounts of water; e.g., cobalt (II) and nickel (II) perchlorates in hydrous 1-butanol. Some studies have indicated that solvation of transition metal perchlorates in the alcohol phases after extraction is primarily due to hydration (28). The coextracted water in such cases exceeds the normal coordination numbers of the cations, leading to large "hydration numbers". 1-Butanol was chosen as the solvent for the study because it is the alcohol of lowest molecular weight which can be used as an extractant of aqueous solutions, and it also has very favorable thermal properties, which will be discussed later.

Quite a variety of opinion exists as to the detailed nature of transition metal aquocomplexes in nonaqueous solvents (8,15,17,19). One of the best approaches to a theoretical treatment of such species, and without which no argument would be really complete, is through thermodynamic information. Formation constants have been determined for a very limited number of transition metal aquocomplexes in only a few solvents and solvent mixtures (8,15,17,19,20,21). The method of Bjerrum (2) has been most widely used for calculating the formation constants.

Spectroscopy is the method most often chosen for aquocomplexing studies. However, spectroscopic information is inherently linked to molar extinction coefficients which nearly always are small in the visible region for aquocomplexes. It is generally difficult to find a metal-water-solvent system which has an infrared absorption band dependent only on the water-metal interactions and not complicated by other vibrational modes. At best the data has considerable scatter which leads to uncertainty in the formation constants (8,17).

Polarography has been used as a companion method to spectroscopy, but some reservations also must be held about its use (17,20). An inherent difficulty in using polarography for studying aquocomplexing is that a high concentration of a second or supporting electrolyte is necessary. Whereas such an electrolyte might not strictly affect the polarographic measurements as such, it is difficult to imagine that the chemical hydration process would be totally unaffected. Nelson and Iwamoto (20) have recognized that lithium perchlorate might compete with copper (II) perchlorate for free water in the solution, but stated that no quantitative evidence was available to show that it did; they, therefore, ignored the (likely) interaction of lithium perchlorate in the interpretation of their polarographic results.

Even at best, formation constants, with perhaps a temperature dependence, can be determined by spectroscopy and polarography. However, these two methods give no information about the stepwise enthalpies and entropies of formation, which usually give the best insight into the nature of the species.

To obtain a complete thermodynamic description, it is necessary to use some form of calorimetry. In order for Bjerrum's method to be used for obtaining successive formation constants, the system should be capable of passing through successive equilibrium states as repetitive additions are made to the same solution. Thermometric titrations offer a convenient linking of these two requirements.

Most analytical procedures are ultimately free energy methods, i.e., they depend on a property related to the equilibrium constants. For example, the pH change in a conventional acid-base titration depends on the relevant ionization constants of the system. But reaction systems with a small free energy change are also capable of measurement if the entropy term in equation (1.1) is favorable.

$$\Delta H = \Delta G + T\Delta S \qquad (1.1)$$

Since a measurable heat of reaction is a very general property of chemical processes, thermometric titrations have considerable applicability to both thermodynamic studies and analytical chemistry. One of the advantages of using thermometric titrations for the study of aquocomplexing is the possibility of obtaining both formation constants and enthalpies from the same set of data. With the formation constants and enthalpies experimentally determined, free energies and entropies are defined by equations (1.1) and (1.2).

$$\Delta G = -RT \ln K \qquad (1.2)$$

Another important advantage of thermometric titrations lies in the sensitivity of the method. Precise data are reasonably simple to obtain and yield more easily to quantitative interpretation than do absorption spectra.

There are some disadvantages to thermometric titrations for fundamental thermodynamic measurements, however. One of these is the necessity of making a correction for the heat of mixing of the solvent with the titrant. In this study of aquocomplexing of cobalt (II) and nickel (II) perchlorates, 1-butanol was a fortunate choice of solvent because the integral heat of mixing of water with 1-butanol is a linear function of the water concentration. Consequently, the heat of hydration of cobalt (II) and nickel (II) perchlorates is easily obtained from the overall experimental heat of reaction of the 1-butanol solutions by subtraction of a simple linear function for the heat of mixing of water with 1-butanol. However, in other systems, such as ethanol-water, the integral heat of mixing of water with solvent may not be a simple linear function at low water concentrations, thereby making such a correction difficult, although not at all impossible (6).

CHAPTER II

THEORY OF THE PROPOSED METHOD

Corresponding Solutions - For the calculation of stepwise formation constants, an adaptation of Bjerrum's (2) method of "corresponding solutions" to calorimetric measurements was employed. This is developed in detail in the following derivation, which is applicable to 2:1 metal salts.

Assume that the reaction of ligand L with metal M occurs with equal ease for solvated ion (M^{++}) or ion-associate ($M^{++}\cdot 2X^{-}$). It will be shown later, however, that the latter predominates in the low dielectric solvent 1-butanol. Assume also that in the calorimeter there are z moles of central metal ion (as salt MX_2) at total molar concentration C_M and that the addition of y moles of ligand produces a total ligand concentration C_L. Consider now the reaction

$$zM(\text{soln.}) + yL(\text{liq.}) \rightarrow x_1 zML(\text{soln.}) + x_2 zML(\text{soln.}) + \cdots + x_N zML_N(\text{soln.}) + Q_{rx} \qquad (2.1)$$

where x_n is the fraction of M in aquocomplex ML_n at equilibrium, and Q_{rx} is the heat of reaction of M with L. The mixing of water with solvent produces Q_{sol} calories according to the relation

$$\overline{H}_L^{o} = \overline{H}_L^{*} + Q_{sol} \qquad (2.2)$$

where $\overline{H}_L^{o}$ is the standard molar enthalpy of pure liquid L, $\overline{H}_L^{*}$ is the partial molar enthalpy of L in binary solution at C_L, and Q_{sol} is the heat of mixing of L with solvent.

Dividing equation (2.1) by z and formulating the corresponding equation gives

$$\begin{aligned}\bar{H}^*_M + \tfrac{y}{z}\bar{H}^\circ_L = \; & (x_1\bar{H}_{ML} + x_2\bar{H}_{ML_2} + \cdots + x_N\bar{H}_{ML_N}) \\ & + (\bar{H}_M - x_1\bar{H}_M - x_2\bar{H}_M - \cdots - x_N\bar{H}_M) \\ & + (\tfrac{y}{z}\bar{H}_L - x_1\bar{H}_L - 2x_2\bar{H}_L - \cdots - Nx_N\bar{H}_L) \\ & + Q_{rx}/z \qquad (2.3)\end{aligned}$$

where $\bar{H}^*_M$ is the partial molar enthalpy of M in the binary reference solution, and $\bar{H}_M$, $\bar{H}_L$ and $\bar{H}_{ML_n}$ are the partial molar enthalpies in the equilibrium mixture. Equation (2.3) can be rearranged and combined with (2.2) to give

$$\begin{aligned}\sum_1^N (\bar{H}_{ML_n} - \bar{H}^*_M - n\bar{H}^*_L)x_n = \; & (1 - \sum_1^N x_n)(\bar{H}^\circ_M - \bar{H}_M) \\ & + (\tfrac{y}{z} - \sum_1^N nx_n)(\bar{H}^\circ_L - \bar{H}_L) \\ & + (yQ_{sol} - Q_{rx})/z \qquad (2.4)\end{aligned}$$

The first two terms on the right represent, in effect, the corrections for excess (free) metal and ligand, respectively. Such terms will be small for dilute solutions, and at infinite dilution will be zero.

Consider now a second concentration of metal and ligand, C'_M and C'_L, and the corresponding thermal equation to (2.4). By taking the difference between the new equation and (2.4) one has

$$\begin{aligned}\Delta\sum_1^N \eta_n x_n = \; & \Delta(1 - \sum_1^N x_n)(\bar{H}^\circ_M - \bar{H}_M) + \Delta(\tfrac{y}{z} - \sum_1^N nx_n)(\bar{H}^\circ_L - \bar{H}_L) \\ & + \Delta(yQ_{sol} - Q_{rx})/z \qquad (2.5)\end{aligned}$$

where $\eta_n = \sum_1^N (\bar{H}_{ML_n} - \bar{H}^*_M - n\bar{H}^*_L)$. When the last term on the right side of (2.5) is made zero, by proper choice of salt and ligand concentrations, equation (2.5) becomes

$$\sum_1^N \eta_n x_n - \sum_1^N \eta_n x'_n = \sum_1^N \eta_n (x_n - x'_n) \approx 0 \qquad (2.6)$$

Consider the case where $\sum_1^N \eta_n (x_n - x'_n) = 0$. Since the η_n's are not all zero, it follows that $x_n = x'_n$ for all the η_n's. Such solutions are said to be corresponding, and the enthalpy change attending the reaction can be written as

$$\Delta H = \sum_1^N C_M \eta_n x_n \qquad (2.7)$$

To find such corresponding solutions a plot of $\Delta H/C_M$ versus C_L is made and the values of C_L and C'_L are found for which $\Delta H/C_M$ and $(\Delta H/C_M)'$ are the same.

Equations (2.5) and (2.6) may be used similarly to find corresponding solutions in the small concentration range, for then equation (2.6) holds with little error. With decreasing concentration (2.6) becomes exact, but even at moderate concentrations the equation may still hold quite well. This is because of the smallness of the $(\bar{H}^o_M - \bar{H}_M)$ and $(\bar{H}^o_L - \bar{H}_L)$ terms in equation (2.5).

For the specific case of complex ML_2, the stepwise formation constants are

$$k_1 = \frac{[ML]}{[M][L]}$$

$$k_2 = \frac{[ML_2]}{[ML][L]} = \frac{[ML_2]}{k_1 [M][L]^2} \qquad (2.8)$$

The overall formation constant is

$$\beta_2 = k_1 k_2 = \frac{[ML_2]}{[M][L]^2} \qquad (2.9)$$

Now the total metal concentration is

$$C_M = [M] + [ML] + [ML_2] + \cdots + [ML_N] \qquad (2.10)$$

and, therefore, the fraction as the second complex is

$$x_2 = \frac{[ML_2]}{C_M} = \frac{\beta_2 [M][L]^2}{[M] + [ML] + \cdots + [ML_N]} \qquad (2.11)$$

By factoring out [M] from equation (2.11) one has

$$x_2 = \frac{\beta_2 [L]^2}{1 + \beta_1 [L] + \beta_2 [L]^2 + \cdots + \beta_N [L]^N} \qquad (2.12)$$

and it is seen that

$$x_n = f(L), \qquad (2.13)$$

a function of the free ligand concentration. When $x_2 = x_2'$

$$\frac{\beta_2 [L]^2}{1 + \beta_1 [L] + \beta_2 [L]^2 + \cdots} = \frac{\beta_2 [L']^2}{1 + \beta_1 [L'] + \beta_2 [L']^2 + \cdots} \qquad (2.14)$$

therefore, $[L] = [L']$. For corresponding solutions, $x_n = x_n'$, for all n, and $[L] = [L']$.

From Bjerrum's treatment of successive complex formation in solution

$$\bar{n} = \frac{\beta_1 [L] + 2\beta_2 [L]^2 + \cdots + N\beta_N [L]^N}{1 + \beta_1 [L] + \beta_2 [L]^2 + \cdots + \beta_N [L]^N} = \frac{\sum_1^N n\beta_n [L]^n}{\sum_0^N \beta_n [L]^n} \qquad (2.15)$$

where $\bar{n}$ is the "average ligand number". Bjerrum called the relationship of equation (2.15) the "formation function" of the system, in which an unambiguous connection between the average ligand number and the free ligand concentration is expressed. If the concentration of free ligand is known, the formation function may be calculated directly from the equation

$$\bar{n} = \frac{C_L - [L]}{C_M} \tag{2.16}$$

By rearranging equation (2.16) to give

$$C_L = \bar{n}C_M + [L] \tag{2.17}$$

one has the familiar equation of a straight line where $\bar{n}$ is the slope, and $[L]$ is the y-intercept.

According to equations (2.7) and (2.14), when $\Delta H/C_M = (\Delta H/C_M)'$ the solutions are corresponding, and therefore $[L] = [L']$. One should then be able to select values of $\Delta H/C_M$ where equation (2.7) holds, make a plot of the corresponding values of C_L and C_M, and obtain a series of straight lines with slopes $\bar{n}$ and intercepts $[L]$. This is illustrated in Figure 1.

Formation Constants and Enthalpies - Once a set of values for $\bar{n}$ and $[L]$ have been determined, either by graphical or some other means, the problem of finding values for the formation constants and overall enthalpies of formation becomes a matter of curve fitting. Bjerrum's formation function may be plotted against $\log[L]$ as shown in Figure 2. The curve should asymtotically approach the maximum coordination number, N, of the central metal ion. Equation (2.15) may then be fitted to the experimental formation function to determine the formation constants.

Poe (22) has proposed that a set of temporary or "pseudo constants" be calculated from the Scatchard function as a starting point

$$k_{ps} = \frac{\bar{n}}{(N - \bar{n})[L]} \tag{2.18}$$

where k_{ps} is the "equilibrium constant" for the chemical

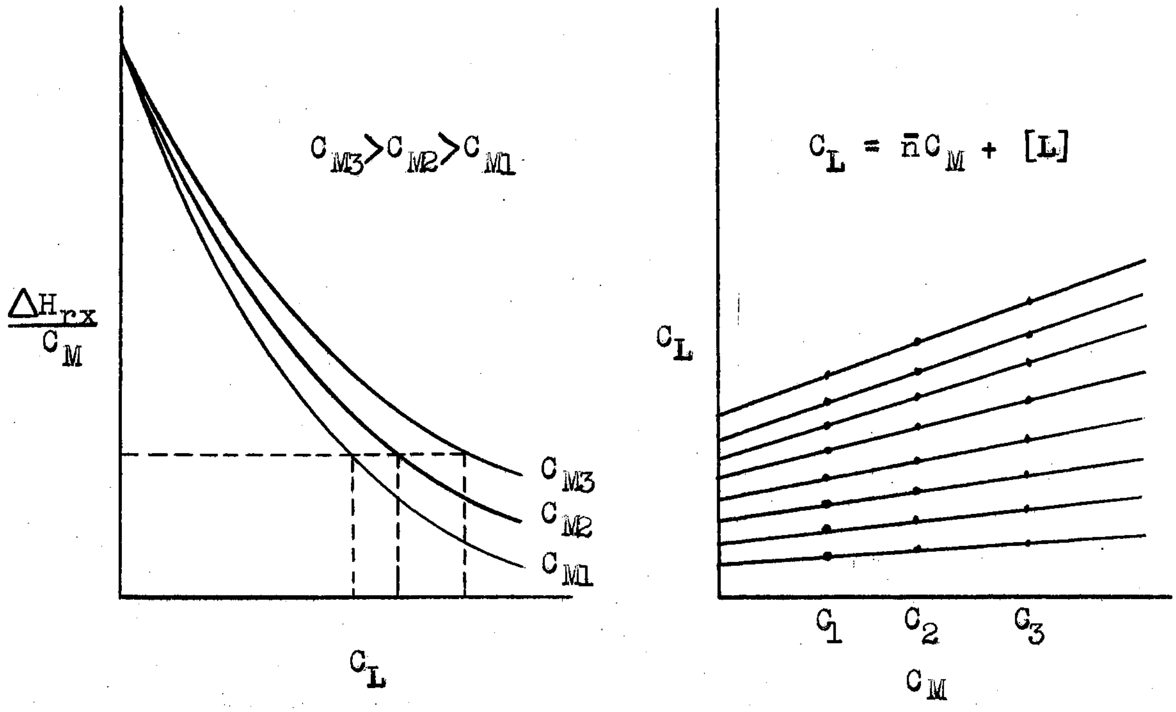

Figure 1. The Corresponding Solutions Method of Determining $\bar{n}$ and [L]

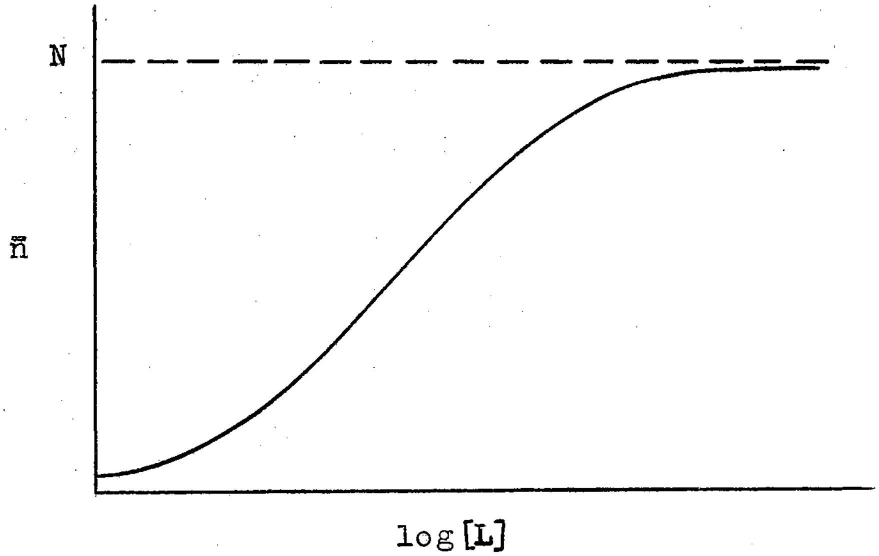

Figure 2. Typical Formation Function of Bjerrum Where $\bar{n}$ Approaches N

equilibrium

$$\text{unoccupied site} + L \rightleftarrows \text{occupied site} \tag{2.19}$$

Since the ease with which a site can be occupied would be expected to be influenced by the number of neighboring sites already occupied, k_{ps} is not expected to be a constant with variation of $\bar{n}$ or $[L]$. An increase of k_{ps} with $\bar{n}$ indicates increasing ease of attachment and vice versa. The pseudo constant is much more sensitive to such effects than the formation function curve. Extrapolation of the k_{ps} curve to $\bar{n} = 0$ gives k_1/N and to $\bar{n} = N$ gives Nk_N.

Values for the enthalpies may be found in a manner similar to that used to find the β's from the equation (if the β's are known)

$$\overline{\Delta H} = \frac{\eta_1\beta_1[L] + \eta_2\beta_2[L]^2 + \cdots + \eta_N\beta_N[L]^N}{1 + \beta_1[L] + \beta_2[L]^2 + \cdots + \beta_N[L]^N} \tag{2.20}$$

If the stepwise attachment of ligands to the central metal ion is purely a statistical function, so that $\eta_n = n\eta_1$, then

$$\overline{\Delta H} = \eta_1\bar{n} \tag{2.21}$$

gives a linear relation between $\overline{\Delta H}$ and $\bar{n}$. From a plot of $\overline{\Delta H}$ versus $\bar{n}$, the limiting slope at $\bar{n} = 0$ should give the value of η_1. In like manner, temporary values for the successive η's may be found by measuring the slope of the curve for η_n at $\bar{n} = n - 1$. Iterative refinement of the η's is necessary for a good fit, as is the case with the β's. Computer techniques are invaluable for such successive approximations, simply because of the labor involved in making the calculations by hand.

Entropies of formation can be calculated in a straightforward manner from the formation constants and enthalpies of formation by the thermodynamic equation

$$\sigma_n = \frac{\eta_n}{T} + R \ln \beta_n \tag{2.22}$$

Assumptions of the Theory - In the foregoing the theory of corresponding solutions has been developed in a general sense, but several assumptions are necessary for the adaptation of the method to the cobalt (II) and nickel (II) perchlorate-water-1-butanol systems.

Consider the following two reaction possibilities. Let X be the perchlorate ion and L be the water ligand.

$$ML_{n-1}X_p + L \rightleftarrows ML_nX_p \quad \text{for which} \quad k_{np} = \frac{[ML_nX_p]}{[ML_{n-1}X_p][L]} \tag{2.23}$$

and

$$ML_nX_{p-1} + X \rightleftarrows ML_nX_p \quad \text{for which} \quad k'_{np} = \frac{[ML_nX_p]}{[ML_nX_{p-1}][X]} \tag{2.24}$$

Then if

$$\beta_n = \prod^{n} k_{n0} = k_{10}k_{20}k_{30}\cdots k_{n0} \tag{2.25}$$

and

$$\beta_p = \prod^{p} k'_{np} = k'_{n1}k'_{n2}k'_{n3}\cdots k'_{np} \tag{2.26}$$

it follows that

$$[ML_nX_p] = [M][L]^n[X]^p\beta_n\beta_p \tag{2.27}$$

The average ligand number may again be formulated

$$\bar{n} = \frac{C_L - [L]}{C_M} = \frac{\sum\limits_0^n \sum\limits_0^p n\beta_n\beta_p [M][L]^n[X]^p}{\sum\limits_0^n \sum\limits_0^p \beta_n\beta_p [M][L]^n[X]^p} \tag{2.28}$$

Let w_{np} be the fraction of M as the complex ML_nX_p. Then

$$w_{np} = [ML_nX_p]/C_M \tag{2.29}$$

and hence

$$\bar{n} = \frac{\sum_0^n \sum_0^p n\,[ML_nX_p]}{C_M} = \sum_0^n \sum_0^p nw_{np} \qquad (2.30)$$

Similarly, for the heat of reaction

$$\overline{\Delta H} = \sum_0^n \sum_0^p \eta_{np}\,[ML_nX_p]/C_M \qquad (2.31)$$

If one finds two solutions such that

$$\overline{\Delta H} = \overline{\Delta H}' \qquad (2.32)$$

then one has from (2.29)

$$(\sum_0^n \sum_0^p \eta_{np}w_{np}) = (\sum_0^n \sum_0^p \eta_{np}w_{np})' \qquad (2.33)$$

Equation (2.33) can hold at all values of η_{np} only if $w_{np} = w'_{np}$, for presumably $\eta_{np} = \eta'_{np}$ always. Since the w_{np}'s are all equal, it follows that $\bar{n} = \bar{n}'$ because, according to equation (2.30), they are the same function of the w_{np}'s. Furthermore, one notes that

$$w_{np} = \frac{\beta_n\beta_p[L]^n[X]^p}{\sum_0^n \sum_0^p \beta_n\beta_p[L]^n[X]^p} \qquad (2.34)$$

w_{np} is independent of [X] if, and only if, [X] can be eliminated from equation (2.34) by cancellation, i.e., if p = 0 or if p is constant, and equation (2.34) reduces to equation (2.11). When p = 0 one has the case of complete dissociation. When p ≠ 0, but is a constant, there results the case of complete ion-association.

It should be emphasized that unless p is a constant (including zero) equation (2.34) will not reduce to the form of equation (2.11), and a plot of C_L versus C_M would not be expected to be linear.

