A THERMODYNAMIC STUDY OF THE AQUOCOMPLEX FORMATION OF SELECTED FIRST ROW TRANSITION AND ALKALINE EARTH METAL PERCHLORATES IN 1-BUTANOL

By

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1966

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
DOCTOR OF PHILOSOPHY
July, 1972

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ACKNOWLEDGEMENT

I wish to extend my deepest appreciation to Dr. Tom E. Moore for his guidance throughout the course of this study, and in the writing and proof reading of the manuscript. I wish also to thank Drs. L. P. Varga and H. A. Mottola for their counsel on computational and analytical procedures. I wish to thank my parents and friends for their encouragement.

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

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CHAPTER I

PURPOSE OF STUDY AND STATEMENT OF PROBLEM

This research was undertaken as part of a program to study the solvation behavior of divalent metal perchlorates in binary solvent systems in which there is evidence of selective ion-solvent interaction. The term "selective ion-solvent interaction" (83,102) is applied when the composition of the solvent components in the neighborhood of the ions is different from the composition of the bulk solvent.

The solvent system chosen for study was 1-butanol:water. Water is, of course, the most common solvent while 1-butanol is the lowest molecular weight primary alcohol that can be used for solvent extraction owing to miscibility limitations.

Previous studies (19,57,77,99,115) indicate that many divalent metal salts preferentially solvate water in mixed water:organic-solvent systems, i.e., form "aquocomplexes". Solvation by water is pronounced even when the amount of water present is as small as 0.1% by weight, which is roughly the amount present in commercially available "dry" organic solvents. This quantity of water is not really small, as is obvious when expressed on the chemically more significant molal scale, for it represents a concentration of about 0.06 molal.

It was the objective of the present study to obtain as nearly a complete thermodynamic description of the aquocomplex formation process as possible. This requires the evaluation of the step-wise free energies, enthalpies, and entropies of aquocomplex formation. In the course of the study these quantities were evaluated for the formation of aquocomplexes of calcium, copper(II), zinc, magnesium, manganese(II), and strontium perchlorates in anhydrous 1-butanol.

Method of Study

Incremental thermometric titration calorimetry (18,29,32,48,114) was chosen as the method of study. Thermometric titrations, first reported being performed in 1909 (38,117), are unique among titration methods in that they depend on an entropy term (70). Most titration methods are "free energy" methods in that they depend entirely on equilibrium constants which are correlated logarithmically with free energies by the well-known equation

$$\Delta G^{o} = -RT\ln K . \qquad (1.1)$$

By employing the thermometric titration method, one takes advantage of the fact that the reaction enthalpy is one of the most general properties of a chemical reaction. It is an additive function of the two reaction parameters ΔG and $T\Delta S$

$$\Delta H = \Delta G + T\Delta S \qquad (1.2)$$

Since the two terms on the right side of Equation (1.2) are essentially independent of each other (20,47,66), it is quite conceivable that an unfavorable free energy term may be compensated for by a favorable entropy term.

Usually, data from two different experiments are needed to calculate free energy, enthalpy, and entropy changes associated with a chemical reaction. For example, the free energy change may be calculated from equilibrium constant measurements, and the enthalpy change from calorimetric data or through the van't Hoff isochore, requiring measurements of equilibrium constants as a function of temperature. The "van't Hoff isochore" method of obtaining enthalpies is less preferable as it is often subject to considerable error (82).

However, for certain classes of reactions, free energy, enthalpy, and entropy changes can be determined from a single set of calorimetric data (15,16,18,28,69,97,104,105). The thermometric titration method depends on calculation of the extent of reaction from the quantity of heat evolved. Its successful application to a given system depends on satisfaction of the following conditions:

1. The enthalpy change for the reaction must be measureably different from zero.
2. The equilibrium constant and the reaction conditions must be such that at equilibrium a measurable, but not quantitatively complete, amount of reaction has taken place.

The thermometric titration method should then be of general usefulness in studying weak colorless complexes and reactions in nonaqueous solvents (29).

Many organic liquids, such as 1-butanol, have a heat capacity significantly less than that of water (103). This makes the temperature change for a given quantity of heat evolved greater, and hence the method more sensitive.

There are certain disadvantages to using thermometric titrations for fundamental thermodynamic measurements. One of these is the necessity of making a correction for the heat of mixing of the solvent with the titrant.

1-Butanol was a fortunate choice of solvent for this study because the integral heat of mixing of water with 1-butanol is a linear function of water concentration at low water concentrations (57). Consequently, the heat of complexation of the metal ion is easily obtained from the overall heat of reaction and a correction term, which is a simple linear function of the heat of mixing of water with 1-butanol.

The activity of water in 1-butanol has been thoroughly investigated by Thomson et. al. (119), and by Weber and Randall (124). These groups of workers each found the activity coefficient of water in 1-butanol to be 1.00 up to a water mole fraction of about 0.25. This corresponds roughly to the upper limit of water concentration considered in this study.

In order to eliminate the unknown heat of dilution of the products of the reaction and permit calculation of the enthalpy of reaction referred to the customary ideal standard state of the solutes, extrapolation of the measured heat of reaction to infinite dilution and zero ionic strength is required (29). Maintaining a constant (approximately zero) ionic strength was no problem in the present study as conductivity studies by Cheung (24) and Rands (112) have indicated that 2:1 perchlorate salts are almost completely associated in 1-butanol up to much higher water concentrations than those investigated here. Extending the measurements to salt concentrations much less than 0.01 molar was not possible, however, because of the small values of the heat of formation of the aquocomplexes. This may not introduce serious error, for studies by Christensen and coworkers (25) have indicated that the value of ΔH for acid-base reactions changes very little in the range of ionic strengths from 0.0M to 0.01M.

Literature Survey of Earlier Aquocomplex Studies

Investigation of the solvation of salts in mixed aqueous-alcohol solvents dates back to 1909 when Jones and Anderson (67) reported that the absorption spectra of many transition metal and rare earth salts in methanol and ethanol solution containing small amounts of water showed features of the spectra of the same salts in water alone as well as features observed in alcohol alone. The spectra were found to be virtually independent of anion concentration, and were, therefore, assumed to be caused by changes in solvation of the cation only.

The first quantitative study of the stability of aquocomplexes in aqueous-alcohol solutions was carried out in 1953 by Bjerrum and Jorgensen (13). They calculated the stability constant for the formation of the first (1:1) aquocomplex of a mixture of praesodymium(III) and neodymium(III) chlorides (42% Pr, 58% Nd) in aqueous methanol from spectral data, employing the method of "corresponding solutions" developed earlier by Bjerrum (12). A value of 1.7 was obtained for k_1, where k_1 is defined by

$$k_1 = [M(H_2O)]/[M][H_2O] \; . \tag{1.3}$$

Jorgensen (72), using the same technique employed in the earlier work with Bjerrum, studied the formation of aquocomplexes of copper(II), cobalt(II), and nickel nitrates in aqueous ethanol. He was able only to evaluate an "average formation constant", which he defined as

$$K_{av} = [\sum_1^N (k_n)]^{1/N} \tag{1.4}$$

Values of K_{av} obtained were 0.19, 1.08, and 0.82, respectively, for the above three metal nitrates. The maximum coordination number was assumed to be six. In this study Jorgensen assumed the nitrate salts to be dissociated electrolytes in anhydrous ethanol, with the observed spectral changes due only to changes in solvation of the cation. This assumption was challenged by Katzin and Gebert (73) on the basis of their work with cobalt(II) nitrate and perchlorate in organic media (74). These authors argued that the spectrum change was due to replacement of nitrate by water in the first coordination shell of the cation. Bjerrum and Jorgensen (14) later agreed with the contention of Katzin and Gebert regarding the inner sphere coordination of nitrates but presented evidence that the spectral changes for cobalt(II) perchlorate in ethanol must be due to hydration and not to perchlorate coordination. This is in agreement with the findings of Yates, et. al. (127) in a study of the hydration of divalent perchlorates and chlorides in 2-octanol. The apparent degree of hydration of cobalt(II) perchlorate and nickel perchlorate in 2-octanol was determined by solvent extraction. Up to 12 moles of hydrate water per mole of salt were found to be coextracted with 2-octanol. This seems to confirm the inability of the perchlorate anion to function effectively as a coordinating ligand or to approach the cation closely. The cation is thus left free to exert its maximum influence on the solvent molecules.

Minc and Libus (94) also have studied aquocomplexing of copper(II) nitrate in ethanol by infrared spectroscopy. They obtained a value of K_{av} of 0.15, which is in fairly good agreement with the value obtained by Jorgensen (72).

In 1958, Vasil'ev (123) measured dissociation constants for the stepwise dissociation of the aquocomplexes of cadmium, lead(II), and thallium(I) in aqueous ethanol solution by polarography. For cadmium, values of 34, 47, and 50 were obtained for the stability constants k_3 through k_5, respectively. For lead(II), values of 26, 44, 46, and 51 were obtained for k_2 thru k_5, respectively. For thallium(I), values of 30 and 46 were obtained for k_2 and k_3, respectively.

Larson and Iwamoto (80), in 1961, evaluated the consecutive formation (stability) constants for the copper(II) perchlorate aquocomplexes in nitromethane both polarographically and spectroscopically in the infrared. Formation constants obtained by the two methods are in close agreement and indicate that the copper(II) ion has a much greater affinity for water than for nitromethane. Values obtained were 950, 96, 34, 9.7, 7.2, and 7.0 for k_1 through k_6, respectively.

In 1962, Friedman and Plane (44) studied the formation of aquocomplex of copper(II) perchlorate in acetone:water and ethanol:water mixtures by spectroscopy. Constants were obtained for the stepwise replacement of two water molecules in the primary hydration sphere by the organic solvent. From this data one calculates the stability constants for the fifth and sixth aquocomplexes to be 1.8 and 3.9×10^{-2}, respectively. For acetone, corresponding values of 3.7 and 3.1×10^{-3} are obtained. The magnitude of the equilibrium constants indicate that acetone and ethanol are preferred over water only for the sixth coordination site.

Nelson and Iwamoto (100) have also studied the solvation by water of copper(II) in acetone. Measurements were made by polarography and, of necessity, a carrier electrolyte was included in the solution. One-tenth molar lithium perchlorate was used in one set of measurements, and

0.1M tetra-n-butyl ammonium perchlorate in another. Therefore, a strict comparison of the formation constants obtained by Nelson and Iwamoto (100) with those obtained by Friedman and Plane (44) is not as meaningful as it might be because of the difference in the solvent medium caused by the presence of the carrier electrolyte. With lithium perchlorate as carrier electrolyte the values 56, 32, 9.9, and 3.2 were obtained for the formation constants, k_1 through k_4, respectively. With tetra-n-butyl ammonium perchlorate as carrier, values of 56, 18, 6.3, and 4.5 were obtained for k_1 through k_4, respectively.

In 1963, Luz and Meiboom (87) studied the solvation of cobalt(II) perchlorate in methanol-water mixtures at low temperatures by nuclear magnetic resonance. The data best fit a model consisting of a monoaquated complex in equilibrium with the <u>cis</u> and <u>trans</u> isomers of a diaquated species. Values of 44, 1.5×10^2, and 2.4×10^2 were obtained for β_1, β_2^{trans}, and β_2^{cis}, (see the Glossary in Appendix E for the meaning of the symbols).

Jayne and King (65) have studied the solvation of chromium(III) in acidified water:methanol solvents. Equilibrium constants were obtained from ion-exchange data for the stepwise replacement of water by methanol. Values obtained were 6.0×10^{-1}, 3.3×10^{-1}, 4×10^{-2}, and 3×10^{-2} for the replacement of the first four water molecules by alcohol, respectively. Pasternack and Plane (106), in 1965, extended the earlier work of Friedman and Plane (44) to include cobalt(II) and nickel perchlorates. The results are similar to those for copper(II) in that there appears to be a marked disparity in the magnitude of k_5 and k_6, six coordination being assumed. Values of k_5 and k_6 for cobalt(II) in ethanol were 2.9 and 6.0×10^{-3}, respectively. For cobalt(II) in acetone, corresponding values of 3.6 and 1.5 x 10^{-2} were obtained. For nickel in ethanol, values of 5.7 x 10^{-1} and 4.9 x 10^{-3} were found. In acetone the values were 6.2 and 2.1 x 10^{-2}, respectively.

Aquocomplexing of monovalent cations in acetonitrile has been investigated by Chantooni and Kohlthoff (23). Formation constants for aquocomplexes of lithium, sodium, potassium, and cesium salts were evaluated by solubility measurements. Values of the formation constants were small, ranging from 0.5 to 2.0.

Kemp and King (76) have extended earlier investigations of the solvation behavior of chromium(III) to include acidified water:ethanol solvent mixtures. The slow exchange rate of solvent molecules in the first solvation sphere of chromium(III) allowed separation of differently solvated species by ion exchange. Equilibrium constants were calculated for the replacement of water by ethanol in the first coordination shell. Values obtained were 4.2 x 10^{-1}, 1.3 x 10^{-1}, and 4.0 x 10^{-2} for replacement of the first three water molecules, respectively.

Probably the most complete thermodynamic study of aquocomplex formation of metal ions in organic solvents is that of Harris and Moore (58). Formation constants, enthalpies, and entropies were evaluated for the stepwise formation of the assumed six aquocomplexes of cobalt(II) and nickel perchlorates in 1-butanol. The assumption of six coordination is in agreement with the findings of McManemy (92) in a solvent-extraction study of cobalt(II), copper(II), and zinc nitrates in water:1-butanol mixtures. McManemy calculated apparent hydration numbers of 7.0, 5.3, and 6.0, respectively, for the three ions.

The magnitude of the formation constants obtained by Harris and Moore (58) indicate that the metal ions studied have a much greater affinity for water than for the organic solvent. The present research reports an extension of this work to other metal perchlorates in butanol.

Stability constants reported in the studies discussed above are listed in Table I for convenience.

TABLE I

STABILITY CONSTANTS OBTAINED IN OTHER AQUOCOMPLEX STUDIES

Metal	Solvent	k_{av}	k_1	k_2	k_3	k_4	k_5	k_6	Method	Ref.
Nd/Pr	E	---	1.7×10^{0}	--	--	--	--	--	IR Spect.	72
Cu(II)	E	1.9×10^{-1}	--	--	--	--	--	--	IR Spect.	13
Co(II)	E	1.1×10^{0}	--	--	--	--	--	--	IR Spect.	13
Ni(II)	E	8.2×10^{-1}	--	--	--	--	--	--	IR Spect.	13
Cu(II)	E	1.5×10^{-1}	--	--	--	--	--	--	IR Spect.	94
Cd(II)	E	---	--	--	3.4×10^{1}	4.7×10^{1}	5.0×10^{1}	--	Polarog.	123
Pb(II)	E	---	--	2.6×10^{1}	4.4×10^{1}	4.6×10^{1}	5.1×10^{1}	--	Polarog.	123
Tl(I)	E	---	--	3.0×10^{1}	4.6×10^{1}	--	--	--	Polarog.	123
Cu(II)	N	---	8.0×10^{3}	8.3×10^{1}	1.7×10^{1}	8.7×10^{0}	3.3×10^{0}	3.2×10^{0}	Polarog.	80
Cu(II)	W/A	---	--	--	--	--	3.7×10^{0}	3.1×10^{-3}	IR Spect.	44
Cu(II)	W/E	---	--	--	--	--	1.8×10^{0}	3.9×10^{-2}	IR Spect.	44
Cu(II)	A	---	5.6×10^{1}	1.8×10^{1}	6.3×10^{0}	4.5×10^{0}	--	--	Polarog.	100
Cu(II)	A	---	5.6×10^{1}	3.2×10^{1}	1.0×10^{1}	3.2×10^{0}	--	--	Polarog.	100
Co(II)	M	---	4.4×10^{1}	3.4×10^{0}* 5.5×10^{0}**	--	--	--	--	NMR	87
Co(II)	E	---	--	--	--	--	2.9×10^{0}	6.0×10^{-3}	IR Spect.	106
Co(II)	A	---	--	--	--	--	3.6×10^{0}	1.5×10^{-2}	IR Spect.	106
Ni(II)	E	---	--	--	--	--	4.9×10^{-1}	4.9×10^{-3}	IR Spect.	106
Ni(II)	A	---	--	--	--	--	6.2×10^{0}	2.1×10^{-2}	IR Spect.	106
Cr(III)	E	---	2.5×10^{1}	7.7×10^{0}	2.4×10^{0}	--	--	--	Ion Exch.	76
Cr(III)	M	---	3.3×10^{1}	2.5×10^{1}	3.3×10^{0}	1.6×10^{0}	--	--	Ion Exch.	76
Co(II)	B	---	5.7×10^{1}	2.1×10^{1}	1.1×10^{1}	3.5×10^{0}	9.1×10^{0}	2.5×10^{1}	Calorim.	58
Ni(II)	B	---	6.4×10^{1}	2.7×10^{1}	1.4×10^{1}	7.0×10^{0}	4.0×10^{0}	2.3×10^{0}	Calorim.	58
K	AN	---	1.0×10^{0}	--	--	--	--	--	Solub.	23
Na	AN	---	2.0×10^{0}	--	--	--	--	--	Solub.	23
Cs	AN	---	5.0×10^{-1}	--	--	--	--	--	Solub.	23

Solvent Abbreviations: E - ethanol N - nitromethane A - acetone W - water M - methanol B - 1-butanol
AN - acetonitrole * - cis isomer ** - trans isomer

CHAPTER II

THEORY OF THE PROPOSED METHOD

Corresponding Solutions

For the calculation of stability constants, an adaptation of Bjerrum's method of "corresponding solutions" (12,45,46,62,126) applicable to the calorimetric data was employed. This is developed in detail in what follows in a manner which is strictly applicable to 2:1 metal salts, but which can be easily extended to other types.

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

$$zM(soln) + yL(liq) \rightarrow z\sum_{1}^{N} \alpha_n ML_n(soln) + Q_{rx} \qquad (2.1)$$

where α_n is the fraction of salt M in aquocomplex ML_n at equilibrium and Q_{rx} is the heat of reaction of M with L. The mixing of water (L) with solvent alone produces Q_{mix} calories according to the relation

$$Q_{mix} = \bar{H}_L^o - \bar{H}_L^* \qquad (2.2)$$

where

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

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

Q_{mix} = heat of mixing of L with solvent.

Dividing Equation (2.1) by z and formulating the corresponding thermal equation yields

$$\bar{H}_M^* + \frac{y}{z}\bar{H}_L^o = \sum_1^N \alpha_n \bar{H}_{MLn} + \bar{H}_M - \sum_1^N \alpha_n \bar{H}_M + \frac{y}{z}\bar{H}_L - \sum_1^N n\alpha_n \bar{H}_L + Q_{rx}/z \qquad (2.3)$$

where

$\bar{H}_M^*$ = partial molal enthalpy of M in the binary reference solution.

$\bar{H}_M$, $\bar{H}_L$, $\bar{H}_{MLn}$ = respective partial molar enthalpies in the equilibrium mixture.

Equation (2.3) can be rearranged and combined with (2.2) to give

$$\sum_1^N(\bar{H}_{MLn}-\bar{H}_M^*-n\bar{H}_L^*)\ \alpha_n=(1-\sum_1^N\alpha_n)(\bar{H}_M^*-\bar{H}_M) + (\frac{y}{z} - \sum_1^N n\alpha_n)(\bar{H}_L^*-\bar{H}_L) + (yQ_{min}-Q_{rx}) \qquad (2.4)$$

The first two terms on the right are, 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 thermal equation corresponding to (2.4). By taking the difference between the new equation and (2.4), one has

$$\Delta\sum_1^N h_n\alpha_n = \Delta(1-\sum_1^N\alpha_n)(\bar{H}_M^*-\bar{H}_M) + \Delta(\frac{y}{z} - \sum_1^N n\alpha_n)(\bar{H}_L^*-\bar{H}_L) + \Delta(yQ_{mix}-Q_{rx})/z \qquad (2.5)$$

where

$$h_n = (\bar{H}_{MLn} - \bar{H}^*_M - n\bar{H}^*_L)$$

When the last term on the right side of (2.5) is made zero by proper choice of salt and ligand concentration, Equation (2.5) becomes

$$\sum_1^N h_n\alpha_n - \sum_1^N h_n\alpha'_n = \sum_1^N h_n(\alpha_n - \alpha'_n) \approx 0 \tag{2.6}$$

Consider further the case where the term on the right side of Equation (2.6) is zero. Since the h's are not all zero, it follows that $\alpha_n = \alpha'_n$ for all the n's. Such solutions are said to be <u>corresponding</u>, and the enthalpy change associated with the reaction can be written

$$\Delta H = \sum_1^N C_M h_n \alpha_n = \sum_1^N h_n (ML_n). \tag{2.7}$$

To find such corresponding solutions, a plot of C_L vs $\Delta H/C_M$ 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 equal. This is done by drawing lines parallel to the C_L axis for varying values of $\Delta H/C_M$.

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

For the general case of complex ML_n, the overall formation constant β_n is defined by

$$\beta_n = (ML_n)/(M)(L)^n \tag{2.8}$$

The analytical metal concentration is given by

$$C_M = (M) + (ML) + \cdots + (ML_N) \tag{2.9}$$

and the fraction in the form of the <u>nth</u> complex is given by

$$\alpha_n = (ML_n)/C_M \tag{2.10}$$

By combining (2.8) and (2.10) and factoring out the free metal concentration (M) one has

$$\alpha_n = \beta_n(L)^n/(1 + \sum_1^N \beta_i(L)^i) \tag{2.11}$$

and it is obvious from inspection that since the β's are constants,

$$\alpha = f(L)$$

a function of the free ligand concentration only for a given metal.

When $\alpha_n = \alpha'_n$

$$\alpha_n = \beta_n(L)^n/\sum_0^N \beta_n(L)^n = \beta_n(L')^n/\sum_0^N \beta_n(L')^n = \alpha'_n \tag{2.12}$$

and therefore (L) = (L'). For corresponding solutions, $\alpha_n = \alpha'_n$ for all n, and (L) = (L').

From Bjerrum's treatment of stepwise complex formation in solution

$$\bar{n} = \sum_1^N n\beta_n(L)^n/\sum_0^N \beta_n(L)^n \tag{2.13}$$

by definition, where $\bar{n}$ is the "average ligand number". Bjerrum (12) called the relationship of Equation (2.13) the "formation function" of the system, for it represents the average number of ligands bound per metal atom.

If the concentration of free ligand is known, the formation function may be calculated directly from the defining equation and values of C_M and C_L .

$$\bar{n} = (C_L - (L))/C_M \qquad (2.14)$$

By rearranging Equation (2.14) to give

$$C_L = \bar{n}C_M + (L) \qquad (2.15)$$

one has the familiar equation of a straight line where $\bar{n}$ is the slope and (L) is the intercept.

According to Equations (2.7) and (2.13), when $\Delta H/C_M = \Delta H'/C_M'$, the solutions are corresponding, and therefore (L) = (L'). One should be able to select values of $\Delta H/C_M$ where Equation (2.7) holds, as shown in Figure 1a. From a plot of the corresponding values of C_L and C_M, one obtains a series of straight lines with slopes equal to $\bar{n}$ and intercepts of (L). This is illustrated in Figure 1b.

Once a set of $\bar{n}$ and (L) values have been determined, one can proceed with the calculation of stability constants utilizing Equation (2.13). Details of the calculation are given in a later chapter.

From the set of stability constants, the corresponding enthalpies can be calculated following the relation

$$\Delta H/C_M = \Delta\bar{H} = \sum_1^N h_i \beta_i (L)^i / \sum_0^N \beta_i (L)^i \qquad (2.16)$$

where h_i is the enthalpy change associated with the reaction

$$M + iL \rightarrow ML_i$$

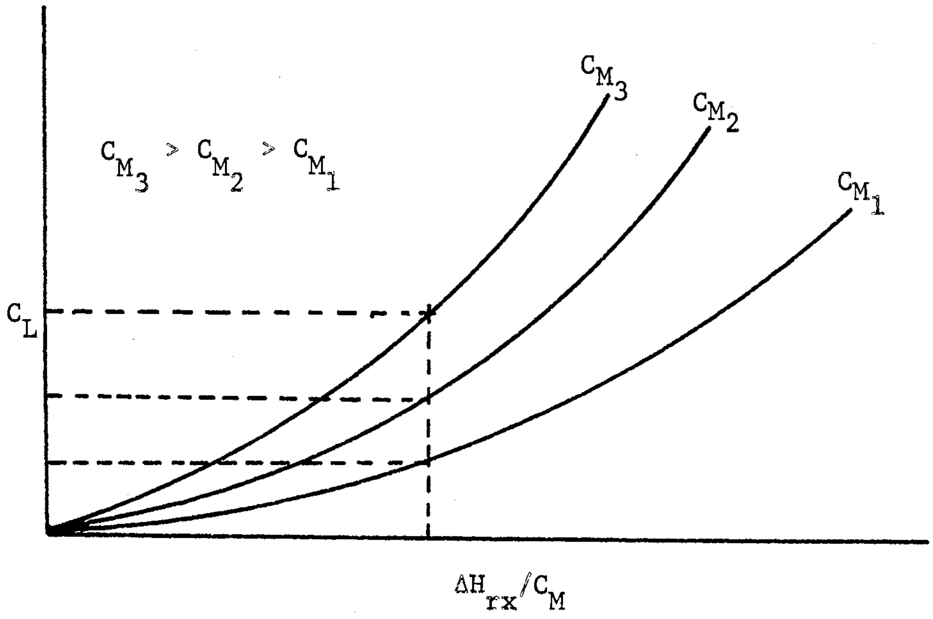


Figure 1a

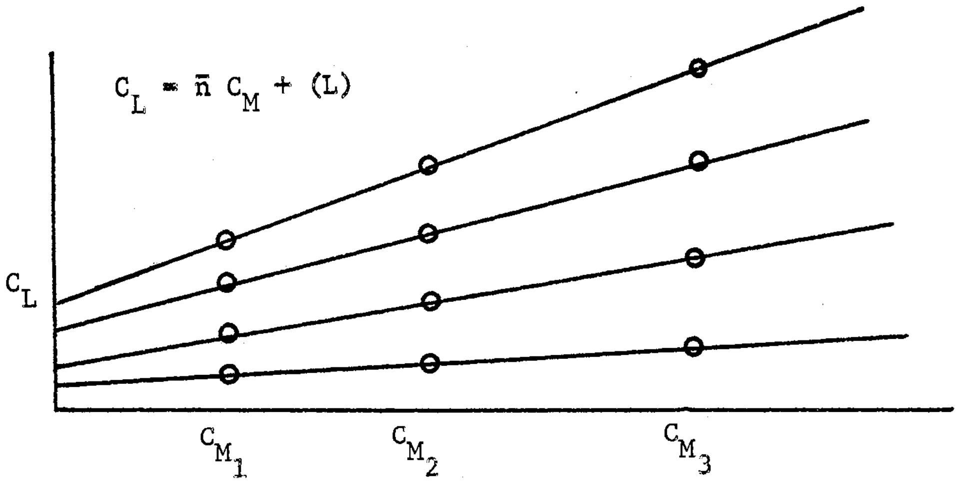


Figure 1b

The Corresponding Solutions Method of Determining $\bar{n}$ and (L)

Equation (2.16) can be expressed in a form more convenient for purposes of calculation.

$$\Delta\bar{H} = \sum_{1}^{N} h_i \alpha_i \tag{2.17}$$

This has the form of a linear equation and the h_i's can be calculated by straightforward least-squares procedures.

Once the stability constants and enthalpies have been determined, calculation of the stepwise entropies of aquocomplex formation can be accomplished easily via the equation

$$\Delta S_i = h_i/T + R \ln \beta_i \tag{2.18}$$

Assumptions of the Theory

In the foregoing discussion the theory of corresponding solutions has been developed in a general sense, but several assumptions are necessary for successful application of the method to specific systems. Although the problem has been considered in detail by Harris and Moore (58), their analysis is reviewed here because of its relevancy.

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

$$ML_{n-1}X_p + L \rightleftarrows ML_nX_p \quad \text{for which} \quad k_{np} = (ML_nX_p)/(ML_{n-1}X_p)(L) \tag{2.19}$$

and

$$ML_nX_{p-1} + X \rightleftarrows ML_nX_p \quad \text{for which} \quad k'_{np} = (ML_nX_p)/(ML_nX_{p-1})(X) \tag{2.20}$$

Then, if one defines

$$\beta_n = \prod_{o}^{n} k_{no} \quad (p = o) \tag{2.21}$$

and

$$\beta_p = \prod_{o}^{p} k_{np}, \tag{2.22}$$

it follows that

$$(ML_nX_p) = (M)(L)^n(X)^p \ \beta_n\beta_p \tag{2.23}$$

The average ligand number again be formulated

$$\bar{n} = (C_L - (L))/C_M = \sum_{o}^{n}\sum_{o}^{p} n\ \beta_n\ \beta_p(M)(L)^n(X)^p/\sum_{o}^{n}\sum_{o}^{p} \beta_n\ \beta_p(M)(L)^n(X)^p \tag{2.24}$$

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

$$w_{np} = (ML_nX_p)/C_M \tag{2.25}$$

and hence

$$\bar{n} = \sum_{o}^{n}\sum_{o}^{p} n(ML_nX_p)/C_M = \sum_{o}^{n}\sum_{o}^{p} nw_{np} \tag{2.26}$$

Similarly, for the heat of reaction

$$\Delta\bar{H} = \sum_{o}^{n}\sum_{o}^{p} h_{np}(ML_nX_p)/C_M \tag{2.27}$$

If one finds two solutions such that

$$\Delta\bar{H} = \Delta\bar{H}' \tag{2.28}$$

then one has from Equation (2.27)

$$\sum_{o}^{n}\sum_{o}^{p} h_{np}w_{np} = \sum_{o}^{n}\sum_{o}^{p} h_{np}\ 'w_{np}' \tag{2.29}$$

Equation (2.29) can hold for all values of h_{np} only if $w_{np} = w_{np}'$, for presumably $h_{np} = h_{np}'$ always. Since the w_{np}'s are all equal, it follows that $\bar{n} = \bar{n}'$, because, according to Equation (2.26), the n's are the same function of the w_{np}'s.

Furthermore, one notes that

$$w_{np} = \beta_n \beta_p (L)^n (X)^p / \sum_o^n \sum_o^p \beta_n \beta_p (L)^n (X)^p \qquad (2.30)$$

Thus, w_{np} is independent of (X) if, and only if, (X) can be eliminated from Equation (2.30) by cancellation, i.e., if $p = 0$ or if p is constant and Equation (2.30) reduces to Equation (2.11). When $p = 0$ one has complete dissociation. When $p \geq 1$ and is constant, one has the case of complete ion-association.

