THERMODYNAMICS OF TRANSFER OF COBALT(II), NICKEL(II), AND COPPER(II) PERCHLORATES FROM AQUEOUS TO 1-BUTANOL PHASES AT EXTRACTION EQUILIBRIUM

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Fort Collins, Colorado

1964

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, 1967

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ACKNOWLEDGMENT

I wish to express my appreciation to Dr. Tom E. Moore for his advice and guidance throughout the research and assistance with reading the entire manuscript. I wish to thank Dr. C. M. Cunningham for his counsel on conductance measurements. I also wish to thank my parents for their help and encouragement.

I am grateful to my wife, Evangeling, for her patience and encouragement.

This study 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

INTRODUCTION

The liquid-liquid extraction system involving water, a transition-metal perchlorate salt and a partially miscible monohydroxyl alcohol is a system of two phases in which water is the primary solvating agent of the salt. An example is the extraction of cobalt and nickel perchlorates by 2-octanol (35). The solvation is more complete when the anion has very little tendency to associate with the cation. Thus the perchlorates are better extracted than the chlorides (31,33,35), probably because chloride ions may displace the solvating molecules from the first coordinate sphere around the metal. This is shown by the thousand-fold better extraction of zinc chloride by 2-octanol compared with that of cadmium chloride (36), the latter showing much higher association between cation and anion.

The study reported here includes the measurement of the concentration dependence of the distribution coefficients of copper, nickel, and cobalt perchlorates at small concentrations and calorimetric measurements of the enthalpies of transfer of the metal salts from aqueous phases to the equilibrium 1-butanol phases. This was also accompanied by a study of the electrical conductance and the viscosity of the solutions in both equilibrium phases.

It is the objective of this study to obtain additional information about ion-solvent interactions which would lead, hopefully, to a useful structural model that would permit a better understanding of the extraction phenomena.

CHAPTER II

LITERATURE SURVEY

Properties and Structures of Solvents - The ability of water to act as the "universal" solvent has been ascribed to its dipole character. Spectroscopic studies of the isolated water molecule in the gaseous state (32) have established that the H-O-H bond angle is 105°, and the O-H internuclear distance 0.97 Å. The isolated molecule has a dipole moment of 1.87×10^{-18} e.s.u. acting along the bisector of the H-O-H angle with the negative end towards the oxygen nucleus. This dipole moment was considered by Bernal and Fowler (9) to arise from an effective charge of -e situated 0.15 Å from the oxygen nucleus, with +0.5e at each hydrogen nucleus. A more elaborate model, due to Verwey (50), in which the tripolar charge distribution of Bernal and Fowler is replaced by a quadrapole arrangement, has led to a very satisfactory prediction of the lattice energy of the ice crystal.

The distinctive structural features of liquid water (46) generally have been ascribed to its partial retention of the tetrahedrally directed hydrogen-bonding involved in the crystalline structure of ice. Not only are the orientations of the water molecules far from random, but the molecules oscillate torsionally with rather small amplitudes instead of rotating freely.

The above view of water structure is supported strongly by the results of X-ray scattering experiments and of studies of the infrared and Raman absorption spectra (27), which indicate that a considerable degree of short-range order and the low coordination characteristic of the tetrahedrally-bonded structure persist in the liquid. Thus, X-ray scattering studies indicate that the average number of nearest-neighbours is 4.4 to 4.6 (probably fluctuating between 4 and 6) and that the average distance between centers is 2.92 Å. The radius of water molecule is 1.36 Å according to Gurney (21). A high concentration of molecules also is found at 4.75 Å to 4.90 Å, which is roughly the expected distance (the length of the tetrahedral edge, i.e., $2.92 \times (8/3)^{\frac{1}{2}}$) for the next-nearest neighbours if the molecules tend to have a tetrahedral arrangement as in ice.

Therefore, liquid water may be regarded as having a rather loose tetrahedrally-bonded ice structure. Due to thermal agitation, the structure is continously broken and formed. The association of water molecules persists, though temporarily, long enough in comparison with the time of X-ray or infrared radiation interactions.

The structure of liquid alcohols has been reviewed recently by Frands and Ives (18). Contrary to expectation, all evidence shows that no more than two (expected number is 3) hydrogen-bonds are formed for each oxygen of an alcohol molecule. Each oxygen acts once as proton donor and once as proton acceptor. This apparent limitation to equality of "give-and-take" may be attributed to the essentially co-operative nature of hydrogen bonding; together with the unfavorable steric effect of the organic group, it restricts the degree of order which can be established in the liquid state, and precludes the kind of three-dimensional association which is dominant in water. X-ray radial distribution curves indicate that, instead, linear polymers of the kind shown in the following figure are formed; in the case of the higher normal alcohols, these may tend to associate non-randomly together, preferred positions for the oxygen atoms lying in planes perpendicular to the parallel hydrocarbon chains (43).