Experimental evidence in the form of conductivity measurements will be given later to support the hypothesis that the perchlorates studied do not exist as dissociated ions in 1-butanol in the concentration range of from 0.08 to 0.01M, but rather as ion-associates.

No attempt was made throughout the measurements to maintain a constant ionic strength medium in order to minimize any change in activity coefficients. In solvents of low dielectric constant, the deviation from ideality for a completely dissociated solute is greater than in solvents of high dielectric constant, and departure from the Debye-Huckel limiting law occurs at lower ionic strengths. However, if ion-association is very pronounced, the ionic strength is then so low that activity coefficients may actually be nearer unity than they are in solvents of high dielectric constant (16). Therefore, at the experimentally investigated salt concentrations in 1-butanol in which mostly ion-associates exist, the total ionic strength should be very close to zero.

A still more important reason for not attempting to maintain a constant high ionic strength by the addition of a second electrolyte is the competition of the supporting salt for the ligand. The reaction of water with the medium could be expected to produce thermal effects overwhelming and masking the primary heat of reaction with cobalt (II) or nickel (II) perchlorate.

A correction for the heat of mixing of water with 1-butanol was necessary. As previously mentioned, the correction function was linear, and hence simple to apply. In making such a correction, it was assumed that the enthalpy of mixing of water with salt solution (assuming no reaction between water and salt occurred) was always the same as for water with butanol. While this assumption is probably not true in the strictest sense, any difference would presumably be small in comparison to the overall effect.

CHAPTER III

APPARATUS AND PROCEDURES

The Calorimeter - The concept of thermometric titrations is a rather old one in view of today's modern analytical methods. The first thermometric titration was performed in 1901 when Steinwehr (26) introduced liquid reagent from a pipette into a dewar flask and measured the temperature change with a thermometer. Since that time refinements have been made in calorimeter design, and new instrumentation has been added. As a consequence, thermometric titrations are no longer the tedious, error-prone experiments they once were. Rather, they are convenient, precise, and capable of high accuracy, depending upon the basic needs of the investigator. For analytical purposes, a thermometric titration can be performed with acceptable precision within a matter of a few minutes (13). For more fundamental work, where exact heats of reaction rather than end-points are desired, more care must be exercised in design and construction of the calorimeter. However, a series of twenty-five sequential additions of titrant, such as were performed in this study, can be made in about an hour.

For a calorimeter to be satisfactory for the proposed study of aquocomplexing, several basic requirements had to be fulfilled:

1. The design of the calorimeter should permit maintenance free operation.
2. The calorimeter should be constructed of materials which have low thermal conductance properties and high chemical resistance.
3. The calorimeter should allow the sample solution to be introduced by means of a syringe, thus avoiding exposure of the sample to atmospheric moisture.
4. Provision should be made for introduction of a large amount of titrant without interruption of the continuous operation of the calorimeter during a titration.
5. The solution in the calorimeter should be continuously mixed so that the reaction may proceed uniformly once titrant is added, and equilibrium may be established rapidly.
6. The temperature of the titrant should continuously be controlled and maintained at the same temperature as the solution, so that a correction factor will not need to be applied.
7. The calorimeter must be sensitive to very small temperature changes, with no appreciable time lag in detection.
8. An electrical heat capacity calibration system should be used.
9. The calorimeter should have an overall accuracy of within ±1% for some suitable standard calibrating reaction involving a total heat change of approximately one calorie.

Several excellent solution calorimeters have been described in the literature, but they do not incorporate all of the desirable properties listed (6,13,14,25). Therefore, a new calorimeter was designed and built specifically to meet the above requirements. A sketch of the calorimeter is shown in Figure 3. The parts illustrated are permanently mounted in an isothermal air chamber.

The calorimeter has been found to give maintenance free operation. Cleaning is effected by simply rinsing with acetone or by immersing the lower part of the calorimeter in a cleaning solvent. The calorimeter vessel itself is a small silvered dewar flask which can be cleaned in any conventional manner.

The calorimeter was constructed of glass because of the good structural stability and relatively low thermal conductance of glass. Some metals are better structurally, but they tend to have high rates of heat transfer. Some plastics have better thermal conductance properties than glass, but they either have less structural stability or are not as chemically resistant. Glass was considered to be the best compromise. All parts which contact the solution are glass except the internal heater wire (A) and the titrant hypodermic needle (D).

The sample injection port (E) is fitted with a serum stopper so that a hypodermic syringe can be used to inject the proper size sample (32-35 cc. of solution). The dewar flask is equipped with a standard taper ground glass fitting (₮ 50/40 mm.) such that when it is sealed in place the entire unit is air tight.

Titrant is introduced with an R-G precision micrometer

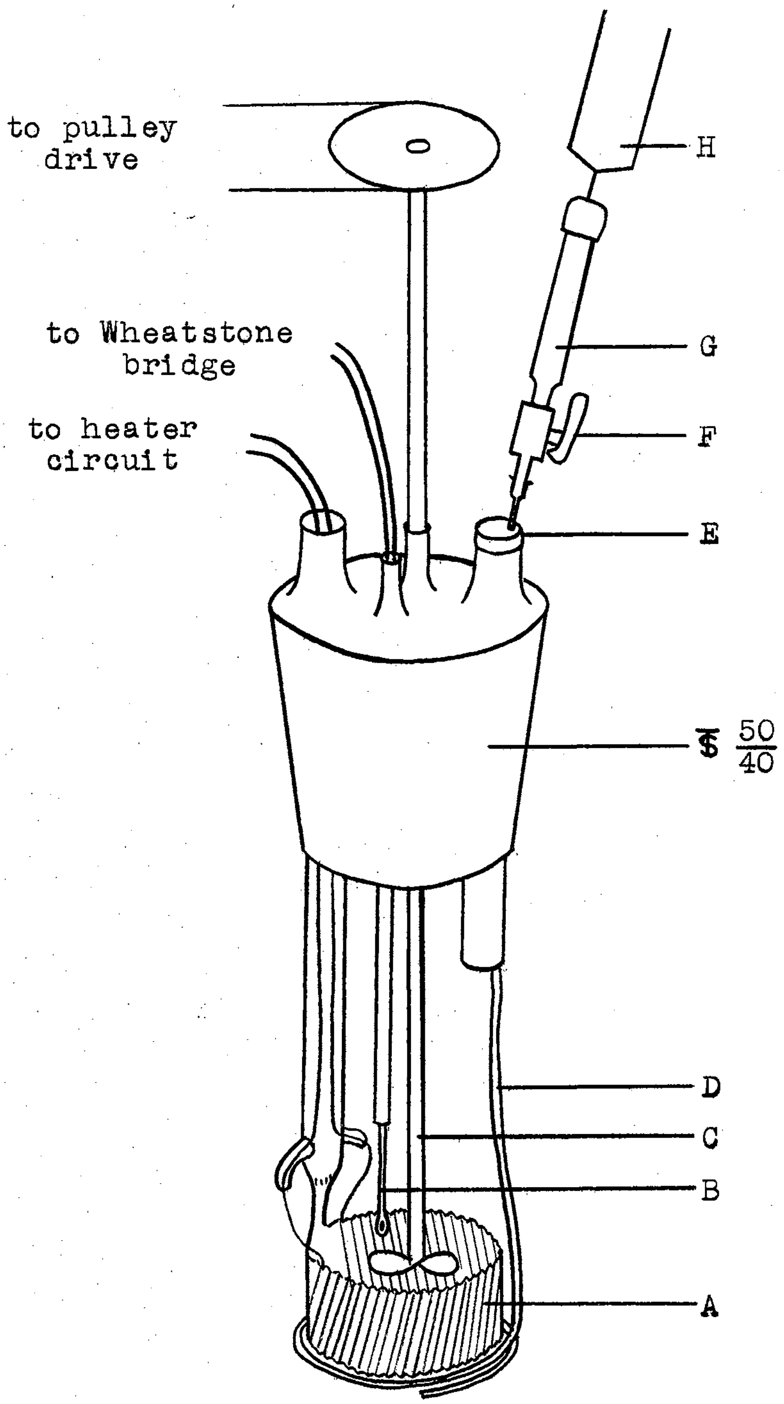

Figure 3. The Internal Parts of the Calorimeter

syringe (0.0001 cc. divisions, 0.02% accuracy, 2.5 cc. capacity) (H) via a twelve-inch Wilkens Instrument and Research Teflon 18 gauge hypocermic needle with a 22 gauge tip inserted into the end. A "piggy back" reservoir (G) attached to a B-D MS01 syringe stopcock (F) is arranged so that the micrometer syringe may be removed from its position for refilling without disturbing the operation of the calorimeter.

Mixing and stirring of the solution is accomplished by a glass rod with paddles molded on the end (C). The rod is mounted in two Teflon bearings, and a pulley at the upper end allows the rod to be rotated by a remote electric motor. Some qualitative tests indicated that liquid solutions of water and 1-butanol became homogeneous within 15 seconds.

An important feature of the calorimeter, and one that greatly improved the precision over previous designs, is the device which guarantees the same temperature for titrant as for solution. The lower half of the Teflon hypodermic needle (D) is coiled around the internal heater body below the surface of the solution. The volume of the coiled portion of the needle is approximately 0.05 cc. Since the injections ranged in volume from 0.0050 to 0.0250 cc., the minimum time that any injected volume spent within the coil was over five minutes. Precautions were taken to see that both solution and titrant were at the same temperature before the titration. However, since the solution will not maintain the same temperature over the entire run (the process is adiabatic), the coiled needle allows the temperature of the titrant and solution to continuously equilibrate. As a consequence, no uncertain correction factor had to be applied for each increment, and the output data could be used directly as they were recorded.

The heart of any calorimeter is its temperature-sensing element. A Victory Engineering Co. 2000 ohm ± 20% thermistor (No. 32A30) formed one arm of a Wheatstone bridge, with the unbalance potential of the bridge measured by a Sargent SR recording potentiometer. The thermistor has a temperature coefficient of -3.9% deg.$^{-1}$ and was operated at a potential of 1.45 volts. The 1 mV. range plug on the recorder was used. The temperature sensing circuit is shown in Figure 4. Variable resistors in the bridge are digital reading Borg Equipment Co. precision helipots, with a linear tolerance of 0.1%.

The bridge was operated at a sensitivity of 0.20 to 0.25 calories per inch of pen travel on the recorder. Measurements were made to the nearest 0.01 inch or ±0.0001°C. Somewhat higher sensitivities are available by applying a greater potential across the thermistor. However, care must be taken not to exceed the maximum operation potential of the thermistor which would cause internal heating of the thermistor to occur. Preliminary experiments showed that the pen displacement was a linear function of temperature.

The calorimeter has an electrical heat capacity calibration system as shown in Figure 4. A constant calibrating current is provided by discharging a Willard six volt lead battery across a General Radio Co. type 1432-F decade resistor, or "dummy heater", which is preset to match the resistance of the heater in the calorimeter. A relay system is

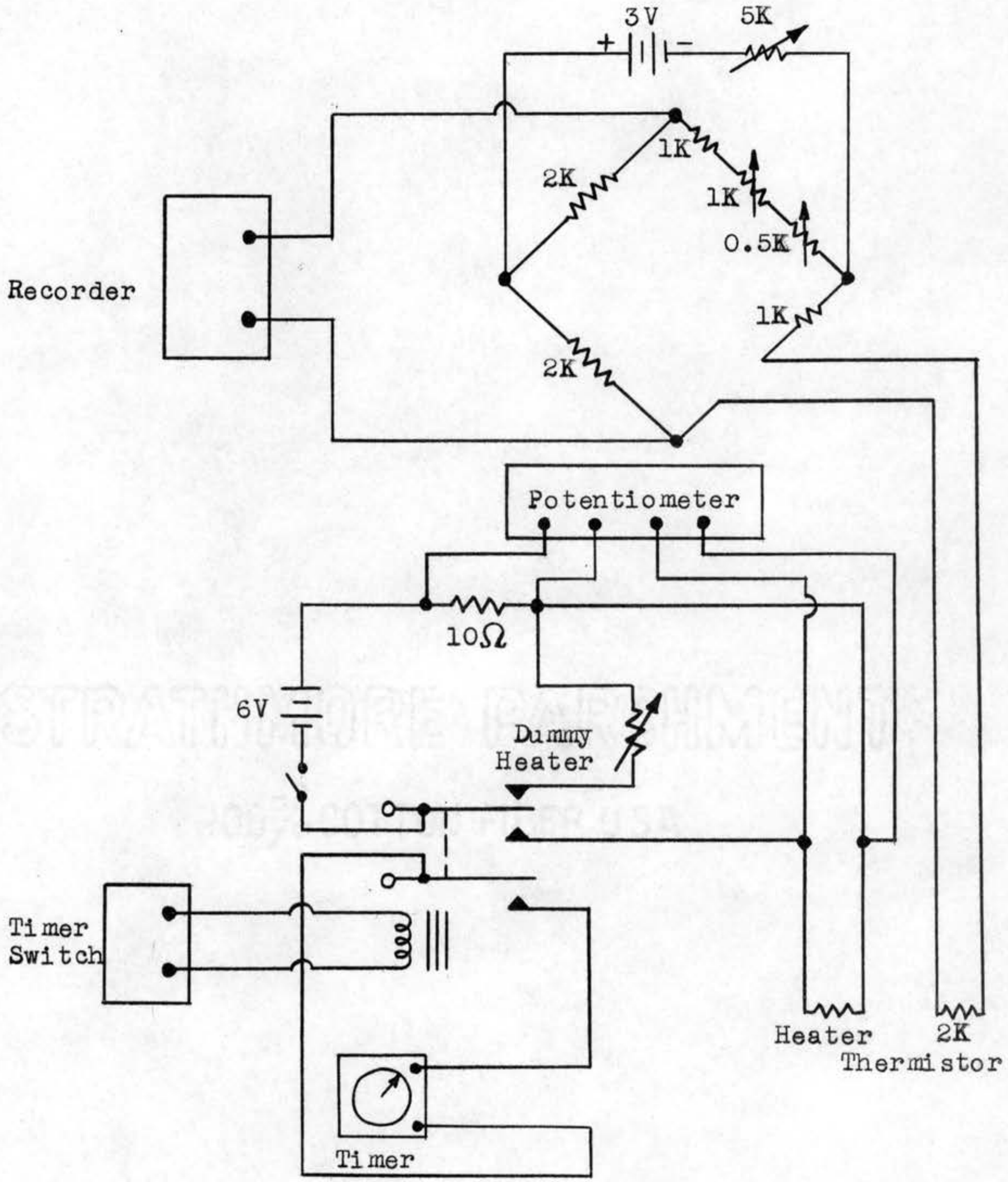

Figure 4. A Schematic of the Temperature Sensing and Heat Capacity Calibration Circuitry

connected from an X-ray timer (0.001 second) and time switch to the heater, which is externally wound with six feet of 0.0034 inch diameter platinum wire having a total resistance of 25 ohms. A Rubicon potentiometer was used to measure the potential across the heater and across a secondary standard General Radio type 500-B ten ohm resistor which was kept in a sealed dewar flask at room temperature. The secondary standard was standardized against a Leeds and Northrup 4025-B National Bureau of Standards type ($10.0000 \pm .0005\Omega$ at 25°C.) primary standard. Its resistance was found to be $10.000 \pm .003$ ohms at 25°C.

The heat capacity was calculated by the formula

$$h = \frac{iEt}{4.186 \cdot s} = \text{number of calories per inch pen travel}$$

where i = current across heater in amperes

E = potential across heater in volts

t = time current was flowing in seconds

s = distance of recorder pen travel in inches

4.186 = number of joules per calorie

The performance of the calorimeter was checked by measurement of the well studied heat of formation of water. A recent careful calorimetric study by Hale, et.al. (9), gave the heat of formation of water as $\Delta H_f = -13.34$ kcal./mole at 25°C.

A titration of 0.14451 molal HCl (aq.) with 3.9937 molar NaOH (aq.) gave the value $\Delta H_f = -13.39$ kcal./mole at 27°C. and $\Delta H_f = -13.50$ kcal./mole at 24°C. By using the listed correction factor for the differences in temperature of 0.04

kcal./mole•deg., an average value of $\Delta H_f = -13.46$ kcal./mole at 25°C. is obtained (23). This value is within the 1% accuracy sought.

Drying Apparatus - One of the experimental difficulties in making a study of the stepwise aquocomplexing of cobalt (II) and nickel (II) perchlorates is that of preparing a zero water concentration reference solution. Common techniques for drying alcohols produce no less than 0.1% residual water as tested by Karl Fischer titration (12). A 0.1% solution of water in 1-butanol, however, represents a molar concentration larger than some of the salt concentrations used in this study. It was obvious from the beginning that some method of obtaining "dry" solutions (no residual water) would have to be found for the results to have much significance.

Perchlorate salts are always obtained as hydrates in the solid state. Attempts to prepare dry salts by heating in an oven results in decomposition of the perchlorates, often explosively. Dry solutions, therefore, cannot be prepared by simply adding dry salt to dry solvent, i.e., the water must be removed after the solution is prepared.

Attempts by Fielder (6) to obtain dry solutions by direct contact with Molecular Sieve 4A (Linde Co., Division of Union Carbide) (10) resulted in very low water content, but there was some loss of metal ions and contamination due to an ion exchange with the sieves. The presence of any species in the solution other than the pure cobalt (II) or nickel (II) perchlorates was considered highly undesirable for the proposed calorimetric studies.

Arthur, et.al. (1), developed a very effective method for drying salt solutions with Molecular Sieves using a modified Soxhlet extractor. The technique used in this study is basically the same as theirs, with the addition of apparatus for refluxing under vacuum conditions as illustrated in Figure 5.

Because of the potential danger involved in drying the nickel perchlorate solution by heating to boiling (117° C.), it was decided in this study to use as low a temperature as possible for refluxing. 1-Butanol solutions will readily distill at 25° C. at 1 mm. Hg, but the temperature differential between the butanol vapors and the condensing coolant was found to be too small to give a good reflux rate; furthermore, too much vapor was lost from the column. In the procedure finally adopted the solutions were heated with a heating mantle to 35° C. and refluxed at 15 mm. Hg. Once the distillation was in progress, vapor loss was negligible; therefore, no concentrating of solutions occurred.

Drying Procedure - The Molecular Sieves 3A must be wetted with predried solvent before use. The solution to be dried was placed in the distillation flask, and the system from Valve A to the vacuum pump was evacuated. Air was then bled from the flask by carefully opening Valve A to prevent bumping of the solution. Once the air had been pumped out of the flask, and the pressure at the manometer had reached 10 to 15 mm. Hg, the stopcock on the vacuum regulator was closed, and the heating mantle was switched on.

Care was taken to fill the flask no more than half full

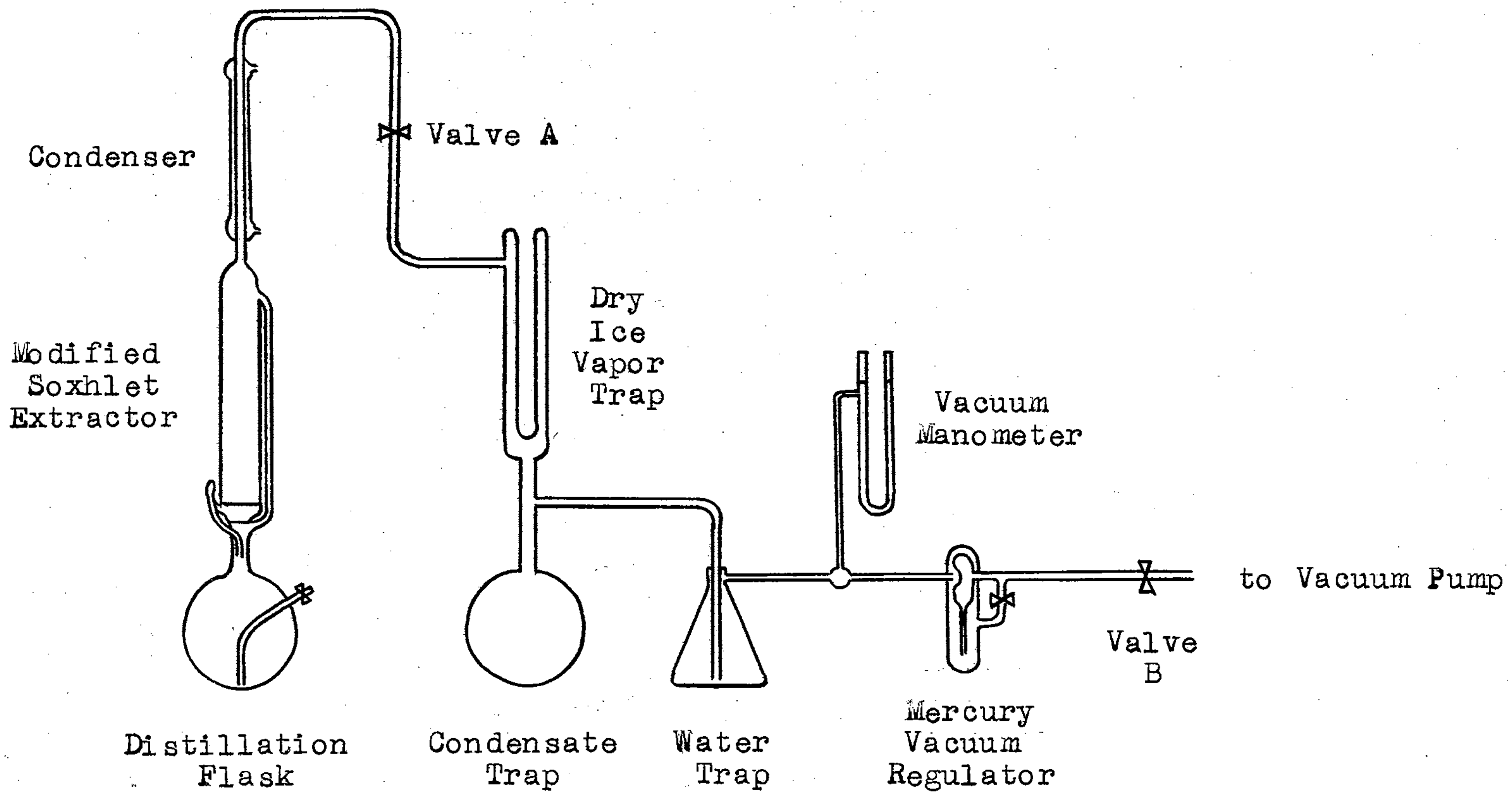

Figure 5. Solution Drying Apparatus

as the 1-butanol solutions of the perchlorates were very prone to bump at low pressure. Moderate bumping can be expected, and due precautions should be observed.