It should be emphasized that unless p is constant (including zero) Equation (2.30) will not reduce to the form of Equation (2.11), and a plot of C_L vs C_M would not be expected to be linear.

Experimental evidence in the form of conductivity measurements and spectral studies will be presented later to support the hypothesis that in butanol solution the perchlorates studied are only slightly ionized over the concentration range investigated.

CHAPTER III

APPARATUS AND PROCEDURE

Materials

1-butanol (J. T. Baker). Reagent grade was used after removal of water by a method to be explained later; b.p. 117.5°C. Chromatographic analysis showed no significant impurities.

Di sodium Ethylenediaminetetraacetate (J. T. Baker). Analyzed reagent grade was used without further purification.

Karl Fischer Reagent (Baker and Adamson). Stabilized solution was used after dilution with absolute methanol.

Nitrogen (Linde). Lamp grade was used for purging equipment after being passed through a molecular sieve trap.

Methanol, Absolute (J. T. Baker, analyzed). Reagent grade was used without further purification.

Molecular Sieve (Union Carbide Corporation). Type 4A was used after being reactivated at 400°C. in a drying over for 48 hours.

Perchlorates of copper (II), calcium, manganese (II), zinc, magnesium, strontium, and barium (Hydrated) (G. F. Smith Co.). Reagent grade was placed directly in the solvent and the solution was dried by a procedure to be explained later.

Tetra-n-Butylammonium Perchlorate (G. F. Smith Co.). Reagent grade was used after drying under vacuum at 70°C. in a drying pistol for 48 hours.

Water. Laboratory distilled water was further purified by passing through a Deeminac mixed bed ion exchange column.

Potassium Chloride (J. T. Baker). Reagent grade was dried for 24 hours at 110°C. prior to use.

Zinc (J. T. Baker). Electrolytic grade was dried at 130°C. for 24 hours prior to use.

The Calorimeter

The calorimeter (Figure 2) used in this study was essentially the same as that described by Moore (96), which was patterned closely after other incremental thermometric titration calorimeters of proven design (5, 32, 48, 111, 114). All parts of the calorimeter in contact with the solution were made of glass except for the internal heater wire (A) and the Teflon titrant injection needle (B). The calorimeter vessel was a silvered-glass dewar flask having a volume of about 35 cc.

The 18-gauge Teflon titrant injection needle was fitted through a serum-stoppered opening (C) where it was attached through a luer-lok to a RG precision micrometer syring (0.001 cc divisions, 0.02% accuracy, 2.5 cc capacity). The lower half of the needle was coiled around the internal heater body below the surface of the solution. This insured that the titrant and solution would be very close to thermal equilibrium at the time of mixing. The minimum time spent by titrant in the coiled immersed part of the needle was over five minutes, which should have been ample time for the small volume of titrant and the solution to reach thermal equilibrium.

The stirrer (D) was a glass rod with paddles molded to the end. The rod was mounted in two teflon bearings and connected to the pulley

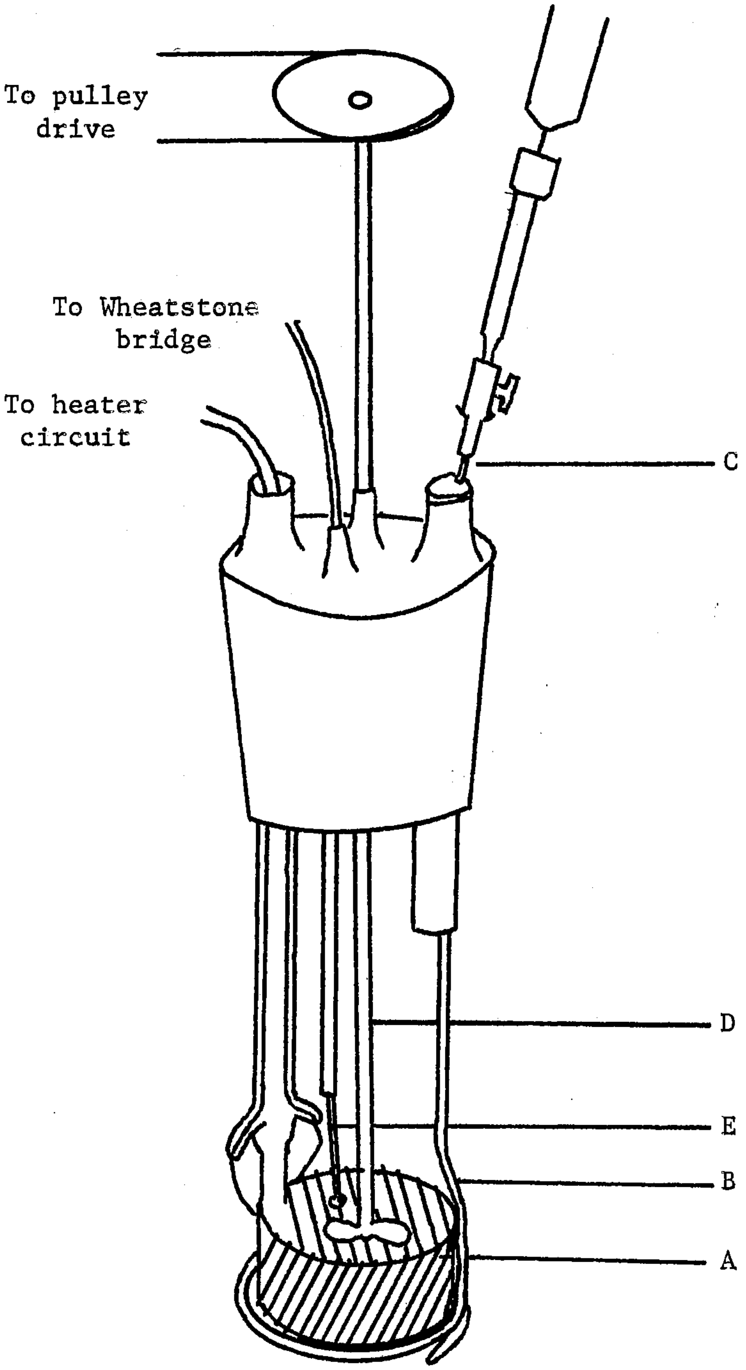


Figure 2. The Internal Parts of the Calorimeter

by a one-inch length of tygon tubing. The stirrer was powered by a Gerald K. Heller model GT21 electric motor. The rpm of the motor was closely controlled by a Cole-Parmer model GT21 Thyratron motor controller. The stirrer was operated at 600 rpm. This speed was the best compromise between a short mixing time and a minimal amount of stirring noise and heating.

The temperature sensing element (E) was a 10^5 ohm Victory Engineering Co. thermistor. The thermistor formed one arm of a wheatstone bridge. The unbalanced potential of the bridge was measured by a Sargent model SRG recording potentiometer operating in the 10 millivolt range. The thermistor had a temperature coefficient of resistance of $-4.6\%/^{\circ}C.$ and was operated at a potential of 10.0 volts to the bridge. A Trygon Electronics Co. constant voltage source supplied voltage to the thermistor.

Variable resistors in the bridge were digital reading Borg Equipment Co. precision helipots with a linear tolerance of 0.1%. The bridge was operated at a sensitivity of 0.10 to 0.25 calories per inch of pen travel on the recorder. Measurements were made to the nearest hundredth of an inch. Higher sensitivities could be obtained by applying a greater potential across the thermistor. Stirrer noise, however, quickly became a problem if the bridge voltage were greater than ten volts. Stirrer noise at higher bridge voltages caused the recorder pen to oscillate about its drift line to such an extent that the accuracy of measuring the pen travel after addition of titrant became less accurate than the aforementioned 0.01 inch. Preliminary experiments showed that the pen displacement was a linear function of temperature for small temperature changes. The resistance of a thermistor is known to be a logarithmic function of temperature (2, 8, 17, 36, 61, 68, 98) but can be considered linear for very small temperature changes such as those encountered in the present study.

The calorimeter was equipped with the electrical calibrating circuit shown in Figure 3. A constant calibrating voltage was supplied by the laboratory dc line (provided by a battery bank) which was run through a Valor Instrument Co. voltage regulator. Approximately 28 volts were supplied to the voltage regulator which reduced the voltage to about five volts before entering the calibration circuit. The voltage regulator was connected to a General Radio Co. type 1432-f decade resistance box serving as a "dummy heater". This was adjusted to match the resistance of the heater in the calorimeter. A relay system connects an X-ray timer and time switch to the heater. The heater is externally wound with six feet of 3.4×10^{-3} inch diameter platinum wire on a concentric glass form. The heater provided a total resistance of about thirty ohms. In operation the voltage across the heater was of the order of 0.9 volts.

A Rubicon potentiometer was used to measure the potential across a secondary standard General Radio type 500-B resistor sealed in a dewar flask at room temperature. This resistance was connected in series with the heater. The secondary standard was standardized against a Leeds and Northrup 4025-B National Bureau of Standards type resistor (10.000 ± 0.0005 ohms at 25°C). The secondary standard had a resistance of 10.000 ± 0.003 ohms at 25°C.

The calorimeter vessel was a silvered dewar flask with a Standard Taper 50/40 mm top, closed except for ports for stirrer and thermistor. When sealed in place, the entire unit was gas tight. The dewar flask was placed in a specially designed glass water jacket through which

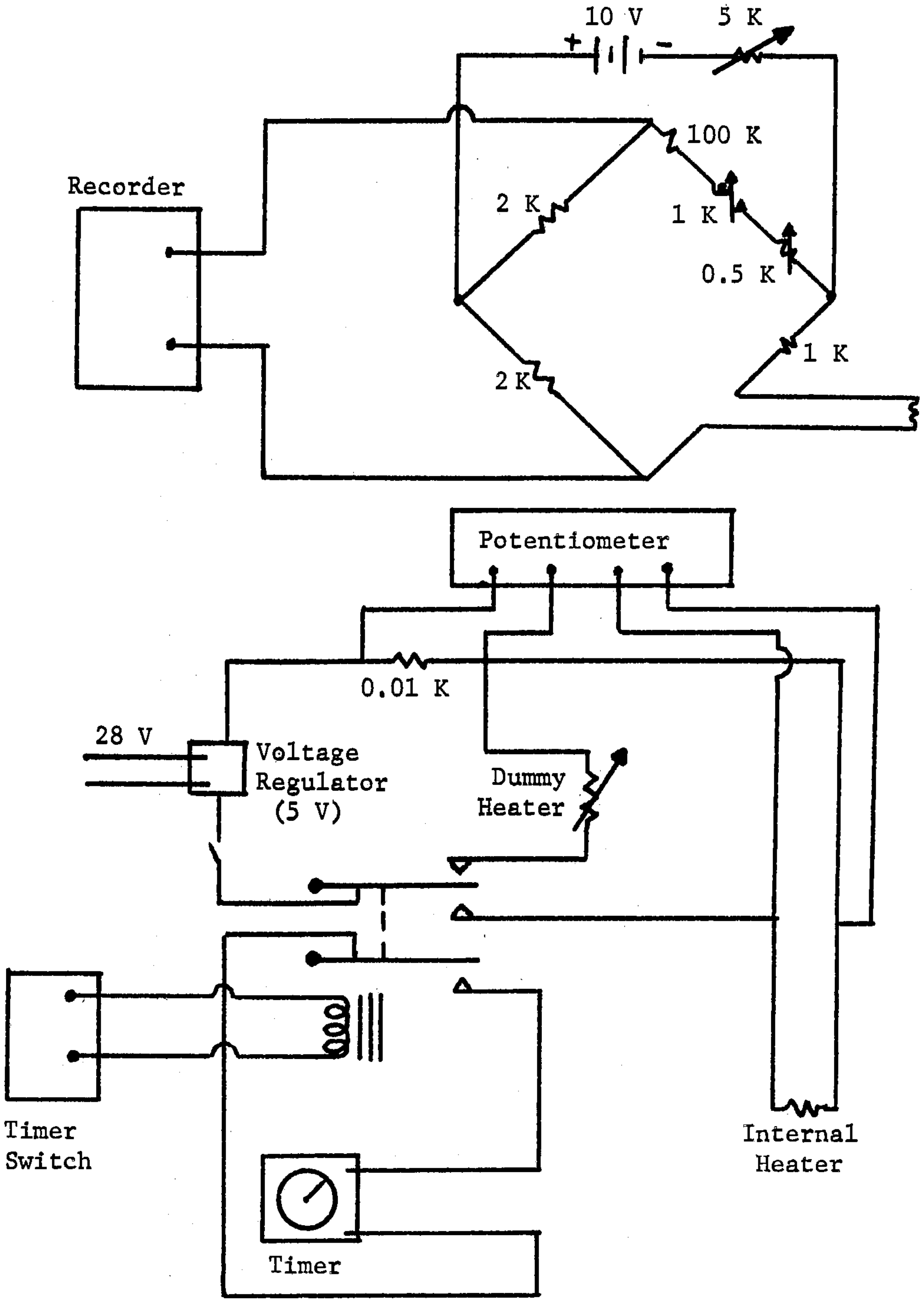


Figure 3. A Schematic of the Temperature Sensing and Heat Capacity Calibration Circuitry

constant temperature water was circulated. There was a small annular air space between the water jacket and the dewar flask. This provided a controlled environment for the flask.

The dewar flask was held rigidly in place by a styrofoam plastic ring. The air space and styrofoam ring allowed for limited conduction of the mechanical heat of stirring away from the dewar. The temperature of the water in the jacket was then adjusted so that the drift line of the recorder pen was flat (no net heating or cooling).

The heat capacity of the system was calculated by the equation

$$Cp = iEt/4.185s \text{ calories/inch of pen travel} \qquad (3.1)$$

where

i = current across the heater in amperes. This can be calculated by dividing the potential drop (in volts) across the standard resistor by 10.0.

E = potential drop across the heater in volts.

t = length of time current is flowing in seconds.

s = distance of pen travel in inches.

4.185 = joules per calorie.

The performance of the calorimeter was checked by Harris (57) by measurement of the well-studied heat of formation of water (54,56). Conditions were made as nearly like those in the nonaqueous titration as possible. A titration of 0.14452 molal HCl with 3.9937 molar NaOH, for example, gave a value of -13.46 kcal/mole at 25°C. This is in agreement with 1% of the calorimetrically determined value determined by Hale, et. al. (54).

The overall performance of the calorimeter was also checked by a measurement of the endothermic heat of mixing of water with 1-butanol.

A value of 432 cal $(\text{mole water})^{-1}$ $(\text{kg 1-butanol})^{-1}$ was obtained. This is in close agreement with the value of 432 ± 2 determined by Harris (57).

Preparation of Dry Solutions

In order to determine the constants (k_1, k_2, etc.) for the formation of the lowest aquocomplexes, it is necessary to start with a salt solution which is anhydrous. As perchlorate salts are hydrated in the solid state and are generally unstable to heating to the temperatures necessary to remove the hydrate water, it was necessary to dry the solutions after the hydrated salt had been dissolved in the solvent 1-butanol.

Arthur, Haynes, and Varga (4) have developed a very effective method for drying salt solutions employing molecular sieves and a modified soxhlet extractor. Harris (57) used this technique with the addition of an apparatus for refluxing under vacuum conditions. Solutions used in the present study were also dried by this method.

After preliminary distillation to remove the water-rich azeotrope, (boiling point = 96°C at 760 torr) (120) it was necessary to carry out the remainder of the reflux operation at reduced pressure because of the high boiling point of 1-butanol (117°C) at atmospheric pressure. With extremely dry solutions at this temperature there is danger that the perchlorate salts will be unstable in solution toward reduction by the solvent. Harris (57) refluxed solutions of cobalt (II) and nickel perchlorates at 35°C. and 15 torr and obtained solutions containing less than 10^{-3}% water by weight in four to six hours. Solutions used in this study required longer refluxing times at higher temperatures (less vacuum).

Solutions of calcium perchlorate in 1-butanol could be dried satisfactorily in 12 to 14 hours by refluxing at a temperature of 60°C. over type 4A molecular sieve.

In the case of copper(II) perchlorate in 1-butanol, prolonged refluxing (up to 50 hours) at temperatures up to 80°C. produced solutions no drier than 0.09% water by weight as determined by Karl Fischer titration. The copper(II) concentration in the solution was about 0.43 molal, giving a salt/water ratio of about ten to one. At temperatures much above 80°C the color of the solution darkened and took on a brownish hue. This was taken to be evidence of decomposition. Dried solutions had the characteristic blue-green color of the solvated copper(II) ion.

Zinc perchlorate in 1-butanol required approximately 30 hours of refluxing at 65°C. The solutions remained colorless throughout the drying process.

Manganese(II) perchlorate in 1-butanol required approximately 30 hours of refluxing at a temperature of 65°C. The dry solutions had the characteristic light pink color of the solvated manganese(II) ion.

Magnesium perchlorate in 1-butanol required approximately 30 hours of refluxing. The reflux was carried out at atmospheric pressure. The solution remained colorless throughout the drying process.

Strontium, barium, and lithium perchlorates in 1-butanol required approximately 20 hours of refluxing at atmospheric pressure. The solutions remained colorless throughout the drying process. The molal salt concentrations and final weight percent water of the stock solutions are listed in Table II.

TABLE II

CONCENTRATION AND WEIGHT PERCENT WATER IN
METAL PERCHLORATE STOCK SOLUTIONS

	Cu	Ca	Mn	Li	Mg	Sr	Ba	Zn
Molal salt con.	0.43	0.56	0.57	0.28	0.53	0.50	0.34	0.57
Weight percent water	.091	.004	.008	.003	.010	.015	.006	.018

Determination of Metal Concentrations

Strontium was determined with ethylenediaminetetraacetic acid (EDTA), disodium salt, via a displacement titration (9). Two milliliters of magnesium-EDTA solution was added to the solution to be titrated. The solution was buffered to pH 10 and titrated to an Eriochrome Black T end point.

Barium was determined by direct titration with EDTA in a solution of pH 12.8 using 3'-3" Bis N,N-bis(carboxymethyl) amino methyl thymolsulfonethalein pentasodium salt as the indicator. The color change was from blue to clear (78). Best results were obtained by overtitrating with EDTA, adding barium solution until the color just changed back to blue, and then proceeding to the end point with EDTA.

Manganese(II), magnesium, and zinc were determined directly as described by Flaschka (41). The solutions were titrated at pH 10 with EDTA using Eirochrome Black T as the indicator.

Copper(II) was determined with EDTA in a 50% water:ethanol solution. The solution was buffered to pH 5 and titrated with 1-(2-pyridylazo)-2-naphthol (PAN). The color change was from deep red-violet to canary yellow.

Lithium was determined indirectly by gravimetry by precipitating lithium perchlorate with tetraphenylarsonium chloride hydrochloride (79).

Calcium was determined at pH 12 with EDTA using Eirochrome Blue SE (Lamont Laboratories) as the indicator. This indicator gives a very sharp pink-to-blue end point. The pH 12 buffer was prepared from an aqueous solution of ethylamine by adding ammonium chloride to attain the desired pH.

Metal concentrations were first determined as moles/kg of solution and then converted to molar concentrations via density measurements. A linear relation was found between moles of salt per kg. of solution and the density of the solution for all salt solutions except copper(II) over the entire concentration range studied. Plots of concentration vs. density are shown in Figure 4.

Water Analysis

The water content of "dried" stock solutions was determined by Karl Fischer titration (40,95) employing polarized electrodes and a Backman Expanded Scale pH meter as a null-point indicator (84).

All the metal perchlorate solutions except copper(II) could be analyzed for water directly. After Karl Fischer reagent has undergone partial reaction with water, iodide ions are generated which will react with copper(II) in the manner shown in the following reaction.

$$2Cu^{++} + 4I^{-} = 2CuI + I_2$$

As the molecular iodine is one of the components of Karl Fischer reagent that reacts stoichiometrically with water, it is obviously essential that it participate in no other chemical reactions. The

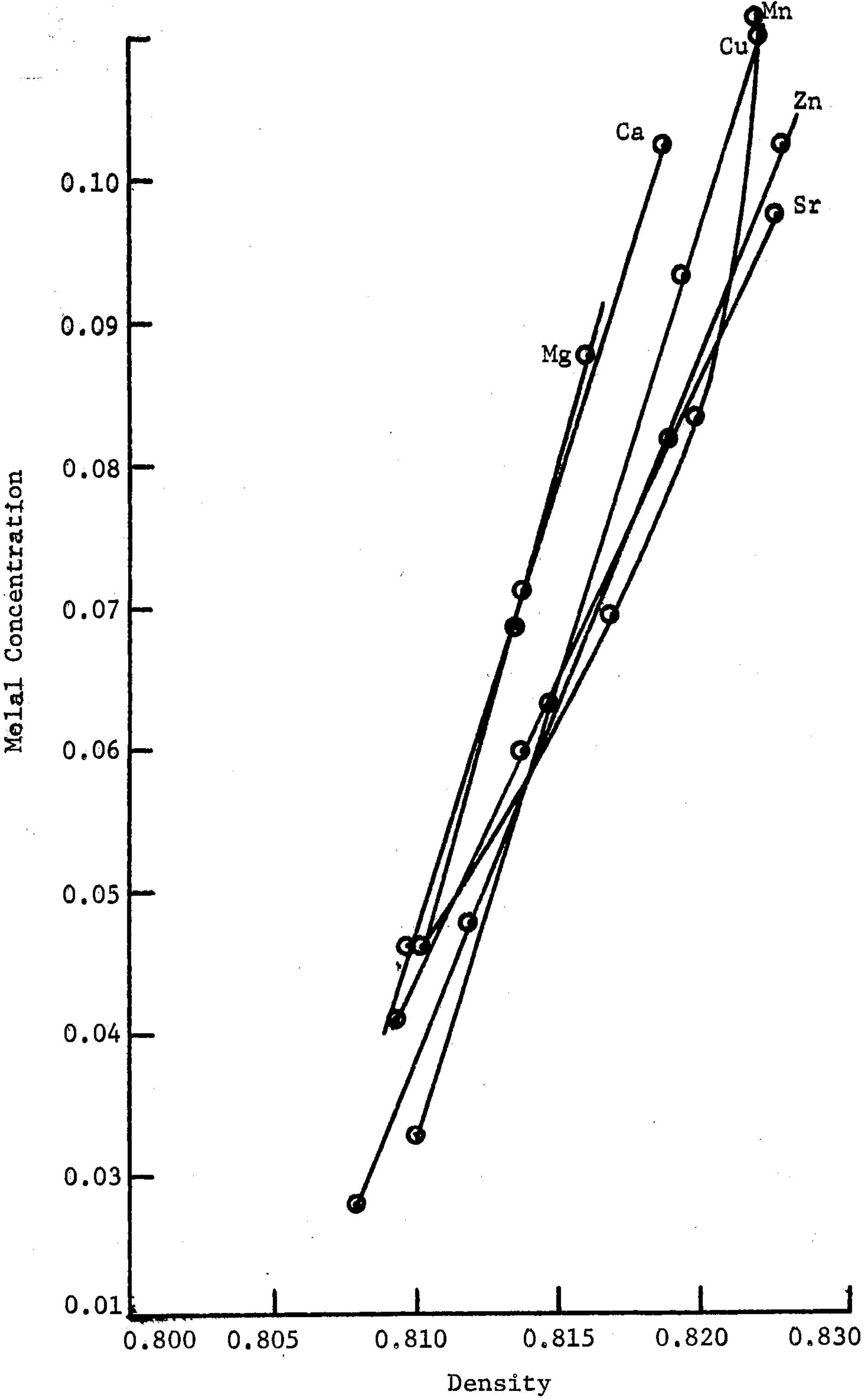


Figure 4. Molal Concentration vs. Density

interference by copper(II) can be avoided by preliminary reduction to the metal with oven-dried zinc powder, as described by Haynes (59). Copper metal is precipitated from solution and the resultant zinc perchlorate solution can then be drawn off and analyzed for water.

Thermometric Titration Procedure

At the start of a thermometric titration, the 2.5 ml microliter syringe was filled with titrant, the luer-lok stopcock was opened, and titrant was forced through the teflon needle until all bubbles were expelled. The stopcock was closed to prevent premature mixing of titrant and solution before the beginning of the run.

The dewar flask, which had been predried and stored in a vacuum dessicator between runs, was placed in the water jacket inside the calorimeter housing. Tank nitrogen predried by passing the gas through a three-foot long glass column filled with Linde 4A molecular sieve, was used to flush the calorimeter. Flushing was carried out for 15 to 20 minutes. The chamber was then sealed to exclude atmospheric water.

Approximately 35 cc of a perchlorate solution was next weighed on a Mettler balance in a 50 cc BD syringe. This solution was then injected into the calorimeter and the stirrer switched on. Thirty minutes to one hour was required for the calorimeter and solution to reach thermal equilibrium.

As the composition of the solution changes during the course of a thermometric titration, a series of heat capacity measurements must be made at various intervals during the titration. In making a heat capacity measurement, the recorder was started, and a temperature-time base line established. The timer was set for two minutes and the current switched on. The corresponding quantity of heat generated was about 0.8 calories. After two initial heat capacity measurements at "zero" water concentration, the titrant syringe stopcock was opened and the titration begun.

Titrant was delivered in increments ranging from 0.005 ml at the start of the titration to 0.02 ml near the end. Titrant was added incrementally until a concentration of about 1.0 molar was reached, varying somewhat depending upon the salt concentration. A typical enthalpogram (C_L vs. $\Delta\bar{H}$) is shown in Figure 1a.

The number of calories per increment of titrant was determined in the following manner. The time base lines were extrapolated as shown in Figure 5. A vertical line was drawn through point A, the mid-point of the slope. This gave the length of pen travel, s. The distance s, in inches, was then multiplied by the heat capacity (calories/inch) to give the number of calories generated.

The time required for a titrimetric run varied from four to twelve hours, depending on the amount of water added.

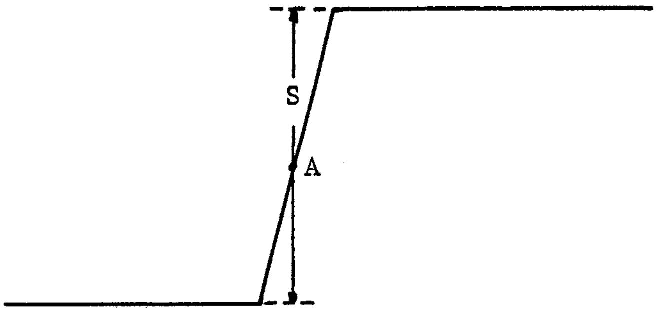


Figure 5. Temperature-Time Base Line

CHAPTER IV

EXPERIMENTAL PROCEDURE AND TREATMENT OF DATA

Titration Data

The heat liberated in the calorimeter had to be first apportioned to the various contributing sources (25,26,51). For the reaction of water with the butanol solvated metal ion in dilute solution the measured heat is the sum of two contributions. When the quantity of water added is small, only the heat of aquocomplex formation, $\underline{Q}_{rx}$, and the heat of mixing of water with 1-butanol, $\underline{Q}_{mix}$, contribute significantly to the heat measured in the calorimeter.

$$Q_{cal} = Q_{rx} + Q_{mix} \qquad (4.1)$$

Since $\underline{Q}_{cal}$ is the experimental heat measured in the thermometric titration of the metal perchlorate in 1-butanol with water, $\underline{Q}_{mix}$, the heat of mixing of water with 1-butanol must be determined before Q_{rx}, the heat of reaction of the ligand water with the metal salt can be found.

Harris (57) had earlier measured the heat of mixing of water with butanol and reported an average value of 432 cal (mole of water)$^{-1}$ (kg butanol)$^{-1}$. The determination was repeated and essentially the same value was obtained. The heat of mixing was found to be a very nearly linear function of the water concentration over the range covered by the thermometric titrations. Figure 6 is a plot of the integral heat of mixing vs the number of moles of water per kilogram of 1-butanol. Experimental data for the titration of water into 1-butanol is given in Table VI (Appendix A). The slope of the curve in Figure 6 also gives an average value of the partial molal enthalpy of mixing of water in 1-butanol of 0.432 kcal (mole of water)$^{-1}$ (kg 1-butanol)$^{-1}$ in the range 0.0 to 1.0 molal in water.

After determining the heat of mixing, salt solutions were titrated thermometrically to determine the heat of reaction per mole of salt per liter, $\Delta\bar{H}$. Titrations were carried out at four to five concentrations of each metal perchlorate, ranging from 0.01 to 0.10 molar. Replicate determinations were made at each salt concentration.

Values of $\Delta\bar{H}$ for all the metal perchlorates in 1-butanol except copper(II) could be calculated in a straightforward manner. In the case of copper(II) solutions it was necessary to extrapolate the first measurements back to zero water concentration since these solutions could not be prepared satisfactorily anhydrous. The extrapolation procedure is discussed in the next section.

Sample Calculations

The following is a sample calculation showing how $\Delta\bar{H}$ is obtained from the experimental data.