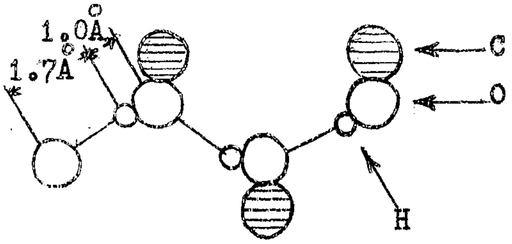


Figure 1. Hydrogen-Bonded Chain Association of Alcohols

Normally, however, association in liquid alcohols seems to be of a kind to which the formal thermodynamic treatment of the "ideal associated solution" applies (44), and is well described in terms of equilibria between polymeric species. These are usually considered to be fragments of the polymeric chains which, though unlimited in length in the crystalline state, do not, in the liquid, exceed a complexity of 5-7 molecules. They may be less for sterically hindered alcohols.

After studying the thermodynamic excess functions of a series of alcohol-water mixtures Franks and Ives (18) concluded that in the low alcohol mole-fraction region, the mixture is essentially an aqueous solution: one in which a resistance to depolymerisation and a preservation of structure is based upon the three-dimensional cooperative hydrogen bonding so fundamental to the nature of liquid water. This means that water is able to act as host to molecules which, although alien, have a certain affinity for water. With increasingly extensive invasion by the foreign species, however, rather sudden "cooperative failure" of structure retention is to be expected.

Ionic Solvation - The problem of solvation has always been one of the most important and fundamental aspects of the chemistry of aqueous solutions. From solubility data, Frank and Evans (17) found that non-polar gases are more structure-forming in water than in other non-polar solvents. They described this by saying that "the water builds a microscopic iceberg round the non-polar molecule". Aqueous ionic solutions present a much more complicated picture. Frank and Evans (17) found that the entropy of solution of monatomic ions in water can be represented by the following equation

$$-S^\circ = 22\ Z^2/(r_i + 2.8), \qquad (2.1)$$

where Z is the valency and r_i is the radius of the bare ion in Å, to which 2.8Å is added to allow for the first rigidly-held layer of water molecules. For mono-valent monatomic ions they have defined a quantity called the 'structure-breaking entropy', ΔS^{st}. All that this amounts to, qualitatively, is that beyond the first layer of water molecules, which are frozen-in by the ions, there is a region where the water structure is broken down; it is pointed out that this could arise from the manner in which the first layer of water molecules is arranged. Around a positive ion the water molecules would be oriented with all the hydrogens outwards; they could not, therefore, all participate in the normal tetrahedral water arrangement, for this arrangement would require two of the water molecules to be oriented with the hydrogens inwards. For polyvalent monatomic ions such as Al^{+++}, the entropy loss is much greater than that for monvalent ions; part of this increase is ascribed to an extension of the 'frozen' region to layers beyond the first. For 'structure breaking' salts the water lattice becomes increasingly random with increasing concentration (16,45). In general, the nature of the salt on the solvent structure may be studied using viscosity data (46).

For calculating thermodynamic properties of ionic solutions, Born's equation (46) provides the simplest mathematical treatment. According to Born, the free energy change of transferring a gaseous ion of radius r and valence Z from vacuum to a large volume of structureless solvent is given by

$$\Delta G^{\circ} = -N_0 Z^2 e^2 (1-1/D)/2r, \qquad (2.2)$$

where N_0 is the Avogadro number, and D the dielectric constant of the solvent. The theory assumes the following:

(1) The ion is a sphere with radius r and with charge Ze uniformly distributed over its surface, and

(2) The ion is immersed in a continuous medium with dielectric constant D.

For one mole of a salt furnishing ν_α, ν_β ... moles of ions of charges $Z_\alpha e$, $Z_\beta e$ ... and of radii r_α, r_β ... the Born's equation becomes

$$\Delta G^{\circ} = -(N_0 e^2/2)\ (\Sigma \nu_\alpha Z_\alpha^2/r_\alpha)\ (1-1/D). \qquad (2.3)$$

The corresponding enthalpy change and entropy change can be obtained by applying thermodynamic relations to the Born's equation.

In many cases, results predicted from the above equations are inconsistent with experiment (2,19,24,26). The general explanations offered are:

(1) The spherical model is not adequate.

(2) It is not permissible to neglect all forces other than the electrostatic forces round the ion. This is shown by Lannung's experiments (30).

(3) Born's theory ignores any dependence on the sign of the charge on the ion.