Solutions can be dried from 0.1% to less than 0.001% water in four to six hours using the vacuum techniques. All solutions were carefully stored and handled by syringes. Although rigid precautions were taken, it seemed impossible to prevent at least some contamination from atmospheric moisture. However, from comparative titrations and back extrapolations it is estimated that the solutions before titration in the calorimeter contained less than 0.001% residual water.

Karl Fischer titration, using polarized electrodes and a Beckman Expanded Scale pH meter as a null-point detector, was used in determining water concentrations. The direct titration procedure becomes insensitive below 0.0001% water, so a lower limit has not been established for the drying technique, but it appears to be less than 0.0001%.

The cobalt (II) and nickel (II) concentrations were determined by EDTA titration as described by Flaschka (7), using murexide as an end-point indicator. The concentrations were determined first on a weight basis as molalities and then converted to molarities by density measurements. A linear relation between density and molality is shown in Figure 6.

<u>Thermometric Titration Procedure</u> - The heater and thermistor batteries were switched on 15 minutes prior to a run to allow time for the current to become constant.

Much attention had to be given to the preparation and

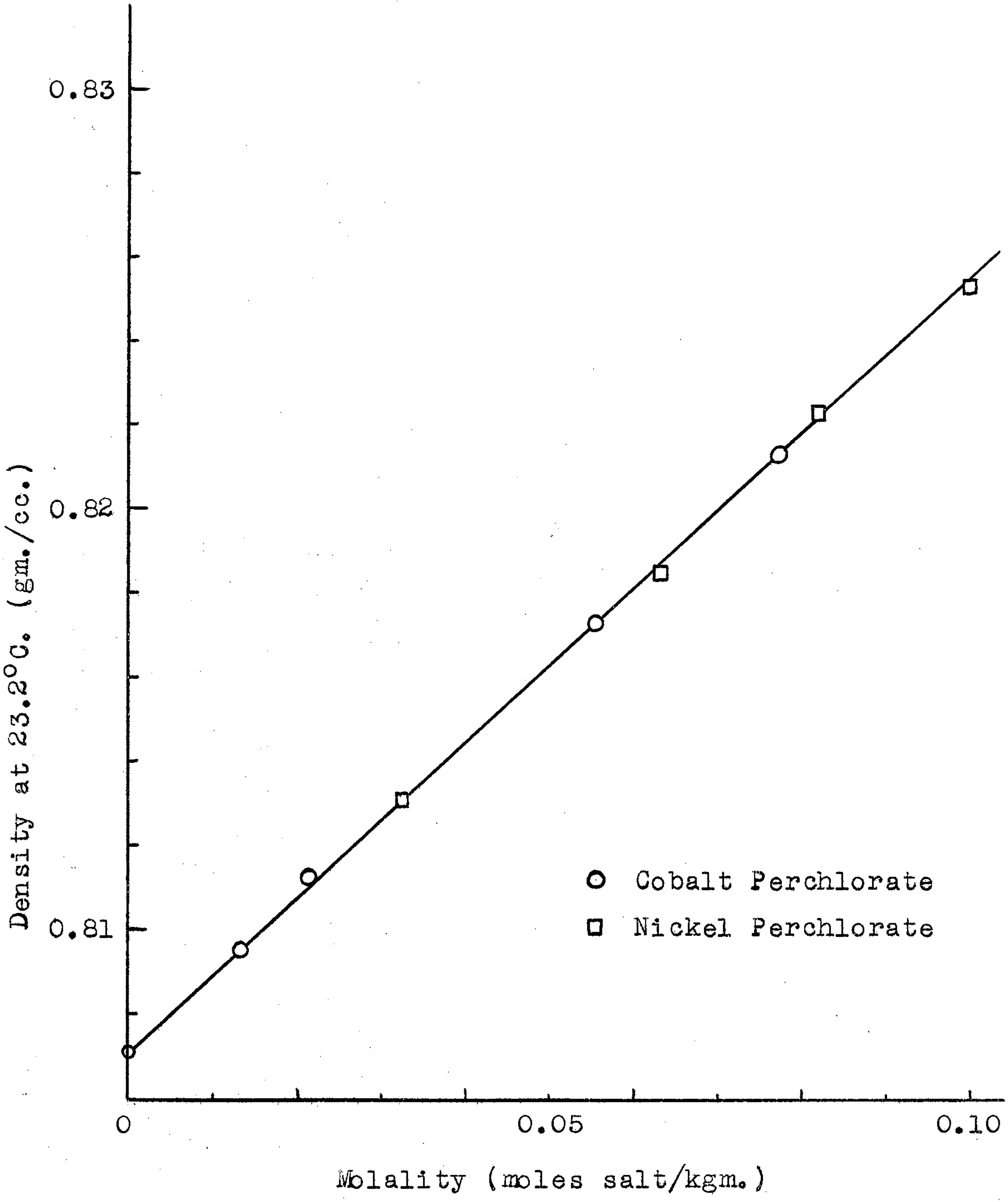

Figure 6. Densities of Cobalt (II) and Nickel (II) Perchlorate Solutions in 1-Butanol

handling of solutions to insure the exclusion of water in the aquocomplexing studies. Equal precautions had to be taken in preparation of the calorimeter, or the solutions would once again take up water from merely contacting the calorimeter before any measurements were made.

The "piggy back" reservoir was first filled with titrant and then connected to the Teflon needle. Additional titrant was forced through the reservoir and Teflon Needle until excess titrant emerged from the tip of the needle at the bottom of the coil showing that all air had been expelled. The syringe stopcock was closed, the drop of water on the tip removed, and a small bit of silicone grease placed over the tip to prevent premature mixing of titrant with solution before the beginning of the run.

The small dewar flask was first cleaned and rinsed with acetone; it was then placed in a vacuum desiccator overnight. The dewar flask was next positioned inside the calorimeter air jacket. Dry tank nitrogen at room temperature was passed through a desiccant tube filled with Drierite and the calorimeter flushed with the dried gas. After 15 minutes the stream of nitrogen was removed and the calorimeter chamber immediately sealed to exclude any atmospheric moisture.

Approximately 32cc. of a perchlorate solution was weighed in a 50cc. B-D syringe. The solution was injected into the calorimeter, and the stirrer motor switched on. A few minutes were allowed for the calorimeter and solution to reach thermal equilibrium.

Because of the change in composition of the solution throughout a thermometric titration, a series of heat capacity calibrations had to be made at various points in the run. Generally two calibrations at each point have been found to be sufficient.

In making a calibration, the recorder was started, and a temperature base line established. The timer switch was set at a predetermined time so that, according to the current and voltage settings, about one calorie of heat was added to the solution.

After two heat capacity calibrations were made at zero water concentration, the syringe stopcock was opened and the titration begun. Titrant was delivered from the micrometer syringe in increasing increments of 0.0050, 0.0100 and 0.0150 cc. in a typical titration up to 0.2500 cc. total water content (~0.43 molar in water). In the 1-butanol solutions of cobalt and nickel perchlorates, the calorimetric reaction was observed to be initially exothermic due to the greater heat effect of the reaction between water and the salt. Later, after this reaction was partially completed, the overall effect became endothermic due to the endothermic heat of mixing of water with 1-butanol. Typical enthalpograms are shown in Figure 7.

The temperature base lines were extrapolated back to the mid-point of the slope. A vertical line was drawn through the mid-point of the slope to give the height, s. This height, in inches, was multiplied by the heat capacity, in calories per inch, to give the number of calories for each increment.

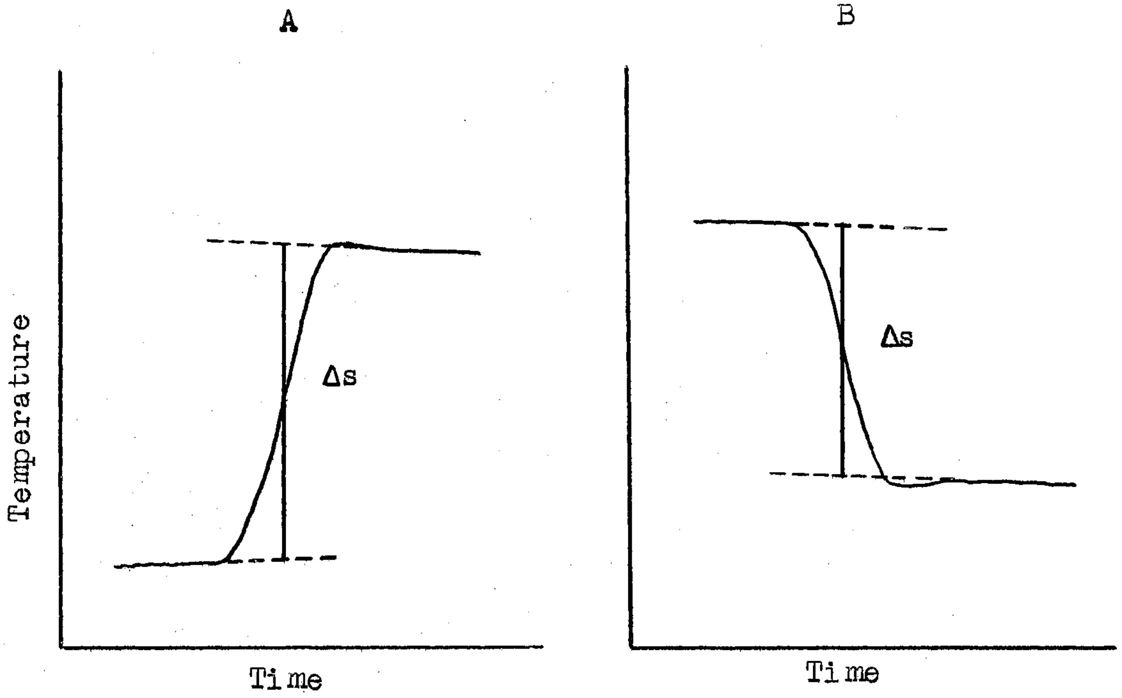

Figure 7. Typical Enthalpograms
A - Exothermic
B - Endothermic

CHAPTER IV

EXPERIMENTAL AND TREATMENT OF DATA

Solutions Used - All of the solutions used in the study were prepared with Baker A.R. grade 1-butanol. The 1-butanol was dried over Linde Molecular Sieves 3A for a minimum of 24 hours. Reagent grade cobalt (II) and nickel (II) perchlorate hexahydrates (G. F. Smith Chemical Co.) were used without further treatment in preparing concentrated (0.5M) solutions in 1-butanol. The concentrated solutions were dried as described in Chapter III and used in preparation of dilute solutions for study in the calorimeter. The dilute solutions (0.08 to 0.01M) were further dried and final concentrations and densities measured before reaction in the calorimeter.

Calorimetry Data - The heat liberated in the calorimeter for the reaction

$$M(\text{soln}) + L(\text{liq}) \rightarrow ML(\text{soln}) + ML_2(\text{soln}) + \ldots + ML_N(\text{soln}) + L(\text{soln}) + Q_{cal} \qquad (4.1)$$

in dilute solution consists of two main parts. When the total quantity of water added is small, only the heat of aquocomplex formation and the heat of mixing of water with 1-butanol contribute significantly to the Q_{cal} measured in the calorimeter

$$Q_{cal} = Q_{rx} + Q_{sol} \qquad (4.2)$$

Since Q_{cal} is the experimental quantity of heat measured in the thermometric titration of cobalt (II) or nickel (II) perchlorate in 1-butanol with water, Q_{sol}, the heat of mixing of water with 1-butanol, must be determined before Q_{rx}, the heat of reaction of L with M, can be determined.

A series of five thermometric titrations of 1-butanol with water was made in order to gain thermodynamic information about the heat of mixing. Young, et.al. (30), have measured the mixing of 1-butanol with water at high water concentrations and found it to be a linear function of butanol concentration from 0.0 to 0.12M 1-butanol in water. The heat of mixing was also found here to be very nearly linear with water concentration at low water concentrations as shown in Figure 8. Experimental data for two typical thermometric titrations selected from the five are given in Table I along with the calculated heats of mixing. From the five sets of data, the partial molal enthalpy of solution of water in 1-butanol was found to be 0.432±.002 kcal./mole water.kgm. butanol.

Once the enthalpy of mixing had been determined, salt solutions were titrated thermometrically to determine the heat of reaction, $\overline{\Delta H}$. Five solutions of $Co(ClO_4)_2$ in 1-butanol ranging in concentration from 0.0171 to 0.0803M and four solutions of $Ni(ClO_4)_2$ ranging in concentration from 0.0260 to 0.0803M were studied. Duplicate titrations were made at each salt concentration, as shown in Figures 9 and 10. The experimental data and calculated heats of reaction are given in Table II.

<u>Sample Calculation</u> - A sample calculation illustrating how $\overline{\Delta H}$ is obtained from the experimental data is given on page 45.

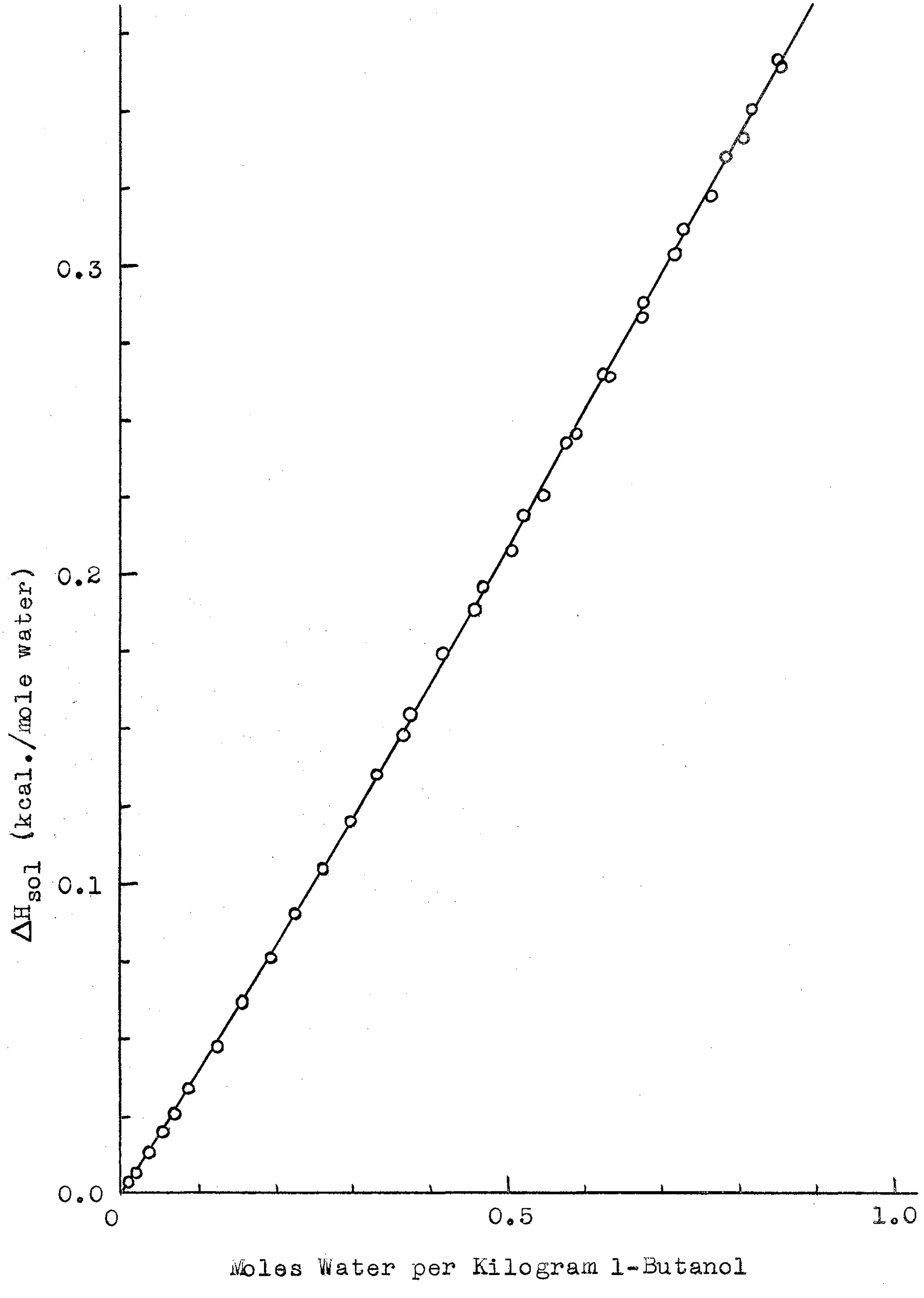

Figure 8. Heat of Mixing of Water with 1-Butanol

TABLE I

HEAT OF MIXING OF WATER AND 1-BUTANOL

32.034g 1-Butanol				32.023g 1-Butanol			
ml H_2O	s, in	h	$\overline{\Delta H}_{sol}$	ml H_2O	s, in	h	$\overline{\Delta H}_{sol}$
0.0050	-0.26	0.3075	2.5	0.0050	-0.34	0.3073	3.3
0.0100	-0.34	0.3075	5.8	0.0100	-0.33	0.3075	6.4
0.0200	-0.68	0.3076	12.3	0.0200	-0.66	0.3080	12.8
0.0300	-0.69	0.3077	18.9	0.0300	-0.69	0.3086	19.4
0.0400	-0.69	0.3077	25.6	0.0400	-0.69	0.3091	26.1
0.0500	-0.71	0.3078	32.4	0.0500	-0.73	0.3096	33.2
0.0700	-1.45	0.3080	46.3	0.0700	-1.43	0.3107	47.0
0.0900	-1.48	0.3083	60.6	0.0900	-1.46	0.3117	61.2
0.1100	-1.48	0.3086	74.8	0.1100	-1.48	0.3127	75.7
0.1300	-1.48	0.3089	89.1	0.1300	-1.53	0.3137	90.7
0.1500	-1.50	0.3093	103.6	0.1500	-1.54	0.3143	105.8
0.1700	-1.52	0.3097	118.3	0.1700	-1.49	0.3152	120.4
0.1900	-1.50	0.3101	132.8	0.1900	-1.50	0.3158	135.2
0.2100	-1.53	0.3106	147.6	0.2150	-1.91	0.3165	154.1
0.2400	-2.32	0.3114	170.2	0.2400	-1.93	0.3172	173.2
0.2650	-1.91	0.3121	188.8	0.2700	-2.32	0.3177	196.3
0.2900	-1.92	0.3129	207.5	0.3000	-2.32	0.3184	219.3
0.3150	-1.95	0.3137	226.6	0.3300	-2.32	0.3190	242.4
0.3400	-1.95	0.3145	245.8	0.3600	-2.32	0.3196	265.6
0.3650	-1.93	0.3154	264.8	0.3900	-2.31	0.3201	288.7
0.3900	-1.93	0.3164	283.8	0.4200	-2.35	0.3206	312.2
0.4150	-1.95	0.3174	303.2	0.4500	-2.33	0.3210	335.6
0.4400	-1.93	0.3185	322.4	0.4700	-1.59	0.3213	351.5
0.4650	-1.96	0.3196	341.9	0.4900	-1.57	0.3216	367.3
0.4950	-2.35	0.3210	365.5				