To 27.039 grams of copper(II) perchlorate in 1-butanol at a concentration of 0.0275 moles/kg of solution is added 0.0100 ml of water, producing a 1.83 inch deflection of the recorder pen. The heat capacity of the system is 0.247 calories/inch over the interval. The number of calories liberated over the increment is accordingly

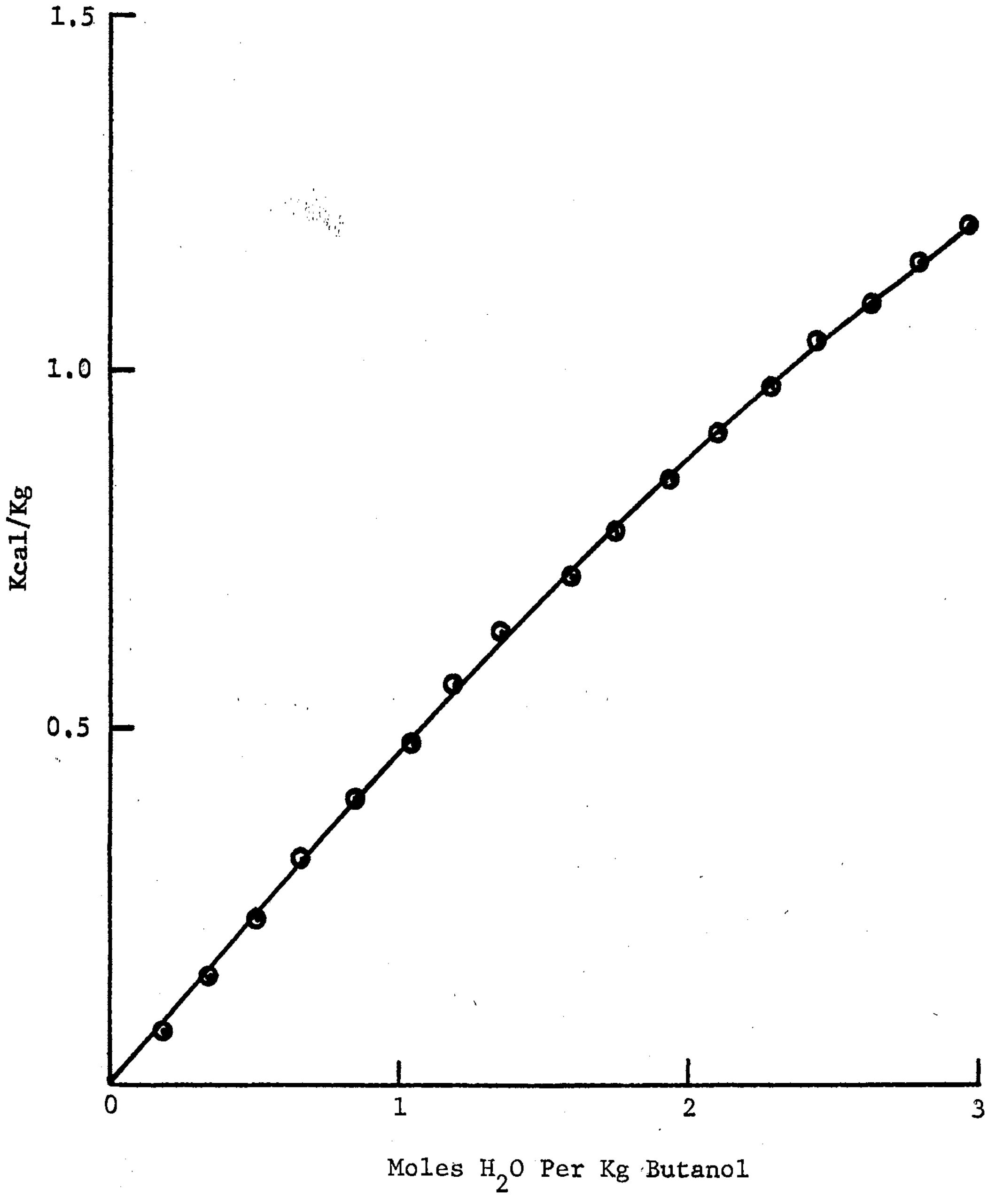


Figure 6. Heat of Mixing of Water Into 1-Butanol

$$\begin{aligned}\delta q_{cal} &= s\cdot C_p \\ &= (-1.83 \text{ in.})(0.247 \text{ cal./in.}) \qquad (4.2) \\ &= -0.452 \text{ cal.}\end{aligned}$$

The correction for the heat of mixing of water with the solvent 1-butanol is +432 cal (mole water)$^{-1}$ (kg 1-butanol)$^{-1}$. Since there is less than one mole of water added, the correction to the experimental heat must be adjusted accordingly. The number of moles of water added is

$$\text{moles water} = 0.0100 \text{ g.}/18.016 \text{ g./mole} = 0.000556 \text{ moles}$$

$$\delta q_{mix} = (0.432 \text{ cal/mole})(0.000556 \text{ mole}) = 0.240 \text{ cal}$$

The heat of reaction of water with copper(II) perchlorate in the interval is then

$$\begin{aligned}\delta q_{rx} &= \delta q_{cal} - \delta q_{mix} \qquad (4.3) \\ &= -0.452 \text{ cal} - (+0.240 \text{ cal}) \\ &= -0.692 \text{ cal}\end{aligned}$$

To obtain the heat of reaction $\Delta\bar{H}$, in terms of calories per mole of salt, one finds the number of moles of salt in the given volume of solution

$$\begin{aligned}\text{moles salt} &= (\text{moles salt/kg soln})(\text{kg soln}) \\ &= (0.0275 \text{ moles/kg})(0.027039 \text{ kg}) \\ &= 0.000753 \text{ moles salt}\end{aligned}$$

Finally, the heat of reaction is

$$Q_{rx} = \delta q_{rx}/\text{moles salt}$$

$$= -0.692 \text{ cal}/0.000753 \text{ moles salt}$$

$$= -919 \text{ cal/mole salt}$$

At each addition of titrant

$$\Delta\bar{H} = \Sigma Q_{rx} \tag{4.4}$$

where the sum is over all the increments of water.

This is the complete calculation for a solution which is initially "dry". Since the copper(II) solutions contained measurable water at the beginning of the titration, the titration data had to be extrapolated back to "zero water content" to correctly evaluate $\Delta\bar{H}$. This was done in the following manner. A plot of the analytical water concentration vs $\Delta\bar{H}_e$, the experimentally measured integral heat of reaction, was found to be quite linear at low water concentrations, as shown in Figure 7.

In this figure, point (2) represents the initial concentration of water corresponding to $\Delta\bar{H}_e = 0$. By obtaining the number of calories between points (2) and (3), one can, by simple proportionality, obtain the number of calories between points (1) and (2). The correction, $\Delta\bar{H}_c$, for the heat of reaction can then be added to $\Delta\bar{H}_e$. Thus,

$$\Delta\bar{H}_{rx} = \Delta\bar{H}_c + \Delta\bar{H}_e \tag{4.5}$$

Calculation of Average Ligand Number and Free Ligand Concentration

Once the experimental heats of reaction have been measured, values of the average ligand number, $\bar{n}$, and the free ligand concentration (L)

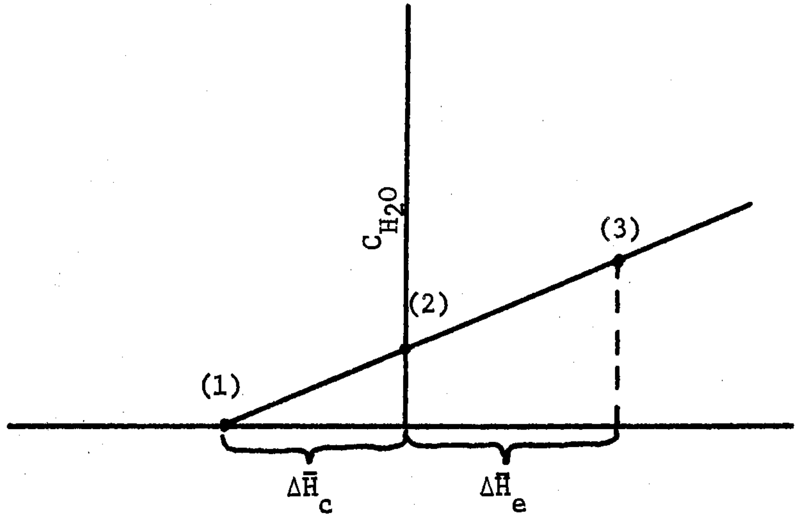


Figure 7. Extrapolation of Heat of Reaction to Zero Water Content

may be determined by employing Bjerrum's method of "corresponding solutions" (12). This was discussed at length in Chapter II. Values of the analytical water concentration C_L were found for each salt concentration at equal values of $\Delta\bar{H}$ from $\Delta\bar{H}$ vs C_L plots. If the solutions are "corresponding", straight lines should be obtained for plots of C_L vs C_M at given values of $\Delta\bar{H}$. By rearranging the defining equation for $\bar{n}$, one obtains the relation

$$C_L = \bar{n}C_M + (L) \qquad (4.6)$$

This has the form of a straight line equation with slope of $\bar{n}$ and intercept of (L). A least squares calculation was performed to obtain $\bar{n}$ and (L) at from 20 to 40 values of $\Delta\bar{H}$. An illustration of the graphical analysis was given in Figures 1a and 1b, with calculated values listed in Table VIII (Appendix C).

The $\bar{n}$,(L) values obtained from the corresponding solutions plots were tested for fit to the experimental data by the following equation

$$ERR = \sum_{1}^{N}[(C_{L_{calc}} - C_{L_{exp}})^2/N]^{1/2} \qquad (4.7)$$

The value of ERR was small for all pairs of $\bar{n}$,(L) values obtained.

After values of $\bar{n}$ and (L) have been determined, the formation function curve may be drawn by plotting $\bar{n}$ vs log (L) as shown in Figure 8.

A property of the formation function curve is that it should, in principle, show an inflection and asymptotically approach the maximum coordination number N.

The experimental $\bar{n}$ vs log (L) curves obtained by both Harris (57) and in the present work show no inflection up to the maximum value of $\bar{n}$

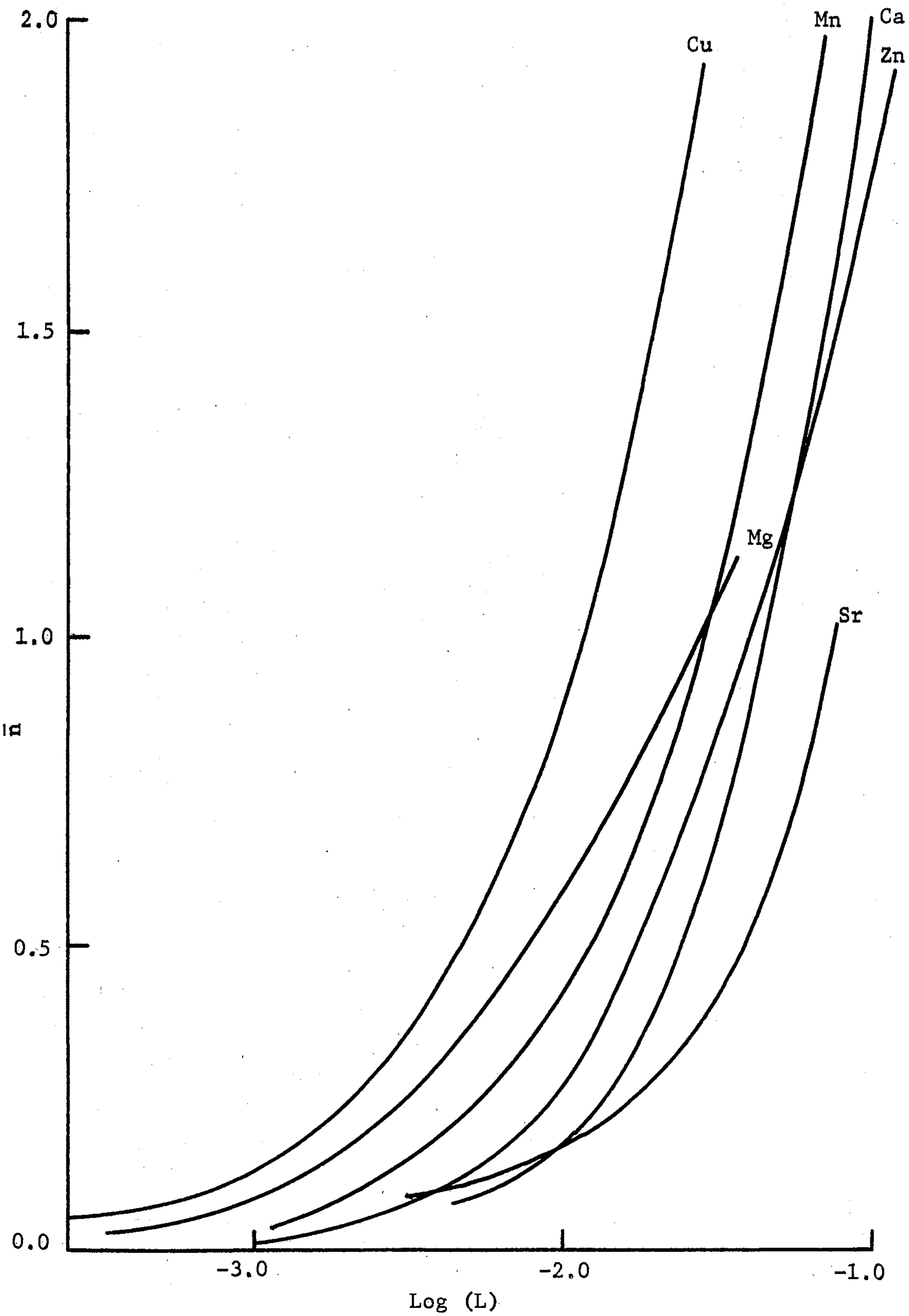


Figure 8. $\bar{n}$ vs Log (L)

obtainable from the experimental data. It was therefore necessary to assume a value for N in order to proceed with the calculation of the stepwise stability constants and other relevant thermodynamic parameters.

A value of six was assumed for all the metal ions studied. Justification for this is the fact that the normal coordination number observed for their aquocations in aqueous solution and in salt hydrates is six (108).

Calculation of Stability Constants

The calculation of stability constants for mononuclear complexes from $\bar{n}$,(L) data is accomplished by a least-squares iterative method (118) based on Bjerrum's equation (116)

$$\sum_{0}^{N} (\bar{n} - i)\beta_i(L)^i = 0 \qquad (4.8)$$

where $\beta_0 \equiv 1.0$.

By utilizing m sets of $\bar{n}$,(L) data and reduction to the N+1 normal equations, the β_i can be calculated by a straightforward least-squares procedure.

As all experimental data have some inherent, presumably random error, it is desirable to calculate the variance associated with each experimental measurement and to weight the measurement accordingly. It is assumed that both $\bar{n}$ and (L) have associated with them random error which can be expressed as

$$\sigma_{\bar{n}} = P\bar{n} \qquad (4.9)$$

$$\sigma_{(L)} = P(L) \qquad (4.10)$$

where P is an estimate of the upper bound of the average fractional error of the data set. An assumed value of P = 0.1 was used in all data treatment in this study. Because there are several numerical and graphical steps involved in the calculation of $\bar{n}$ and (L) from the raw data, it is impossible to closely estimate the error in any given pair of $\bar{n}$, (L) values. Since the experimental $\Delta\bar{H}$ values are reproducible within 1%, an average fractional error of 10% should be a reasonable upper bound for the error in a given pair of $\bar{n}$, (L) values.

The mathematical model for the system is Bjerrum's Equation (4.8) above. This has the general form

$$Y = f(\bar{n},(L)) \tag{4.11}$$

$$= \sum_{o}^{N} (\bar{n} - i)\beta_i (L)^i \tag{4.12}$$

Any variance in Y due to random error in $\bar{n}$ and (L) may be calculated according to error propagation theory (31) by the relation

$$\sigma_Y^{\,2} = [\frac{\partial Y}{\partial \bar{n}}]\,\sigma_{\bar{n}}^{\,2} + [\frac{\partial Y}{\partial (L)}]\,\sigma_L^{\,2} \tag{4.13}$$

Here $\sigma_Y^{\,2}$ is evaluated by taking the appropriate derivatives

$$\frac{\partial Y}{\partial \bar{n}} = \sum_{o}^{N} \beta_i (L)^i \tag{4.14}$$

$$\frac{\partial Y}{\partial (L)} = \sum_{1}^{N} i(\bar{n}-i)\,\beta_i (L)^{i-1} \tag{4.15}$$

Substituting Equations (4.14) and (4.15) into Equation (4.13), the working equation for error estimation is obtained

$$\sigma_{Y_k}^{\,2} = P^2\bar{n}_k^{\,2}\,\{\sum_{o}^{N} \beta_i (L)^i\}^2 + P^2\,\{\sum_{1}^{N} i(\bar{n}_k - i)\,\beta_i (L_k)^i\}^2 \tag{4.16}$$

The weight of each experimental measurement is given by

$$W_k = 1/\sigma_{Y_k} \tag{4.17}$$

The weighted least-squares method (122) requires that a set of constants be determined which will minimize the following relation

$$S_{min} = \sum_{j=1}^{M} W_j \{\sum_{o}^{N} (\bar{n}_j - i)\ \beta_i (L_j)^{-i} Y_j\}^2 \tag{4.18}$$

where, as stated previously, all $Y_j = 0$.

The normal equations which result from the minimization of S with respect to variation in the β_i are, in matrix notation (118)

$$\begin{bmatrix} \Sigma w_i x_i^o & \Sigma w_i x_i & \ldots & \Sigma w_i x_i^N \\ \vdots & & & \vdots \\ \Sigma w_i x_i^N & \Sigma w_i x_i^{N+1} & \ldots & \Sigma w_i x_i^{2N} \end{bmatrix} \begin{bmatrix} \beta_o \\ \beta_1 \\ \vdots \\ \beta_N \end{bmatrix} = \begin{bmatrix} \Sigma w_i y_i x_i^o \\ \Sigma w_i y_i x_i \\ \vdots \\ \Sigma w_i y_i x_i^N \end{bmatrix} \tag{4.19}$$

where $x_i = (\bar{n} - i)(L)^i$. The Gauss-Jordan method (91) was employed to solve for the (N + 1) dimensional column of beta values.

Since the weight parameter is a function of the unknown β_i, an approximate set of β's was calculated for all $W_k = 1$, and an iterative procedure was used to successively refine the estimate of W and the corresponding stability constants. Four iterations were sufficient to yield a consistent solution.

The computer program used for the calculation of stability constants from $\bar{n}$, (L) data (122) contained an option in which different models, corresponding to different numbers of complexes formed in solution, could be tested for fit to the experimental data. Models corresponding

TABLE III

THERMODYNAMIC CONSTANTS AND STANDARD DEVIATIONS CALCULATED BY LEAST SQUARES ADJUSTMENT

	n	β_n and Std. Dev.	SMIN/DF	h	ΔS	$(\Delta H_{exp} - \Delta H_{calc}) \times 100/\Delta H_{exp}$
Copper						
	1.	$(1.2 \pm 0.1) \times 10^2$	0.014 to $\bar{n} = 2.9$	1.9 ± 0.2	+3.3	1.57 to ΔH = 4.7 kcal.
	2.	$(3.9 \pm 0.9) \times 10^3$		5.4 ± 1.1	-1.8	
	3.	$(5.0 \pm 5.0) \times 10^4$		7.5 ± 3.4		
	4.	$(3.4 \pm 0.7) \times 10^6$				
Calcium						
	1.	$(1.7 \pm 0.1) \times 10^1$	0.09 to $\bar{n} = 2.5$	1.2 ± 0.2	+1.5	1.09 to ΔH = 3.1
	2.	$(2.1 \pm 0.5) \times 10^2$		2.4 ± 0.6	+2.4	
	3.	$(2.0 \pm 0.8) \times 10^3$		0.8 ± 0.8		
	4.	$(8.0 \pm 3.0) \times 10^3$				
Manganese						
	1.	$(4.8 \pm 0.1) \times 10^1$	0.06 to $\bar{n} = 3.0$	2.3 ± 0.1	-0.1	1.00 to ΔH = 4.0
	2.	$(7.0 \pm 1.0) \times 10^2$		2.6 ± 0.5	+4.3	
	3.	$(7.0 \pm 3.0) \times 10^3$		7.0 ± 2.0		
	4.	$(5.0 \pm 3.0) \times 10^4$		1.0 ± 3.0		
	6.	$(1.4 \pm 0.9) \times 10^6$		10. ± 6.0		
Cobalt						
	1.	$(5.0 \pm 0.2) \times 10^1$	0.26 to $\bar{n} = 4.1$	3.4 ± 0.1	-3.4	0.70 to ΔH = 4.8
	2.	$(1.5 \pm 0.2) \times 10^3$		3.3 ± 0.1		

TABLE III (Continued)

	n	β_n and Std. Dev.	SMIN/DF	h	ΔS	$(\Delta H_{exp} - \Delta H_{calc}) \times 100/\Delta H_{exp}$
Cobalt						
	3.	$(1.2 \pm 0.3) \times 10^4$		8.4 ± 0.3		
	4.	$(1.5 \pm 0.2) \times 10^7$		4.9 ± 0.1		
Nickel						
	1.	$(6.4 \pm 0.1) \times 10^1$	0.013 to $\bar{n} = 4.0$	3.2 ± 0.1	-2.3	1.23 to ΔH = 5.1
	2.	$(1.4 \pm 0.1) \times 10^3$		5.1 ± 0.2	-3.3	
	3.	$(4.0 \pm 0.2) \times 10^4$		4.7 ± 0.1		
	4.	$(2.4 \pm 0.1) \times 10^7$		6.4 ± 0.2		
Zinc						
	1.	$(5.2 \pm 0.1) \times 10^1$	0.30 to $\bar{n} = 2.2$	5.0 ± 0.1	-11.	0.90 to ΔH = 4.3
	2.	$(7.1 \pm 0.4) \times 10^2$		3.0 ± 0.1	+3.0	
	3.	$(5.7 \pm 0.3) \times 10^3$		8.3 ± 0.1		
Strontium						
	1.	$(1.7 \pm 0.2) \times 10^1$	1.83 to $\bar{n} = 1.1$	0.6 ± 0.2	+3.6	7.89 to ΔH = 1.1
	2.	$(1.2 \pm 0.3) \times 10^2$		2.1 ± 0.3	+2.8	
Magnesium						
	1.	$(9.4 \pm 0.1) \times 10^1$	0.083 to $\bar{n} = 1.1$	3.40 ± 0.01	-2.5	2.37 to ΔH = 3.6
	2.	$(1.3 \pm 0.5) \times 10^3$		5.80 ± 0.08	-5.2	

to N = 1 through N = 6 were tested for fit. A model was rejected if any of the constants were negative, or, if the standard deviation of any of the constants was larger than the constant itself.

The standard deviation of each constant is calculated by Equation (4.20)

$$\sigma_{\beta_i} = \left[X_{ii}^{-1} \frac{S_{min}}{I-1}\right]^{\frac{1}{2}} \qquad (4.20)$$

where X_{ii}^{-1} is the ith diagonal element of the inverse of the matrix of the coefficients of the normal equations. The quantity I - N is the number of degrees of freedom of the system (35), where I corresponds to the number of pairs of $\bar{n}$,(L) values used in the calculation and N is, of course, the number of stability constants. The quantity S_{min} is defined by Equation (4.18).

The best values of the stability constants, their standard deviation, and the associated enthalpies and entropies of reaction are listed in Table VI. Harris's (57) data on cobalt(II) and nickel are included for comparison.

None of the systems fit the model for six stability constants. This is perhaps due to the fact that the experimental value of $\bar{n}$ does not become much larger than four in the range of measurements for any of the systems studied.

Once the stepwise stability constants have been calculated, the stepwise enthalpies of reaction, h_i, can be evaluated as a function of $\Delta\bar{H}$, the β_i, and (L). Writing $\Delta\bar{H}$ as a linear function of the h's one has

$$\Delta\bar{H} = \sum_{1}^{N} h_i\alpha_i \qquad (4.21)$$

where

h_i = enthalpy change associated with the reaction

$$M + iL \rightarrow ML_i$$

$\alpha_i = \dfrac{\beta_i(L)^i}{\sum_o^N \beta_i(L)^i}$ = concentration fraction of M complexed as ML_i

The h_i can be calculated using the same linear least-squares procedure and weighting procedure used for the stability constants.

Stepwise entropies can now be calculated from the following thermodynamic relation

$$\Delta S_i = \frac{h_i}{T} - R \ln \beta_i \qquad (4.22)$$

For comparison, a second calculational method (33) was employed for those systems for which the best fit was obtained with N=2. Two systems, magnesium and strontium, satisfied this criterion best.

The method, called Variable Metric Minimization (VMM) does not appear to be capable of convergence if N is greater than two. This method utilizes the experimental enthalpy of reaction in the following equation:

$$Q_{rx} = V\sum_{i}^{N} h_i[ML_i] \qquad (4.23)$$

where

V = volume of solution

h_i = enthalpy for the reaction $M + iL \rightarrow ML_i$

Q_{rx} = heat of reaction in calories

ML_i = molar concentration of ith complex

In the calculation, initial values of the β_i are guessed and then used to calculate the free ligand concentration at each experimental value of Q_{rx} based upon Newton's iterative method (86). The stability constants and the free ligand concentration are next used to calculate α_o and thus obtain the free metal concentration. With a knowledge of the β's, (L), and α_o, the concentration of each complex can then be calculated. These quantities are used in turn in Equation (4.23) to calculate the h_i. The experimental Q_{rx} is finally compared with Q_{rx} calculated from Equation (4.23) using the calculated h_i. If the comparison is not satisfactory, each stability constant is incremented randomly in turn and the whole process repeated. As this method involves semi-random searching for minima, the number of minima must necessarily be small if the method is to be useful.

The principal advantage of the Variable Metric Minimization method is that the stability constants and enthalpies of reaction are obtained simultaneously and directly from one set of experimental data without intermediate graphical treatment. One disadvantage of this method is that it appears to be restricted to systems forming no more than two complexes. Another is that the corresponding solutions check on the validity of the assumptions regarding the nature of the complexes is given up.

Values of the stability constants and enthalpies for magnesium and strontium calculated by the VMM method are listed in Table IV.

Values of β_2 obtained by the VMM procedure are an order of magnitude smaller than those obtained by the least squares procedure. The VMM calculated stability constants appear to be better than the least-squares

TABLE IV

THERMODYNAMIC CONSTANTS CALCULATED BY VMM METHOD

	β_1	β_2	ΔH_1	ΔH_2	ΔS_1	ΔS_2
Magnesium	7.0×10^1	9.3×10^2	3.6×10^3	5.8×10^3	-3.3	-8.7
Strontium	1.3×10^1	1.2×10^1	9.6×10^2	6.6×10^3	-12	-17

calculated constants in that they lead to calculated values of $\Delta\bar{H}$ which are more nearly consistent with the experimental values over the entire range of data used for the calculation of stability constants.

Conductivity Studies

One of the assumptions made by Harris and Moore (58) in applying the theory of corresponding solutions to the systems studied is that the degree of ion-association does not change significantly over the range of ligand concentrations studied. It is further assumed that in the anhydrous solutions the salts are essentially undissociated, existing as associated ions of composition $M(ROH)_N(ClO_4)_2$.

These assumptions were tested by measuring the conductivity of solutions of each metal perchlorate as a function of concentration of both salt and water.

A Leeds and Northrup precision Jones-type conductivity bridge was used in conjunction with a dilution cell at a frequency of 1000 Hz. The measurements were performed by adding water from a micrometer syringe to 40 gram samples of the solutions in the dilution cell. The range of water concentrations studied was from zero to approximately four molar. The results are plotted as equivalent conductance vs weight percent water in Figure 9.

The weight percent of water corresponding to the maximum value used in calculating thermodynamic constants is indicated by a dashed line in each figure.