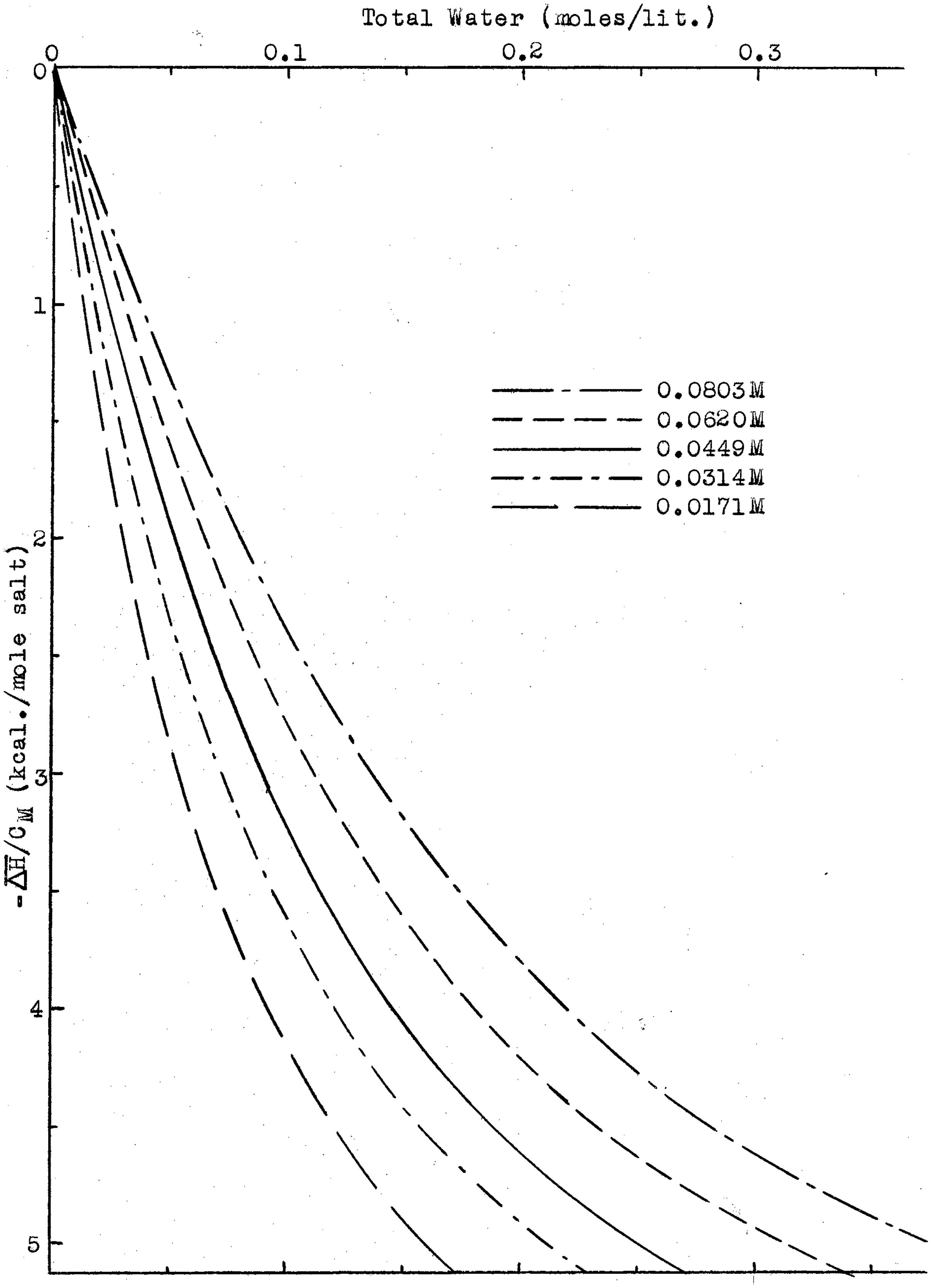

Figure 9. Heat of Reaction of Water With $Co(ClO_4)_2$

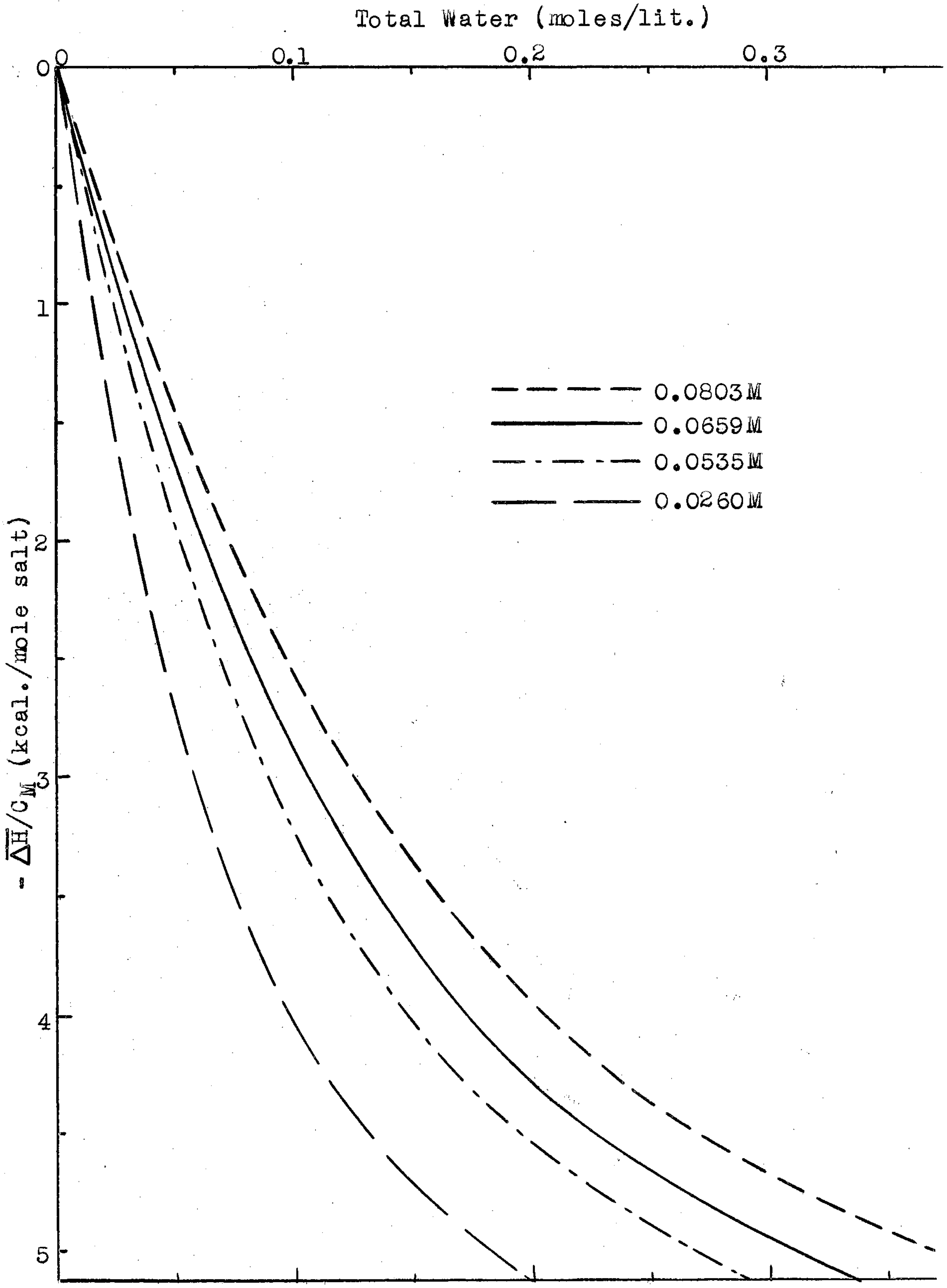

Figure 10. Heat of Reaction of Water With $Ni(ClO_4)_2$

TABLE II

EXPERIMENTAL DATA AND CALCULATED HEATS OF REACTION FOR THERMOMETRIC TITRATIONS

26.505g of 0.0620M $Co(ClO_4)_2$				26.499g of 0.0620M $Co(ClO_4)_2$				26.453g of 0.0449M $Co(ClO_4)_2$			
ml H_2O	s, in	h	$\overline{\Delta H}$, cal	ml H_2O	s, in	h	$\overline{\Delta H}$, cal	ml H_2O	s, in	h	$\overline{\Delta H}$, cal
0.0065	2.45	0.2603	- 389	0.0050	2.06	0.2482	- 310	0.0050	1.68	0.2583	- 376
0.0115	1.80	0.2604	- 678	0.0100	1.92	0.2483	- 603	0.0100	1.64	0.2584	- 745
0.0165	1.69	0.2605	- 953	0.0150	1.84	0.2485	- 886	0.0150	1.51	0.2585	-1091
0.0215	1.59	0.2606	-1215	0.0200	1.70	0.2486	-1152	0.0200	1.40	0.2586	-1418
0.0265	1.51	0.2608	-1467	0.0250	1.55	0.2488	-1400	0.0250	1.26	0.2587	-1721
0.0315	1.33	0.2609	-1696	0.0300	1.49	0.2489	-1641	0.0300	1.17	0.2588	-2008
0.0365	1.24	0.2610	-1914	0.0350	1.43	0.2491	-1875	0.0350	0.96	0.2589	-2258
0.0415	1.14	0.2611	-2119	0.0400	1.32	0.2492	-2095	0.0400	0.90	0.2590	-2497
0.0465	1.10	0.2612	-2318	0.0450	1.17	0.2493	-2297	0.0450	0.81	0.2591	-2721
0.0515	1.00	0.2613	-2505	0.0500	1.07	0.2495	-2487	0.0500	0.74	0.2592	-2932
0.0565	0.90	0.2614	-2680	0.0550	0.97	0.2496	-2664	0.0550	0.58	0.2594	-3116
0.0665	1.53	0.2616	-2994	0.0650	1.70	0.2499	-2990	0.0650	1.00	0.2596	-3455
0.0765	1.30	0.2619	-3278	0.0750	1.44	0.2502	-3285	0.0750	0.77	0.2598	-3753
0.0865	1.14	0.2621	-3543	0.0850	1.17	0.2505	-3546	0.0850	0.50	0.2599	-4004
0.0965	0.84	0.2623	-3768	0.0950	0.90	0.2507	-3775	0.0950	0.32	0.2599	-4223
0.1065	0.60	0.2625	-3963	0.1050	0.73	0.2510	-3982	0.1050	0.18	0.2601	-4418
0.1215	0.63	0.2629	-4221	0.1200	0.76	0.2514	-4253	0.1200	0.05	0.2604	-4671
0.1365	0.34	0.2632	-4441	0.1350	0.44	0.2519	-4484	0.1350	-0.21	0.2607	-4878
0.1515	0.11	0.2636	-4632	0.1500	0.15	0.2523	-4679	0.1500	-0.41	0.2609	-5049
0.1665	-0.10	0.2639	-4796	0.1650	-0.09	0.2527	-4844	0.1650	-0.55	0.2612	-5196
0.1815	-0.25	0.2642	-4940	0.1800	-0.25	0.2531	-4989	0.1800	-0.64	0.2615	-5326
0.1965	-0.40	0.2646	-5064	0.1950	-0.40	0.2535	-5116	0.1950	-0.73	0.2618	-5441
0.2115	-0.53	0.2649	-5172	0.2100	-0.52	0.2540	-5228	0.2100	-0.82	0.2620	-5538
0.2265	-0.64	0.2653	-5265	0.2250	-0.64	0.2544	-5324	0.2250	-0.88	0.2623	-5626
0.2415	-0.66	0.2656	-5355	0.2400	-0.70	0.2548	-5413	0.2400	-0.95	0.2626	-5701
0.2565	-0.76	0.2659	-5433	0.2550	-0.81	0.2553	-5488	0.2550	-0.99	0.2629	-5769

TABLE II (Continued)

26.421g of 0.0803M $Co(ClO_4)_2$				26.371g of 0.0803M $Co(ClO_4)_2$				26.245g of 0.0449M $Co(ClO_4)_2$			
ml H_2O	s, in	h	$\overline{\Delta H}$, cal	ml H_2O	s, in	h	$\overline{\Delta H}$, cal	ml H_2O	s, in	h	$\overline{\Delta H}$, cal
0.0040	1.62	0.2534	- 192	0.0018	0.78	0.2524	- 91	0.0033	1.06	0.2581	- 241
0.0090	2.01	0.2536	- 431	0.0068	2.11	0.2528	- 340	0.0083	1.62	0.2581	- 609
0.0140	1.97	0.2537	- 667	0.0118	2.03	0.2532	- 581	0.0133	1.54	0.2582	- 963
0.0190	1.81	0.2538	- 886	0.0168	1.93	0.2536	- 813	0.0183	1.42	0.2582	-1296
0.0240	1.78	0.2540	-1104	0.0218	1.76	0.2540	-1028	0.0233	1.27	0.2582	-1602
0.0290	1.65	0.2541	-1308	0.0268	1.76	0.2543	-1244	0.0283	1.13	0.2582	-1884
0.0340	1.64	0.2543	-1512	0.0318	1.64	0.2547	-1449	0.0333	1.04	0.2583	-2150
0.0390	1.55	0.2544	-1707	0.0368	1.56	0.2550	-1645	0.0383	0.93	0.2583	-2396
0.0440	1.43	0.2545	-1891	0.0418	1.47	0.2554	-1833	0.0433	0.83	0.2583	-2625
0.0490	1.39	0.2546	-2071	0.0468	1.38	0.2557	-2014	0.0483	0.73	0.2583	-2836
0.0540	1.27	0.2548	-2239	0.0518	1.30	0.2561	-2186	0.0533	0.64	0.2584	-3031
0.0640	2.29	0.2551	-2552	0.0618	2.29	0.2568	-2501	0.0633	1.04	0.2584	-3379
0.0740	2.01	0.2553	-2838	0.0718	2.02	0.2574	-2790	0.0733	0.72	0.2585	-3670
0.0840	1.72	0.2556	-3096	0.0818	1.74	0.2580	-3052	0.0833	0.51	0.2585	-3924
0.0940	1.46	0.2558	-3329	0.0918	1.47	0.2586	-3287	0.0933	0.36	0.2586	-4152
0.1040	1.29	0.2560	-3545	0.1018	1.29	0.2591	-3506	0.1033	0.21	0.2586	-4353
0.1140	1.06	0.2562	-3739	0.1168	1.54	0.2599	-3795	0.1183	0.06	0.2587	-4610
0.1240	0.89	0.2563	-3917	0.1318	1.14	0.2606	-4045	0.1333	-0.18	0.2588	-4824
0.1340	0.71	0.2565	-4077	0.1468	0.81	0.2611	-4262	0.1483	-0.38	0.2588	-5003
0.1440	0.53	0.2566	-4220	0.1618	0.54	0.2616	-4452	0.1633	-0.55	0.2589	-5152
0.1540	0.42	0.2568	-4352	0.1768	0.30	0.2620	-4619	0.1783	-0.63	0.2590	-5286
0.1690	0.43	0.2570	-4530	0.1918	0.14	0.2623	-4770	0.1933	-0.76	0.2591	-5397
0.1840	0.20	0.2572	-4686	0.2068	-0.09	0.2626	-4898	0.2083	-0.77	0.2591	-5507
0.1990	0.02	0.2574	-4825	0.2218	-0.21	0.2628	-5014	0.2233	-0.89	0.2592	-5595
0.2140	-0.16	0.2576	-4945	0.2368	-0.37	0.2630	-5113	0.2383	-0.94	0.2593	-5674
0.2290	-0.28	0.2577	-5055	0.2518	-0.46	0.2632	-5204	0.2533	-0.97	0.2594	-5748
0.2440	-0.38	0.2578	-5154								
0.2540	-0.30	0.2579	-5216								

TABLE II (Continued)

26.135g of 0.0314M $Co(ClO_4)_2$				26.139g of 0.0314M $Co(ClO_4)_2$				25.974g of 0.0171M $Co(ClO_4)_2$			
ml H_2O	s, in	h	$\overline{\Delta H}$, cal	ml H_2O	s, in	h	$\overline{\Delta H}$, cal	ml H_2O	s, in	h	$\overline{\Delta H}$, cal
0.0025	0.73	0.2444	- 234	0.0015	0.52	0.2406	- 158	0.0050	1.01	0.2359	- 650
0.0075	1.39	0.2444	- 685	0.0065	1.57	0.2406	- 646	0.0100	0.87	0.2361	-1241
0.0125	1.35	0.2445	-1126	0.0115	1.35	0.2407	-1083	0.0150	0.66	0.2363	-1742
0.0175	1.22	0.2445	-1537	0.0165	1.21	0.2407	-1486	0.0200	0.55	0.2368	-2196
0.0225	1.02	0.2446	-1899	0.0215	1.04	0.2408	-1849	0.0250	0.39	0.2370	-2582
0.0275	0.89	0.2446	-2230	0.0265	0.85	0.2408	-2168	0.0300	0.25	0.2372	-2907
0.0325	0.73	0.2446	-2523	0.0315	0.75	0.2409	-2462	0.0350	0.15	0.2374	-3189
0.0375	0.57	0.2447	-2777	0.0365	0.63	0.2409	-2729	0.0400	0.11	0.2376	-3454
0.0425	0.49	0.2447	-3013	0.0415	0.55	0.2410	-2976	0.0450	0.04	0.2378	-3689
0.0475	0.42	0.2448	-3231	0.0465	0.43	0.2411	-3196	0.0500	-0.05	0.2380	-3886
0.0525	0.34	0.2448	-3430	0.0515	0.36	0.2411	-3399	0.0550	-0.08	0.2383	-4069
0.0625	0.43	0.2449	-3769	0.0615	0.45	0.2412	-3740	0.0650	-0.29	0.2387	-4379
0.0725	0.22	0.2450	-4057	0.0715	0.22	0.2413	-4028	0.0750	-0.40	0.2390	-4641
0.0825	0.06	0.2451	-4307	0.0815	0.06	0.2414	-4277	0.0850	-0.50	0.2394	-4859
0.0925	-0.12	0.2452	-4513	0.0915	-0.08	0.2415	-4493	0.0950	-0.58	0.2397	-5042
0.1025	-0.23	0.2453	-4693	0.1015	-0.20	0.2416	-4681	0.1050	-0.64	0.2400	-5199
0.1175	-0.50	0.2454	-4926	0.1165	-0.49	0.2418	-4918	0.1200	-1.03	0.2403	-5403
0.1325	-0.69	0.2456	-5112	0.1315	-0.65	0.2419	-5116	0.1350	-1.10	0.2407	-5575
0.1475	-0.83	0.2457	-5265	0.1465	-0.78	0.2420	-5284	0.1500	-1.16	0.2411	-5721
				0.1615	-0.88	0.2422	-5428	0.1650	-1.24	0.2416	-5830
				0.1765	-0.96	0.2424	-5552	0.1800	-1.26	0.2420	-5929
				0.1915	-1.05	0.2425	-5655	0.1950	-1.29	0.2424	-6015
				0.2065	-1.07	0.2427	-5753	0.2100	-1.32	0.2427	-6086
				0.2215	-1.12	0.2428	-5839	0.2250	-1.33	0.2431	-6152
				0.2365	-1.18	0.2430	-5911	0.2400	-1.36	0.2435	-6204
				0.2515	-1.21	0.2431	-5975	0.2550	-1.41	0.2438	-6234

TABLE II (Continued)

25.971g of 0.0171M $Co(ClO_4)_2$				26.375g of 0.0803M $Ni(ClO_4)_2$				26.434g of 0.0803M $Ni(ClO_4)_2$			
ml H_2O	s, in	h	$\overline{\Delta H}$, cal	ml H_2O	s, in	h	$\overline{\Delta H}$, cal	ml H_2O	s, in	h	$\overline{\Delta H}$, cal
0.0020	0.43	0.2457	- 279	0.0050	2.45	0.2393	- 268	0.0030	1.41	0.2468	- 159
0.0070	0.96	0.2457	- 925	0.0100	2.41	0.2396	- 532	0.0080	2.40	0.2470	- 429
0.0120	0.78	0.2458	-1491	0.0150	2.29	0.2399	- 786	0.0130	2.31	0.2471	- 690
0.0170	0.56	0.2458	-1959	0.0200	2.15	0.2402	-1027	0.0180	2.13	0.2473	- 934
0.0220	0.44	0.2459	-2373	0.0250	2.01	0.2405	-1256	0.0230	2.09	0.2474	-1175
0.0270	0.33	0.2459	-2738	0.0300	1.94	0.2408	-1478	0.0280	1.92	0.2475	-1400
0.0320	0.21	0.2460	-3050	0.0350	1.82	0.2411	-1690	0.0330	1.77	0.2476	-1612
0.0370	0.11	0.2460	-3317	0.0400	1.68	0.2414	-1890	0.0380	1.68	0.2478	-1814
0.0420	0.06	0.2460	-3561	0.0450	1.58	0.2416	-2080	0.0430	1.59	0.2479	-2009
0.0470	-0.03	0.2461	-3766	0.0500	1.48	0.2419	-2261	0.0480	1.50	0.2481	-2195
0.0520	-0.08	0.2461	-3948	0.0550	1.37	0.2421	-2432	0.0530	1.38	0.2482	-2370
0.0620	-0.25	0.2462	-4271	0.0650	2.47	0.2426	-2750	0.0630	2.42	0.2484	-2688
				0.0750	2.10	0.2430	-3035	0.0730	2.22	0.2487	-2988
				0.0850	1.74	0.2434	-3286	0.0830	1.77	0.2489	-3245
				0.0950	1.45	0.2438	-3511	0.0930	1.46	0.2491	-3473
				0.1050	1.20	0.2442	-3713	0.1030	1.26	0.2493	-3683
				0.1200	1.36	0.2447	-3976	0.1180	1.47	0.2496	-3958
				0.1350	0.95	0.2451	-4200	0.1330	1.00	0.2499	-4188
				0.1500	0.62	0.2455	-4394	0.1480	0.65	0.2502	-4386
				0.1650	0.33	0.2458	-4561	0.1630	0.37	0.2504	-4557
				0.1800	0.12	0.2461	-4709	0.1780	0.17	0.2507	-4709
				0.1950	-0.10	0.2463	-4836	0.1930	-0.04	0.2509	-4852
				0.2100	-0.23	0.2466	-4951	0.2080	-0.20	0.2511	-4959
				0.2250	-0.36	0.2468	-5054	0.2230	-0.33	0.2513	-5063
				0.2400	-0.51	0.2470	-5142	0.2380	-0.46	0.2515	-5156
				0.2500	-0.57	0.2472	-5225	0.2530	-0.56	0.2517	-5238

TABLE II (Continued)

26.574g of 0.0659M $Ni(ClO_4)_2$				26.682g of 0.0659M $Ni(ClO_4)_2$				26.004g of 0.0260M $Ni(ClO_4)_2$			
ml H_2O	s, in	h	$\overline{\Delta H}$, cal	ml H_2O	s, in	h	$\overline{\Delta H}$, cal	ml H_2O	s, in	h	$\overline{\Delta H}$, cal
0.0034	1.53	0.2420	- 207	0.0036	1.53	0.2543	- 217	0.0100	2.72	0.2446	-1074
0.0084	2.27	0.2423	- 514	0.0086	2.12	0.2544	- 518	0.0150	1.37	0.2447	-1614
0.0134	2.23	0.2427	- 817	0.0136	2.17	0.2545	- 825	0.0200	1.09	0.2448	-2073
0.0184	2.05	0.2430	-1100	0.0186	2.01	0.2546	-1113	0.0250	0.87	0.2449	-2469
0.0234	1.99	0.2433	-1377	0.0236	1.89	0.2547	-1387	0.0300	0.66	0.2450	-2803
0.0284	1.80	0.2435	-1633	0.0286	1.72	0.2548	-1642	0.0350	0.49	0.2451	-3088
0.0334	1.67	0.2439	-1875	0.0336	1.57	0.2549	-1879	0.0400	0.34	0.2452	-3329
0.0384	1.54	0.2441	-2102	0.0386	1.41	0.2550	-2098	0.0450	0.29	0.2452	-3556
0.0434	1.41	0.2444	-2315	0.0436	1.31	0.2551	-2305	0.0500	0.20	0.2453	-3756
0.0484	1.30	0.2447	-2516	0.0486	1.21	0.2552	-2501	0.0550	0.10	0.2454	-3928
0.0534	1.23	0.2449	-2709	0.0536	1.10	0.2554	-2684	0.0600	0.04	0.2455	-4082
0.0634	2.02	0.2454	-3046	0.0636	1.94	0.2556	-3019	0.0700	-0.06	0.2456	-4349
0.0734	1.67	0.2459	-3344	0.0736	1.62	0.2558	-3318	0.0800	-0.20	0.2458	-4574
0.0834	1.42	0.2463	-3614	0.0836	1.28	0.2560	-3577	0.0900	-0.35	0.2460	-4757
0.0934	1.03	0.2467	-3841	0.0936	0.95	0.2562	-3797	0.1000	-0.42	0.2461	-4919
0.1034	0.83	0.2471	-4044	0.1036	0.73	0.2565	-3992	0.1100	-0.50	0.2463	-5058
0.1184	0.84	0.2476	-4305	0.1186	0.82	0.2568	-4252	0.1250	-0.86	0.2466	-5233
0.1334	0.44	0.2481	-4520	0.1336	0.45	0.2571	-4469	0.1400	-0.99	0.2468	-5370
0.1484	0.18	0.2486	-4705	0.1486	0.19	0.2574	-4656	0.1550	-1.04	0.2471	-5492
0.1634	-0.06	0.2490	-4863	0.1636	-0.07	0.2577	-4812	0.1700	-1.10	0.2473	-5596
0.1784	-0.24	0.2494	-5000	0.1786	-0.26	0.2579	-4945	0.1850	-1.16	0.2476	-5682
0.1934	-0.39	0.2498	-5121	0.1936	-0.41	0.2581	-5061	0.2000	-1.22	0.2478	-5750
0.2084	-0.50	0.2501	-5228	0.2086	-0.52	0.2583	-5164	0.2150	-1.23	0.2481	-5815
0.2234	-0.60	0.2505	-5324	0.2236	-0.61	0.2585	-5256	0.2300	-1.28	0.2483	-5864
0.2384	-0.70	0.2508	-5409	0.2386	-0.71	0.2588	-5337	0.2450	-1.27	0.2486	-5916
0.2534	-0.75	0.2512	-5487	0.2536	-0.77	0.2591	-5410	0.2600	-1.27	0.2488	-5968

TABLE II (Continued)

26.281g of 0.0260M $Ni(ClO_4)_2$				26.270g of 0.0535M $Ni(ClO_4)_2$				26.402g of 0.0535M $Ni(ClO_4)_2$			
ml H_2O	s, in	h	$\overline{\Delta H}$, cal	ml H_2O	s, in	h	$\overline{\Delta H}$, cal	ml H_2O	s, in	h	$\overline{\Delta H}$, cal
0.0060	1.78	0.2486	- 689	0.0042	1.85	0.2450	- 317	0.0033	1.44	0.2422	- 243
0.0110	1.45	0.2486	-1253	0.0092	2.20	0.2450	- 693	0.0083	2.21	0.2423	- 616
0.0160	1.24	0.2487	-1756	0.0142	2.06	0.2451	-1050	0.0133	2.00	0.2424	- 960
0.0210	0.98	0.2488	-2183	0.0192	1.81	0.2452	-1373	0.0183	1.90	0.2425	-1290
0.0260	0.76	0.2488	-2546	0.0242	1.70	0.2453	-1679	0.0233	1.80	0.2427	-1607
0.0310	0.61	0.2489	-2865	0.0292	1.53	0.2454	-1963	0.0283	1.63	0.2428	-1900
0.0360	0.49	0.2490	-3149	0.0342	1.37	0.2455	-2223	0.0333	1.40	0.2429	-2162
0.0410	0.37	0.2491	-3398	0.0392	1.26	0.2456	-2469	0.0383	1.32	0.2431	-2412
0.0460	0.24	0.2491	-3609	0.0442	1.11	0.2457	-2693	0.0433	1.15	0.2432	-2640
0.0510	0.18	0.2492	-3802	0.0492	0.98	0.2458	-2899	0.0483	1.01	0.2433	-2848
0.0560	0.10	0.2493	-3972	0.0542	0.85	0.2459	-3087	0.0533	0.90	0.2435	-3040
0.0660	0.02	0.2494	-4260	0.0642	1.41	0.2461	-3423	0.0633	1.47	0.2437	-3380
0.0760	-0.17	0.2495	-4492	0.0742	1.06	0.2463	-3709	0.0733	1.10	0.2440	-3669
0.0860	-0.30	0.2497	-4685	0.0842	0.72	0.2465	-3947	0.0833	0.79	0.2443	-3916
0.0960	-0.40	0.2498	-4850	0.0942	0.49	0.2467	-4154	0.0933	0.57	0.2445	-4131
0.1060	-0.50	0.2500	-4984	0.1042	0.33	0.2469	-4337	0.1033	0.37	0.2448	-4319
0.1210	-0.81	0.2502	-5169	0.1192	0.20	0.2472	-4571	0.1183	0.27	0.2452	-4561
0.1360	-0.92	0.2504	-5321	0.1342	-0.08	0.2475	-4765	0.1333	-0.05	0.2456	-4759
0.1510	-1.01	0.2506	-5446	0.1492	-0.27	0.2477	-4933	0.1483	-0.22	0.2460	-4933
0.1660	-1.08	0.2508	-5550	0.1642	-0.43	0.2480	-5077	0.1633	-0.42	0.2464	-5078
0.1810	-1.13	0.2510	-5639	0.1792	-0.59	0.2483	-5199	0.1783	-0.53	0.2468	-5208
0.1960	-1.16	0.2512	-5720	0.1942	-0.67	0.2486	-5309	0.1933	-0.67	0.2472	-5319
0.2110	-1.21	0.2515	-5785	0.2092	-0.77	0.2489	-5406	0.2083	-0.72	0.2476	-5422
0.2260	-1.26	0.2517	-5835	0.2242	-0.85	0.2492	-5490	0.2233	-0.81	0.2480	-5512
0.2410	-1.25	0.2519	-5887	0.2392	-0.88	0.2495	-5570	0.2383	-0.90	0.2484	-5589
0.2560	-1.28	0.2521	-5931	0.2542	-0.93	0.2498	-5643	0.2533	-0.92	0.2488	-5664

Sample Calculation

From Table II, page 40:

To 26.421 g. of 0.0803M $Co(ClO_4)_2$ in 1-butanol was added 0.0040 ml. of water producing a 1.62 in. deflection of the recorder pen. The heat capacity was 0.2534 cal./in. over the interval. The number of calories liberated in the increment was

$$dq_{cal} = s \cdot h$$
$$= 1.62 \text{ in.} \cdot 0.2534 \text{ cal./in.} = 0.4105 \text{ calories}$$

The correction for the heat of mixing of water with 1-butanol is -432 cal./mole H_2O • kgm. butanol. But since there is less than 1 mole of water added, the correction to the experimental heat must be adjusted accordingly. The number of moles of water added is

$$(H_2O)_{mol} = 0.0040 \text{ g.} / (18.016 \text{ g./mole})$$
$$= 0.000222 \text{ moles } H_2O$$

The correction therefore becomes

$$dq_{sol} = -432 \text{ cal./mole} \cdot 0.000222 \text{ mole}$$
$$= -0.0959 \text{ calories}$$

The heat of reaction of H_2O with $Co(ClO_4)_2$ in the interval is then

$$dq_{rx} = dq_{cal} - dq_{sol}$$
$$= 0.4105 + 0.0959 = 0.5064 \text{ calories}$$

To obtain the heat of reaction, $\overline{\Delta H}$, in terms of cal. per mole of salt, one finds the number of moles of salt in the solution to be

$$\text{moles salt} = \text{salt molarity} \cdot \text{kgm. of solution} \cdot \frac{1}{\rho}$$

where ρ is the density of the solution in kilograms per liter of solution. The density of the perchlorate solutions was found to increase linearly with salt concentration as shown in Figure 6. The volume of solution containing 1000 g. of butanol has the approximately constant value of 1.241 lit. per kgm. of solution. Therefore,

$$\text{moles salt} = 0.0803 \text{ mole/lit.} \cdot 1.241 \text{ lit./kgm.} \cdot 0.026421 \text{ kgm.}$$

$$= 0.002634 \text{ moles}$$

Finally, the heat of reaction is

$$Q_{rx} = dq_{rx} / \text{moles salt}$$

$$= 0.5064 \text{ cal.} / 0.002634 \text{ moles} = 192 \text{ cal./mole}$$

or, by convention

$$\overline{\Delta H} = -192 \text{ cal./mole}$$

Constants of the Systems - Once the experimental heats of reaction have been determined, values of the average ligand number, $\bar{n}$, and the free ligand concentration, $[L]$ or $[H_2O]_{free}$, may be determined according to the principle of "corresponding solutions". Values of total water concentration were found for each salt concentration at equal $\overline{\Delta H}$ values. According to Rossotti and Rossotti (24), if the solutions are corresponding

$$C_L = \bar{n}C_M + [L] \tag{4.3}$$

and a straight line should be obtained for each series of points for any particular value of $\overline{\Delta H}$. It should be clearly realized that if straight lines are not obtained (within experimental error), then the "corresponding solutions" treatment may not be considered to be valid for the system under study. A least squares calculation was performed to obtain $\bar{n}$ and $[L]$ for each value of $\overline{\Delta H}$ from 100 to 5300 calories in 100 calorie intervals. The standard error of estimate of the fit was in all cases better than 0.3% for $Co(ClO_4)_2$ and 0.6% for $Ni(ClO_4)_2$ (11). A graphical illustration of the analysis is given in Figures 11 and 12, with the calculated values listed in Table III.

After values of the average ligand number and the free ligand concentration have been determined by least squares procedure, the formation function curve may be drawn by plotting $\bar{n}$ versus $\log[H_2O]_{free}$. Experimental results are shown in Figures 13 and 14.

Since

$$\bar{n} = \frac{\beta_1[L] + 2\beta_2[L]^2 + \dots + N\beta_N[L]^N}{1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_N[L]^N} \tag{4.4}$$

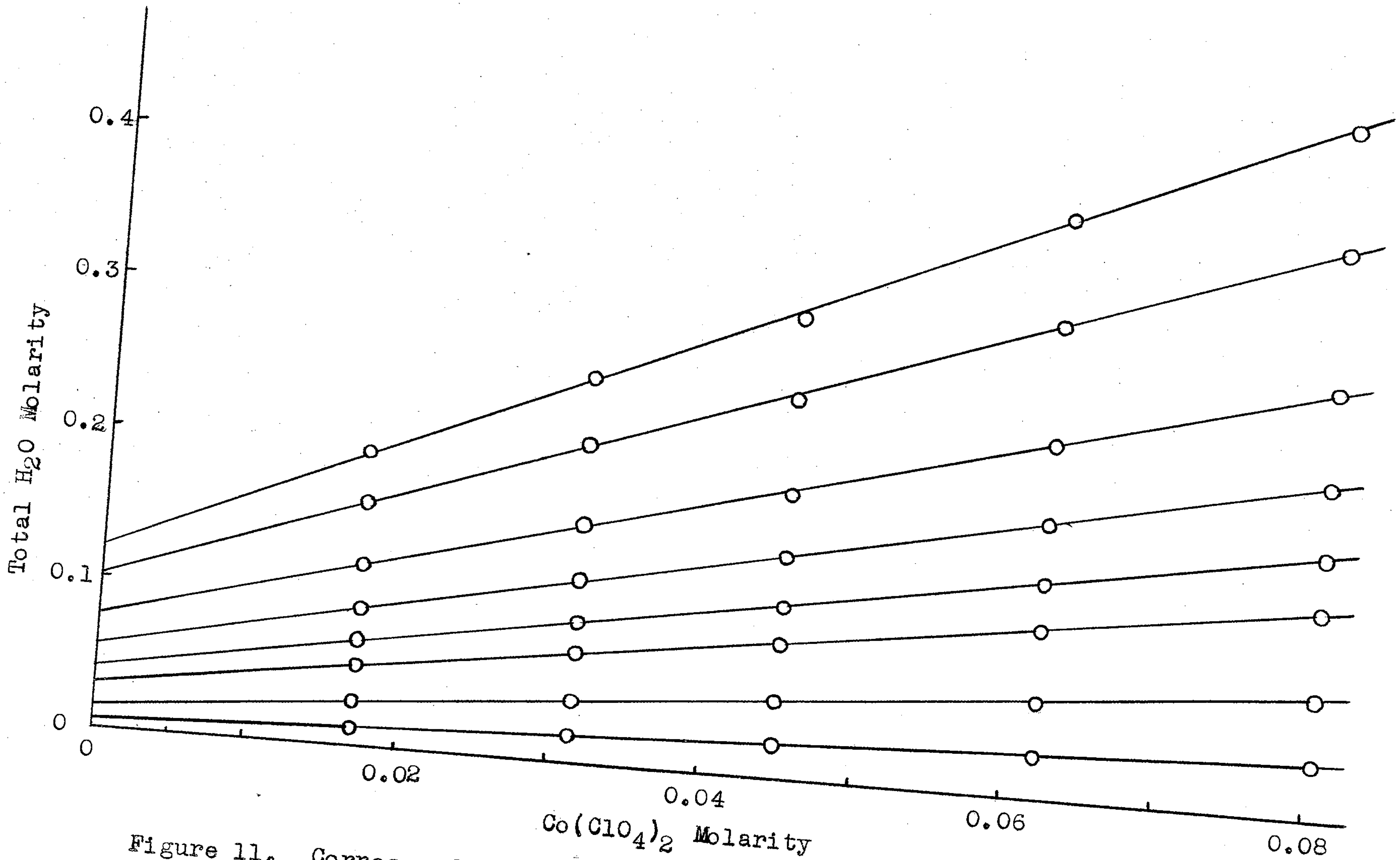

Figure 11. Corresponding Solutions Treatment for Cobalt (II) Perchlorate

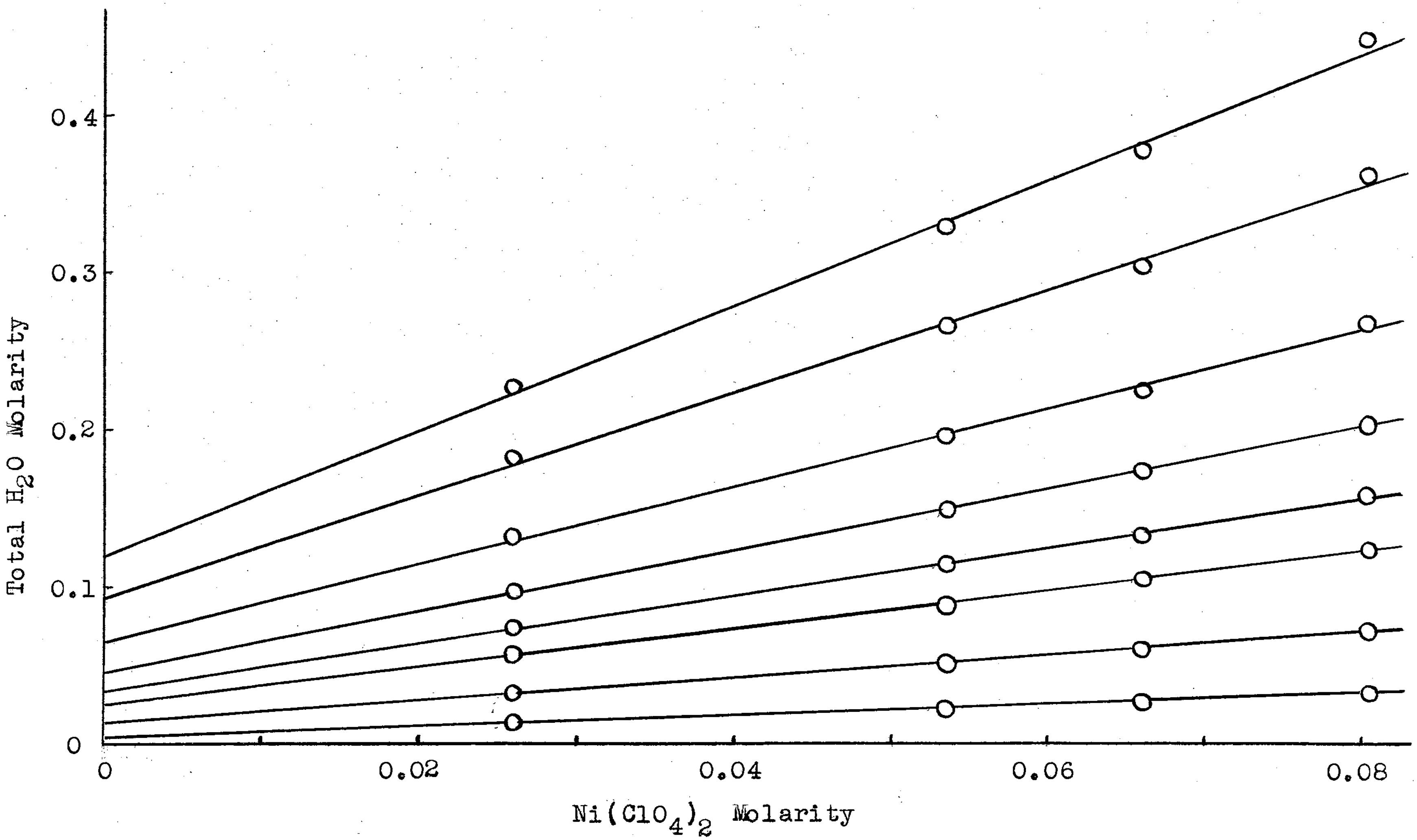

Figure 12. Corresponding Solutions Treatment for Nickel (II) Perchlorate

TABLE III

LEAST SQUARES CURVE FIT FOR $\bar{n}$ AND [L]

$Co(ClO_4)_2$ in 1-Butanol				$Ni(ClO_4)_2$ in 1-Butanol			
$-\overline{\Delta H}$	$\bar{n}$	$[H_2O]$	$\log[H_2O]$	$-\overline{\Delta H}$	$\bar{n}$	$[H_2O]$	$\log[H_2O]$
100	0.0355	0.00103	-2.9872	200	0.0669	0.00106	-2.9747
200	0.0712	0.00150	-2.8239	400	0.1305	0.00212	-2.6737
300	0.1058	0.00203	-2.6925	600	0.1986	0.00322	-2.4921
400	0.1428	0.00251	-2.6003	800	0.2694	0.00432	-2.3645
500	0.1803	0.00300	-2.5229	1000	0.3357	0.00579	-2.2373
600	0.2187	0.00359	-2.4450	1200	0.4041	0.00740	-2.1308
700	0.2543	0.00441	-2.3556	1400	0.4780	0.00885	-2.0531
800	0.2912	0.00507	-2.2950	1600	0.5583	0.01024	-1.9897
900	0.3278	0.00595	-2.2255	1800	0.6396	0.01175	-1.9300
1000	0.3646	0.00671	-2.1733	2000	0.7304	0.01308	-1.8834
1200	0.4380	0.00849	-2.0711	2100	0.7781	0.01377	-1.8611
1400	0.5195	0.01021	-1.9910	2200	0.8273	0.01446	-1.8398
1600	0.6023	0.01225	-1.9119	2300	0.8734	0.01542	-1.8119
1800	0.6925	0.01419	-1.8480	2400	0.9239	0.01636	-1.7862
2000	0.7789	0.01660	-1.7799	2500	0.9707	0.01753	-1.7562
2100	0.8260	0.01776	-1.7506	2600	1.0229	0.01857	-1.7312
2200	0.8730	0.01903	-1.7206	2700	1.0714	0.02011	-1.6966
2300	0.9169	0.02046	-1.6891	2800	1.1234	0.02144	-1.6688
2400	0.9648	0.02190	-1.6596	2900	1.1769	0.02292	-1.6398
2500	1.0121	0.02343	-1.6302	3000	1.2370	0.02420	-1.6162
2600	1.0613	0.02505	-1.6012	3100	1.2970	0.02567	-1.5906
2700	1.1145	0.02664	-1.5745	3200	1.3566	0.02738	-1.5626
2800	1.1696	0.02828	-1.5485	3300	1.4211	0.02912	-1.5358
2900	1.2418	0.02912	-1.5358	3400	1.4864	0.03104	-1.5081
3000	1.2909	0.03159	-1.5004	3500	1.5552	0.03300	-1.4815
3100	1.3540	0.03339	-1.4734	3600	1.6286	0.03510	-1.4547
3200	1.4164	0.03547	-1.4501	3700	1.7076	0.03743	-1.4268
3300	1.4807	0.03754	-1.4255	3800	1.7852	0.04016	-1.3962
3400	1.5445	0.03987	-1.3994	3900	1.8719	0.04285	-1.3680
3500	1.6155	0.04205	-1.3762	4000	1.9670	0.04536	-1.3433
3600	1.6870	0.04458	-1.3509	4100	2.0639	0.04827	-1.3163
3700	1.7574	0.04750	-1.3233	4200	2.1671	0.05129	-1.2900
3800	1.8351	0.05054	-1.2964	4300	2.2711	0.05505	-1.2592
3900	1.9154	0.05373	-1.2698	4400	2.3843	0.05910	-1.2284
4000	2.0053	0.05677	-1.2459	4500	2.4975	0.06412	-1.1930
4100	2.0926	0.06053	-1.2180	4600	2.6192	0.06966	-1.1570
4200	2.1965	0.06382	-1.1950	4700	2.7581	0.07550	-1.1220
4300	2.3043	0.06775	-1.1691	4800	2.9220	0.08085	-1.0923
4400	2.4222	0.07158	-1.1452	4900	3.0991	0.08680	-1.0615
4500	2.5403	0.07613	-1.1184	5000	3.3060	0.09291	-1.0319
4600	2.6771	0.08080	-1.0926	5100	3.5263	0.10073	-0.9968
4700	2.8231	0.08580	-1.0665	5200	3.7624	0.10950	-0.9606
4800	2.9773	0.09157	-1.0382	5300	4.0317	0.11889	-0.9248
4900	3.1478	0.09743	-1.0113				
5000	3.3491	0.10307	-0.9869				
5100	3.5933	0.10865	-0.9640				
5200	3.8646	0.11466	-0.9406				
5300	4.1383	0.12195	-0.9138				