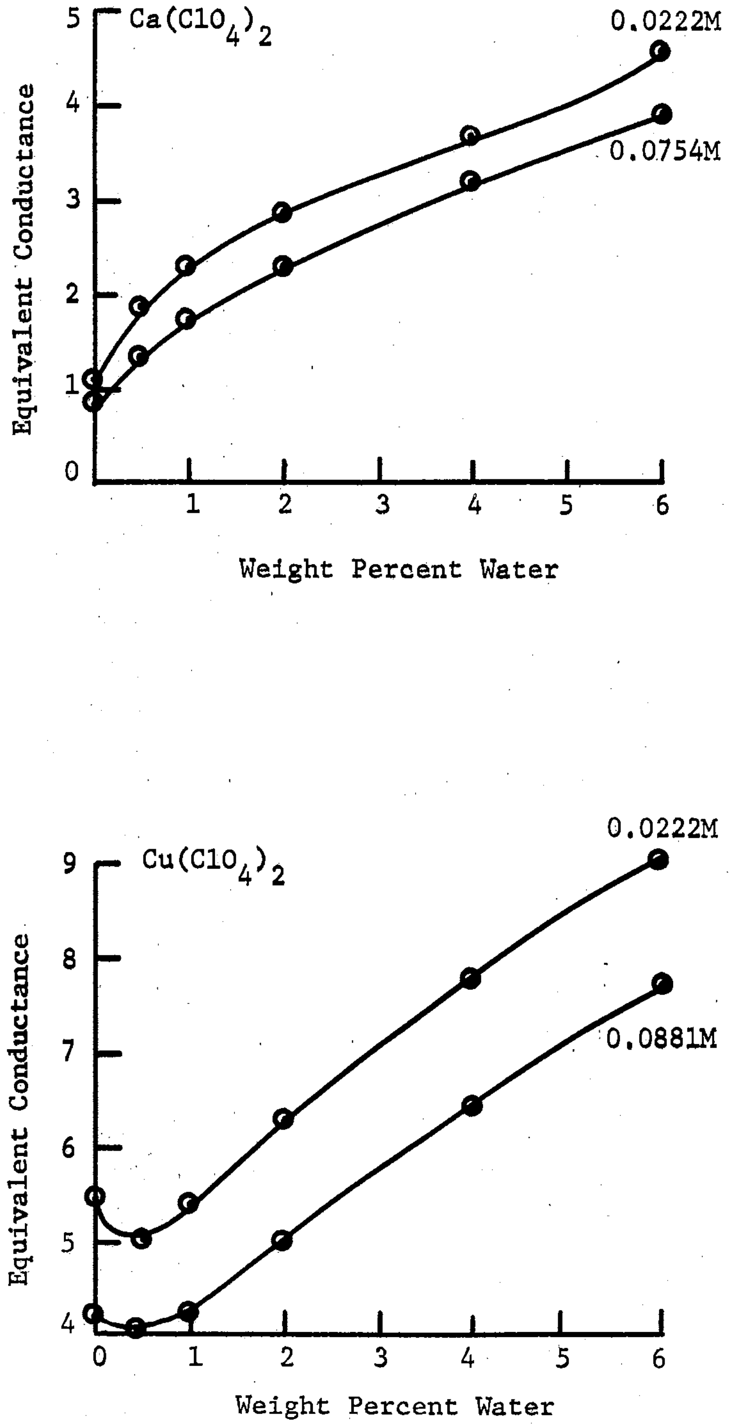
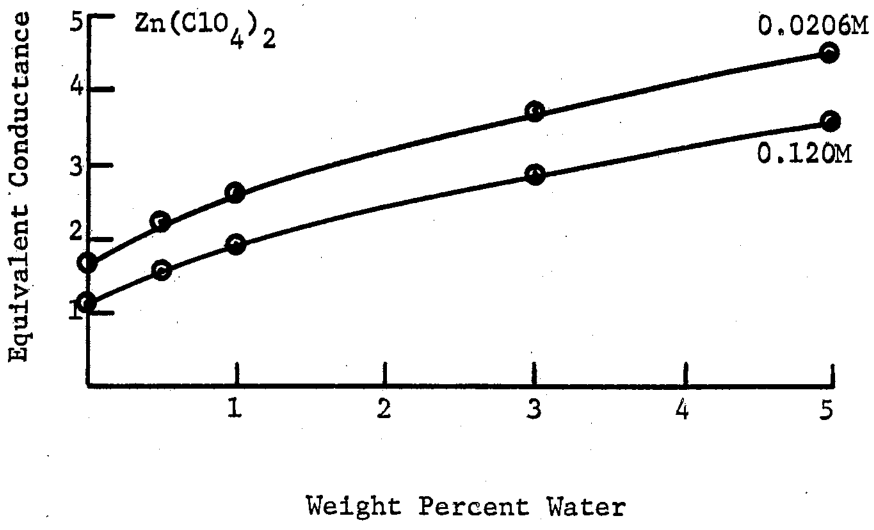


Figure 9. Equivalent Conductance of Metal Perchlorate in 1-Butanol Solutions as a Function of Added Water



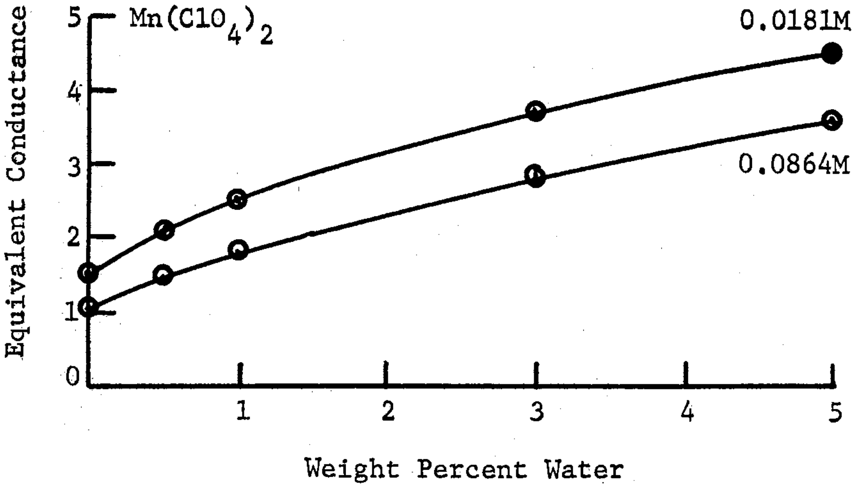
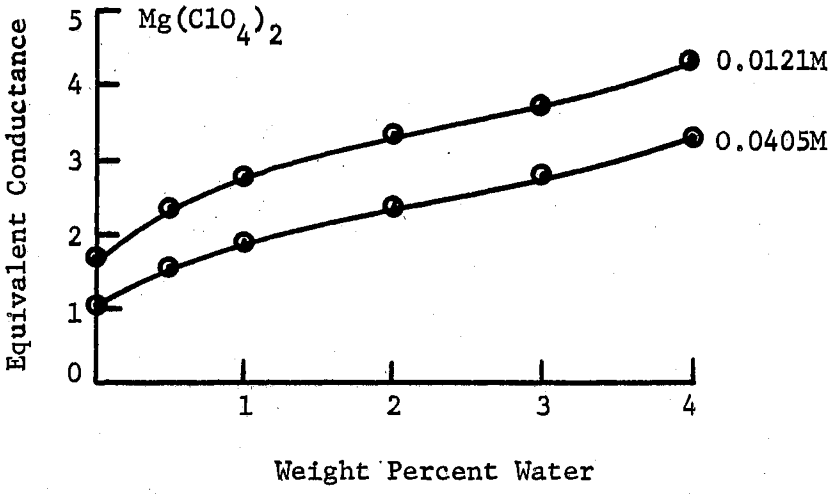


Figure 9 (Continued)



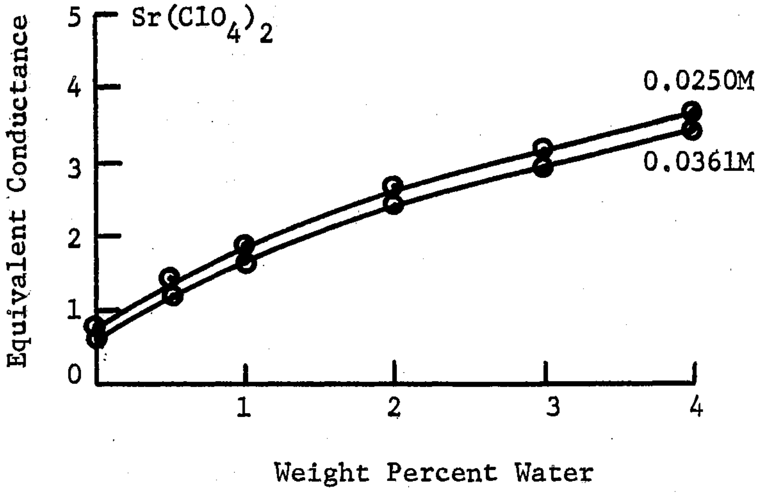


Figure 9 (Continued)

CHAPTER V

DISCUSSION OF RESULTS

Data Interpretation

The results from this study, like those of most investigations of reactions in solution, are not subject to unambiguous interpretation. Thus, it has been assumed throughout that the measurements have related to displacement reactions in which only ligand exchange of water for coordinated butanol occurs. For such reactions the maximum coordination number for the fully aquated salts would be expected to be equal to or larger than the value when butanol is the ligand since water is a smaller molecule and should be favored stereochemically.

In the absence of an experimental value, a maximum coordination number of six has been assumed, based in part upon the fact that this value represents the normal coordination number for water in the solid perchlorate hydrates of each of the salts studied (108). In these the water molecules form octahedrally disposed clusters about the metal ions. Although there seems to be some justification for assuming that similar octahedrally aquated complexes would be formed in butanol solvent by reaction with water (50), nothing is known about the structure of the butanol coordinated molecules before reaction nor about any of the butanol coordinated molecules before reaction nor about any of the intermediate aquocomplexes. For example, if the salts are initially inner sphere perchlorate complexes the reaction will certainly involve displacement of perchlorate as well as butanol. Further complications arise in the interpretation of results due to the possibility of forming cis and trans isomers of the complexes as well as other geometrically distinguishable forms of the intermediates. In addition to the nine possible aquocomplexes with water and butanol as the only ligands, there are eleven with one monodentate perchlorate, fourteen with two monodentate perchlorates, six with one bidentate perchlorate, and four with two bidentate perchlorates (not including optical isomers).

The consequences of mixed ligand intermediates have been considered by Harris and Moore (58) who point out that it is only in the limiting case of complete association or complete dissociation that the correspoding solutions treatment can be applied to extract information about the formation constants of the squocomplexes. This point was discussed in detail in Chapter II.

If one assumes no inner-sphere perchlorate ligands, the effect of the existence of isomers upon the values of the formation constants β_1, β_2, ... β_N computed from Bjerrum's formation function curve is easily shown to be $\beta_n = \beta_n' + \beta_n'' + \ldots$, where β_n is the value reported in Table VI, and β_n', β_n'', etc. are the formation constants of the individual isomers.

Similarly, the values of the enthalpy of formation calculated and reported are related to the enthalpies of formation of the isomers of ML_n through the relation $\alpha_n h_n = \alpha_n' h_n' + \alpha_n'' h_n'' + \ldots$. For a completely dissociated complex at large dilution one would expect that $h_n = h_n' = h_n'' = \ldots$ but the α_n's and the β_n's would be related to the number of ways in which a cis or a trans isomer of ML_n can be formed from ML_{n-1} through the statistical contribution to the entropy. For a completely associated complex, even though outer-sphere perchlorate, the coordination positions in "octahedral" geometry are not all equivalent and the M-L-X (X = perchlorate) positions are energetically distinct from normal M-L positions. The symmetry of the electric field at the metal is thus lowered to tetragonal or less.

A question of fundamental importance is that of the reality of complexation equilibria when the complexes detected in solution by a given method are "weak". Only methods which directly measure a property of a particular complex can be said to establish the existence of that complex. Thus, although the molar enthalpy of formation is an intensive property of characteristic magnitude for each complex, it lacks the "fingerprint" quality of a new Raman line or U.V. absorption band. However, since the heat of solution of water in butanol is independent of water concentration in the range studied, the difference between the heats of solution with and without salt present should be a valid measure of the degree of complexing by water in the system. A necessary condition for assuming the existence of complexes formed by reaction with water is then conformity of the experimental data with the requirement that the analytical concentration of metal salt C_M and water C_L corresponding to the same values of the heat of reaction per mole of salt always be linearly related, as expressed by equation (5.1)

$$C_L = \bar{n}\, C_M + (L) \tag{5.1}$$

This requirement, which is the basis for Bjerrum's <u>Method of Corresponding Solutions</u> (12), is based upon stoichiometric concentrations rather than activities but does presume that the intensive factors (enthalpies of formation in this case) do not vary with composition of the medium.

$\bar{n}$, log(L) Curves

Agreement of the experimental data with the predictions of equation (5.1) is very satisfactory at all metal concentrations studied and up to water concentrations below about 0.5 molar. For water concentrations smaller than about 0.5 molar, plots of the slope of the corresponding solutions lines against the logarithm of the intercept ($\bar{n}$ vs. log (L)) have the shape characteristic of "formation curves" in complex equilibria. With further increase in water concentration above this value, however, the curves continue to rise and $\bar{n}$ fails to approach the expected limiting value corresponding to the maximum coordination number. Plots of $\bar{n}$ vs. log (L) are shown in Figure 8.

Behavior at High Water Concentration

The failure of the $\bar{n}$ vs. log (L) curves to approach a maximum value of $\bar{n}$ is due to an unresolved heat effect at high (above two molar) water concentration.

It was expected that as the water/salt ratio became large, the heat of reaction would become insignificantly small and the measured heat would approach the endothermic heat of mixing of water with 1-butanol. This did not prove to be the case. Figure 10 shows the shape of a typical thermometric titration curve in which the titration is carried out to high water concentration. The unexpected heat effect at high water concentration was exhibited by all of the metal salts over the complete range of metal concentrations covered in this study.

The reaction with water is seen to be initially strongly exothermic because of the heat of aquocomplex formation. The reaction becomes predictably less exothermic in the range of one to two molar in water,

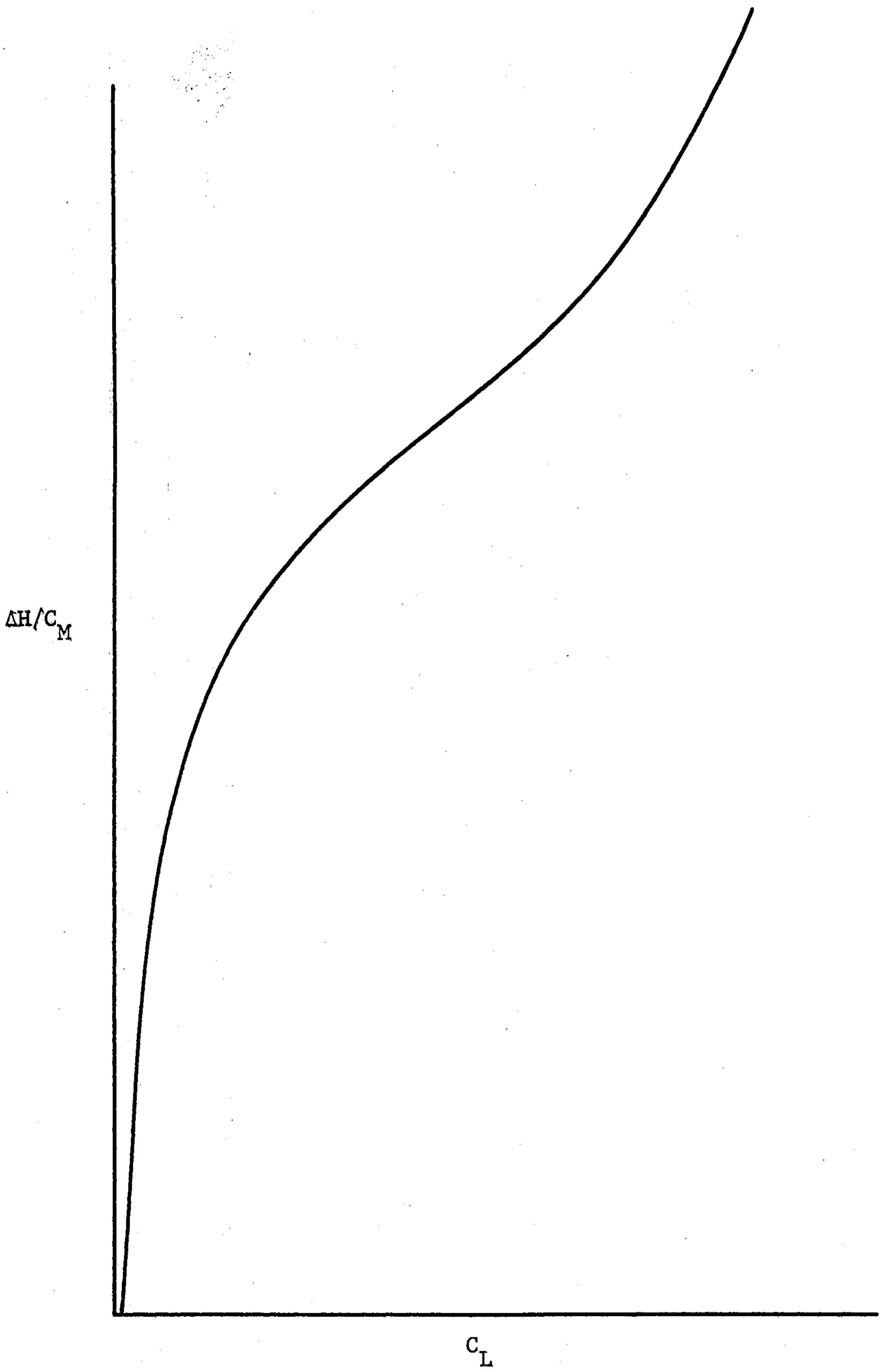


Figure 10. Enthalpy Titration Curve to High Water Concentration

as aquocomplexation approaches completion, and then (unexpectedly) becomes increasingly exothermic at water concentrations greater than about two molar. It would appear that another exothermic process starts (or becomes more predominant) at high water concentrations. This would, as mentioned earlier, account for the observation that the $\bar{n}$ vs. log (L) curves do not asymptotically approach a maximum value, corresponding to a maximum coordination number.

Althoug the C_L,C_M data show excellent linearity up to free water concentrations of about 0.2 moles/liter (varying somewhat, from metal to metal), only data for concentrations less than this value (again, the maximum value depending upon the metal) were used for the evaluation of the stability constants. In this way any contributions from the process responsible for the divergence of the titration curves at high water concentration would be minimized. Experimental data and calculated $\Delta\bar{H}$ values for thermometric titrations to high water content are listed in Table IX (Appendix D).

Preferential Solvation

A possible explanation of the exothermic heat effect at high water concentration is that it represents the heat of preferential reordering of the solvent envelope about the metal ion. As water is apparently preferred as a ligand over 1-butanol, there should be a gradual replacement of 1-butanol by water in the outer solvation spheres of the metal ion as water is added to the solution.

The preferential solvation shown by electrolytes in mixed solvents is a direct consequence of the specific interaction between an ion and one of the components of the mixed solvent. Preferential solvation refers to the change in the composition of the mixed solvent in the vicinity of the ion. This has been defined by Padova (102) as

$$(n_1/n_2)/(n_1^o/n_2^o) = 10^\gamma \qquad (5.2)$$

where

n_1/n_2 = mole ratio of the two solvent components in the vicinity of the ion.

n_1^o/n_2^o = mole ratio in the bulk solvent mixture.

The exponent γ is called the "index of preferential solvation". It is obvious that for $\gamma>0$, the ion is selectively solvated by component 1: for $\gamma<0$, the ion is selectively solvated by component 2: and for $\gamma = 0$ there is no preferential solvation.

Based upon a thermodynamic treatment of a mixed fluid in an electrostatic field, Padova (102) derived the following thermodynamic expression for the case of organic solvents containing a large percentage of water.

$$\gamma = -(\Delta\bar{G}_1 + \Delta\bar{G}_2)/2.3RT \qquad (5.3)$$

where

$\Delta\bar{G}_i$ = partial molar free energy of the ion in component i of the mixture at infinite dilution.

It follows that the preferential solvation depends only upon the difference between the partial molar free energy of the electrolyte in each component of the solvent mixture.

If water is taken as component one and 1-butanol as component two, γ will be positive for metal ions preferentially solvated by water.

Using data gathered from the literature, Padova (102) calculated γ for som 1:1 salts in the mixed solvent system water:1-butanol. Values ranged from 1.1 for lithium bromide to 5.63 for rubidium chloride.

Insufficient data exists to calculate γ for the systems included in this study, but it would be expected from the magnitude of the stability constants that γ would be large and positive in all cases.

As mentioned earlier, only data chosen from the lower end of titration curves were used in the calculation of stability constants. Unfortunately, this restricted the range of values of $\bar{n}$ which could be used in evaluating the stability constants and consequently limited the number of stability constants that could be reliably calculated.

Truncation Errors

Calculation of fewer stability constants than the (assumed) maximum coordination number dictates is equivalent to truncation of some of the latter terms of the linear homogeneous equation constituting the Bjerrum formation function

$$\sum_{0}^{N} (\bar{n} - i)\beta_i(L)^i = 0 \tag{5.4}$$

If J stability constants are calcualted, where J $\leq$ N, the truncation error will be given by R, as defined by equation (5.5)

$$\begin{aligned} R &= \sum_{1}^{N} (\bar{n} - i)\beta_i(L)^i - \sum_{1}^{J} (n - i)\beta_i(L)^i \\ &= \sum_{J+1}^{N} (\bar{n} - i)\beta_i(L)^i \end{aligned} \tag{5.5}$$

Obviously, one wishes to minimize R. It is evident upon inspection of equation (5.5) that R will be small for small values of (L). The maximum value of (L) cannot be restricted too severely, however, as this also restricts the value of $\bar{n}$, which, as pointed out above, limits the number of stability constants that can be reliably calculated.

It is usually assumed, based upon chemical experience, that successive or stepwise formation constants, k_n, become smaller as n increases (12).

Subject to this restriction, there will always be a range of values of (L) where truncation of higher order terms in (L) is justified. If, in such a case, retention of only j terms is necessary, then the "true" formation curve over this range can be written as

$$\bar{n} = \sum_1^j n\beta_n(L)^n/(1+\sum_1^j \beta_n(L)^n) \qquad (5.6)$$

and a fit of a Bjerrum function containing j parameters to good experimental data by least squares adjustment ought to optimize these parameters, i.e., if the β_n's are the "true" parameters and the β_n^*'s are those found by least squares adjustment, β_1^* should correspond closely to β_1, β_2^* to β_2, etc. This is illustrated in Figure 11.

In the case where the function being fit to the data has more parameters than are necessary (β_n^*, $n \geq j$), the higher order terms $\beta_n^*(L)^n$ should make minor contributions, and the β_n^*'s where $n \leq j$, should still be valid. The range of validity might thus be defined by the condition that the contribution of the terms in β_{j+1}^* satisifes the relation

$$[(j+1)\beta_{j+1}^*(L)^{j+1}]/[\bar{n}(1+\sum_1^{j+1} \beta_n(L)^n)] < f \qquad (5.7)$$

where f is an arbitrary number of the order of 5% or less. This follows from the definition of $\bar{n}$ in equation (2.14).

As mentioned previously, no "fingerprint type" method is applicable to determine the number or type of aquocomplexes in solution for a given analytical lingand concentration, C_L. Therefore, due to a lack of sufficient information, the complexes were assumed to be mononuclear and formed by the stepwise replacement of solvent by ligand water. Also,

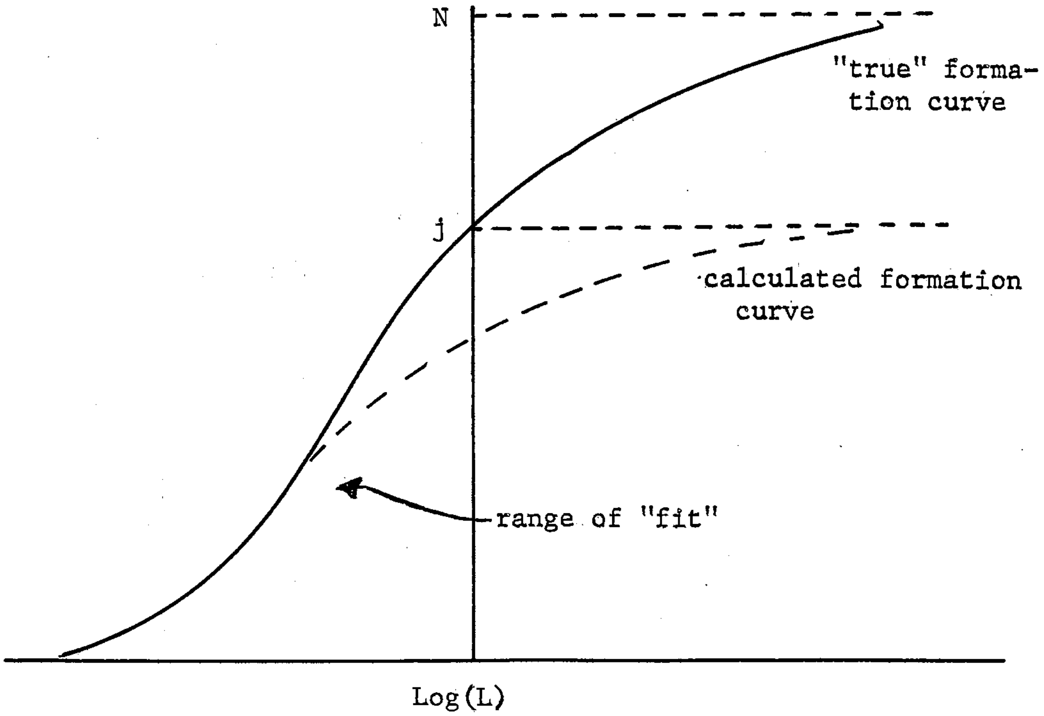


Figure 11. Range of "fit" of the Calculated Stability Constants to the Experimental Data

for a lack of a better criterion, the number of complex species to be considered in the calculations was taken to be equal to that number of β_n values which gave the best fit to the experimental data, i.e., gave the lowest value of S_{min} as defined by equation (4.18).

Conductivity Measurements

As was described in Chapter IV, conductivity measurements were made on all metal perchlorate solutions in 1-butanol in order to test certain of the basic assumptions made in applying the theory of corresponding solutions to the treatment of the experiment data. These assumptions were:

1. In the anhydrous solutions, the salts are essentially undissociated, existing as ion-aggregates of the type $M(ROH)_N(ClO_4)_2$.
2. The degree of ion-association does not change significantly over the water concentration range studied.
3. The substitution of water for coordinated 1-butanol is the reaction occurring exclusively upon the addition of water.

Support for assumption (1) was gained by the observation that the equivalent conductances of the anhydrous solutions were in all cases quite small, being of the order of 1-2 mho cm^2 $equiv.^{-1}$ over the metal concentration range 0.02 to 0.10 molar. These values are very similar to those found by Harris and Moore (58) for cobalt(II) and nickel perchlorates in 1-butanol.

Support for assumption (2) was gained by the observation that the equivalent conductances of all the metals show little change (less than one mho cm^2 $equiv.^{-1}$ in most cases) over the range of water concentration considered in the evaluation of the formation constants. Conductivity studies by Cheung (24) and Rands (112) indicate that transition metal perchlorates in 1-butanol remain largely associated even at much higher water concentrations (~50 mole percent) than those that were covered in the present study. The conductivity-concentration curves at fixed water concentration resemble those of weak electrolytes in water. Literature data (7) further show that the dielectric constant of butanol-rich water:butanol mixtures changes very little over the entire miscible range. Brown (19) has estimated the dielectric constant of the water:butanol mixtures, varying from zero to 0.25 mole fraction in water, to be approximately 18 over this range with an estimated error of estimate of no more than five percent. Graphical extrapolation of the data of Åkerlof (1) (Figure 12) on the dielectric constants of aqueous mixtures of methyl, ethyl, and n-proply alcohols, gives a value of ~18 for a 90%/10% w/w mixture of 1-butanol and water at 20°C. This would account in part for the failure of the equivalent conductance to increase very rapidly with water concentration in this range of water mole fractions.

Assumption (3) is supported by spectral studies. The IR spectrum of the perchlorate ion in anhydrous solution indicates T_{4d} symmetry. Lower symmetry such as C_{2v} or C_{3v} would be expected if the perchlorate anions were bonded as bidentate or monodentate ligands, respectively. A study of concentrated (0.5M) solutions failed to show any splitting of the strong perchlorate band at 1100 cm^{-1} (121). However, the limiting solubility in anhydrous 1-butanol for most of the salts studied is about 0.5 molar and if there were inner sphere coordination by perchlorate it might not be detectable at the salt concentrations available for study.

It is of some interest to compare the equivalent conductances of the metal perchlorates studied in 1-butanol with that of tetra n-butyl

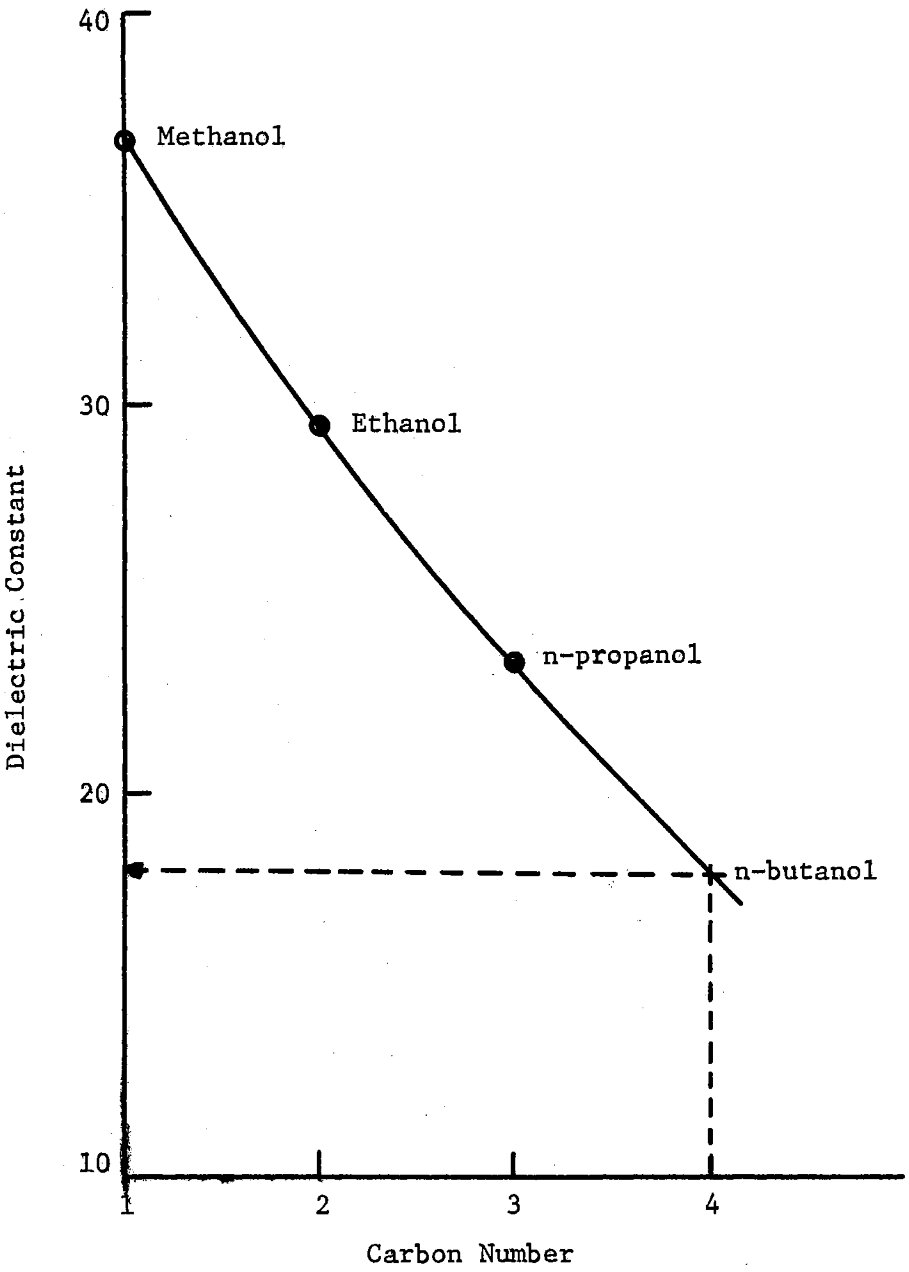


Figure 12. Extrapolated Dielectric Constant of 90/100 Weight Percent Butanol: Water Mixture

ammonium perchlorate (TNBAP) in 1-butanol (99). TNBAP would be expected to be more highly ionized in 1-butanol than divalent metal perchlorates because of the lower charge density of the large monovalent cation and thus, perhaps, be representative of the state of the divalent metal perchlorates in more dilute solution. Figure 13 shows plots of equivalent conductance vs. weight percent water for two concentrations of TNBAP in the range of metal concentrations covered in this study. It may be noted that the equivalent conductance for both concentrations is initially small and does not change greatly in the range of zero to one percent water. This would indicate that the degree of ionization for this salt changes relatively little throughout the range of added water covered by the measurements.

Specific Conductance of the Solvent

An important consideration in conductance measurements in solution is the specific conductance of the solvent medium. A plot of specific conductance vs. weight percent water is shown in Figure 14. The conductance of the solvent is found to be, at most, about one to two percent of that of the solutions. After correction for solvent conductance, the equivalent conductance of the salt solutions is in all cases only about two percent of the limiting conductance estimated from Walden's viscosity rule.