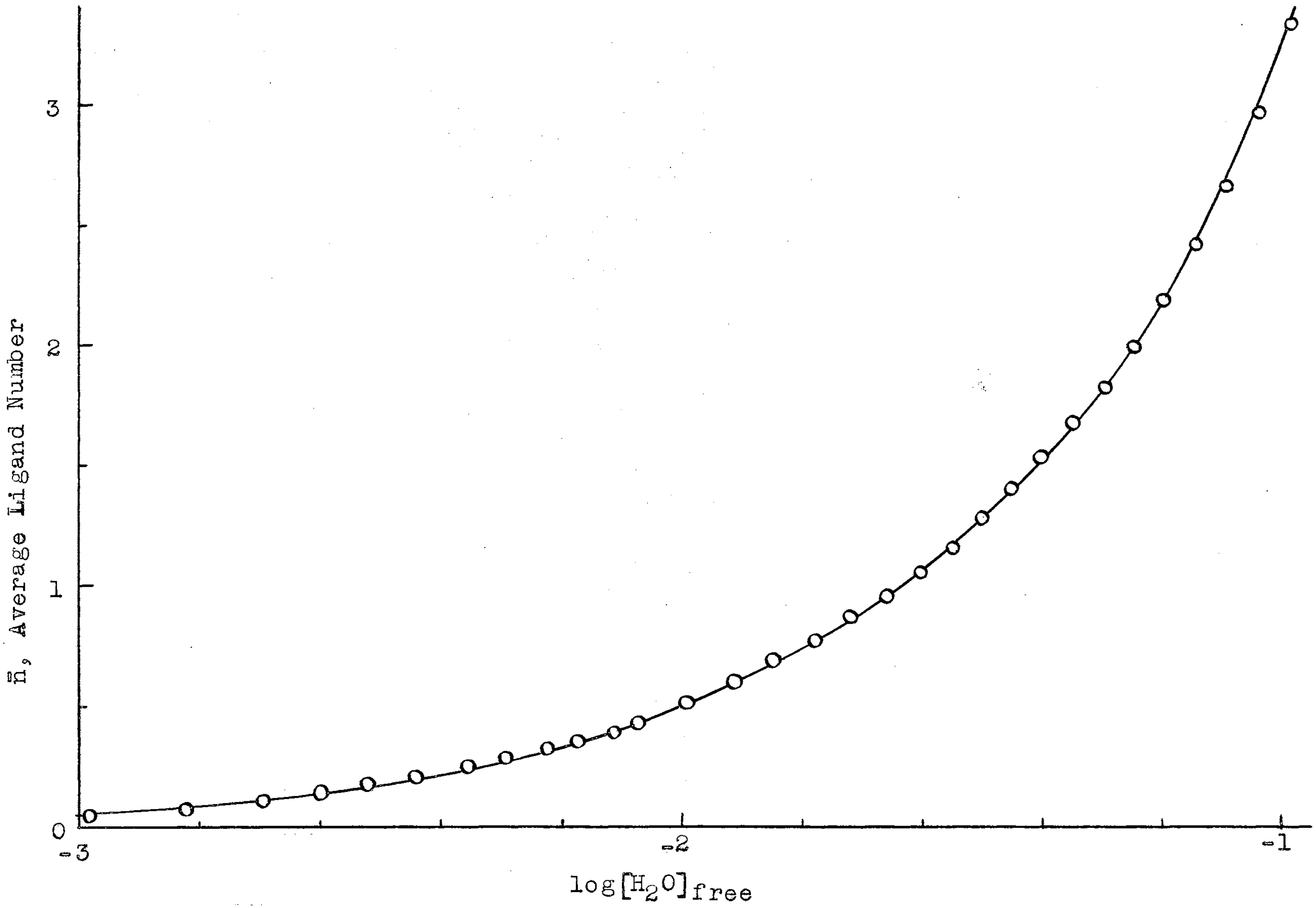

Figure 13. Formation Function Curve for Cobalt (II) Perchlorate

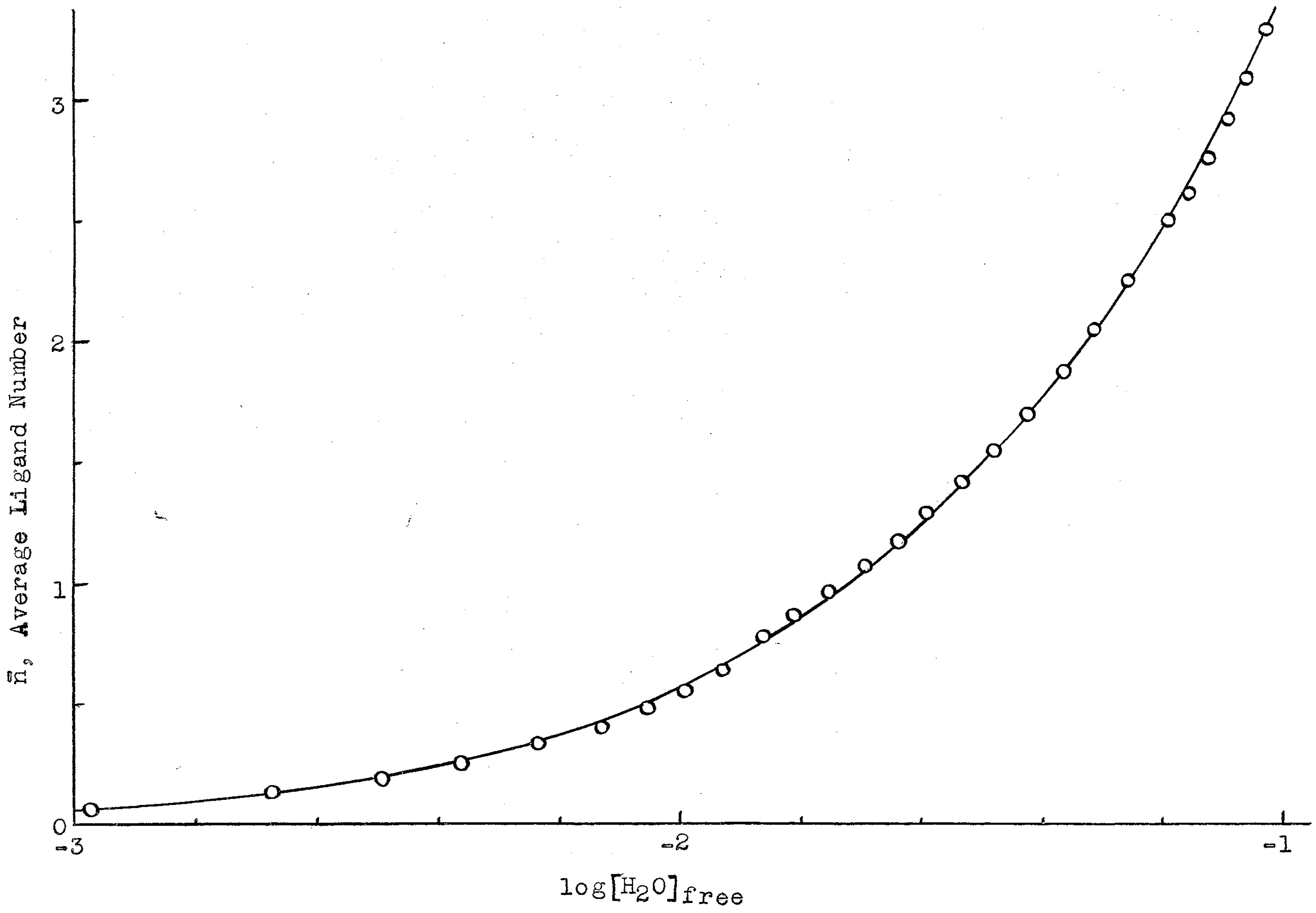

Figure 14. Formation Function Curve for Nickel (II) Perchlorate

and values of $\bar{n}$ and $[H_2O]_{free}$ are available from the corresponding solutions treatment, in principle one should be able to calculate the formation constants.

In order to calculate the formation constants after the procedure of Poe (22), one needs first to obtain a set of pseudo constants, k_{ps}.

$$k_{ps} = \frac{\bar{n}}{(N - \bar{n})[L]} \tag{4.5}$$

The pseudo constants are themselves related to the stepwise formation constants by

$$\begin{aligned} k_1 &= N \cdot k_{ps} \\ k_2 &= (N - 1) / 2 \cdot k_{ps} \\ k_3 &= (N - 2) / 3 \cdot k_{ps} \\ &\vdots \\ k_N &= k_{ps} / N \end{aligned} \tag{4.6}$$

Unfortunately, one has to assume a value for the maximum coordination number, N, unless this information is indicated by the shape of the formation function curve or has been found otherwise. In this study, data were obtained at $\bar{n}$ values only slightly above $\bar{n} = 4$, and there was no apparent tendency for the curve to bend over and approach a limiting value of $\bar{n} = N$. The maximum coordination must certainly be greater than four, but it was not possible to determine N from the data. Therefore, it seemed reasonable to suppose that N would be six, the normal coordination of divalent cobalt and nickel compounds. Support for this choice comes from the visible absorption spectra which clearly show six coordination about the metal. Pseudo formation constants were, however, calculated for assumed values of $N = 4, 6, 8, 9$ and 10. It was found that when k_{ps} was extrapolated back to $\bar{n} = 0$ and k_1 calculated, values of k_1 were very nearly the same regardless of the value of N. Plots of the pseudo constant curves for $N = 6$ are shown in Figures 15 and 16 with the calculated values given in Table IV.

It should be pointed out that both graphs indicate by their nearly horizontal slope between $\bar{n} = 0$ and $\bar{n} = 2$ that the first two attachment sites are roughly equivalent. The increasing slope beyond $\bar{n} = 2$ indicates that the remaining attachment sites are more easily occupied, once the first two sites are filled. Thus there is indication that two of the positions are different, either chemically, sterically or both, from the others. The pseudo formation constant curves were extrapolated to $\bar{n} = N$ to obtain values for k_5 and k_6.

The stepwise formation constants are related to the overall formation constants by

$$\beta_n = k_1 k_2 \ldots k_n \tag{4.7}$$

Final fit of equation (4.4) to the data required refinement of the constants calculated from the pseudo constants by iteration. Thereby, a set of overall formation constants, β_n, were obtained which were used to calculate the solid lines in Figures 13 and 14. Experimental values are shown by the circles. The calculated formation constants are tabulated in Table V.

Once the formation constants are available, the overall enthalpies of formation should be calculable from

$$\overline{\Delta H} = \frac{\eta_1\beta_1[L] + \eta_2\beta_2[L]^2 + \cdots + \eta_N\beta_N[L]^N}{1 + \beta_1[L] + \beta_2[L]^2 + \cdots + \beta_N[L]^N} \tag{4.8}$$

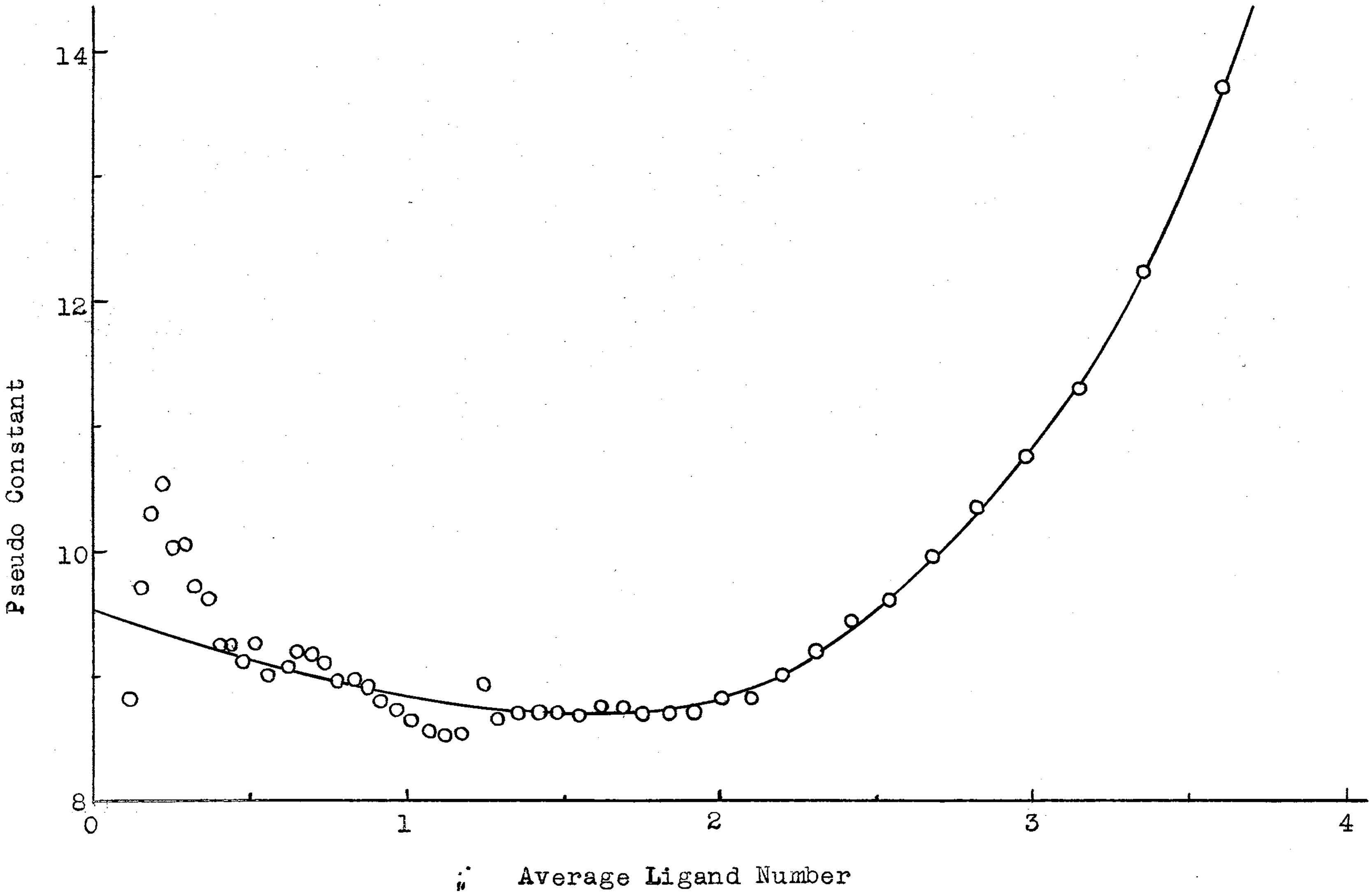

Figure 15. Pseudo Formation Constant Curve for $Co(ClO_4)_2$ Aquocomplexes

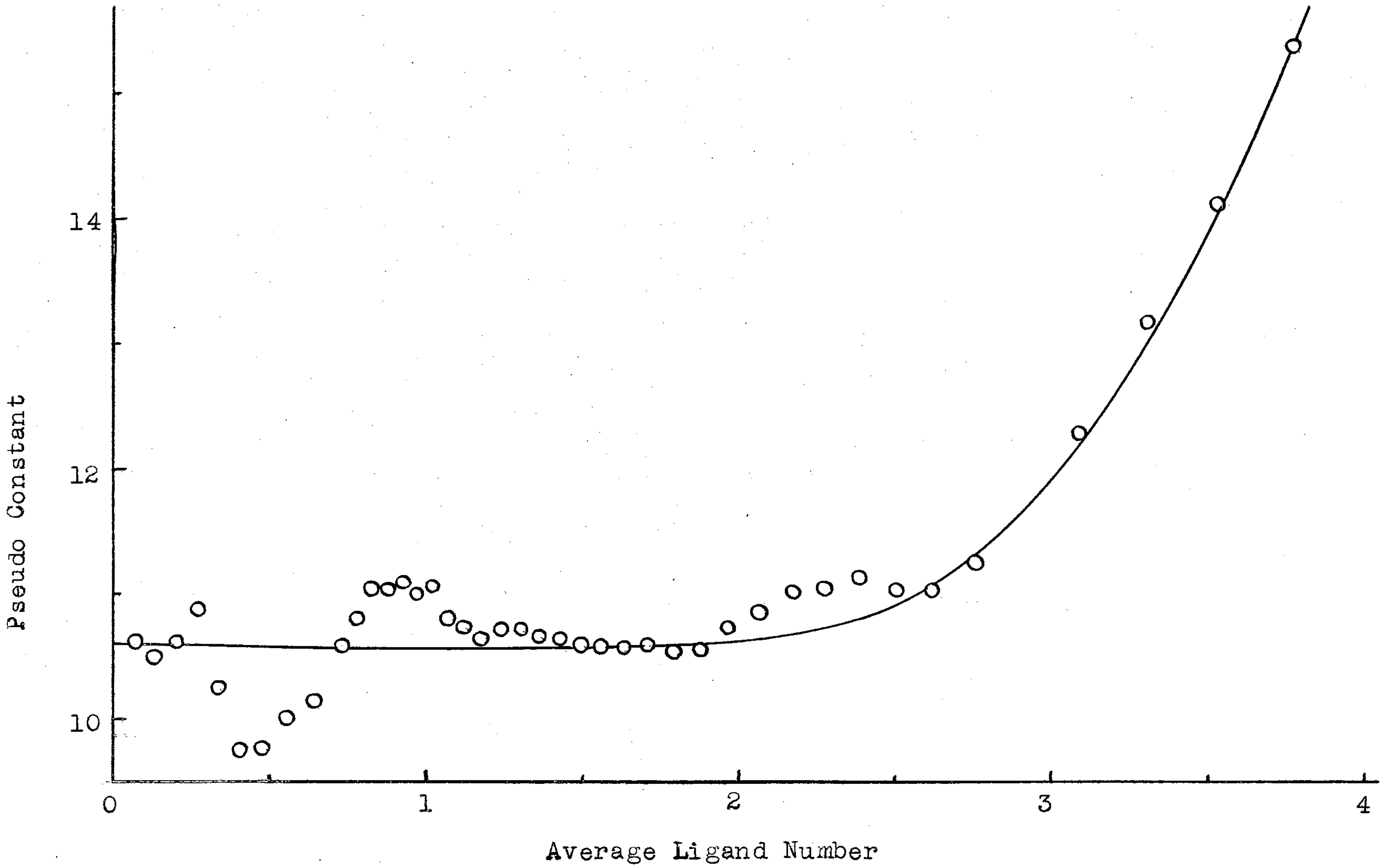

Figure 16. Pseudo Formation Constant Curve for $Ni(ClO_4)_2$ Aquocomplexes

TABLE IV

PSEUDO FORMATION CONSTANTS

$Co(ClO_4)_2$	
$\bar{n}$	k_{ps}
0.1058	8.84
0.1428	9.71
0.2543	10.04
0.3278	9.71
0.3646	9.64
0.3998	9.28
0.4380	9.28
0.4769	9.13
0.5195	9.28
0.5569	9.03
0.6023	9.11
0.6480	9.21
0.6925	9.20
0.7358	8.99
0.8260	8.99
0.8730	8.95
0.9169	8.82
0.9648	8.75
1.0121	8.66
1.0613	8.58
1.1145	8.56
1.1696	8.56
1.2418	8.96
1.2909	8.68
1.3540	8.73
1.4164	8.71
1.4807	8.73
1.5445	8.70
1.6155	8.76
1.6870	8.77
1.7574	8.72
1.8351	8.72
1.9154	8.73
2.0053	8.84
2.0926	8.85
2.1965	9.05
2.3043	9.20
2.4222	9.46
2.5403	9.64
2.6771	9.97
2.8231	10.36
2.9773	10.76
3.1478	11.33
3.3494	12.26
3.5933	13.74
3.8646	15.78
4.1483	18.37

$Ni(ClO_4)_2$	
$\bar{n}$	k_{ps}
0.0669	10.64
0.1305	10.49
0.1986	10.63
0.2694	10.88
0.3357	10.24
0.4041	9.76
0.4780	9.78
0.5583	10.02
0.6396	10.15
0.7304	10.60
0.7781	10.82
0.8273	11.06
0.8734	11.05
0.9239	11.13
0.9707	11.01
1.0229	11.07
1.0714	10.81
1.1234	10.74
1.1769	10.65
1.2370	10.73
1.2970	10.74
1.3566	10.67
1.4211	10.66
1.4864	10.61
1.5552	10.60
1.6286	10.61
1.7076	10.63
1.7852	10.55
1.8719	10.58
1.9670	10.75
2.0639	10.86
2.1671	11.02
2.2711	11.06
2.3843	11.16
2.4975	11.12
2.6192	11.12
2.7581	11.27
2.9220	11.74
3.0991	12.31
3.3060	13.21
3.5263	14.15
3.7642	15.42
4.0317	17.23

TABLE V

CALCULATED FORMATION CONSTANTS

	$Co(ClO_4)_2$	$Ni(ClO_4)_2$
β_1	5.70×10^1	6.37×10^1
β_2	1.20×10^3	1.71×10^3
β_3	1.26×10^4	2.30×10^4
β_4	4.40×10^4	1.60×10^5
β_5	4.0×10^5	6.4×10^5
β_6	1.0×10^7	1.5×10^7
k_1	57.0	63.7
k_2	21.0	26.8
k_3	10.5	13.4
k_4	3.5	7.0
k_5	9.1	4.0
k_6	25.0	23.4

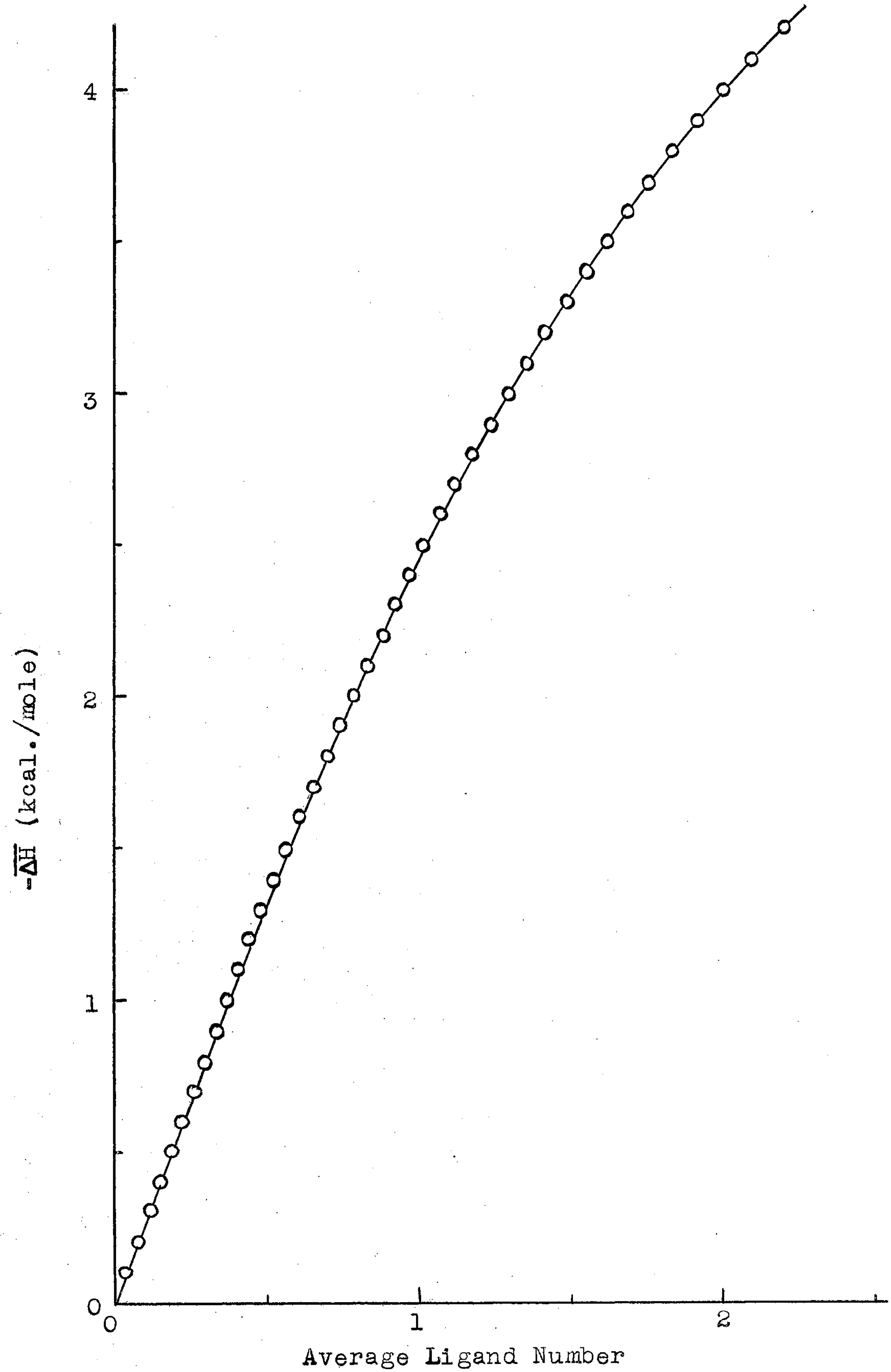

Figure 17. Heat of Reaction of $Co(ClO_4)_2$ with H_2O as a Function of Average Ligand Number

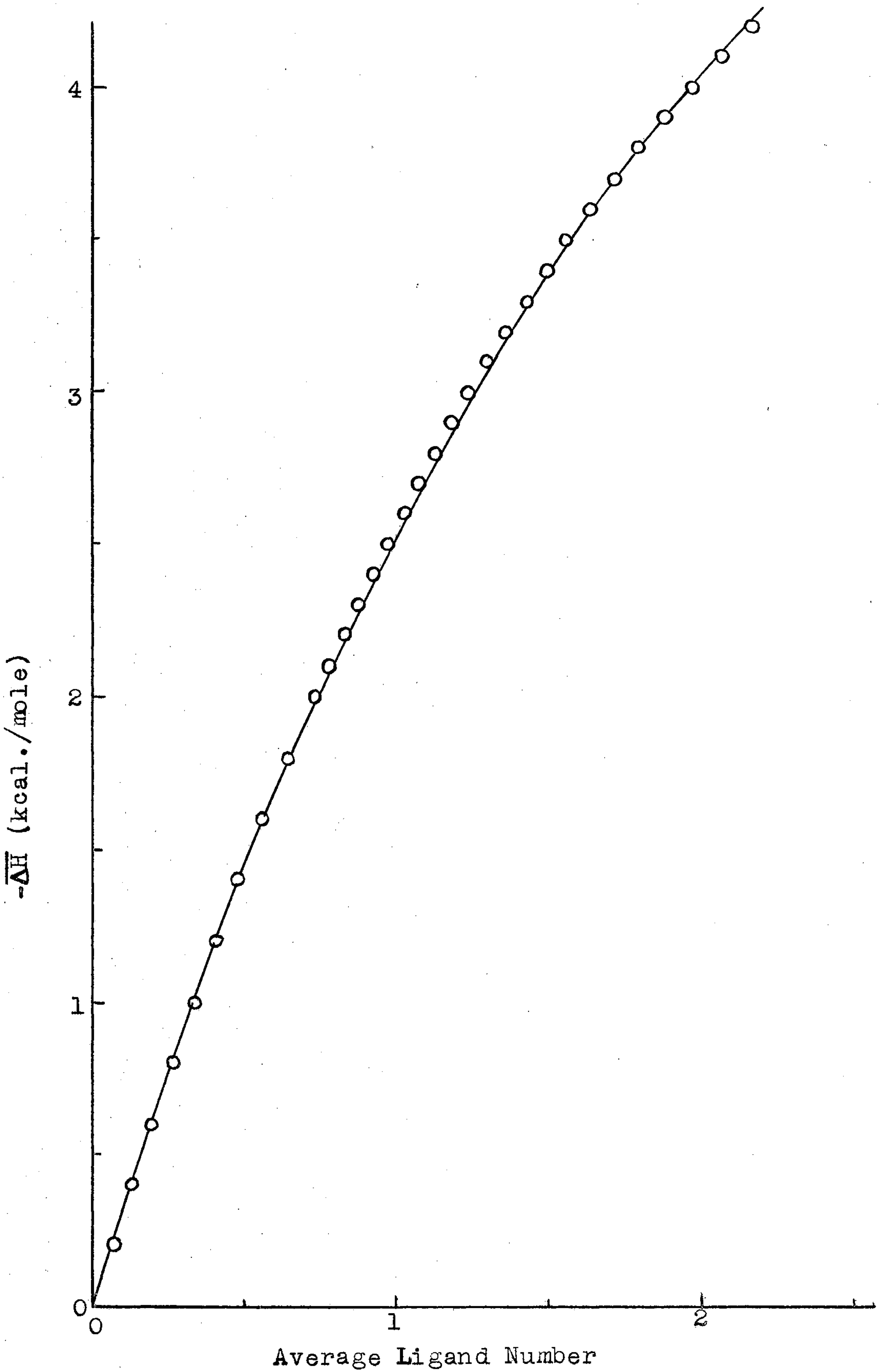

Figure 18. Heat of Reaction of $Ni(ClO_4)_2$ with H_2O as a Function of Average Ligand Number

if the η's can be estimated. If the stepwise formation of the aquocomplexes is a statistical process, then it is easily shown since $\eta_n = n\eta_1$ that

$$\overline{\Delta H} = \eta_1 \bar{n} \qquad (4.9)$$

and η_1 would be given by the limiting slope at $\bar{n} = 0$ of a $\overline{\Delta H}$ versus $\bar{n}$ plot. Such a plot is shown in Figures 17 and 18. By taking the limiting slope of the curve for η_n at $\bar{n} = n - 1$, a set of temporary enthalpies of formation was found.

It should be pointed out that the $\overline{\Delta H}$ versus $\bar{n}$ plots are not linear as expected statistically, indicating a difference in energies of attachment. In the thermometric titrations which were carried to a sufficiently large total water concentration to allow $\overline{\Delta H}$ to reach a minimum value, $\overline{\Delta H}_{min}$ was approximately -6.6 kcal./mole for $Co(ClO_4)_2$, and -6.4 kcal. per mole for $Ni(ClO_4)_2$. It is interesting to note that at $\bar{n} = 2$ over sixty per cent of the total energy of reaction has been released. The values of $\overline{\Delta H}$ rapidly fall off beyond $\bar{n} = 2$. This is further evidence which indicates a difference in the first two sites of attachment.

The overall enthalpies of formation were calculated by successive approximation, and the final values are listed in Table VI.

Consideration has been given to the precision of the numbers listed in Tables V and VI. The numbers tabulated there are those which were used to give the closest fit to the experimental points by equation (4.8). However, the procedure by which these values were obtained (i.e., η's are calculated with the β's and $[L]$'s; β's are calculated with

TABLE VI

EXOTHERMIC OVERALL ENTHALPIES OF AQUOCOMPLEX FORMATION (CALORIES PER MOLE)

	$Co(ClO_4)_2$	$Ni(ClO_4)_2$
η_1	2.85×10^3	3.05×10^3
η_2	4.70×10^3	4.80×10^3
η_3	5.35×10^3	5.25×10^3
η_4	5.60×10^3	5.45×10^3
η_5	5.8×10^3	5.65×10^3
η_6	5.9×10^3	5.8×10^3

the the [L]'s; [L]'s are determined graphically) embodies a multiplication of errors. It is therefore, virtually impossible to evaluate the overall error in the values of η because of the interdependence of the factors entering into equation (4.8). One would naturally assume the greatest degree of confidence in the $\bar{n}$ and $[H_2O]_{free}$ values, less in the β values, and the least confidence in the η values. The standard error of estimate for the $\bar{n}$ versus log[L] curve fitted with the formation constants of Table V was less than 2% for $Co(ClO_4)_2$ and less than 2.5% for $Ni(ClO_4)_2$. The greatest error is seen to lie in the higher $\bar{n}$ regions of the curve where the less certain values for β_5 and β_6 play an important role in the calculation. The enthalpies of formation listed in Table VI gave an overall curve fit with standard error of estimate less than 3.5% for $Co(ClO_4)_2$ and 5.5% for $Ni(ClO_4)_2$. A revised set of values of β and η is given in Table VII.

With the formation constants and enthalpies of formation determined, calculation of the entropies of aquocomplex formation is straightforward by the equation

$$\sigma_n = \frac{\eta_n}{T} - R\ln\beta_n \qquad (4.10)$$

Entropies of aquocomplex formation are listed in Table VII.

<u>Conductivity</u> <u>Studies</u> - One of the assumptions made in the discussion of the theory of corresponding solutions in Chapter II was that the degree of ion-association does not change significantly over the concentration range of the measurements. In order to test this assumption conductivity titrations were performed on 1-butanol solutions of $Co(ClO_4)_2$ and $Ni(ClO_4)_2$. A Leeds and Northrup precision Jones type

TABLE VII

REVISED FORMATION CONSTANTS, OVERALL ENTHALPIES AND ENTROPIES OF AQUOCOMPLEX FORMATION

	$Co(ClO_4)_2$	$Ni(ClO_4)_2$
$\log \beta_1$	1.76	1.80
$\log \beta_2$	3.08	3.23
$\log \beta_3$	4.10	4.36
$\log \beta_4$	4.64	5.20
$\log \beta_5$	5.6	5.8
$\log \beta_6$	7.0	7.2
$\log \eta_1$	3.45	3.48
$\log \eta_2$	3.67	3.68
$\log \eta_3$	3.73	3.72
$\log \eta_4$	3.75	3.74
$\log \eta_5$	3.8	3.8
$\log \eta_6$	(3.8)	(3.8)
σ_1	-1.53 e.u.	-1.98 e.u.
σ_2	-1.68	-1.32
σ_3	+0.81	+2.34
σ_4	+2.45	+5.52
σ_5	+6.2	+7.6
σ_6	+12.2	+13.4

conductivity bridge was used in conjunction with a dilution cell at a frequency of 1000 cps. The titrations were performed by titrating water from the micrometer syringe into 50 cc. volumes of several of the solutions used in the thermometric titrations. The results are presented graphically in Figure 19.

It is apparent from the equivalent conductance values in the range of 0 to 2% water that the solutions have very small conductivity at the concentrations for which the formation constants were determined. The conductivity does increase with water concentration, though it does not exceed 3 $ohms^{-1}$ at a water content of 2% and a salt concentration of 0.02 M. At higher salt concentrations the conductivity is still less.

Some of the increase in conductivity can be attributed to changes in the viscosity and dielectric constant of water and some to increased ionization. However, in a study of the conductance of $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ as a function of concentration in hydrous butanol solvent containing 13.5% water by weight, Cheung (4) showed that the degree of ion-pairing in a solution of concentration as small as 1×10^{-4} M was only of the order of 50%.

It may be reasonably concluded from these results that dissociation must be very small, and hence a small change in the degree of ion-association will not invalidate the treatment of the data by the method of corresponding solutions over the water concentration range studied.

<u>NMR Studies</u> - The structural features of the solvation of $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ in butanol solution, though

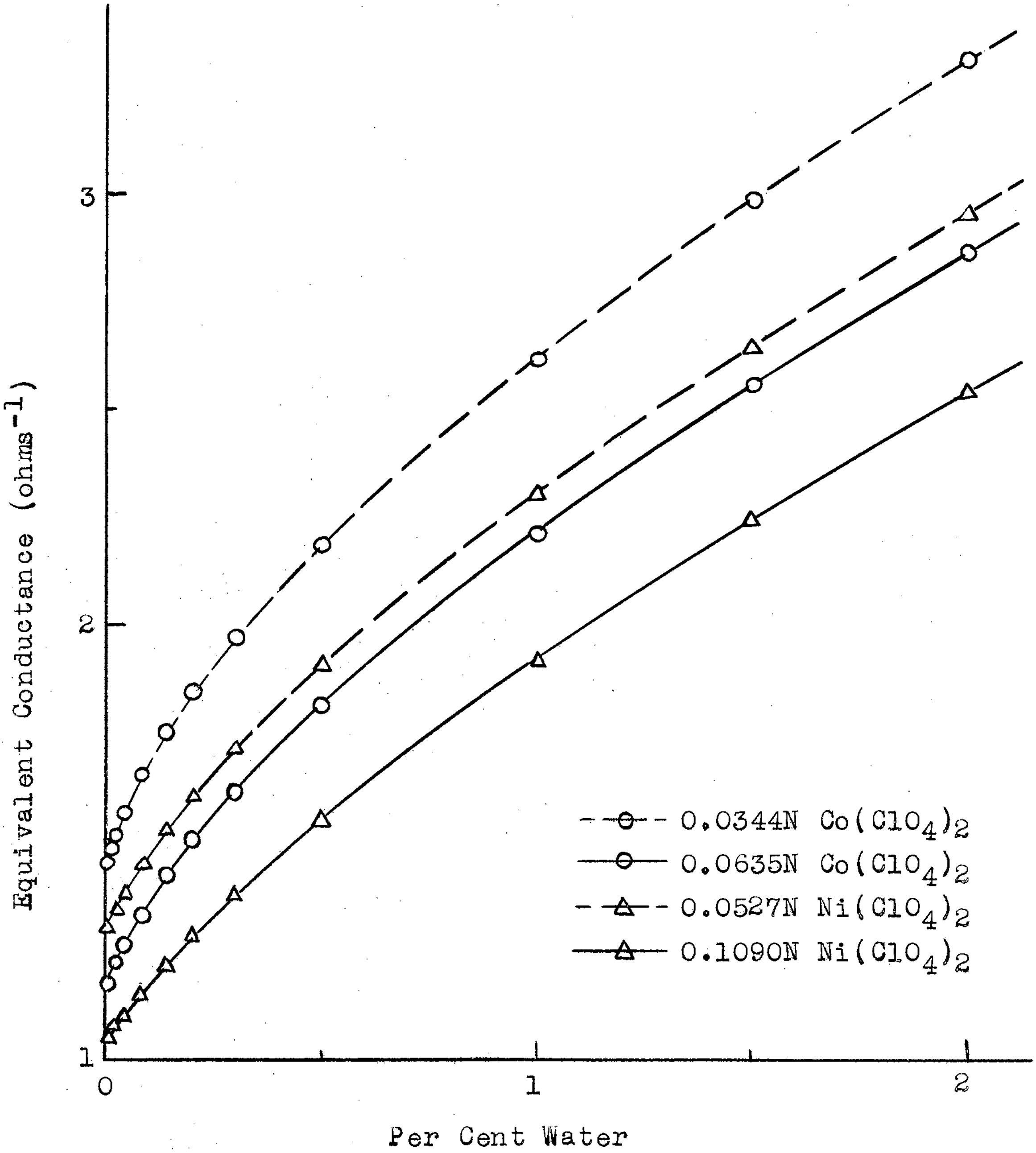

Figure 19. Conductivity of $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ Solutions at 25.0°C.

important to a complete understanding of the thermodynamic properties of the systems, cannot be readily studied. Thus although absorption spectra indicate six-coordination, there exists the possibility that the six sites of octahedral symmetry about Co^{++} and Ni^{++} may be occupied by oxygen atoms of one or all of the butanol molecules, water or the perchlorate anion. It was believed, therefore, that proton magnetic resonance measurements might provide some qualitative structural information about the aquocomplex formation and hydration processes.

In a study of 0.4 molal $Co(ClO_4)_2$ it was found that at 25°C the fine structure of the methylene and methyl groups was destroyed by the influence of the paramagnetic salt and that these resonance peaks were shifted up-field from the hydroxyl proton. By adding water to the solutions it was found that the hydroxyl peak increased in height and was also shifted up-field.

A very weak, broad and diffuse band was observed far down-field of the peaks assigned to water and 1-butanol. This peak was located near the low frequency end of the 2000 cps. chemical shift range of the Varian A-60 Spectrometer. The peak was found to shift up-field with added water and to increase in height. After reaching a maximum height at a water to salt ratio of 50:1, it began to decrease and eventually merge with the hydroxyl peak.

It is possible that one is observing the "bound" solvent in the association complexes. As water replaces the butanol the peak sharpens up due to the greater binding energy of the water with respect to butanol.

It was felt that more could be learned if the peaks could be sharpened by slowing the rates of exchange of water for butanol at equilibrium. Attempts were made to obtain low temperature spectra with the Varian HA-100 Spectrometer, having a cold probe at -60°C. It was found, however, that the chemical shifts are very temperature dependent. Spectra were taken at several intermediate temperatures between 25° and -60°C, but a meaningful correspondence could not be made between the spectra.

Great difficulty was also encountered getting a lock on the frequency with an internal standard, such as TMS, so chemical shifts cannot be reported.

Color of the Solutions - An observation of peculiar interest to chemists regards the color of the dry salt solutions The normal preparation of the solutions by adding the hexahydrate perchlorate salts to butanol yields a rose color for $Co(ClO_4)_2$ and a bright green for $Ni(ClO_4)_2$. Even in solutions with a relatively low water concentration, the colors are the same as before. In removing the last traces of water from the solutions, a slight, yet quite noticeable, color change was observed. The $Co(ClO_4)_2$ showed a slight bluish tinge in addition to the rose color, and the $Ni(ClO_4)_2$ became yellowish-green in appearance. The bluish component of the color in the case of the cobalt salt may be associated with tetrahedral structure, though this is only conjecture. Tetrahedral $CoCl_2$ has bands in the 6000 to 7000 A. range which give the bluish color to this salt in anhydrous solvents.

CHAPTER V

DISCUSSION OF RESULTS AND CONCLUSIONS

Aquocomplex Formation - It was pointed out earlier that the stepwise formation constants, k_5 and k_6, do not appear to follow the normal pattern of descending order. In fact, k_6 seems abnormally large. From the corresponding solutions treatment of the thermometric titration data, values for the average ligand number could be obtained for $\bar{n}$ values only slightly above four. At $\bar{n} = 4$ there was no indication of the $\bar{n}$ versus log[L] curve approaching a limiting value. Since the assumption was made that N = 6, the theory demands that six formation constants be used to fit the data. Several curve fitting routines, including regression analysis, were attempted in an effort to find the formation constants, but these methods calculated one or more of the constants to be negative. If the requirement is imposed that all of the formation constants be positive and in decreasing order, $k_1 > k_2 > \cdots > k_6$, it is not possible to obtain a reasonable fit. A fit was obtained by successive approximation, however, by making $k_6 \sim k_2$. Since k_6 appears to be anomolous, it is possible that the maximum coordination number may be greater than six. If this were the case, it would, in effect, make the tabulated k_6 not a stepwise formation constant, but rather a "residual" formation constant including terms $\bar{n} > 6$.

In a study of aquocomplex formation of $Cu(ClO_4)_2$ in nitromethane, Larson and Iwamoto (17) noted that strict interpretation of the limiting slope for polarographic data required postulation of a limiting "hydration number" of 9. No values were listed for k_6 as all values calculated were larger than for k_5. Their observation seems to be in line with the results of this study.

Formation function curves calculated from the two sets of six tabulated constants are shown in Figure 20. If in aquocomplex formation substitution of water for butanol were a statistical process based upon the equal accessibility of all sites, then the curve should be symmetric about $\bar{n} = N/2$. The curves in Figure 20 are obviously not symmetric about $\bar{n} = 3$. However, as was mentioned earlier, there are good reasons for considering that the formation of the first two aquocomplexes should not be considered on a statistical basis.

Some of the thermometric titrations of the $Co(ClO_4)_2$ solutions were carried out to relatively high water concentrations. A minimum $\overline{\Delta H}$ value was ovserved at a water to salt ratio of about 60±10, and at larger ratios the process started to become slightly endothermic, according to Figure 21. From Figure 20, it may be seen that the aquocomplex formation reaction is essentially completed at the water/salt ratios corresponding to the minimum $\overline{\Delta H}$, and that any further thermal effect is due largely to the mixing of water with the solution of aquocomplexes. It was shown earlier that the experimental heats of reaction must be corrected by subtracting the heat of mixing of water with solvent to give the heat of aquocomplex

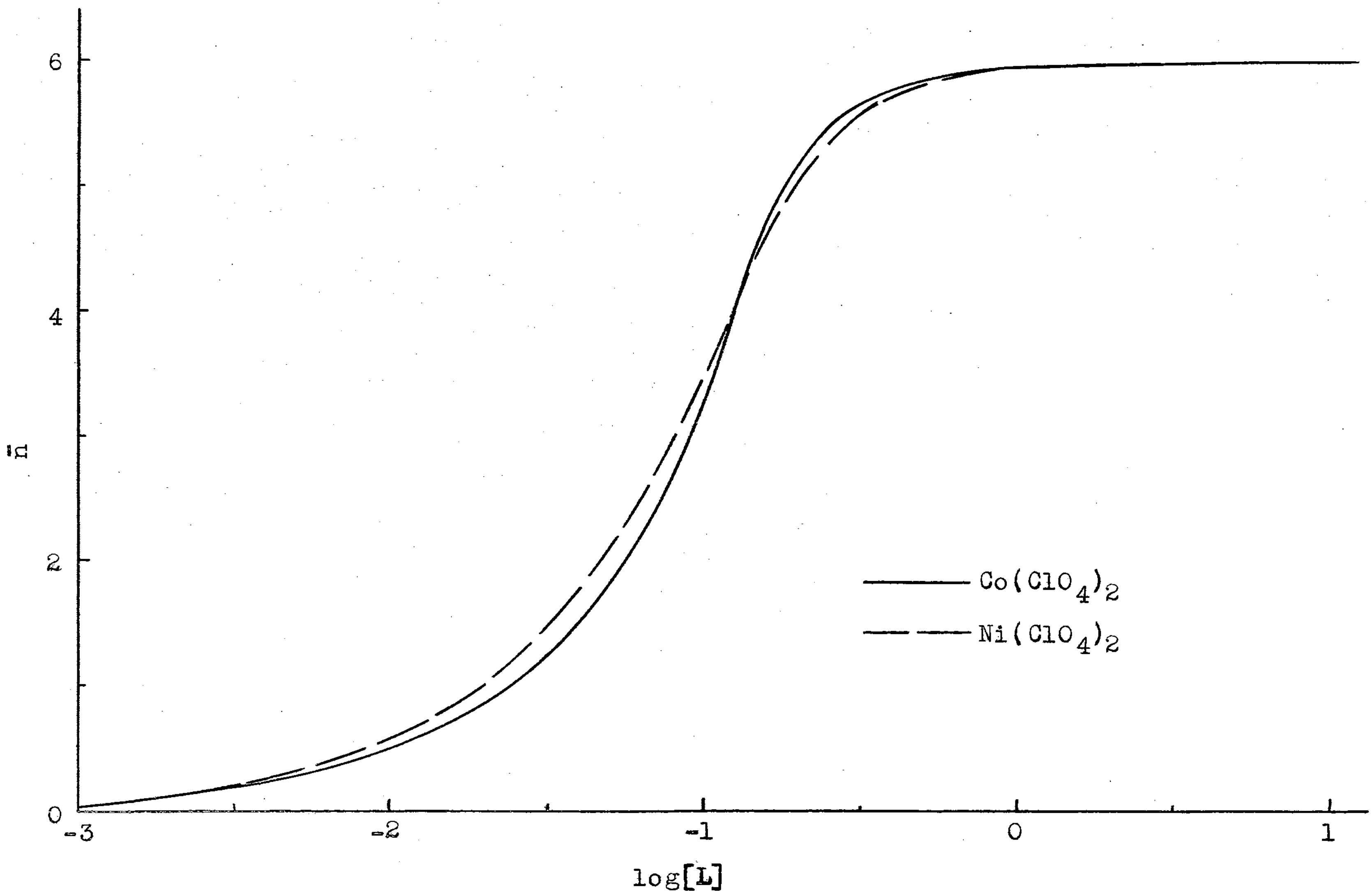

Figure 20. Calculated Formation Function Curves of Cobalt (II) and Nickel (II) Perchlorate Aquocomplexes