Results of conductivity and spectral studies thus lead to the conclusion that in anhydrous butanol solutions the metal ion coordination sites are initially occupied by butanol molecules with the perchlorate anions associated in at least the second coordination sphere. Furthermore, the observation that the conductivity changes only by a small

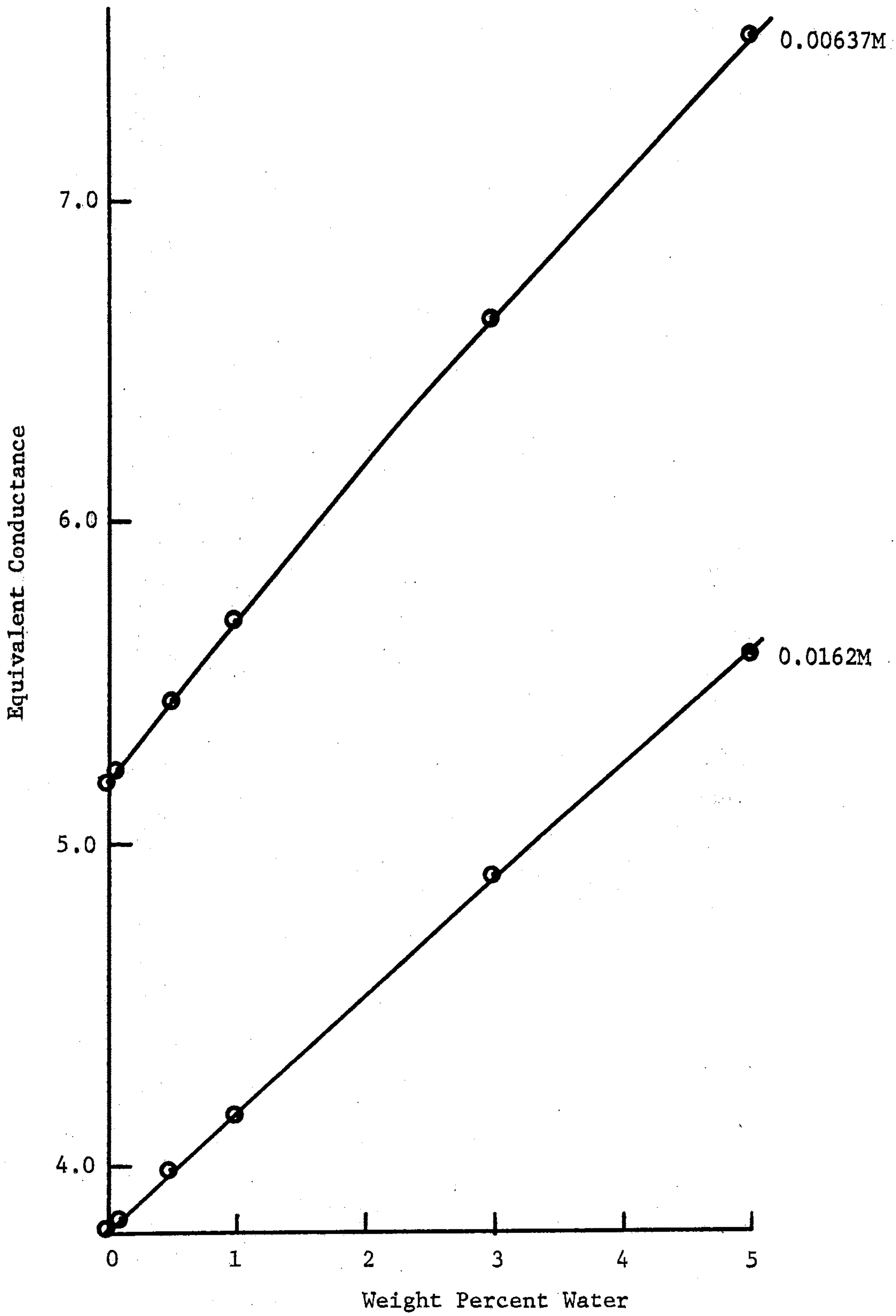


Figure 13. Equivalent Conductance of TNBAP in 1-Butanol as a Function of Added Water

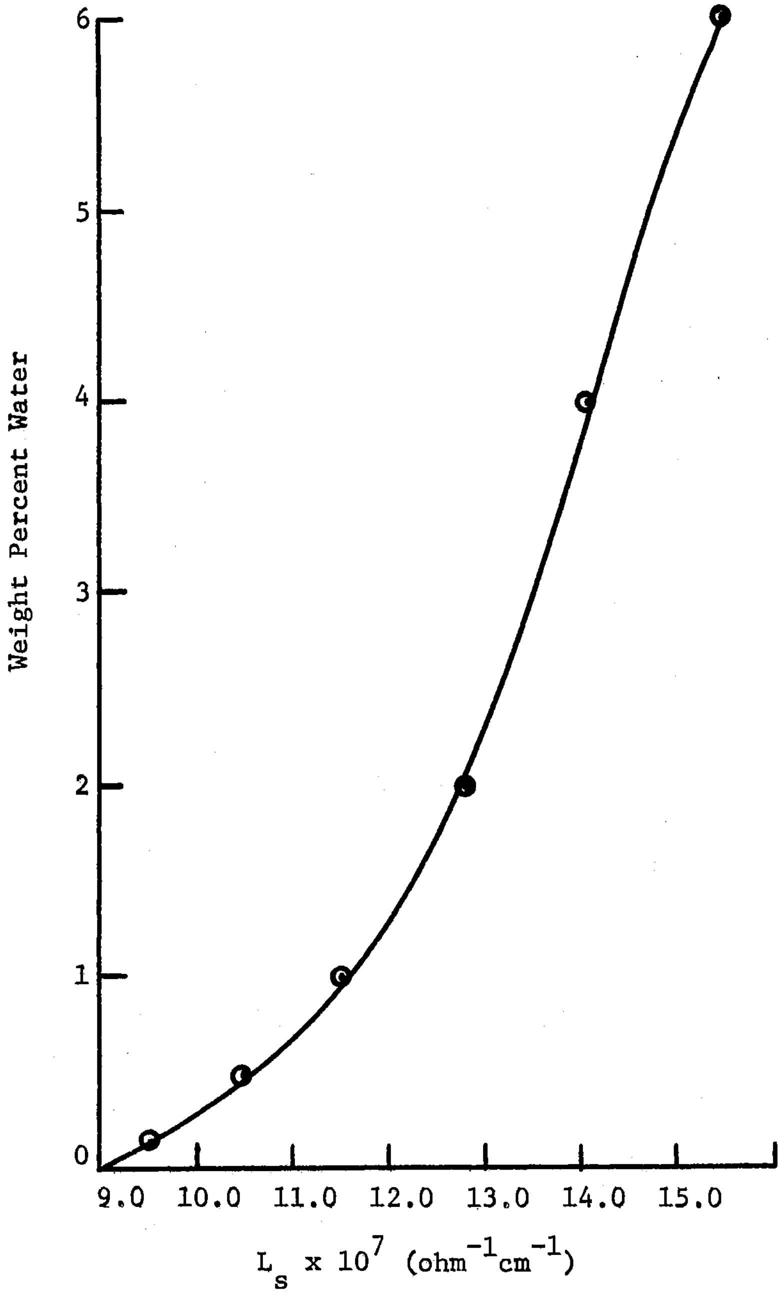


Figure 14. Specific Conductance of Water: Butanol Mixtures

amount upon the addition of small quantities of water (less than three-tenths percent) further indicates that the bulk of the perchlorate ions remain associated with the metal ion throughout the substitution process.

Stability Constants

The stability constants found are in agreement with the "stability order" proposed by Irving and Williams (64), who pointed out that the complex forming tendencies of the first-row transition metal ions often follow the sequence $\mathrm{Mn(II)} < \mathrm{Co(II)} < \mathrm{Ni} < (\mathrm{Cu(II)} > \mathrm{Zn}$. The sequence has been found to hold especially well for oxygen and nitrogen donor ligands (64). This order, first noted by Mellon and Maley in 1947 (93), was rationalized by Irving and Williams through correlation of the magnitude of a given stability constant with the second ionization potential of the ion in question. In complex formation, electrons lost in the ionization process are effectively regained from the ligands. The ionization potentials can, therefore, be regarded as an approximate measure of the electron affinity of the metal ion, and a correlation can be expected between the stability constant of the complex and the ionization potential of the metal. Although this comparison is not always satisfactory, owing in part to ligand-field effects on the electronic configuration as the atomic number of the metal increases, fairly good linear relationships have been found (6,22,30,89).

Log β_n vs. second ionization potential plots for the first, second, and third stability constants of calcium, manganese(II), nickel, cobalt (II), copper(II), and zinc are shown in Figure 15. An approximately linear relationsihp is observed for all the metals except zinc. The position of zinc commonly lies off the "natural order" line, such that

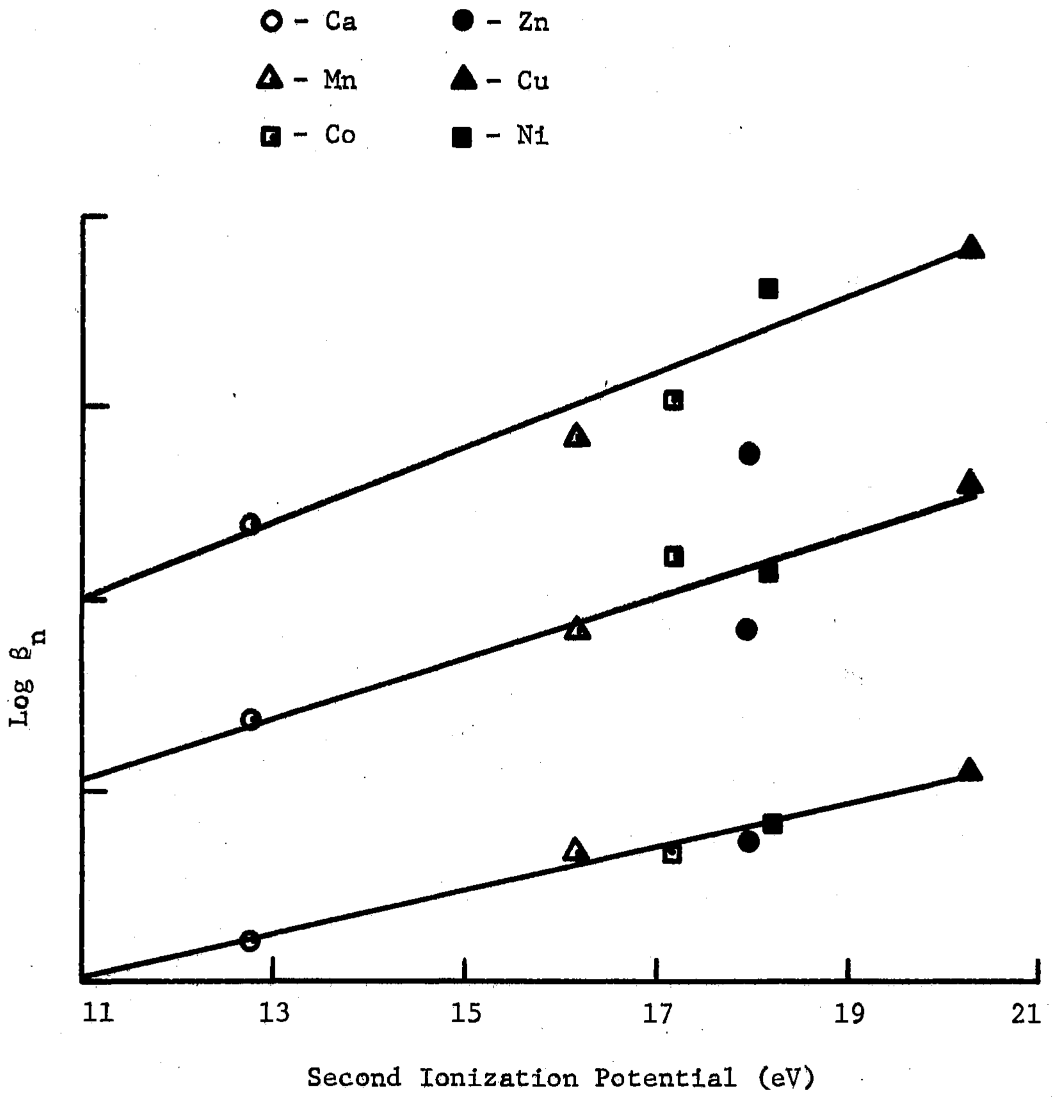


Figure 15. Dependence of Stability Constant on Second Ionization Potential of Metal

often the order Zn<Ni<Cu(II) holds (82).

Another empirical relation which has been found to hold in the case of many simple complexes of the alkaline earth metals with charged ligands is that between the ionic radius ($1/r_i$) of the cation and log β_n (82). The degree of conformity of the empirical data to this type of relation is shown in Figure 16, where values of log β_n for $n = 1$ and $n = 2$ are plotted against the reciprocal of the ionic radius for magnesium, zinc, manganese(II), calcium and strontium. The ions of these metals have empty, half-filled, or filled d-orbitals, and would be expected not to show ligand field effects (101). It is seen that log β_1 correlates well with $1/r_i$. Also shown in the figure are the values for copper(II), cobalt(II), and nickel. It is obvious that, with exception of copper (II), the values for the latter ions lie equally close to the line in the figure. For charged ligands Irving and Williams (63) early proposed that a dependence upon $1/r_i$, the Pauling radius (107), would be a measure of the electrostatic contribution to the enthalpy and entropy. However, in this case where the bonding would seem to be best considered electrostatic, but corresponding to that between an ion and a dipole, a linear dependence upon the first power of the ionic radius cannot be easily rationalized. This is because the leading term in the ion-dipole interaction has an inverse square dependence upon r_i (53). Further discussion of correlations with ion size will be made later, however, and the apparent dependence upon r_i may be in part due to scatter in the data as well as to the relative magnitudes of the radii involved.

Comparison With Other Aquocomplex Studies

It is of interest at this point to compare the stability constants

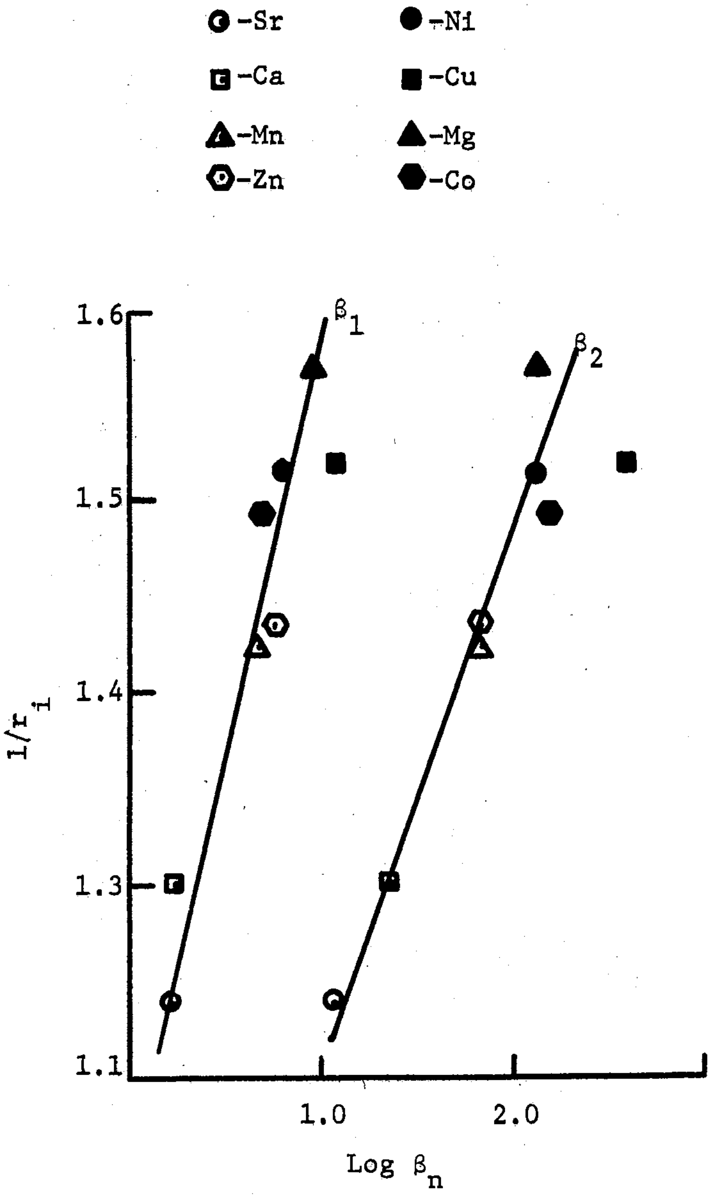


Figure 16. Dependence of Formation Constant Upon Inverse Ionic Radius

for aquocomplexes found in this study with those obtained in similar studies by other workers (see Table I).

Reference has already been made to the work of Harris and Moore (58) on aquocomplexes of cobalt(II) and nickel perchlorates in 1-butanol. As mentioned earlier, their data combined with the data obtained in the present study are in satisfactory agreement with the "stability order" of Irving and Williams (64).

The early work of Bjerrum and Jorgensen (13) on copper(II), cobalt (II), and nickel nitrates in ethanol indicates that these metal ions form weaker aquocomplexes in ethanol than in 1-butanol. It has been shown by Padova (102) that when the activity of water is very nearly given by its mole fraction in the mixed solvent, the preferential solvation of an ion depends only on the difference between the partial molar free energy of solvation of the electrolyte in each component of the mixture (see equation 5.3). To a first and very crude approximation, solvation should involve an ion-dipole interaction as the leading term. The dipole moments of 1-butanol and ethanol are very close (1.70 debye for ethanol and 1.68 debye for 1-butanol), but there may be some steric hindrance in the case of 1-butanol, and this would explain the relatively greater stability of aquocomplexes in butanol compared to those in ethanol.

Perhaps more singificant is the state of the solute. In the measurements of Jorgensen and Bjerrum (13), the salts were at concentrations ranging from less than 0.01 M to over 0.10 M. In this range of concentrations the degree of ionization is likely to be variable and certainly not 100 percent as was assumed by Jorgensen and Bjerrum. Furthermore, as Katzin and Gerbert (74) pointed out, the possibility of nitrato complexes is not excluded.

Stability constants obtained for the formation of the aquocomplexes of copper(II) perchlorate in nitromethane by Larson and Iwamoto (80) by polarographic measurements are even larger than those obtained in this study. These workers report a considerably larger value for k_1, but their values of k_2 and k_3 are of the same order of magnitude as those found in the present study. Meaningful interpretive comparisons of stability constants evaluated in solvents as structurally different as 1-butanol and nitromethane are difficult. The relative values of the dielectric constants and dipole moments for the two solvents are in the wrong order to account for the observed difference in magnitude of the formation constants in the solvents ($\varepsilon = 47$, $u = 3.40$ debye, for nitromethane). Larson and Iwamoto (80) offer the explanation that aquocomplexation constants in nitromethane should be larger than in alcohol (ethanol) because nitromethane and water are "less compatible" as a mixed-solvent pair (lower mutual solubility) than the pair, ethanol and water. The cation should, therefore, solvate water to a greater degree at a given water concentration in nitromethane than in ethanol, owing to the smaller solvation energy of the cation by nitromethane. The smaller solvation energy of copper(II) in nitromethane was evidenced also in the work of Larson and Iwamoto (80) by the more positive half-wave potential of copper(II) ion.

Nelson and Iwamoto (100) further tested the "solvent compatibility" line of reasoning of Larson and Iwamoto (80) by polarographically measuring the constants for aquocomplex formation by copper(II) in acetone. It was reasoned that ethanol and nitromethane represented opposite extremes of behavior toward water, and that acetone, being intermediate between these two in its behavior toward water, would, therefore, be a good solvent for a test of the "solvent compatibility" concept. The formation constants for aquocomplexes evaluated in acetone were, as predicted, intermediate in magnitude between those evaluated in nitromethane and ethanol. Using the stability constants of the aquocomplexes as a criterion, 1-butanol would seem to lie between nitromethane and acetone with respect to "solvent compatibility" with water.

Friedman and Plane (44) applied infrared spectroscopy to find constants for the replacement of two water molecules from the first solvation shell of copper(II) in water by ethanol and by acetone. This study differs from the other aquocomplex studies discussed above in that the salt was initially dissolved in water rather than in the organic solvent of interest. A follow up investigation was made by Pasternack and Plane (106) on cobalt(II) and nickel perchlorates employing the same organic solvents and also using infrared spectroscopy. The results showed that for the three metal ions, copper(II), cobalt(II), and nickel, the organic solvents were preferred over water at the sixth coordination site, i.e., k_6 is less than unity in all three cases. This result appears reasonable when compared with those of the present study where the value of k_n is observed to decrease fairly rapidly with increasing n. A completely valid comparison of the values of k_5 and k_6 for 1-butanol solvent with the values reported in ethanol and acetone is impossible, since the same criticism can be made of these data as was made of the measurements of Bjerrum and Jorgensen (13) in ethanol; namely, the state of the solute is not characterized adequately.

Luz and Meiboom (87) have employed NMR spectroscopy to study cobalt (II) perchlorate in methanol-water mixtures at very low (-80°C.) temperatures. Their value of k_1, listed in Table I, is quite close to the value obtained for cobalt(II) perchlorate in 1-butanol by Harris and Moore (58). Although aquocomplexation constants for a given metal ion would be expected to be larger in 1-butanol than in methanol at a given temperature, it is not impossible for k_1 in methanol at -80°C. to be the same as k_1 in 1-butanol at 25°C. by coincidence. From the thermodynamic dependence of k_1 on temperature as expressed by the van't Hoff isochore,

$$d \ln k_1/dT = \Delta H_1/RT^2 \tag{5.8}$$

and a value of ΔH_1 of -3 kcal mole^{-1}, the value of k_1 in 1-butanol would be an order of magnitude or more larger at -80°C. than at 25°C.

In conclusion, it should be emphasized again that comparison of stability constants evaluated by different methods is frequently not very satisfactory. This is due, in part, to the inherent differences in what is actually measured by different experimental techniques (55) as well as differences in experimental conditions. For example, reported values of β_4 for the tetracyanonickelate(II) complex vary from 10^{12} to 10^{30} (37,43,60,81,87,90,113) depending on the method of measurement and the experimental conditions. In the present case, the heat generated when two reagents are mixed is a very general, i.e., nonspecific quantity. It is only when one is able to make reasonable allowances for the thermal effects of all possible interactions other than that of the reaction in question, and also when such "background" interactions are relatively smaller than that of the specific reaction being investigated, that the calorimetric titration method can be employed successfully (26,29,51).

Enthalpies of Formation

The successive or stepwise enthalpies of replacement of butanol by water would be expected to be small and nearly equal in magnitude (82). This is because of the similarity in the structural features of the two ligands. For both, the metal-ligand bond presumably involves interaction of the metal ion with the hydroxyl group of the ligand dipole. The bonding is, therefore, best considered as electrostatic.

In the absence of complicating factors, such as sterically hindered substitution or change in the nature of the bonding, the stepwise ligational enthalpies for neutral ligands have been found to be constant for a given ligand and metal in aqueous solution (52). For example, the calorimetrically determined values for the reaction of ammonia and amines with aqueous transition metal ions such as copper(II) and nickel are relatively constant and of the order of four to five kilocalories per attached donor atom (49,110,128).

With the exception of the study of the substitution of water for 1-butanol in butanol solutions of cobalt(II) and nickel perchlorates by Harris and Moore (58), there seems to be no enthalpy data for the formation of aquocomplexes in nonaqueous solvents. These authors point out that if the successive enthalpies are equal ($h_n = nh_1$), the overall heat of reaction per mole, $\Delta\bar{H}$, would be given by

$$\Delta\bar{H} = \bar{n}h_1 \qquad (5.9)$$

where h_1 is the enthalpy of formation of the first aquocomplex. Assignment of enthalpies of formation for each complex involves solution of sets of equations dependent upon the calculated values of the stability constants, as well as the experimental $\Delta\bar{H}$ values. A quantity which is independent of the calculation of the stability constants, but which is useful in comparisons of binding energies for different metals with the same ligand is $\bar{h}$, the "apparent average binding energy". This quantity is defined by equation (5.10)

$$\Delta\bar{H}/\bar{n} = \bar{h} \tag{5.10}$$

which reduces to equation (5.9) when the stepwise enthalpies of formation are equal. Furthermore, since

$$\bar{n} = \sum_{1}^{N} i\alpha_i \tag{5.11}$$

$$\Delta\bar{H} = \sum_{1}^{N}\alpha_i h_i \tag{5.12}$$

for sufficiently small free ligand concentrations, it follows that $\Delta\bar{H} \cong \alpha_1 h_1$ and $\bar{n} = \alpha_1$. Then, also $\Delta\bar{H} = \bar{n} \cdot h_1$. The initial slope of the $(\Delta\bar{H},\bar{n})$ curve thus gives a measure of h_1 for the reaction, and since this is not dependent upon calculated values of the formation constants, it serves as a check upon calculations.

Table V shows a comparison of the values of h_1 obtained by extrapolation of $(\Delta\bar{H},\bar{n})$ plots with the calculated values obtained from formation constants and enthalpy titration data. The agreement is quite satisfactory (less than ten percent difference in most cases) especially when it is recalled that there is an estimated error of ten percent in the $\bar{n}$,(L) data.

It is of significance to compare the apparent average binding energy per ligand for each of the metal ions studied. Values were obtained from plots of $\Delta\bar{H}$ vs. $\bar{n}$ similar to those in Figure 17. The value at any point is $\bar{h}$, the apparent average binding energy per ligand at that ligand number. The sequence of values obtained for h_1 (Mg>Zn≃Co≃Ni>Mn>Cu>Ca>Sr) also holds for $\bar{h}$ at $\bar{n} = 1$, with the exception of Mn and Cu, for which the

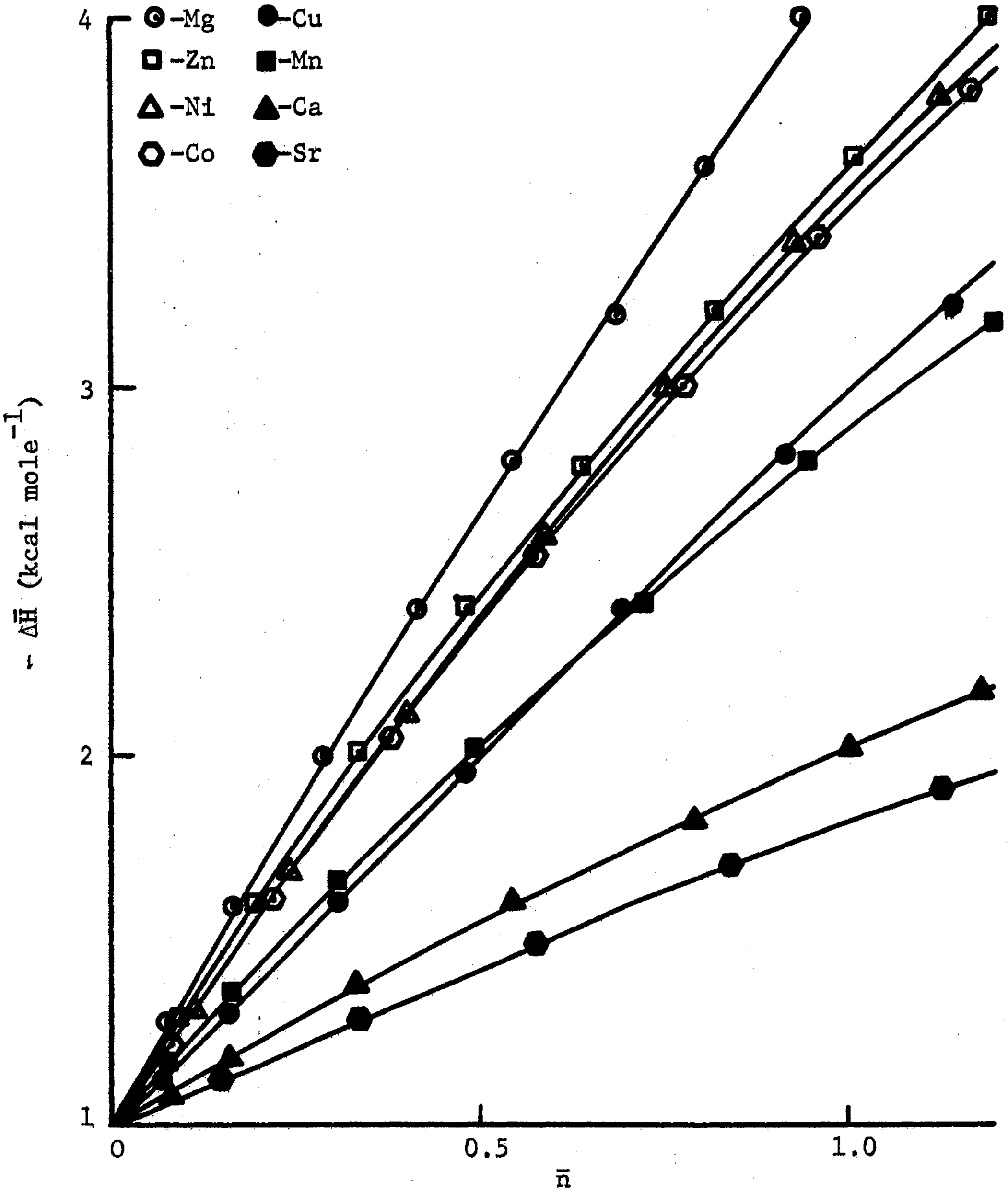


Figure 17. Average Binding Energy Per Ligand ($\Delta\bar{H}/\bar{n}$)

TABLE V

COMPARISON OF GRAPHICAL AND LEAST SQUARES CALCULATED VALUES OF THE ENTHALPY OF FORMATION OF THE FIRST AQUOCOMPLEX

Metal	Calculated	Graphical	Percent Difference
Ni	3.1	3.1	0.0
Co	3.3	2.9	12
Cu	1.9	1.9	0.0
Mn	2.3	2.3	0.0
Ca	1.2	1.2	0.0
Mg	3.4	3.4	0.0
Sr	0.6	0.8	25
Zn	3.1	2.7	13

order is reversed. Thus, the transition series (including zinc) sequence shows no clearly recognizable ligand field effects and appears to be determined largely by size factors. This is strikingly shown in the alkaline earth sequence, Mg>Ca>Sr.

It has been pointed out by Duncan (36) that because of the restricted range in values of ion radii, functions of these which appear in electrostatic calculations of energy are themselves often approximate linear functions of the reciprocal cation radius. Thus, although one would like to be able to attribute the variation in binding energy to some particular factor whose dependence upon cation radius was uniquely $1/r_i$, any observed dependence is more likely the composite of other factors.

Figure 19 shows the variation of the enthalpy of formation of the first aquocomplex with the reciprocal of the cation radius. The linearity is excellent, but perhaps to some degree, fortuitous. The position of copper(II) is anomalous and merits further comment. In Figure 18 the enthalpy of formation of the first complex, h_1, is plotted against the free energy of formation of the same complex. Although there appears to be a good general correlation of stability with enthalpy of formation, the stability of the copper(II) complex is seen to be greater than would be predicted by its heat of formation. That the free energy may not be "normal" either, however, is indicated by the fact that although copper(II) fits well into the correlation with second ionization potential (Figure 15), a plot of g_1 against $1/r_i$ (Figure 20) shows copper(II) to be well off the correlation line for the other metals.