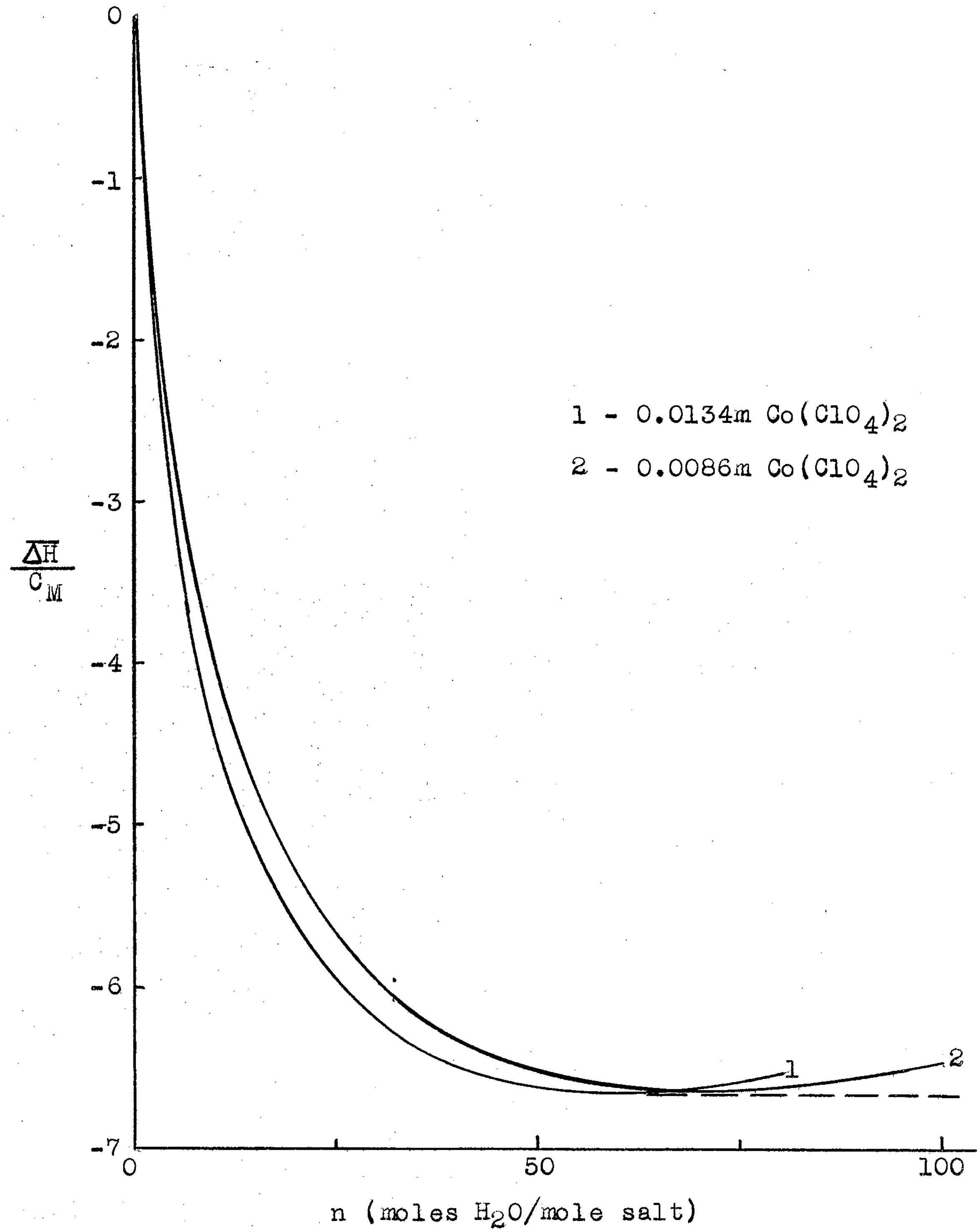

Figure 21. Heat of Reaction of Water with Cobalt (II) Perchlorate in 1-Butanol at 25°C.

formation, $\overline{\Delta H}$. Strictly speaking, the partial molar heat of mixing of water with butanol would not be expected to be identical with the partial molar heat of mixing of water with solution except at infinite dilution. Also, the assumption that they are the same probably does not hold as well at high water concentration as at lower concentration, since the integral heat of mixing is not a perfectly linear function of water concentration. Therefore, a slight deviation may be expected from the dotted horizontal line in Figure 21 which represents the case of no further reaction and perfectly compensated heat of mixing of water with butanol.

In treating the case of aquocomplex formation of ion-associated salts such as $Co(ClO_4)_2$ and $Ni(ClO_4)_2$, it is necessary to arbitrarily assign all of the hydration to the cation. However, this assignment is not without some justification. The electric field is more intense around a small, doubly charged cation than it is in the proximity of a more voluminous, singly charged anion. Moreover, the replacement of butanol ligands around the cation by water is certainly favored sterically. Because of the greater intensity of the cation electric field, the formation of relatively strong $M^{++}{-}OH_2$ coordinate bonds in preference to weaker $O_3Cl{-}O^{-}\cdots H{-}OH$ hydrogen bonds would seem to be thermodynamically favored.

<u>Mechanism of Aquocomplex Formation</u> - A general requirement imposed upon any reaction mechanism is that it be in agreement with the relevant thermodynamic quantities. A proposed mechanism should, therefore, be examined in terms of the known formation constants and enthalpies and entropies

of formation.

There are five proposed structures shown in Figure 22 for cobalt or nickel perchlorate in butanol. Structure (I) represents one extreme, with the metal ion completely solvated by butanol and free of any association with the anion. The low electrical conductivity of the perchlorate solutions effectively rules out structure (I).

Structures (II) and (III) represent the other extreme, with either monodentate or bidentate coordination of the perchlorate anion directly to the cation. The perchlorate ion is well known for its almost complete lack of any tendency to form inner sphere coordinated complexes in aqueous solution. This property of perchlorates is often used by physical and synthetic inorganic chemists when a non-interfering anion is desired. Recently Straub and Yung (27) have found, however, that perchlorato complexes of cobalt (II) and nickel (II) do indeed form in methylene chloride. Their infrared and near infrared measurements have indicated a tetrahedral arrangement of monodentate perchlorate ions about the cobalt, $[Co(ClO_4)_4]^{2-}$, and an octahedral arrangement of both monodentate and bidentate perchlorate ions about the nickel, $[Ni(ClO_4)_4]^{2-}$. Such species, however, are found only in solvents of very low basicity, and, therefore are not expected to be found in alcohol solutions.

Structures (IV) and (V), with the perchlorate anions bound by hydrogen bonding to the hydroxyl groups of the butanol ligands, seem more reasonable and are consistent with the following mechanism for the reaction.

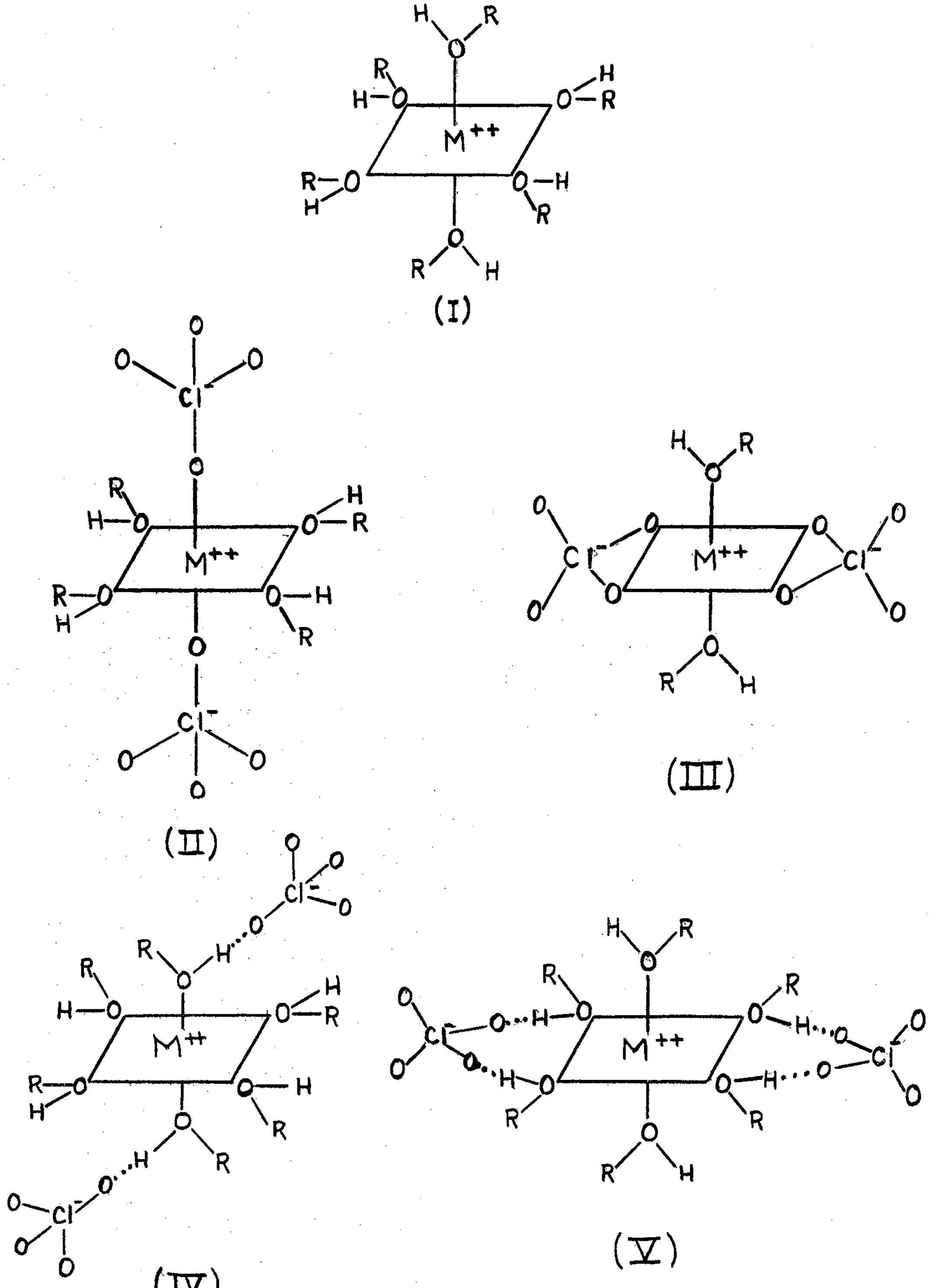

Figure 22. Possible Structures of $M(ClO_4)_2$ in 1-Butanol

From the values of the overall formation constants, β_1 and β_2, (Table VII) and the corresponding enthalpies of formation, it seems logical to infer that the first two sites of attachment are essentially different from the others, yet mutually similar. Both structures (IV) and (V) fulfill this requirement, for the axial positions as shown are obviously sterically different from the remaining positions and equivalent to each other. For the first two replacements of butanol by water, there is a relatively large negative enthalpy change. For structure (V), however, one would qualitatively expect a small negative enthalpy effect, but a positive entropy effect. This follows from the reasoning that the smaller water ligand should have greater steric freedom than the much more bulky butanol molecule, even though more firmly held.

Consideration of the replacement of an axial butanol by water in structure (IV) shows that it would be possible to have a closer approach of the anion to the doubly charged cation, due to the differences in steric bulk of the water and butanol molecules. The closer approach of the charges would certainly alter the electric field intensity and thereby affect the enthalpy.

A negative entropy effect implies a loss of translational and rotational freedom. In a simple exchange of a water molecule for a coordinately bound butanol molecule, one would expect a small positive entropy effect owing to the relatively larger amount of freedom gained by the butanol compared with that lost by the bound water. If the overall entropy change is to be negative, however, this otherwise positive contribution to the entropy of the process must be counterbalanced by a still larger negative entropy contribution from greater restriction in the freedom of the water ligand. Because of the closer approach of the anion to the cation when water replaces butanol, and also because water has a greater dipole moment than does butanol, the water molecule should be more firmly bound than the butanol. This is confirmed by a simple electrostatic calculation of the energy of the system using point charges.

If one considers the stereochemical arrangement of the proposed complex structure as illustrated in Figure 23, he will note that the approximately tetrahedral sp^3 orbitals of the oxygen of water are not in the most favorable configuration to overlap the octahedral sp^3d^2 orbitals of the cation. The oxygen of the water could tilt somewhat to give greater orbital overlap, but this would certainly alter the electrostatic field of the cation-anion interaction as well as cause steric interference with the butanol ligands.

When a model of the proposed complex of Figure 23 was constructed (Framework Molecular Models, Prentice-Hall Inc., Englewood Cliffs, N. J.), one general fact became immediately apparent for the proposed structure as well as for any of the other complex structures shown in Figure 22--there is a considerable amount of steric crowding about the central metal ion. The crowding, owing to the interference at the Van der Waals radius of the hydrogens, is most severe when there are six butanol molecules around the central metal ion. It was noticed from the model that water doubly hydrogen-bonded to

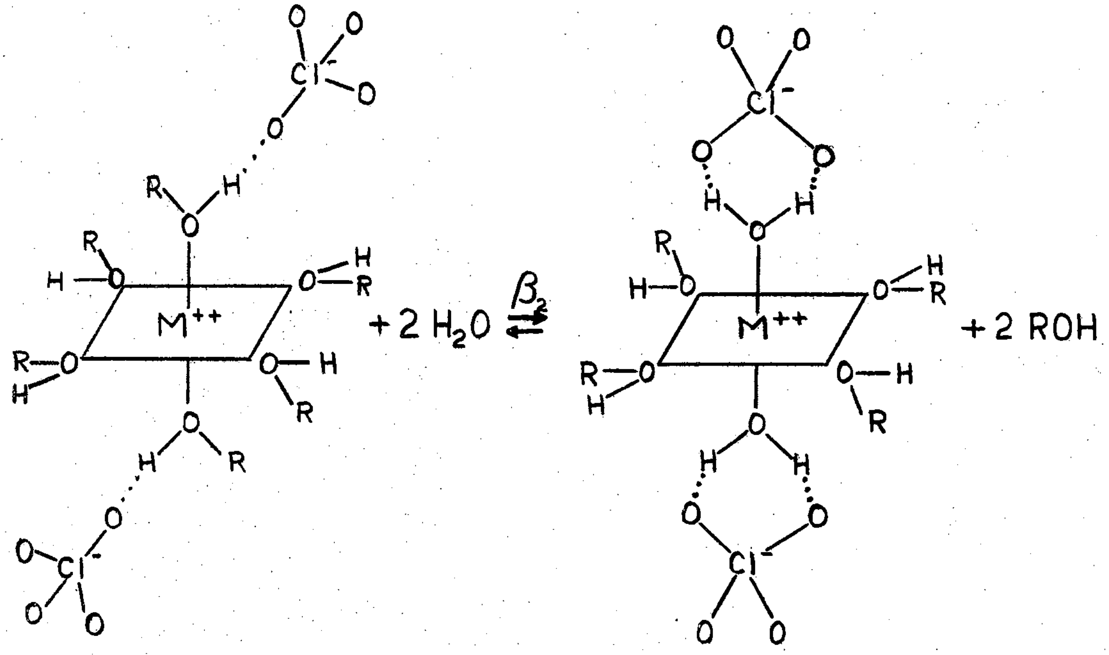

Figure 23. Formation of the n = 2 Aquocomplex

perchlorate ion could not form colinear hydrogen bonds at the normal bond angles of water and perchlorate, but some bond angle deformation would have to take place. Doubly bonded hydrogen-bonding systems are known to exist, however, e.g., acetic acid dimer.

A point which should be noted concerns the magnitude of the formation constants. The formation constants for $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ aquocomplexes are relatively small, indicating that the complexes are rather weak (24). This fact probably reflects more the similarity in the bonding of butanol and water than any failure to achieve maximum overlap of the oxygen-metal orbitals. However, the binding energy may be somewhat less than could be expected for more favorable symmetry.

Substitution at the remaining four ligand sites presumably occurs in a straightforward manner. The small negative enthalpy change for stepwise substitution arises from the replacement of butanol by water at the equatorial positions, with very little difference in the binding energies of water and butanol. The positive entropies arise, as pointed out earlier, from the freedom gained in such a replacement by the butanol compared with that lost by water.

<u>Reliability of the Thermodynamic Quantities</u> - One of the paradoxes encountered in this study involves the relative precision of the data obtained and the thermodynamic quantities calculated from the data. The experimental values were measured with a reproducibility of better than 1%. Because of the high precision and the fact that so many data points

were obtained, a well defined "experimental" curve was obtained. Great difficulty was encountered, however, in finding a set of constants to reproduce a "calculated" curve which fits the experimental curve with the same precision. In fact, this could not be done; however, a set of constants was found which gave a good fit at all but a few points.

A comparison of the formation constants for $Cu(ClO_4)_2$ in acetone (20) with those of $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ in butanol shows that they are all of comparable magnitude; however, comparison of the values for the first and second replacements of water by acetone or ethanol from fully hydrated $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ (21) indicates a reversal in the order of stability from that shown by k_5 and k_6 of this work. In view of the uncertainty in the proper value of N to be used, this point of disagreement cannot be resolved.

A further criticism of the above papers must be raised concerning the assumptions made about the nature of the complex species in organic solvents. It has been generally assumed in previous studies of aquocomplexing that the transition metal perchlorates were completely dissociated in ethanol, acetone and nitromethane solutions. This point appears to be in contradiction to the interpretation of the conductivity measurements made in this study. Even in mixtures of 50 mole per cent water in butanol, calculations indicate that ion-association predominates over the concentration range studied. At small water concentrations still less ionization can be expected (4). The dielectric constant of a 50 mole per cent water in butanol solution is comparable to that of acetone.

CHAPTER VI

SUMMARY AND SUGGESTIONS FOR FURTHER STUDY

Solutions of cobalt (II) and nickel (II) perchlorate in anhydrous 1-butanol, ranging in concentration from 0.0171 to 0.0803M, were titrated thermometrically with water. The results were analysed by the principle of corresponding solutions to give the average ligand number and the free ligand concentration. No upper concentration limit was established for the method.

Values for the first four stepwise formation constants were calculated from Bjerrum's formation function with good precision. The fifth and sixth constants are less certain, being determined on the basis of a smaller number of points at $\bar{n}$ values less than four. The formation constants were used to calculate the overall enthalpies of aquocomplex formation, which were in turn used to calculate the entropies of formation. From the stepwise enthalpies and entropies of formation, a structure is proposed for a reaction mechanism to fit the thermodynamic data.

Thus, it has been shown that in a study of aquocomplex formation by thermometric titration it is possible to determine not only the formation constants, but the enthalpies and entropies of formation as well from a single set of calorimetric values.

One of the more important pieces of information lacking in this study is the experimentally determined maximum coordination number. The assumption of a value of six, although in accord with conventional practice, leaves something to be desired. The only conceivable way of finding such a maximum by thermometric titrations would be to extend the measurements to much higher water concentrations. Unfortunately, considering the degree of reproducibility of the data and the uncertainty involved in correcting for the heat of mixing, the values of the heat of reaction ($\overline{\Delta H}$) at high water concentrations are almost equal to the error involved in their determination. Therefore, with the precision currently available with the calorimeter, extension of the thermometric titrations of cobalt and nickel perchlorate in butanol to high water concentrations is not useful. If a way of improving the precision of the measurements were developed, either by better technique or by modifications to the calorimeter, such a study might prove very informative.

Since this work has shown the applicability of the theory and technique of thermometric titrations to the study of the thermodynamics of aquocomplex formation (at least in principle), a logical step is to study other transition metal perchlorates in other solvent systems. One extension of this work would be to study copper (II) perchlorate and such other solvents as acetone, 2-butanone, other alcohols and other oxygenated solvents. The literature concerning the aquocomplexing of copper perchlorate in organic solvents is the most extensive of any salt at present, and this makes possible a critical evaluation and comparison of methods of study of aquocomplexing.

A possible reevaluation of Fielder's (6) data for the aquocomplex formation of cobalt perchlorate in ethanol, using a non-linear correction for the heat of mixing of titrant and solvent is needed. Fielder found that the cobalt perchlorate aquocomplexes were apparently too stable in ethanol solvent to be amenable to a corresponding solutions analysis. His conclusions seem to contradict the results in this study, since the aquocomplexes of cobalt perchlorate would be expected to be less stable in ethanol than in 1-butanol.

A qualitative study of both hydrous and anhydrous solutions of metal perchlorates by infrared spectroscopy could prove very helpful in confirming the proposed hydration mechanism. If the perchlorate ion does change from a singly to a doubly hydrogen bonded anion, then a vibrational shift in the spectrum should be observed (5,18,27).

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GLOSSARY

C_M = analytical molar concentration of metal, M

C_L = analytical molar concentration of ligand, L

Q_{cal} = experimental heat of reaction of L with solution

Q_{sol} = experimental heat of mixing of L with butanol

Q_{rx} = experimental heat of reaction of L with M

$\overline{H}_L^o$ = standard molar enthalpy of pure liquid L

$\overline{H}_L^*$ = partial molar enthalpy of L in binary solution at C_L

$\overline{H}_M^*$ = partial molar enthalpy of M in binary solution at C_M

$\overline{H}_L$ = partial molar enthalpy of L in the equilibrium mixture

$\overline{H}_M$ = partial molar enthalpy of M in the equilibrium mixture

$\overline{\Delta H}$ = heat of reaction of L with M

β_n = overall formation constant for complex ML_n

η_n = overall enthalpy of formation for complex ML_n

σ_n = overall entropy of formation for complex ML_n

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