The anomaly associated with the thermodynamic functions for the formation for the first aquocomplex of copper(II) may be a consequence of

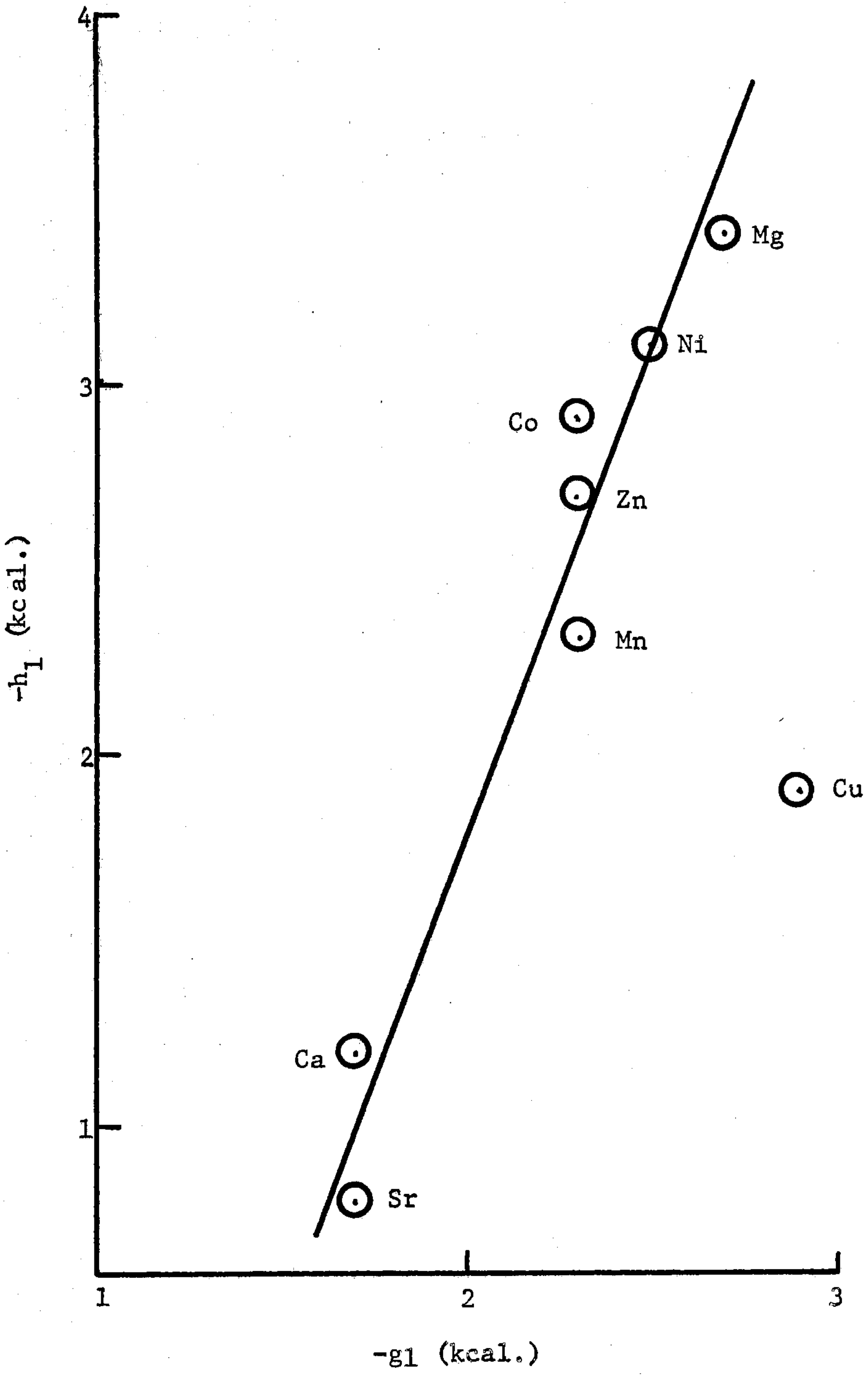


Figure 18. Correlation of Aquocomplex Stability With Enthalpy of Formation

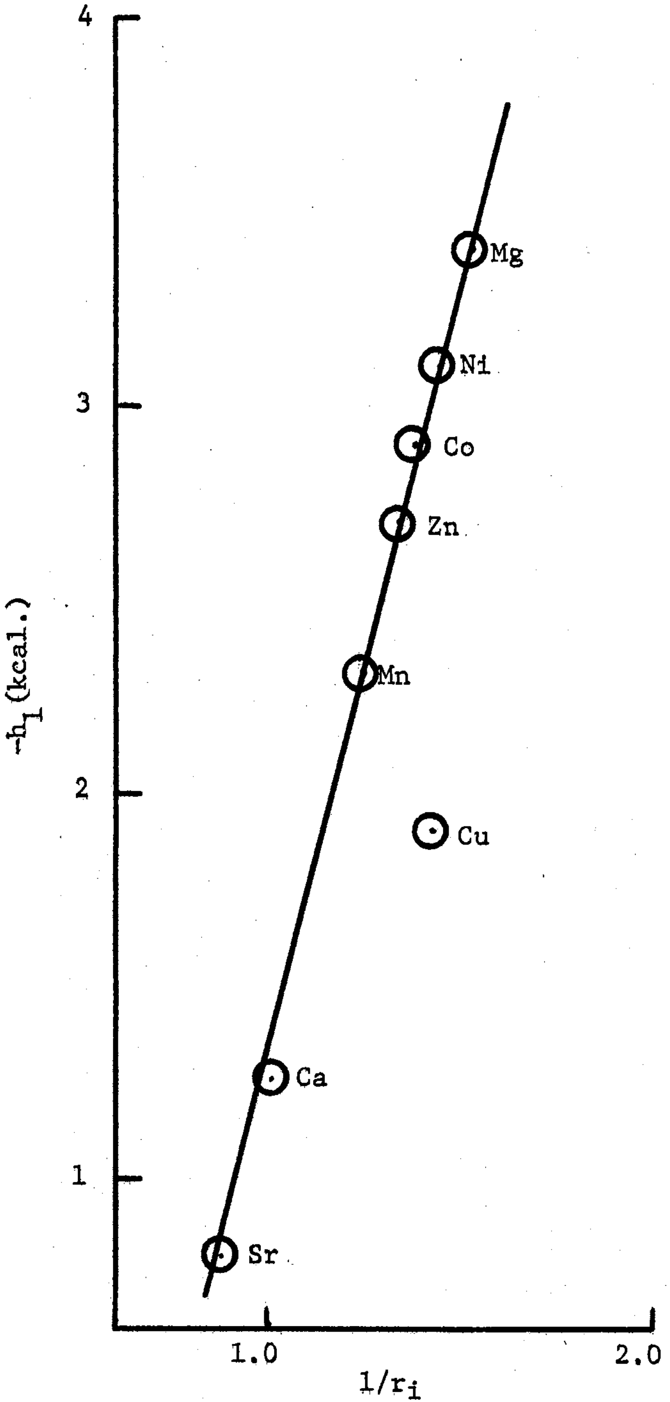


Figure 19. Dependence of Enthalpy of Formation of First Aquocomplex Upon Inverse Ionic Radius

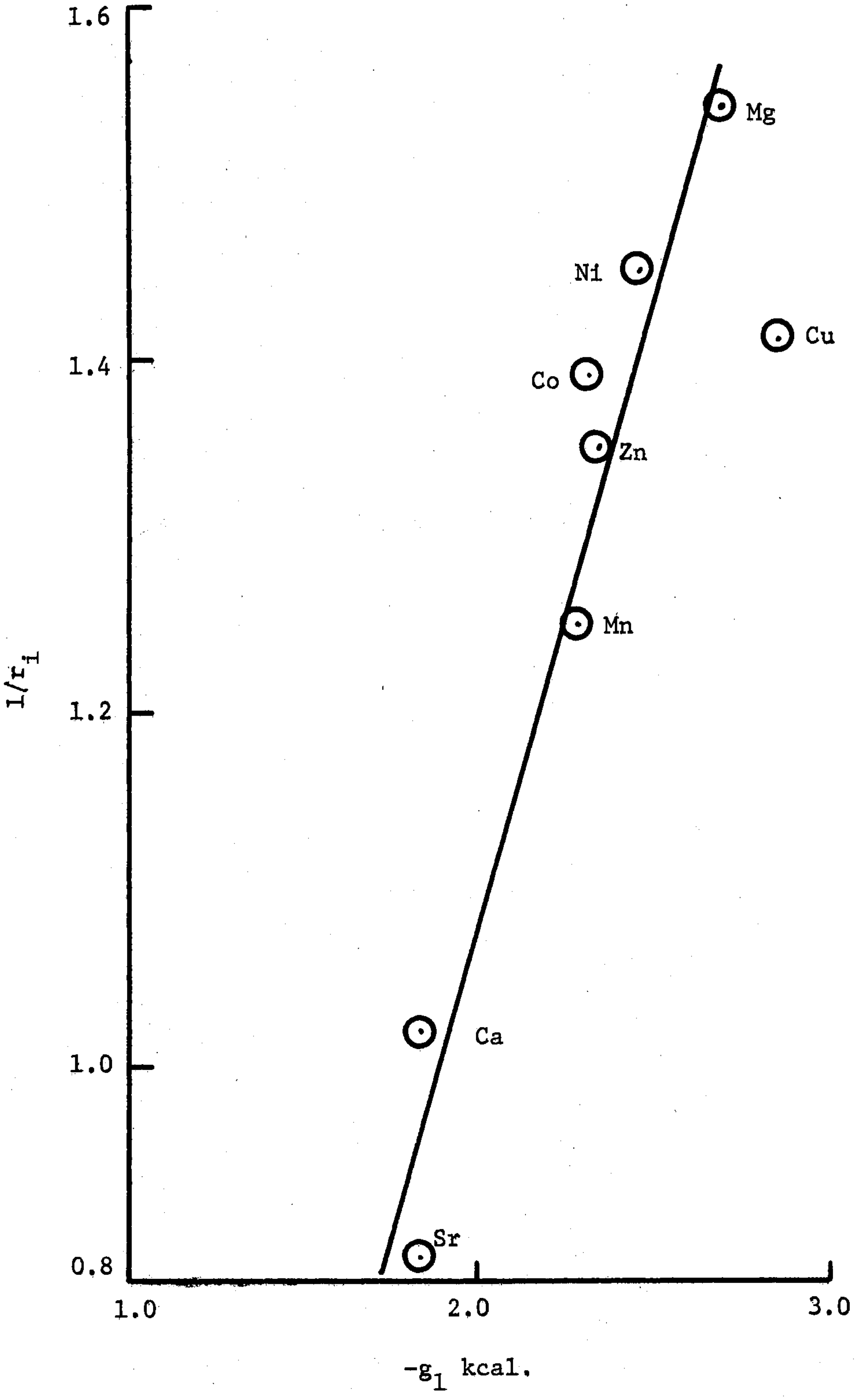


Figure 20. Dependence of Free Energy of Formation of First Aquocomplex Upon Reciprocal Ionic Results

the well established strong tetragonal perturbation of six-coordinated copper(II), the Jahn-Teller effect (101). If the perchlorate ions are <u>trans</u> and thus provide an axial field, the substitution of a smaller water dipole for the bulky butanol in an axial position should stabilize the complex, i.e., $-g_1$ should be larger as a consequence.

Entropies of Formation

Entropies of aquocomplex formation are obtained from enthalpies and free energies and hence are subject to the cumulative errors in the formation constants and enthalpies. The relatively large uncertainties in both of these quantities makes the entropy values of doubtful significance.

Complex formation by uncharged unidentate ligands will not be accompanied by a reduction in the number of particles or charge. As a consequence, the entropy change upon complex formation should be small and approximately the same for all of the metals except in those cases where the structural order of the solvent about the complex is altered (125).

As Figure 21 shows, there is implied an approximately linear relationship between the entropy and enthalpy such that the enthalpy sequence determines the free energy sequence (47,66). Copper(II), as mentioned earlier, fails to conform to this relation.

Water-Butanol Interactions

Thermodynamic excess functions for the 1-butanol:water system have been calculated from the experimental enthalpy data and the data by Thompson, Butler, and Maclennan (119). Excess functions of mixing are

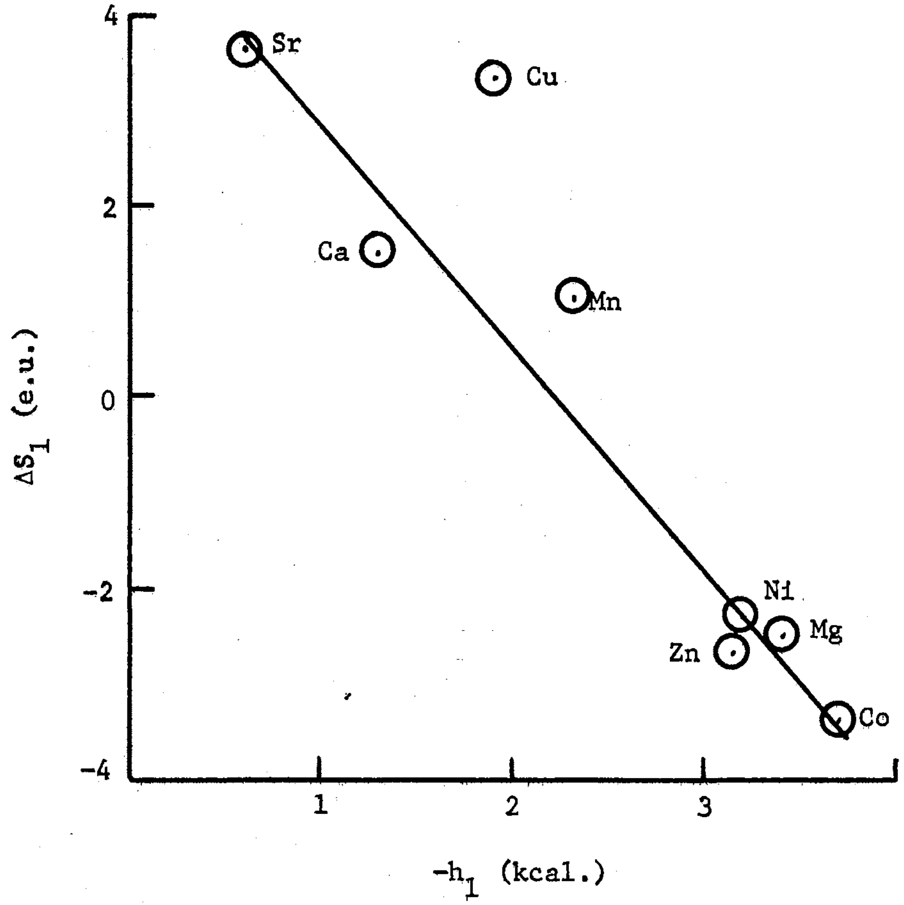


Figure 21. Relationship Between Enthalpy and Entropy of Formation of First Aquocomplex

defined by the following equations (109)

$$H^E = H_{exp} \tag{5.13}$$

$$G^E = G_{exp} - (RTX_1 lnX_1 + TRX_2 lnX_2) \tag{5.14}$$

$$S^E = S_{exp} + RX_1 lnX_1 + RX_2 lnX_2 \tag{5.15}$$

Although the data presented graphically in Figure 22 are for alcohol-rich mixtures only, the curves are somewhat similar to corresponding curves for t-butyl alcohol at high mole fractions (42). Since the mixing of 1-butanol and water at high mole fractions of water is exothermic (129), there is again some similarity to the case of t-butyl alcohol, for which the mixing is also exothermic in the same region of mole fractions.

The type of behavior shown in Figure 22 is similar to that found for the methanol:carbon tetrachloride system where, as pointed out by Ives (42), the endothermic mixing and negative excess entropy are to be associated with changes in the degree of polymerization of methanol with changing mole fraction.

Starting with pure 1-butanol, addition of water dissociates (or depolymerizes) both water and, perhaps, the alcohol endothermically. Water-water hydrogen bonds and butanol-butanol hydrogen bonds are broken and new ones are formed between water and the alcohol. The resulting net decrease in entropy is then ascribed to the "occulsion of the molecules of the diluent in a network of polymer chains" (42).

Summary

Anhydrous butanol solutions of six first-row trnasition and alkaline earth metal perchlorates (manganese(II), copper(II), zinc, magnesium,

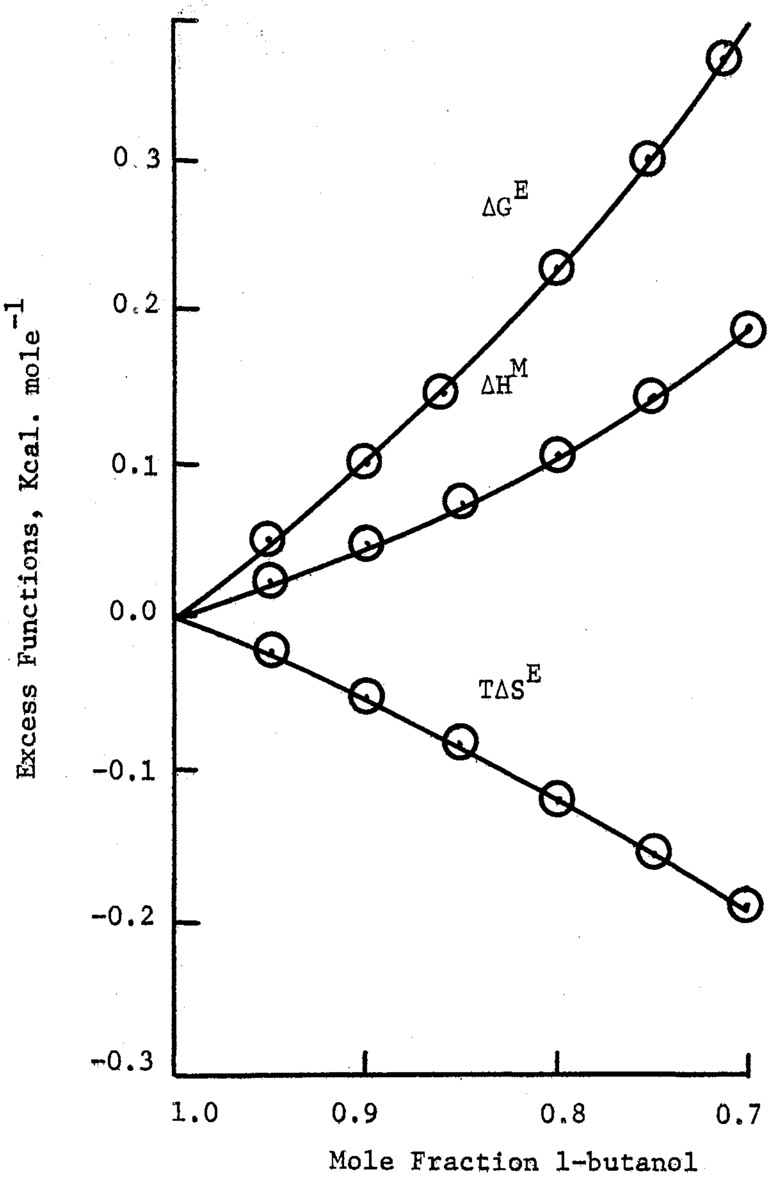


Figure 22. Thermodynamic Excess Functions of Mixing of Water into 1-butanol

calcium, and strontium) have been titrated thermometrically with water. Formation constants were evaluated from the calorimetric data for the stepwise formation of the metal aquocomplexes. The aquocomplexes appear to form in a stepwise manner and the formation constants conform to the "natural order" of Irving and Williams (63).

The logarithms of the first and second stability constants correlate well with the reciprocal cationic radius. This (linear) correlation, however, cannot be rationalized in terms of a simple ion-dipole type interaction.

A linear relationship is also found between the enthalpy of formation of the first aquocomplex and the reciprocal of the cationic radius. A plot of the enthalpy of formation of the first aquocomplex vs. the free energy of formation of the first aquocomplex is, therefore, expectedly linear. In each case, copper(II) lies noticably off the correlation "line". The anomaly associated with the thermodynamic functions for the formation of the first aquocomplex of copper(II) may be a consequence of the well-established strong tetragonal perturbation of six-coordinated copper(II), the Jahn-Teller effect (101).

The approximately linear relationship between the entropy and enthalpy of formation of the first aquocomplex implies that the enthalpy sequence determines the free energy sequence (47,66). Copper(II), as mentioned earlier, fails to conform to this relationship.

The calorimetric data was analyzed using Bjerrum's theory of Corresponding Solutions (12). The data for magnesium and strontium were also analyzed by the Variable Metric Minimization (VMM) method (33). VMM appears to be the more desirable method in terms of satisfactorily fitting the experimental data to the assumed model but, unfortunately, appears to be limited in its application to systems that can be represented by no more than two complexes.

Unfortunately, the experimental data did not yield a value for the maximum coordination number of any of the metal ions studied. The upper end of the formation curves were complicated by an unresolved exothermic process, apparently predominant only at high water concentrations.

It is speculated that the exothermic heat effect at high water concentration is attributable to a preferential reordering of the solvent envelope about the metal ion. As the water concentration becomes large, it can compete successfully with 1-butanol for sites in the outer coordination spheres of the metal ion. Because water is a stronger ligand than 1-butanol, the solvent envelope reordering process would very likely be exothermic.

Conductivity studies indicated that the solutions of metal perchlorates remained virtually undissociated over the range of water concentrations studied. This was a necessary condition for applying the "corresponding solutions" method of analysis to the experimental enthalpy titration data.

Infrared spectra indicated T_{4d} symmetry for the perchlorate ion in the solutions. This would indicate that the perchlorate is either weakly bound in the first coordination sphere of the metal ion, or is in an outer coordination sphere. The spectrum of the perchlorate ion did not change upon the addition of water through the range of water concentrations covered.

Stepwise enthalpies of aquocomplex formation were also calculated from the $\Delta\bar{H}$ curves and the previously calculated stability constants. Calculated values of the enthalpy of formation of the first aquocomplex

(h_1) agreed closely with values obtained by extrapolation of $\Delta\bar{H}$ vs. $\bar{n}$ curves to $\bar{n} = 0$ (see Table IX). This lends a greater degree of confidence to the stability constants calculated from data ($\bar{n}$,(L)) obtained from corresponding solution plots of the enthalpy titration data.

Little significance is attached to the calculated stepwise entropies of aquocomplex formation as they are subject to the cumulative errors in the formation constants and enthalpies.

Suggestions for Further Work

A possible extention of the present work would be a calorimetric investigation of possible complexes formed between transition metal perchlorates in anhydrous 1-butanol and other low molecular weight primary alcohols such as methanol and ethanol. Also, a calorimetric investigation of aquocomplex formation by transition metal perchlorates in other primary alcohols such as ethyl, propyl, amyl, etc. would be of interest.

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APPENDIX A

TABLE VI

HEAT OF MIXING OF WATER INTO 1-BUTANOL

26.908 grams of 1-butanol

ml H_2O	s, in.	$\Delta\bar{H}_{mix}$
0.020	2.82	447
0.040	2.70	438
0.060	2.78	439
0.080	2.82	442
0.100	2.73	441
0.120	2.82	442
0.140	2.81	443
0.160	2.88	446
0.180	2.94	448
0.200	2.86	450
0.220	2.89	451
0.240	2.84	452
0.260	2.89	453
0.280	2.93	454
0.300	2.82	454
0.320	2.94	456
0.340	2.84	456
0.360	2.83	456
0.380	2.90	457
0.400	2.90	458
0.429	2.87	458
0.440	3.00	460
0.460	2.92	461
0.480	2.82	461
0.500	2.87	461
0.520	2.78	461
0.540	2.78	461
0.560	2.79	462
0.580	2.78	461
0.600	2.71	461
0.620	2.72	460
0.640	2.72	460
0.660	2.66	459
0.680	2.66	459
0.700	2.72	459
0.720	2.62	458
0.840	2.57	455
0.860	2.53	454
0.880	2.49	443
0.900	2.49	443
0.920	2.52	443
0.940	2.35	442
0.960	2.45	442
0.980	2.38	441
1.000	2.42	440
1.020	2.32	439
1.040	2.36	439
1.060	2.35	438
1.080	2.32	437
1.100	2.28	437
1.120	2.20	435
1.140	2.23	435
1.160	2.23	434
1.180	2.17	433
1.200	2.17	432
1.220	2.19	431
1.240	2.18	430
1.260	2.14	429
1.280	2.16	428
1.300	2.09	427
1.320	2.09	426
1.340	2.02	425
1.360	2.07	424
1.380	2.03	423
1.400	1.98	422
1.420	2.02	421
1.440	1.93	420
1.460	1.93	419
1.480	1.97	418
1.500	1.90	417
1.520	1.82	416
1.540	1.82	416
1.650	1.82	409
1.670	1.73	408
1.690	1.77	407
1.710	1.73	405
1.730	1.72	404
1.750	1.67	403
1.770	1.69	402
1.790	1.66	401
1.810	1.64	400
1.830	1.60	399
1.850	1.58	397
1.870	1.55	396
1.890	1.57	395
1.910	1.53	394
1.930	1.54	393
1.950	1.520	391
1.970	1.49	390
1.990	1.52	389
2.010	1.48	388
2.030	1.48	387
2.050	1.43	385
2.070	1.42	384
2.090	1.43	383
2.110	1.38	382
2.130	1.36	381
2.150	1.33	379
2.170	1.26	378
2.190	1.32	377
2.210	1.28	376
2.230	1.28	374
2.250	1.28	373
2.270	1.24	372
2.290	1.20	371
2.310	1.20	369
2.330	1.16	368
2.350	1.22	367

TABLE VI (Continued)

ml H_2O	s, in.	$\Delta\bar{H}_{mix}$
0.740	2.62	458
0.760	2.56	457
0.780	2.61	457
0.800	2.58	456
0.820	2.57	455
1.560	1.85	414
1.580	1.89	413
1.600	1.73	411
1.610	1.06	411
1.630	1.76	410
2.370	1.13	365
2.390	1.14	364
2.410	1.17	363
2.430	1.13	362
2.439	0.56	361

APPENDIX B

TABLE VII

EXPERIMENTAL DATA AND CALCULATED HEATS OF REACTION

27.039 grams of
0.022 M $Cu(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0100	+0.83	-1084
0.0140	+0.73	-1458
0.0180	+0.79	-1852
0.0230	+0.70	-2249
0.0280	+0.59	-2608
0.0330	+0.54	-2951
0.0430	+0.78	-3537
0.0530	+0.54	-4034
0.0630	+0.32	-4474
0.0730	+0.12	-4838
0.0830	+0.02	-5169

27.335 grams of
0.0222 M $Cu(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0100	+1.06	-1121
0.0150	+0.93	-1581
0.0200	+0.82	-2007
0.0250	+0.71	-2397
0.0300	+0.63	-2762
0.0350	+0.53	-3095
0.0450	+0.78	-3670
0.0550	+0.53	-4164
0.0650	+0.32	-4589
0.0750	+0.14	-4995
0.0850	+0.03	-5285

28.094 grams of
0.0361 M $Cu(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0110	+1.18	- 841
0.0160	+1.22	-1091
0.0210	+1.07	-1410
0.0260	+1.03	-1720
0.0310	+0.97	-2018
0.0360	+0.87	-2296
0.0460	+1.53	-2807
0.0560	+1.24	-3258
0.0660	+1.04	-3768
0.0760	+0.82	-4031
0.0860	+0.64	-4357
0.0960	+0.48	-4650
0.1060	+0.35	-4915
0.1160	+0.22	-5154

27.369 grams of
0.0407 M $Cu(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0160	+3.22	- 896
0.0260	+3.02	-1465
0.0360	+2.57	-1972
0.0460	+2.24	-2434
0.0660	+3.48	-3219
0.0860	+2.47	-3866
0.1060	+0.97	-4304
0.1260	+0.41	-4666
0.1460	+0.00	-5070

27.896 grams of
0.0598 M $Cu(ClO_4)_4$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0187	+3.02	- 896
0.0280	+2.40	-1300
0.0380	+2.48	-1724
0.0480	+2.35	-2129
0.0580	+2.07	-2501
0.0680	+1.82	-2842
0.0780	+1.58	-3155
0.0880	+1.47	-3453
0.0980	+1.27	-3728
0.1080	+1.13	-3985
0.1180	+0.88	-4211
0.1280	+0.77	-4424
0.1380	+0.63	-4619
0.1480	+0.54	-4804
0.1580	+0.40	-4971
0.1680	+0.31	-5127

28.078 grams of
0.0598 M $Cu(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0180	+2.89	- 870
0.0280	+2.57	-1320
0.0380	+2.33	-1739
0.0480	+2.18	-2138
0.0580	+1.93	-2505
0.0680	+1.57	-2826
0.0780	+1.52	-3140
0.0880	+1.30	-3426
0.0980	+1.16	-3693
0.1080	+1.04	-3946
0.1180	+0.83	-4171

TABLE VII (Continued)

28.467 grams of
0.0361 M $Cu(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0120	+1.16	- 732
0.0170	+1.17	-1166
0.0220	+1.11	-1489
0.0270	+1.03	-1795
0.0320	+0.93	-2080
0.0370	+1.50	-2352
0.0470	+1.50	-2749
0.0570	+1.26	-3298
0.0670	+1.02	-3698
0.0770	+0.81	-4054
010870	+0.62	-4372
0.0970	+0.43	-4650
0.1070	+0.33	-4908
0.1170	+0.20	-5193

27.431 grams of
0.0407 M $Cu(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0160	+3.08	- 871
0.0260	+2.80	-1404
0.0360	+2.53	-1901
0.0460	+2.31	-2368
0.0660	+3.70	-3177
0.0860	+2.54	-3829
0.1060	+1.76	-4374
0.1260	+1.08	-4826
0.1460	+0.60	-5212

28.078 grams of
0.0598 M $Cu(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.1280	+0.72	-4381
0.1380	+0.58	-4574
0.1480	+0.49	-4754
0.1580	+0.37	-4920
0.1680	+0.28	-5073

28.406 grams of
0.0824 M $Cu(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0190	+3.19	- 703
0.0290	+2.93	-1052
0.0390	+2.84	-1408
0.0490	+2.79	-1731
0.0590	+2.48	-2044
0.0690	+2.16	-2340
0.0790	+2.14	-2715
0.0890	+1.99	-2818
0.0990	+1.83	-3135
0.1090	+1.70	-3376
0.1290	+2.83	-3799
0.1490	+2.47	-4182
0.1690	+1.87	-4522
0.1890	+1.49	-4824
0.2090	+1.13	-5092

29.146 grams of
0.0283 M $Ca(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0100	-0.01	- 223
0.0200	-0.07	- 449
0.0300	-0.12	- 654
0.0400	-0.18	- 844
0.0500	-0.21	-1026
0.0600	-0.23	-1201
0.0700	-0.29	-1364
0.0800	-0.30	-1523
0.0900	-0.32	-1677
0.1000	-0.37	-1818
0.110	-0.39	-1954
0.1200	-0.42	-2082
0.1300	-0.44	-2206
0.1400	-0.43	-2331
0.1500	-0.42	-2459
0.1600	-0.48	-2572

28.295 grams of
0.0754 M $Ca(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0100	+0.56	- 146
0.0200	+0.54	- 290
0.0300	+0.48	- 429
0.0400	+0.44	- 563
0.0500	+0.39	- 693
0.0600	+0.34	- 818
0.0700	+0.30	- 939
0.0800	+0.27	-1058
0.0900	+0.25	-1174
0.1000	+0.21	-1287
0.110	+0.17	-1395
0.1200	+0.15	-1502
0.1400	+0.21	-1706
0.1600	+0.13	-1903
0.1800	+0.03	-2090
0.2000	-0.07	-2267
0.2200	-0.14	-2438
0.2400	-0.21	-2601

TABLE VII (Continued)

28.223 grams of
0.0824 M $Cu(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0190	+3.43	- 635
0.0290	+2.93	- 992
0.0400	+2.91	-1331
0.0500	+2.63	-1667
0.0600	+2.52	-1974
0.0700	+2.33	-2253
0.0800	+2.11	-2530
0.0900	+1.99	-2794
0.1000	+1.87	-3043
0.1100	+1.68	-3281
0.1300	+2.82	-3705
0.1500	+2.35	-4098
0.1700	+1.86	-4436
0.1900	+1.45	-4739
0.2100	+1.08	-5010

28.924 grams of
0.0283 M $Ca(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0100	-0.02	- 231
0.0200	-0.08	- 448
0.0300	-0.12	- 654
0.0400	-0.17	- 848
0.0500	-0.22	-1028
0.0600	-0.24	-1204
0.0700	-0.28	-1369
0.0800	-0.30	-1529
0.0900	-0.32	-1684
0.1000	-0.37	-1825
0.1100	-0.40	-1959
0.1200	-0.39	-2096
0.1300	-0.41	-2227
0.1400	-0.42	-2355
0.1500	-0.47	-2470
0.1600	-0.48	-2583

28.359 grams of
0.0754 M $Ca(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0100	+0.52	- 142
0.0200	+0.52	- 285
0.0300	+0.48	- 425
0.0400	+0.42	- 558
0.0500	+0.38	- 687
0.0600	+0.37	- 816
0.0700	+0.31	- 938
0.0800	+0.27	-1057
0.0900	+0.23	-1126
0.1000	+0.20	-1237
0.1100	+0.18	-1347
0.1200	+0.16	-1455
0.1400	+0.19	-1657
0.1600	+0.12	-1853
0.1800	+0.03	-2039
0.2000	-0.07	-2216
0.2200	-0.15	-2384
0.2400	-0.21	-2547

27.434 grams of
0.0216 M $Ca(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0200	-0.57	- 513
0.0400	-0.87	- 952
0.0600	-1.08	-1338
0.0800	-1.18	-1699
0.100	-1.33	-2022
0.1200	-1.49	-2304
0.1400	-1.52	-2579

29.565 grams of
0.0407 M $Ca(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0200	+0.48	- 385
0.0400	+0.19	- 734
0.0600	-0.02	-1055
0.0800	-0.23	-1349
0.1000	-0.41	-1619
0.1200	-0.54	-1873
0.1400	-0.70	-2105
0.1600	-0.78	-2327
0.1800	-0.92	-2530

28.407 grams of
0.0216 M $Ca(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0200	-0.60	- 500
0.0400	-0.86	- 941
0.0600	-1.11	-1325
0.0800	-1.27	-1673
0.100	-1.39	-1992
0.1200	-1.48	-2290
0.1400	-1.58	-2564

26.228 grams of
0.0268 M $Mn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+0.96	- 373
0.0100	+0.73	- 690
0.0200	+1.34	-1295
0.0300	+0.83	-1776
0.0400	+0.53	-2183
0.0600	+0.38	-2830
0.0800	-0.23	-3328
0.100	-0.64	-3724
0.1200	-0.94	-4047

27.884 grams of
0.0405 M $Mn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+1.23	- 281
0.0100	+1.18	- 553
0.0200	+2.00	-1043
0.0300	+1.67	-1482
0.0400	+1.29	-1860
0.0600	+1.92	-2511
0.0800	+1.05	-3024
0.1000	+0.46	-3442
0.1200	+0.02	-3791
0.1400	-0.27	-4093

TABLE VII (Continued)

27.628 grams of
0.0181 M $Mn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+0.73	- 451
0.0100	+0.56	- 842
0.0200	+0.58	-1435
0.0300	+0.33	-1939
0.0400	+0.12	-2369
0.0600	-0.26	-3045
0.0800	-0.78	-3542
0.100	-1.08	-3931
0.1200	-1.32	-4235
0.1400	-1.46	-4487
0.1600	-1.59	-4692
0.1800	-1.68	-4864
0.200	-173	-5016

26.618 grams of
0.0268 M $Mn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+0.86	- 342
0.0100	+0.78	- 666
0.0200	+1.23	-1235
0.0300	+0.89	-1722
0.0400	+0.57	-2132
0.0600	+0.47	-2792
0.0800	-0.13	-3306
0.1000	-0.58	-3712
0.1200	-0.94	-4030

27.229 grams of
0.0639 M $Mn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+1.82	- 240
0.0100	+1.56	- 453
0.0200	+2.26	- 794
0.0300	+2.23	-1132
0.0400	+2.28	-1475
0.0600	+3.34	-2038
0.0800	+2.38	-2505
0.1000	+1.82	-2915
0.1200	+1.14	-3256
0.1400	+0.64	-3546
0.1600	+0.25	-3797
0.1800	-0.10	-4013

28.131 grams of
0.0181 M $Mn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+0.66	- 416
0.0100	+0.47	- 768
0.0200	+0.64	-1368
0.0300	+0.35	-1869
0.0400	+0.12	-2289
0.0600	-0.28	-2953
0.0800	-0.77	-3446
0.1000	-1.03	-3849
0.1200	-1.26	-4170

27.510 grams of
0.0405 M $Mn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+1.53	- 325
0.0100	+1.08	- 581
0.0200	+1.91	-1053
0.0300	+1.54	-1469
0.0400	+1.32	-1851
0.0600	+1.82	-2486
0.0800	+0.98	-2990
0.1000	+0.41	-3404
0.1200	-0.07	-3743
0.1400	-0.46	-4020

26.800 grams of
0.0639 M $Mn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+1.82	- 237
0.0100	+1.48	- 441
0.0200	+2.66	- 819
0.0300	+2.41	-1173
0.0400	+2.05	-1491
0.0600	+3.47	-2066
0.0800	+2.43	-2537
0.1000	+1.66	-2933
0.1200	+1.07	-3269
0.1400	+0.58	-3556
0.1600	+0.19	-3804
0.1800	-0.16	-4017

29.817 grams of
0.0864 M $Mn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+1.52	- 151
0.0100	+1.42	- 295
0.0200	+2.83	- 581
0.0300	+2.78	- 864
0.0400	+2.40	-1119
0.0600	+4.12	-1578
0.0800	+2.73	-1934
0.1000	+2.97	-2308
0.1200	+2.42	-2641
0.1400	+1.83	-2931
0.1600	+1.39	-3188
0.1800	+0.96	-3413

27.446 grams of
0.0141 M $Zn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+2.42	- 6633
0.0100	+1.85	-1229
0.0150	+1.22	-1687
0.0200	+0.53	-2027
0.0250	+0.34	-2335
0.0300	+0.21	-2620
0.0350	+0.08	-2884
0.0400	-0.10	-3116
0.0450	-0.27	-3319
0.0500	-0.34	-3511
0.0550	-0.54	-3668
0.0600	-0.62	-3811

26.954 grams of
0.0321 M $Zn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+1.98	- 485
0.0100	+1.63	- 905
0.0150	+1.47	-1297
0.0200	+1.22	-1642
0.0250	+1.05	-1995
0.0300	+0.87	-2234
0.0350	+0.78	-2497
0.0400	+0.65	-2735
0.0450	+0.51	-2946
0.0500	+0.42	-3140
0.0550	+0.34	-3319
0.0600	+0.23	-3477

TABLE VII (Continued)

29.817 grams of
0.0864 M $Mn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.2000	+0.64	-3614
0.2200	+0.37	-3795
0.2400	+0.12	-3957
0.2600	-0.12	-4101

27.446 grams of
0.0141 M $Zn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0650	-0.72	-3937
0.0700	-0.70	-4067
0.0750	-0.82	-4176
0.0800	-0.86	-4278
0.0900	-1.69	-4487

26.954 grams of
0.0321 M $Zn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0650	+0.17	-3623
0.0700	+0.13	-4006

29.735 grams of
0.0864 M $Mn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+1.50	- 149
0.0100	+1.43	- 297
0.0200	+2.80	- 583
0.0300	+2.75	- 866
0.0400	+2.43	-1115
0.0600	+4.10	-1569
0.0800	+2.76	-1940
0.1000	+2.57	-2313
0.1200	+2.40	-2642
0.1400	+1.86	-2935
0.1600	+1.37	-3179
0.1800	+1.00	-3410
0.2000	+0.67	-3611
0.2200	+0.35	-3790
0.2400	+0.15	-3965
0.2600	-0.10	-4100

28.400 grams of
0.0141 M $Zn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0500	+2.07	- 589
0.0100	+1.73	-1120
0.0150	+1.22	-1567
0.0200	+0.68	-1922
0.0250	+0.50	-2247
0.0300	+0.32	-2542
0.0350	+0.05	-2792
0.0400	-0.14	-3010
0.0450	-0.30	-3200
0.0500	-0.36	-3381
0.0550	-0.43	-3550
0.0600	-0.55	-3698
0.0650	-0.57	-3843
0.0700	-0.73	-3961
0.0750	-0.78	-4070
0.0800	-0.76	-4183
0.0900	-1.83	-4355

27.855 grams of
0.0321 M $Zn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0500	+1.97	- 477
0.0100	+1.63	- 890
0.0150	+1.42	-1266
0.0200	+1.20	-1600
0.0250	+1.03	-1902
0.0300	+0.88	-2176
0.0350	+0.81	-2437
0.0400	+0.58	-2655
0.0450	+0.55	-2867
0.0500	+0.43	-3057
0.0550	+0.38	-3238
0.0600	+0.22	-3388
0.0650	+0.19	-3533
0.0700	+0.16	-3672
0.0800	+0.16	-3921
0.0900	+0.00	-4139

27.953 grams of
0.0535 M $Zn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+2.13	- 308
0.0100	+2.02	- 604
0.0150	+1.89	- 885
0.0200	+1.77	-1152
0.0250	+1.65	-1406
0.0300	+1.57	-1650
0.0350	+1.44	-1880
0.0400	+1.28	-2092
0.0450	+1.21	-2295
0.0500	+1.08	-2484
0.0550	+0.95	-2659
0.0600	+0.83	-2819
0.0650	+0.77	-2973
0.0700	+0.71	-3119

28.888 grams of
0.0858 M $Zn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0500	+3.00	- 255
0.0100	+2.62	-426
0.0150	+2.22	- 682
0.0200	+2.13	- 875
0.0250	+2.02	-1060
0.0300	+1.99	-1243
0.0350	+1.71	-1406
0.0400	+1.86	-1579
0.0450	+1.78	-1747
0.0500	+1.62	-1904
0.0550	+1.56	-2056
0.0600	+1.58	-2209
0.0700	+2.80	-2491
0.0800	+2.35	-2741

27.933 grams of
0.0250 M $Sr(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0076	-0.40	- 108
0.0176	-0.53	- 249
0.0276	-0.56	- 382
0.0376	-0.58	- 509
0.0576	-1.16	- 765
0.0776	-1.27	- 991
0.0976	-1.29	-1211

TABLE VII (Continued)

27.953 grams of
0.0535 M $Zn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0750	+0.63	-3257
0.0800	+0.52	-3382
0.0900	+0.83	-3609
0.1000	+0.67	-3816
0.1100	+0.47	-4002
0.1300	+0.50	-4321

28.888 grams of
0.0858 M $Zn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0900	+2.09	-2971
0.1000	+1.97	-3193
0.1100	+1.73	-3398
0.1200	+1.44	-3582
0.1300	+1.18	-3748
0.1400	+1.04	-3903
0.1600	+1.64	-4181

27.275 grams of
0.0275 M $Sr(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	-0.28	- 73
0.0100	-0.31	- 138
0.0200	-0.58	- 279
0.0300	-0.56	- 424
0.0400	-0.64	- 549
0.0500	-0.65	- 672
0.0700	-1.31	- 914
0.0900	-1.35	-1145

27.610 grams of
0.0535 M $Zn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+2.36	- 333
0.0100	+2.08	- 635
0.0150	+2.10	- 940
0.0200	+1.96	-1228
0.0250	+1.60	-1476
0.0300	+1.53	-1717
0.0350	+1.47	-1951
0.0400	+1.38	-2174
0.0450	+1.15	-2372
0.0500	+1.14	-2568
0.0550	+0.94	-2742
0.0600	+1.00	-2923
0.0650	+0.82	-3083
0.0700	+0.73	-3233
0.0800	+1.14	-3497
0.0900	+0.93	-3737
0.1000	+0.72	-3952
0.1100	+0.57	-4151
0.1200	+0.37	-4327

28.734 grams of
0.0858 M $Zn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+2.62	- 224
0.0100	+2.26	- 423
0.0150	+2.22	- 619
0.0200	+2.25	- 818
0.0250	+2.18	-1011
0.0300	+2.08	-1198
0.0350	+2.08	-1385
0.0400	+1.85	-1555
0.0450	+1.70	-1715
0.0500	+1.55	-1865
0.0550	+1.48	-2010
0.0600	+1.43	-2151
0.0700	+2.80	-2429
0.0800	+2.61	-2695
0.0900	+2.33	-2940
0.1000	+1.82	-3150
0.1100	+1.58	-3342
0.1200	+1.47	-3527
0.1300	+1.27	-3698
0.1500	+1.60	-3973
0.1700	+1.27	-4224

26.911 grams of
0.0361 M $Sr(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	-0.17	- 70
0.0100	-0.21	- 133
0.0200	-0.41	- 261
0.0300	-0.42	- 387
0.0400	-0.45	- 507
0.0600	-0.96	- 737
0.0800	-1.06	- 949
0.1000	-1.10	-1154

27.118 grams of
0.0361 M $Sr(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	-0.18	- 68
0.0100	-0.18	- 135
0.0200	-0.38	- 267
0.0300	-0.39	- 397
0.0500	-0.88	- 640
0.0700	-0.97	- 866
0.0900	-1.07	-1074

27.141 grams of
0.0581 M $Sr(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	-0.04	- 58
0.0100	-0.06	- 114
0.0200	-0.12	- 226
0.0300	-0.16	- 334
0.0400	-0.19	- 439
0.0600	-0.45	- 641
0.0800	-0.56	- 832
0.1000	-0.63	-1015

26.926 grams of
0.0121 M $Mg(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+1.78	-1273
0.0100	+0.73	-1971
0.0200	+0.63	-2911
0.0300	-0.10	-3450
0.0400	-0.22	-3922
0.0600	-0.93	-4596

27.192 grams of
0.0375 M $Mg(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+3.81	- 748
0.0100	+2.04	-1193
0.0200	+3.92	-2057
0.0300	+3.03	-2769
0.0400	+2.19	-3337
0.0600	+3.04	-4244

TABLE VII (Continued)

27.156 grams of
0.0581 M $Sr(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	-0.02	- 60
0.0100	-0.06	- 116
0.0200	-0.12	- 227
0.0300	-0.17	- 334
0.0400	-0.18	- 439
0.0600	-0.42	- 643
0.0800	-0.55	- 832
0.1000	-0.63	-1013

25.932 grams of
0.0121 M $Mg(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+1.50	-1147
0.0100	+0.72	-1859
0.0200	+0.78	-2913
0.0300	+0.14	-3608
0.0400	-0.22	-4100
0.0600	-1.02	-4758

26.532 grams of
0.0495 M $Mg(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+3.08	- 485
0.0100	+2.53	- 897
0.0200	+4.44	-1640
0.0300	+3.79	-2297
0.0400	+3.06	-2856
0.0600	+4.54	-3764
0.0800	+2.66	-4420

26.963 grams of
0.0763 M $Sr(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+0.06	- 52
0.0100	+0.02	- 102
0.0200	+0.02	- 200
0.0300	-0.04	- 292
0.0400	-0.03	- 386
0.0600	-0.11	- 586
0.0800	-0.29	- 736
0.1000	-0.36	- 897
0.1200	-0.47	-1050

26.517 grams of
0.0274 M $Mg(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0500	+2.23	- 653
0.0100	+1.94	-1240
0.0200	+3.04	-2218
0.0300	+2.16	-2990
0.0400	+1.48	-3604
0.0600	+1.42	-4471

27.157 grams of
0.0495 M $Mg(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+3.34	- 511
0.0100	+2.32	- 888
0.0200	+4.57	-1632
0.0300	+3.83	-2279
0.0400	+3.22	-2847
0.0600	+4.63	-3745
0.0800	+2.82	-4406

28.126 grams of
0.0763 M $Sr(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+0.05	- 50
0.0100	+0.00	- 96
0.0200	0.00	- 188
0.0300	-0.05	- 276
0.0400	-0.07	- 361
0.0600	-0.14	- 533
0.0800	-0.27	- 694
0.1000	-0.33	- 849
0.1200	-0.42	- 997
0.1400	-0.48	-1139

27.055 grams of
0.0274 M $Mg(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+2.43	- 697
0.0100	+2.02	-1299
0.0200	+3.03	-2268
0.0300	+2.06	-3012
0.0400	+1.42	-3607
0.0600	+1.36	-4449

26.665 grams of
0.0629 M $Mg(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+3.34	- 389
0.0100	+3.82	- 825
0.0150	+2.96	-1177
0.0200	+2.37	-1470
0.0300	+5.07	-2090
0.0400	+3.92	-2596
0.0500	+3.55	-3065
0.0700	+5.50	-3847
0.0900	+3.66	-4446

TABLE VII (Continued)

27.515 grams of
0.0629 M $Mg(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+3.97	- 462
0.0100	+2.90	- 815
0.0150	+2.63	-1140
0.0200	+2.18	-1420
0.0300	+4.41	-1984
0.0400	+3.96	-2504
0.0500	+3.52	-2978
0.0700	+5.23	-3743
0.0900	+3.43	-4323

27.226 grams of
0.0375 M $Mg(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+3.89	- 750
0.0100	+2.10	-1197
0.0200	+4.00	-2066
0.0300	+2.95	-2761
0.0400	+2.10	-3330
0.0600	+3.10	-4251

APPENDIX C

TABLE VIII

AVERAGE LIGAND NUMBER AND FREE LIGAND CONCENTRATION

$Cu(ClO_4)_2$ in 1-butanol			$Ca(ClO_4)_2$ in 1-butanol			$Mn(ClO_4)_2$ in 1-butanol		
$\Delta\bar{H}$	$\bar{n}$	$(L)x10^2$	$\Delta\bar{H}$	$\bar{n}$	$(L)x10^2$	$\Delta\bar{H}$	$\bar{n}$	$(L)x10^2$
100	0.06	0.04	100	0.08	0.42	100	0.04	0.11
200	0.11	0.09	200	0.16	0.89	200	0.09	0.20
300	0.15	0.15	300	0.24	1.38	300	0.14	0.30
400	0.20	0.20	400	0.33	1.81	400	0.19	0.41
500	0.25	0.26	500	0.44	2.25	500	0.24	0.50
600	0.30	0.29	600	0.55	2.67	600	0.28	0.64
700	0.35	0.35	600	0.67	3.09	700	0.33	0.76
800	0.41	0.38	800	0.80	3.48	800	0.38	0.91
900	0.45	0.45	900	0.89	4.06	900	0.43	1.05
1000	0.51	0.50	1000	1.00	4.59	1000	0.48	1.21
1100	0.55	0.56	1100	1.12	5.13	1100	0.54	1.36
1200	0.60	0.63	1200	1.22	5.73	1200	0.59	1.53
1300	0.66	0.70	1300	1.33	6.35	1300	0.64	1.72
1400	0.70	0.78	1400	1.45	6.96	1400	0.70	1.89
1500	0.76	0.86	1500	1.56	7.59	1500	0.75	2.09
1600	0.81	0.93	1600	1.70	8.21	1600	0.81	2.28
1700	0.86	1.00	1700	1.80	9.02	1700	0.87	2.48
1800	0.92	1.08	1800	1.92	9.75	1800	0.94	2.65
1900	0.97	1.15	1900	2.05	10.3	1900	1.01	2.88
2000	1.03	1.24	2000	2.16	11.3	2000	1.07	3.12
2100	1.08	1.33	2100	2.28	12.1	2100	1.14	3.34
2200	1.13	1.45	2200	2.41	13.1	2200	1.21	3.61
2300	1.19	1.53	2300	2.53	13.9	2300	1.28	3.88
2400	1.25	1.61	2400	2.68	14.7	2400	1.36	4.15
2500	1.31	1.70	2500	2.82	15.6	2500	1.43	4.44
2600	1.37	1.82				2600	1.51	4.73
2700	1.43	1.95				2600	1.59	5.06
2800	1.48	2.05				2800	1.67	5.40
2900	1.56	2.10				2900	1.75	5.75
3000	1.63	2.22				3000	1.83	6.14
3100	1.70	2.29				3100	1.93	6.54
3200	1.77	2.43				3200	2.01	6.99
3300	1.83	2.59				3300	2.10	7.47

TABLE VIII (Continued)

$Cu(ClO_4)_2$ in 1-butanol

$\Delta\bar{H}$	$\bar{n}$	(L)x10^2
3400	1.91	2.71
3500	1.99	2.76
3600	2.05	2.99
3700	2.13	3.14
3800	2.21	3.31
3900	2.28	3.51
4000	2.39	3.60
4100	2.46	3.81
4200	2.56	3.95
4300	2.64	4.18
4400	2.73	4.38
4500	2.84	4.58
4600	2.93	4.81
4700	3.03	5.06
4800	3.13	5.30
4900	3.24	5.66

$Ca(ClO_4)_2$ in 1-butanol

$\Delta\bar{H}$	$\bar{n}$	(L)x10^2

$Mn(ClO_4)_2$ in 1-butanol

$\Delta\bar{H}$	$\bar{n}$	(L)x10^2
3400	2.20	7.98
3500	2.31	8.46
3600	2.43	8.98
3700	2.55	9.54
3800	2.69	10.1
3900	2.83	10.7
4000	2.98	11.3

$Sr(ClO_4)_2$ in 1-butanol

$\Delta\bar{H}$	$\bar{n}$	(L)x10^2
50	0.10	0.31
100	0.15	0.75
150	0.19	1.24
200	0.24	1.65
250	0.30	2.11
300	0.34	2.59
350	0.39	3.07
400	0.45	3.55
450	0.51	4.00
500	0.58	4.46
550	0.64	4.94
600	0.71	5.39
650	0.76	5.89
700	0.84	6.35
750	0.92	6.77
800	0.99	7.26
850	1.03	7.96
900	1.13	8.19
950	1.20	8.80
1000	1.27	9.28

$Mg(ClO_4)_2$ in 1-butanol

$\Delta\bar{H}$	$\bar{n}$	(L)x10^2
100	0.03	0.03
200	0.06	0.05
300	0.08	0.09
400	0.11	0.14
500	0.14	0.16
600	0.17	0.20
700	0.19	0.25
800	0.22	0.29
900	0.26	0.34
1000	0.29	0.38
1100	0.32	0.43
1200	0.35	0.49
1300	0.38	0.54
1400	0.42	0.61
1500	0.45	0.68
1600	0.49	0.74
1700	0.52	0.82
1800	0.55	0.90
1900	0.58	1.00
2000	0.62	1.08
2100	0.65	1.18
2200	0.69	1.28
2300	0.71	1.39
2400	0.75	1.51
2500	0.78	1.65

$Zn(ClO_4)_2$ in 1-butanol

$\Delta\bar{H}$	$\bar{n}$	(L)x10^2
100	0.03	0.07
200	0.07	0.12
300	0.09	0.23
400	0.13	0.29
500	0.16	0.38
600	0.19	0.45
700	0.24	0.48
800	0.28	0.55
900	0.33	0.60
1000	0.37	0.71
1100	0.41	0.81
1200	0.44	0.95
1300	0.48	1.08
1400	0.51	1.19
1500	0.54	1.35
1600	0.58	1.49
1700	0.62	1.66
1800	0.66	1.78
1900	0.70	1.96
2000	0.74	2.11
2100	0.78	2.27
2200	0.84	2.41
2300	0.87	2.60
2400	0.93	2.76
2500	0.97	2.95

TABLE VIII (Continued)

$Sr(ClO_4)_2$ in 1-butanol			$Mg(ClO_4)_2$ in 1-butanol			$Zn(ClO_4)_2$ in 1-butanol		
$\Delta\bar{H}$	$\bar{n}$	$(L)x10^2$	$\Delta\bar{H}$	$\bar{n}$	$(L)x10^2$	$\Delta\bar{H}$	$\bar{n}$	$(L)x10^2$
			2600	0.81	1.78	2600	1.02	3.13
			2700	0.84	1.93	2700	1.07	3.34
			2800	0.88	2.07	2800	1.12	3.56
			2900	0.91	2.23	2900	1.16	3.89
			3000	0.94	2.41	3000	1.21	4.15
			3100	0.97	2.60	3100	1.25	4.48
			3200	1.00	2.79	3200	1.30	4.84
			3300	1.03	2.99	3300	1.36	5.15
			3400	1.06	3.22	3400	1.39	5.56
			3500	1.09	3.46	3500	1.46	5.86
			3600	1.12	3.70	3600	1.51	6.26
						3700	1.57	6.69
						3800	1.63	7.16
						3900	1.71	7.62
						4000	1.79	8.12
						4100	1.87	8.66
						4200	1.94	9.31
						4300	2.02	9.84

APPENDIX D

TABLE IX

ENTHALPY TITRATION DATA TO HIGH WATER CONCENTRATION

25.990 grams of 0.0161 M $Cu(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0280	+2.85	-2151
0.0480	+1.03	-3409
0.0680	-0.14	-4286
0.0880	-0.82	-4941
0.1080	-1.32	-5433
0.1280	-1.60	-5832
0.1480	-1.86	-6145
0.1680	-2.03	-6402
0.1880	-2.14	-6621
0.2080	-2.26	-6800
0.2280	-2.37	-6942
0.2480	-2.33	-7096
0.2680	-2.40	-7225
0.2880	-2.53	-7311
0.3080	-2.58	-7379
0.3280	-2.58	-7445
0.3480	-2.66	-7484
0.3680	-2.62	-7534
0.3880	-2.42	-7651
0.4080	-2.65	-7689
0.4280	-2.68	-7761
0.4480	-2.67	-7745
0.4680	-2.68	-7770
0.4880	-2.72	-7780
0.5080	-2.63	-7818
0.5280	-2.72	-7826
0.5480	-2.72	-7832
0.5680	-2.66	-7857
0.5880	-2.74	-7845
0.6080	-2.66	-7876
0.6280	-2.68	-7891
0.6480	-2.68	-7904
0.6680	-2.65	-7927
0.7880	-2.62	-8031
0.8080	-2.58	-8069
0.8280	-2.59	-8102
0.8480	-2.55	-8147
0.8680	-2.54	-8195
0.8880	-2.57	-8305
0.9080	-2.46	-8306
0.9280	-2.47	-8373
0.9480	-2.47	-8441
0.9680	-2.47	-8507
0.9880	-2.51	-8558
1.0080	-2.38	-8653
1.0280	-2.38	-8748
1.0480	-2.43	-8823
1.0680	-2.38	-8915
1.0880	-2.40	-8999
1.1080	-2.32	-9109
1.1280	-2.33	-9115
1.1480	-2.32	-9324
1.1680	-2.32	-9431
1.1880	-2.28	-9551
1.2080	-2.23	-9688
1.2280	-2.08	-9877
1.2480	-2.25	-10005
1.2680	-2.18	-10156
1.2880	-2.18	-10307
1.3080	-2.16	-10464
1.3280	-2.18	-10612
1.3480	-2.12	-10718
1.3680	-2.08	-10963
1.3880	-2.06	-11151
1.4080	-2.06	-11379
1.4280	-2.07	-11521
1.5480	-1.92	-12806
1.5680	-1.89	-13047
1.5880	-1.93	-13273
1.6080	-1.83	-13533
1.6280	-1.83	-13793
1.6480	-1.84	-14040
1.6680	-1.77	-14329
1.6880	-1.83	-14587
1.7080	-1.74	-14876
1.7280	-1.73	-15168
1.7480	-1.73	-15460
1.7680	-1.68	-15769
1.7880	-1.72	-16062
1.8080	-1.66	-16377
1.8280	-1.66	-16691
1.8480	-1.69	-16993
1.8680	-1.62	-17320
1.8880	-1.63	-17643
1.9080	-1.59	-17979
1.9280	-1.57	-18323
1.9480	-1.59	-18658
1.9680	-1.52	-19018
1.9880	-1.53	-19374
2.0080	-1.53	-19729
2.0280	-1.52	-20087
2.0480	-1.47	-20463
2.0680	-1.43	-20847
2.0880	-1.49	-20221
2.1080	-1.43	-20610
2.1280	-1.42	-22002
2.1480	-1.41	-22397
2.1680	-1.35	-22814
2.1880	-1.37	-23223

TABLE IX (Continued)

ml H_2O	s, in.	$\Delta\bar{H}$	ml H_2O	s, in.	$\Delta\bar{H}$	ml H_2O	s, in.	$\Delta\bar{H}$
0.6880	-2.73	-7921	1.4480	-2.03	-11718	2.2080	-1.29	-23661
0.7080	-2.63	-7947	1.4680	-2.03	-11913	2.2280	-1.32	-24087
0.7280	-2.65	-7966	1.4880	-2.02	-12110	2.2480	-1.33	-24509
0.7480	-2.66	-7980	1.5080	-1.88	-12357	2.2680	-1.38	-24912
0.7680	-2.62	-8006	1.5280	-1.96	-12575			

TABLE IX (Continued)

26.081 grams of 0.0598 M $Cu(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0180	+2.87	- 893
0.0280	+2.82	-1381
0.0380	+2.63	-1841
0.0480	+2.34	-2271
0.0580	+2.13	-2671
0.0680	+1.88	-3039
0.0780	+1.58	-3368
0.0880	+1.41	-3676
0.0980	+1.18	-3954
0.1080	+1.15	-4229
0.1180	+0.89	-4470
0.1280	+0.69	-4685
0.1380	+0.58	-4886
0.1480	+0.43	-5086
0.1580	+0.33	-5237
0.1680	+0.24	-5394
0.1780	+0.17	-5524
0.1880	+0.08	-5678
0.1980	+0.05	-5811
0.2080	-0.05	-5930
0.2280	-0.28	-6146
0.2480	-0.46	-6337
0.2680	-0.62	-6508
0.2880	-0.74	-6662
0.3080	-0.87	-6800
0.3280	-0.97	-6924
0.3480	-1.00	-7043
0.3680	-1.18	-7139
0.3880	-1.16	-7237
0.4080	-1.29	-7138
0.4280	-1.28	-7399
0.4480	-1.30	-7478
0.4680	-1.39	-7544
0.4880	-1.33	-7618
0.5080	-1.43	-7678
0.5280	-1.47	-7733
0.5480	-1.42	-7794
0.5680	-1.53	-7839
0.5880	-1.51	-7887
0.6080	-1.48	-7939
0.6280	-1.58	-7977
0.6480	-1.53	-8021
0.6680	-1.58	-8050
0.6880	-1.56	-8098
0.7080	-1.63	-8127
0.7280	-1.63	-8156
0.7480	-1.53	-8199
0.7780	-2.43	-8243
0.8080	-2.35	-8298
0.8380	-2.43	-8340
0.8680	-2.42	-8383
0.8980	-2.34	-8437
0.9280	-2.45	-8474
0.9580	-2.32	-8528
0.9880	-2.36	-8576
1.0180	-2.37	-8622
1.0480	-2.27	-8681
1.0780	-2.37	-8725
1.1080	-2.21	-8790
1.1380	-2.33	-8838
1.1680	-2.25	-8857
1.1980	-2.23	-8957
1.2280	-2.23	-9017
1.2580	-2.13	-9090
1.2880	-2.14	-9160
1.3180	-2.16	-9227
1.3480	-2.12	-9299
1.3780	-2.08	-9377
1.4080	-2.02	-9462
1.4380	-2.03	-9545
1.4680	-2.03	-9628
1.4980	-1.96	-9720
1.5280	-1.97	- 9810
1.5480	-1.87	- 9913
1.5880	-1.90	-10012
1.6180	-1.92	-10170
1.6480	-1.89	-10205
1.6780	-1.83	-10312
1.7080	-1.75	-10431
1.7380	-1.75	-10549
1.7680	-1.82	-10665
1.7980	-1.73	-10775
1.8280	-1.74	-10892
1.8580	-1.63	-11025
1.8880	-1.66	-11153
1.9180	-1.67	-11279
1.9480	-1.58	-11417
1.9780	-1.58	-11556
2.0080	-1.54	-11699
2.0380	-1.57	-11838
2.0680	-1.53	-11982
2.0980	-1.46	-12137
2.1280	-1.50	-12284
2.1580	-1.40	-12442
2.1880	-1.46	-12595
2.2180	-1.42	-12754
2.2480	-1.36	-12921
2.2780	-1.38	-13085
2.3080	-1.30	-13260
2.3380	-1.36	-13426
2.3680	-1.33	-13496
2.3980	-1.24	-13780
2.4280	-1.29	-13995
2.4580	-1.22	-14141
2.4880	-1.27	-14319
2.5180	-1.20	-14507
2.5480	-1.17	-14699

TABLE IX (Continued)

27.434 grams of 0.0216 M $Ca(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$	ml H_2O	s, in.	$\Delta\bar{H}$	ml H_2O	s, in.	$\Delta\bar{H}$
0.0200	-0.57	- 513	0.7600	-2.33	-5579	1.5000	-1.85	- 8800
0.0400	-0.87	- 952	0.7800	-2.29	-5634	1.5200	-1.90	- 8931
0.0600	-1.08	-1338	0.8000	-2.33	-5677	1.5400	-1.84	- 9077
0.0800	-1.18	-1699	0.8200	-2.30	-5728	1.5600	-1.79	- 9237
0.1000	-1.33	-2022	0.8400	-2.29	-5780	1.5800	-1.77	- 9402
0.1200	-1.49	-2305	0.8600	-2.31	-5826	1.6000	-1.87	- 9539
0.1400	-1.52	-2579	0.8800	-2.28	-5880	1.6200	-1.76	- 9705
0.1600	-1.67	-2816	0.9000	-2.30	-5927	1.6400	-1.75	- 9873
0.1800	-1.67	-3051	0.9200	-2.28	-5978	1.6600	-1.68	-10060
0.2000	-1.77	-3261	0.9400	-2.28	-6029	1.6800	-1.70	-10241
0.2200	-1.82	-3458	0.9600	-2.28	-6079	1.7000	-1.68	-10427
0.2400	-1.90	-3634	0.9800	-2.19	-6152	1.7200	-1.60	-10635
0.2600	-1.96	-3794	1.0000	-2.30	-6194	1.7400	-1.63	-10834
0.2800	-2.02	-3939	1.0200	-2.16	-6274	1.7600	-1.52	-11063
0.3000	-2.03	-4080	1.0400	-2.20	-6341	1.7800	-1.66	-11252
0.3200	-2.09	-4205	1.0600	-2.04	-6451	1.8000	-1.58	-11463
0.3400	-2.12	-4321	1.0800	-2.15	-6530	1.8200	-1.57	-11676
0.3600	-2.18	-4422	1.1000	-2.09	-6624	1.8400	-1.57	-11888
0.3800	-2.14	-4532	1.1200	-2.16	-6701	1.8600	-1.48	-12126
0.4000	-2.21	-4624	1.1400	-2.23	-6756	1.8800	-1.52	-12351
0.4200	-2.17	-4724	1.1600	-2.10	-6846	1.9000	-1.53	-12574
0.4400	-2.24	-4806	1.1800	-2.10	-6935	1.9200	-1.47	-12812
0.4600	-2.24	-4887	1.2000	-2.12	-7018	1.9400	-1.49	-13045
0.4800	-2.31	-4950	1.2200	-2.12	-7100	1.9600	-1.43	-13294
0.5000	-2.28	-5019	1.2400	-2.00	-7214	1.9800	-1.47	-13530
0.5200	-2.33	-5074	1.2600	-2.02	-7321	2.0000	-1.48	-13764
0.5400	-2.38	-5116	1.2800	-1.96	-7444	2.0200	-1.43	-14003
0.5600	-2.27	-5185	1.3000	-2.02	-7550	2.0400	-1.43	-14248
0.5800	-2.30	-5246	1.3200	-1.87	-7696	2.0600	-1.42	-14498
0.6000	-2.37	-5287	1.3400	-2.02	-7801	2.0800	-1.42	-14747
0.6200	-2.41	-5318	1.3600	-2.03	-7902	2.1000	-1.38	-15006
0.6400	-2.33	-5368	1.3800	-1.97	-8019	2.1200	-1.45	-15245
0.6600	-2.34	-5415	1.4000	-1.93	-8146	2.1400	-1.30	-15527
0.6800	-2.38	-5451	1.4200	-1.93	-8272	2.1600	-1.35	-15757
0.7000	-2.36	-5491	1.4400	-1.95	-8391	2.1800	-1.33	-16065
0.7200	-2.38	-5525	1.4600	-1.92	-8519	2.2000	-1.33	-16336
0.7400	-2.47	-5534	1.4800	-1.89	-8654			

TABLE IX (Continued)

25.732 grams of 0.0407 M $Ca(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0200	+0.44	- 441
0.0400	+0.13	- 834
0.0600	-0.10	-1190
0.0800	-0.27	-1519
0.1000	-0.46	-1818
0.1200	-0.60	-2095
0.1400	-0.74	-2349
0.1600	-0.84	-2587
0.1800	-0.94	-2809
0.2000	-1.11	-3003
0.2200	-1.12	-3196
0.2400	-1.32	-3356
0.2600	-1.33	-3514
0.2800	-1.38	-3664
0.3000	-1.39	-3811
0.3200	-1.52	-3938
0.3400	-1.55	-4059
0.3600	-1.57	-4176
0.3800	-1.62	-4284
0.4000	-1.62	-4393
0.4200	-1.72	-4484
0.4400	-1.72	-4575
0.4600	-1.77	-4658
0.5800	-1.83	-4730
0.5000	-1.76	-4813
0.5200	-1.83	-4884
0.5400	-1.84	-4953
0.5600	-1.91	-5009
0.5800	-1.94	-5061
0.6000	-1.80	-5134
0.6200	-1.96	-5181
0.6400	-1.88	-5241
0.6600	-1.89	-5298
0.6800	-1.93	-5349
0.7000	-1.90	-5403
0.7200	-1.97	-5446
0.7400	-1.88	-5503
0.7600	-1.93	-5551
0.7800	-1.96	-5693
0.8000	-1.87	-5651
0.8200	-1.94	-5695
0.8400	-1.88	-5750
0.8600	-1.93	-5796
0.8800	-1.93	-5841
0.9000	-1.87	-5895
0.9200	-1.87	-5949
0.9400	-1.83	-6009
0.9600	-1.84	-6067
0.9800	-1.92	-6111
1.000	-1.82	-6172
1.0200	-1.89	-6220
1.0400	-1.82	-6279
1.0600	-1.78	-6345
1.0800	-1.87	-6395
1.1000	-1.77	-6461
1.1200	-1.81	-6520
1.1400	-1.73	-6593
1.1600	-1.77	-6658
1.1800	-1.78	-6721
1.2000	-1.68	-6801
1.2200	-1.72	-6873
1.2400	-1.68	-6952
1.2600	-1.70	-7026
1.2800	-1.75	-7092
1.3000	-1.62	-7180
1.3200	-1.67	-7259
1.3400	-1.61	-7348
1.3600	-1.68	-7434
1.3800	-1.68	-7510
1.4000	-1.55	-7608
1.4200	-1.61	-7702
1.4400	-1.57	-7788
1.4600	-1.56	-7883
1.4800	-1.58	-7974
1.5000	-1.47	-8085
1.5200	-1.52	-8185
1.5400	-1.52	-8286
1.5600	-1.49	-8391
1.5800	-1.52	- 8490
1.6000	-1.38	- 8615
1.6200	-1.47	- 8722
1.6400	-1.42	- 8838
1.6600	-1.37	- 8963
1.6800	-1.41	- 9081
1.7000	-1.32	- 9214
1.7200	-1.33	- 9345
1.7400	-1.33	- 9475
1.7600	-1.32	- 9607
1.7800	-1.37	- 9730
1.8000	-1.27	- 9857
1.8200	-1.30	-10004
1.8400	-1.28	-10143
1.8600	-1.25	-10286
1.8800	-1.28	-10423
1.9000	-1.19	-10576
1.9200	-1.26	-10710
1.9400	-1.22	-10864
1.9600	-1.22	-11010
1.9800	-1.26	-11150
2.0000	-1.15	-11309
2.0200	-1.20	-11458
2.0400	-1.17	-11613
2.0600	-1.13	-11775
2.0800	-1.16	-11930
2.1000	-1.08	-12101
2.1200	-1.12	-12264
2.1400	-1.08	-12430
2.1600	-1.07	-12605
2.1800	-1.10	-12771
2.2000	-1.03	-12949
2.2200	-1.07	-13120
2.2400	-1.02	-13300
2.260	-1.02	-13479
2.2800	-1.02	-13658
2.3000	-0.97	-13847

TABLE IX (Continued)

25.921 grams of 0.0166 M $Zn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+1.10	- 653
0.0100	+0.82	-1197
0.0200	+0.96	-2020
0.0300	+0.43	-2637
0.0500	+0.08	-3118
0.0600	-0.52	-3812
0.0800	-1.01	-4314
0.1000	-1.38	-4669
0.1200	-1.52	-4969
0.1400	-1.77	-5168
0.1600	-1.85	-5455
0.1800	-1.97	-5453
0.2000	-1.97	-5570
0.2200	-1.99	-5677
0.2400	-2.08	-5747
0.2600	-2.10	-5808
0.2800	-2.07	-5880
0.3000	-2.14	-5923
0.3200	-2.12	-5972
0.3400	-2.15	-6008
0.3600	-2.18	-6031
0.3800	-2.17	-6056
0.4000	-2.22	-6061
0.4200	-2.23	-6060
0.4400	-2.21	-6066
0.4600	-2.22	-6070
0.4800	-2.21	-6070
0.5000	-2.19	-6081
0.5200	-2.22	-6078
0.5400	-2.18	-6090
0.5600	-2.17	-6105
0.5800	-2.17	-6119
0.6000	-2.22	-6111
0.6200	-2.14	-6134
0.6400	-2.18	-6140
0.6600	-2.22	-6128
0.6800	-2.05	-6184
0.7000	-2.18	-6185
0.7200	-2.17	-6189
0.7400	-2.18	-6187
0.7600	-2.14	-6201
0.7800	-2.06	-6246
0.8000	-2.12	-6256
0.8200	-2.08	-6300
0.8400	-2.04	-6349
0.8600	-2.06	-6390
0.8800	-1.94	-6478
0.9000	-2.03	-6528
0.9200	-2.02	-6581
0.9400	-1.96	-6656
0.9600	-1.97	-6729
0.9800	-1.88	-6837
1.0000	-1.95	-6914
1.0200	-1.91	-7007
1.0400	-1.90	-7103
1.0600	-1.90	-7197
1.0800	-1.82	-7324
1.1000	-1.88	-7425
1.1200	-1.83	-7545
1.1400	-1.78	-7686
1.1600	-1.85	-7796
1.1800	-1.74	-7951
1.2000	-1.77	-8092
1.2200	-1.73	-8249
1.2400	-1.68	-8427
1.2600	-1.76	-8569
1.2800	-1.72	-8728

TABLE IX (Continued)

26.971 grams of 0.0717 M $Zn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0500	+2.45	- 274
0.0100	+2.16	- 522
0.0150	+1.76	- 734
0.0200	+1.96	- 964
0.0300	+3.92	-1423
0.0400	+3.15	-1813
0.0600	+5.13	-2486
0.0800	+3.54	-3014
0.1000	+2.52	-3450
0.1200	+1.72	-3811
0.1400	+1.00	-4107
0.1600	+0.48	-4355
0.1800	+0.04	-4563
0.2000	-0.27	-4742
0.2200	-0.57	-4893
0.2400	-0.78	-5025
0.2600	-0.96	-5140
0.2800	-1.10	-5242
0.3000	-1.21	-5334
0.3200	-1.33	-5414
0.3400	-1.37	-5490
0.3600	-1.54	-5551
0.3800	-1.54	-5611
0.4000	-1.57	-5668
0.4200	-1.63	-5720
0.4400	-2.00	-5738
0.4600	-1.86	-5769
0.4800	-1.82	-5804
0.5000	-1.72	-5848
0.5200	-1.66	-5897
0.5400	-1.80	-5933
0.5600	-1.84	-5965
0.5800	-1.84	-5997
0.6000	-1.84	-6029
0.6200	-1.83	-6062
0.6400	-1.86	-6092
0.6600	-1.88	-6120
0.6800	-1.94	-6142
0.7000	-1.97	-6161
0.7200	-1.89	-6187
0.7400	-1.93	-6209
0.7600	-1.67	-6256
0.7800	-1.80	-6290
0.8000	-1.75	-6329
0.8200	-1.83	-6360
0.8400	-1.87	-6387
0.8600	-1.83	-6418
0.8800	-1.91	-6441
0.9000	-1.90	-6465
0.9200	-1.92	-4686
0.9400	-1.87	-6512
0.9600	-1.78	-6547
0.9800	-1.84	-6576
1.0000	-1.90	-6598
1.0200	-1.84	-6626
1.0400	-1.79	-6659
1.0600	-1.82	-6689
1.0800	-1.81	-6719
1.1000	-1.82	-6749
1.1200	-1.74	-6785
1.1400	-1.82	-6814
1.1600	-1.75	-6849
1.1800	-1.72	-6887
1.2000	-1.74	-6923
1.2200	-1.63	-6964
1.2400	-1.72	-7002
1.2600	-1.67	-7044
1.2800	-1.66	-7086
1.3000	-1.73	-7122
1.3200	-1.64	-7166
1.3400	-1.73	-7201
1.3600	-1.62	-7247
1.3800	-1.62	-7292
1.4000	-1.60	-7339
1.4200	-1.56	-7390
1.4400	-1.61	-7436
1.4600	-1.53	-7489
1.4800	-1.57	-7538
1.5000	-1.52	-7591
1.5200	-1.44	-7653
1.5400	-1.54	-7705
1.5600	-1.42	-7767
1.5800	-1.48	-7824
1.6000	-1.43	-7886

TABLE IX (Continued)

27.628 grams of 0.0181 M $Mn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+0.73	- 451
0.0100	+0.56	- 843
0.0200	+0.58	-1435
0.0300	+0.33	-1939
0.0400	+0.12	-2369
0.0600	-0.28	-3045
0.0800	-0.78	-3542
0.1000	-1.08	-3932
0.1200	-1.32	-4235
0.1400	-1.46	-4487
0.1600	-1.59	-4691
0.1800	-1.68	-4864
0.2000	-1.73	-5017
0.2200	-1.92	-5100
0.2400	-1.92	-5222
0.2600	-1.98	-5291
0.2800	-1.89	-5381
0.3000	-1.96	-5445
0.3200	-2.04	-5479
0.3400	-1.94	-5548
0.3600	-2.03	-5583
0.3800	-2.06	-5606
0.4000	-2.00	-5649
0.4200	-2.04	-5677
0.4400	-2.03	-5707
0.4600	-2.10	-5710
0.4800	-2.05	-5730
0.5000	-2.02	-5761
0.5200	-2.10	-5761
0.5400	-2.03	-5786
0.5600	-2.04	-5806
0.5800	-2.08	-5810
0.6000	-.204	-5827
0.6200	-2.08	-5829
0.6400	-2.06	-5837
0.6600	-2.06	-5844
0.6800	-2.12	-5827
0.7000	-1.98	-5862
0.7200	-2.02	-5880
0.7400	-1.96	-5921
0.7600	-2.10	-5907
0.7800	-2.02	-5922
0.8000	-2.00	-5944
0.8200	-2.02	-5957
0.8400	-1.96	-5992
0.8600	-2.03	-5999
0.8800	-1.93	-6043
0.9000	-1.93	-6085
0.9200	-1.95	-6120
0.9400	-1.88	-6179
0.9600	-1.93	-6219
0.9800	-1.88	-6276
1.0000	-1.82	-6330
1.0200	-1.92	-6396
1.0400	-1.82	-6473
1.0600	-1.86	-6534
1.0800	-1.88	-6586
1.1000	-1.83	-6657
1.1200	-1.78	-6746
1.1400	-1.74	-6849
1.1600	-1.79	-6932
1.1800	-1.74	-7034
1.2000	-1.70	-7150
1.2200	-1.73	-7253
1.2400	-1.75	-7348

TABLE IX (Continued)

27.229 grams of 0.0639 M $Mn(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+1.82	- 240
0.0100	+1.56	- 453
0.0200	+2.26	- 794
0.0300	+2.23	-1132
0.0400	+2.28	-1475
0.0600	+3.34	-2038
0.0800	+2.38	-2505
0.1000	+1.82	-2915
0.1200	+1.13	-3256
0.1400	+0.64	-3546
0.1600	+0.25	-3797
0.1800	-0.10	-4013
0.2000	-0.36	-4201
0.2200	-0.60	-4365
0.2400	-0.83	-4505
0.2600	-0.96	-4632
0.2800	-1.09	-4745
0.3000	-1.22	-4844
0.3200	-1.34	-4931
0.3400	-1.40	-5012
0.3600	-1.43	-5089
0.3800	-1.52	-5157
0.4000	-1.62	-5214
0.4200	-1.62	-5270
0.4400	-1.64	-5325
0.4600	-1.76	-5367
0.4800	-1.68	-5416
0.5000	-1.84	-5449
0.5200	-1.78	-5488
0.5400	-1.83	-5522
0.5600	-1.87	-5551
0.5800	-1.84	-5583
0.6000	-1.87	-5611
0.6200	-1.81	-5646
0.6400	-1.97	-5663
0.6600	-1.92	-5686
0.6800	-1.79	-5722
0.7000	-1.91	-5745
0.7200	-1.92	-5767
0.7400	-1.93	-5787
0.7600	-1.93	-5808
0.7800	-1.88	-5833
0.8000	-1.88	-5858
0.8200	-1.92	-5879
0.8400	-1.90	-5901
0.8600	-1.87	-5927
0.8800	-1.92	-5947
0.9000	-1.91	-5968
0.9200	-1.87	-5993
0.9400	-1.86	-6018
0.9600	-1.87	-6043
0.9800	-1.85	-6069
1.0000	-1.83	-6097
1.0200	-1.87	-6121
1.0400	-1.82	-6150
1.0600	-1.78	-6183
1.0800	-1.78	-6216
1.1000	-1.77	-6250
1.1200	-1.76	-6284
1.1400	-1.76	-6319
1.1600	-1.77	-6352
1.1800	-1.74	-6388
1.2000	-1.73	-6425
1.220	-1.67	-6468
1.2400	-1.68	-6511
1.2600	-1.72	-6548
1.2800	-1.72	-6586
1.3000	-1.66	-6629
1.3200	-1.72	-6666
1.3400	-1.67	-6708
1.3600	-1.65	-6753
1.3800	-1.64	-6798
1.4000	-1.64	-6843
1.4200	-1.57	-6910
1.4400	-1.57	-6977
1.4600	-1.62	-7039
1.4800	-1.56	-7107
1.5000	-1.58	-7172
1.5200	-1.56	-7240
1.5400	-1.55	-7308
1.5600	-1.52	-7379
1.5800	-1.47	-7455
1.6000	-1.48	-7530
1.6200	-1.44	-7609
1.6400	-1.43	-7688
1.6600	-1.43	-7768
1.6800	-1.44	-7846
1.7000	-1.43	-7925

TABLE IX (Continued)

27.993 grams of 0.0250 M $Sr(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{\bar{H}}$	ml H_2O	s, in.	$\Delta\bar{\bar{H}}$
0.0076	-0.40	- 108	0.6776	-1.96	-3745
0.0176	-0.53	- 249	0.6976	-1.96	-3774
0.0276	-0.56	- 382	0.7176	-1.85	-3832
0.0376	-0.58	- 509	0.7376	-1.93	-3868
0.0576	-1.16	- 765	0.7576	-1.87	-3921
0.0776	-1.27	- 991	0.7776	-1.93	-3956
0.0976	-1.29	-1212	0.7976	-1.96	-3982
0.1176	-1.35	-1416	0.8186	-1.92	-4019
0.1376	-1.42	-1603	0.8376	-1.94	-4050
0.1576	-1.47	-1775	0.8576	-1.86	-4102
0.1776	-1.47	-1948	0.8776	-1.87	-4150
0.1976	-1.57	-2093	0.8976	-1.87	-4198
0.2176	-1.58	-2236	0.9176	-1.89	-4240
0.2376	-1.66	-2357	0.9376	-1.87	-4287
0.2576	-1.69	-2470	0.9576	-1.85	-4339
0.2776	-1.76	-2564	0.9776	-1.79	-4407
0.2976	-1.73	-2666	0.9976	-1.86	-4455
0.3176	-1.77	-2756	1.0176	-1.75	-4532
0.3376	-1.78	-2844	1.0376	-1.77	-4604
0.3576	-1.82	-2920	1.0576	-1.79	-4670
0.3776	-1.84	-2991	1.0776	-1.75	-4746
0.3976	-1.84	-3061	1.0976	-1.80	-4808
0.4176	-1.84	-3130	1.1176	-1.72	-4891
0.4376	-1.90	-3183	1.1376	-1.73	-4971
0.4576	-1.90	-3236	1.1576	-1.76	-5042
0.4776	-1.89	-3290	1.1776	-1.69	-5132
0.4976	-1.86	-3352	1.1976	-1.73	-5210
0.5176	-1.89	-3406	1.2176	-1.70	-5297
0.5376	-1.92	-3450	1.2376	-1.67	-5391
0.5576	-1.96	-3484	1.2576	-1.71	-5473
0.5776	-1.86	-3544	1.2776	-1.59	-5588
0.5976	-1.89	-3596	1.2976	-1.64	-5689
0.6176	-1.93	-3635	1.3176	-1.58	-5806
0.6376	-1.90	-3682	1.3376	-1.62	-5912
0.6576	-1.95	-3716	1.3576	-1.62	-6017

TABLE IX (Continued)

25.932 grams of 0.0121 M $Mg(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{H}$	ml H_2O	s, in.	$\Delta\bar{H}$
0.0050	+1.50	-1147	0.5000	-2.28	-6135
0.0100	+0.72	-1852	0.5200	-2.23	-6112
0.0200	+0.78	-2913	0.5400	-2.23	-6087
0.0300	+0.14	-3608	0.5600	-2.22	-6066
0.0400	-0.22	-4100	0.5800	-2.16	-6078
0.0600	-1.02	-4758	0.6000	-2.20	-6064
0.0800	-1.42	-5183	0.6200	-2.15	-6079
0.1000	-1.67	-5512	0.6400	-2.17	-6080
0.1200	-1.82	-5757	0.6600	-2.15	-6091
0.1400	-1.90	-5955	0.6800	-2.09	-6135
0.1600	-1.98	-6108	0.7000	-2.15	-6144
0.1800	-2.07	-6208	0.7200	-2.10	-6180
0.2000	-2.09	-6295	0.7400	-2.05	-6243
0.2200	-2.14	-6353	0.7600	-2.05	-6306
0.2400	-2.21	-6369	0.7800	-2.05	-6367
0.2600	-2.13	-6427	0.8000	-2.08	-6410
0.2800	-2.22	-6434	0.8200	-2.07	-6458
0.3000	-2.20	-6449	0.8400	-2.06	-6510
0.3200	-2.26	-6429	0.8600	-2.05	-6568
0.3400	-2.28	-6396	0.8800	-1.97	-6670
0.3600	-2.22	-6394	0.9000	-2.02	-6742
0.3800	-2.27	-6362	0.9200	-1.95	-6854
0.4000	-2.19	-6373	0.9400	-1.92	-6981
0.4200	-2.24	-6354	0.9600	-1.98	-7073
0.4400	-2.30	-6299	0.9800	-1.90	-7211
0.4600	-2.32	-6231	1.0000	-1.97	-7307
0.4800	-2.28	-6184			

TABLE IX (Continued)

27.515 grams of 0.0629 M $Mg(ClO_4)_2$

ml H_2O	s, in.	$\Delta\bar{\bar{H}}$	ml H_2O	s, in.	$\Delta\bar{\bar{H}}$
0.0050	+3.97	- 462	0.6500	-1.83	-7203
0.0100	+2.90	- 815	0.6700	-1.88	-7225
0.0150	+2.63	-1140	0.6900	-1.83	-7252
0.0200	+2.18	-1419	0.7100	-1.83	-7278
0.0300	+4.41	-1984	0.7300	-1.92	-7295
0.0400	+3.96	-2504	0.7500	-1.82	-7322
0.0500	+3.52	-2978	0.7700	-1.90	-7340
0.0700	+5.23	-3743	0.7900	-1.87	-7361
0.0900	+3.43	-4323	0.8100	-1.84	-7386
0.1100	+2.27	-4784	0.8300	-1.84	-7410
0.1300	+1.31	-5146	0.8500	-1.85	-7432
0.1500	+0.63	-5437	0.8700	-1.82	-7458
0.1700	+0.11	-5675	0.8900	-1.86	-7478
0.1900	-0.27	-5873	0.9100	-1.84	-7501
0.2100	-0.58	-6038	0.9300	-1.85	-7523
0.2300	-0.79	-6181	0.9500	-1.78	-7552
0.2500	-0.98	-6304	0.9700	-1.79	-7552
0.2700	-1.14	-6410	0.9900	-1.76	-7610
0.2900	-1.32	-6496	1.0100	-1.77	-7639
0.3100	-1.34	-6581	1.0300	-1.78	-7666
0.3300	-1.52	-6645	1.0500	-1.75	-7696
0.3500	-1.52	-6710	1.0700	-1.76	-7726
0.3700	-1.52	-6774	1.0900	-1.70	-7762
0.3900	-1.67	-6823	1.1100	-1.72	-7795
0.4100	-1.71	-6866	1.1300	-1.68	-7832
0.4300	-1.71	-6918	1.1500	-1.72	-7865
0.4500	-1.74	-6958	1.1700	-1.73	-7896
0.4700	-1.77	-6994	1.1900	-1.67	-7934
0.4900	-2.05	-7000	1.2100	-1.68	-7970
0.5100	-1.87	-7025	1.2300	-1.68	-8006
0.5300	-1.86	-7051	1.2500	-1.64	-8046
0.5500	-1.83	-7080	1.2700	-1.66	-8084
0.5700	-1.81	-7111	1.2900	-1.64	-8123
0.5900	-1.91	-7130	1.3100	-1.61	-8166
0.6100	-1.87	-7154	1.3300	-1.63	-8207
0.6300	-1.89	-7175	1.3500	-1.62	-8248

APPENDIX E

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_{mix} = experimental heat of mixing of L with 1-butanol

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

$\bar{H}^o_L$ = standard molar enthalpy of pure liquid L

$\bar{H}_L$ = partial molar enthalpy of L in binary solution at concentration C_L

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

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

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

$\bar{H}$ = molar heat of reaction of L with M

β_n = overall formation constant of complex ML_n

h_n = overall enthalpy of formation of complex ML_n

S_n = overall entropy of formation of complex ML_n

α_n = concentration fraction of M complexed as ML_n

$\bar{n}$ = average ligand number

(L) = free ligand concentration

ERR = standard error of estimate of a pair of $\bar{n}$, (L) values

P = average fractional error of data set

σ = standard deviation

GLOSSARY (Continued)

σ^2 = variance

W = weight of an experimental point

S_{min} = minimum sum of squares

γ = index of preferential solvation

R = truncation error

Λ = equivalent conductance

L_s = specific conductance

r_i = ionic radius

k_n = constant for formation of ML_n from ML_{n-1}

g_n = overall free energy of formation of ML_n

K_{av} = average formation constant

n = number of moles

y = moles of ligand L

z = moles of metal M

X^- = perchlorate anion

S = molecule of solvent

w_{np} = concentration fraction of M as ML_nX_p

C_p = heat capacity in calories/inch

i = amperes

E = voltage

t = time in seconds

s = distance of recorder pen travel in inches

V = volume of solution

ε = dielectric constant

μ = dipole moment

$\bar{h}$ = average binding energy

VITA

Gordon Foy Wallace

Candidate for the Degree of

Doctor of Philosophy

Thesis: A THERMODYNAMIC STUDY OF THE AQUOCOMPLEX FORMATION OF SELECTED FIRST ROW TRANSITION AND ALKALINE EARTH METAL PERCHLORATES IN 1-BUTANOL

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