(4) In the derivation of Born's equation no consideration is given to the order-producing, order-destroying nature of ions on the solvent.

(5) Born's theory ignores the electrostriction and the dielectric saturation effects near an ion.

(6) The effective radius of an ion depends on the nature of solvent.

(7) Bjerrum-type of ion association can and does occur at finite concentrations.

The basic Born equation can be extended to calculate thermodynamic functions for the transfer of a completely ionized electrolyte from one solvent to another. From an alternative point of view, Gladden and Fanning (19) have considered the process of transfer of a salt from one medium to another as follows:

Salt (aqueous solution) ⟶ Salt (ideal water solution) ⟶

Salt (ideal non-aqueous solution) ⟶ Salt (non-aqueous solution).

If the free energy change for each step could be found, then upon adding the terms, there would result

$$\Delta G_t = \Delta G_t^{\circ} + 2RT \ln(f_2/f_1) , \qquad (2.4)$$

where f_1, f_2 are the activity coefficients of the salt in the nonaqueous solution and in the aqueous solution, respectively. In equation (2.4) ΔG_t° is the value of ΔG_t at infinite dilution of the salt. The activity coefficients can be calculated in terms of Debye-Hückel Theory provided the solutions are sufficiently dilute. When this is done, the resulting equation becomes the "limiting law" for the transfer process. However, this "limiting law" is not satisfactory because of failure to take into explicit account factors quite similar to those that cause deviations from Born's equation. Thus ΔG_t° must be estimated theorectically in a manner similar to the Born's equation.

It should be noted that both of the approaches discussed above are based on idealized models and, therefore, do not depend in any way on the detailed structure of electrolytic solutions. Indeed, their inadequacy signifies the importance of this aspect. In order to gain an understanding of the microscopic structure of electrolyte solutions, two essential questions have to be answered: (1) how many solvent molecules can be considered to be bound to a ion - i.e., the solvation number and (2) how are they bound?

Bernal and Fowler were among those who have pioneered in this field. Along with early studies on the structure of water, they also studied the structure of ionic solutions, both experimentally and theoretically (9). Their theory assumes (1) a continuous solvent medium beyond the region about the ions, (2) all forces and energies involved are electrostatic in nature, (3) their own model for the structure of water, and (4) ion-solvent orientation models such as shown in Figure 2.

For cation

For anion

Figure 2. Ion-solvent Orientation Models

According to Bernal and Fowler, the general features of ion-solvent interaction depend mainly on the size of ions. Therefore, ions of similar sizes would have similar hydration numbers,and similar heats of solvation. This is, of course, not even approximately true (2).

Many studies of hydration numbers ccan be found in literature.

However, results from different authors in many cases do not agree with one another (4,5). This causes one to conclude that different types of experiments measure the numbers of different types of solvation water molecules.

Frank and Evans (17), from a re-analysis of the entropy of hydration, have developed a fundamental classification of solvation water. These authors claimed that a spherical ion is surrounded by three concentric regions which are:

(1) the region of immobilized water molecules,
(2) the water structure-breaking region,
(3) the structurally 'normal' water region.

Quite recently, Azzam has developed another possible classification (3,4,5) which bears some similarity to that of Frank and Evans. His definition of the different types of solvation is given as follows:

(1) Permanent Solvation - This term refers to solvent molecules which are firmly associated with the ion through the formation chemical bonds, e.g., co-ordinated water of crystallization.

(2) Primary Solvation - This term refers to solvent molecules which are firmly associated with the ion by electrostatic attraction. They have lost their translational degree of freedom and move as one entity with the ion during its Brownian motion.

(3) Secondary Solvation - This term refers to solvent molecules which undergo electrostatic attraction to the primary solvated ions. These molecules are much more weakly held, but the electrostatic attraction predominates over the separating action of thermal motion sufficiently to affect solvation-dependent quantities, e.g., salting-out.

(4) Hydrodynamical Solvation - This term refers to solvent molecules which could be transferred hydrodynamically as the hydrated ion moves under the influence of an applied electrostatic field. This effect is mainly due to transfer of momentum between the solvated ion and the solvent molecules.

These different types of solvation play parts of different order of degree in the various experimental phenomena depending on specific factors (11). For example the first type of solvation is not relevant with the alkali and halide ions (4). However the number of solvent molecules in both the permanent and the primary solvation sheaths have definite values, while the number of solvent molecules in the secondary solvation sheath have variable values depending on the phenomena observed. Hydrodynamical solvation is relevant only in dynamic experiments such as in measurements of transport number.

Based on a Boltzman-type statistical-mechanical analysis and solvation models shown as follows

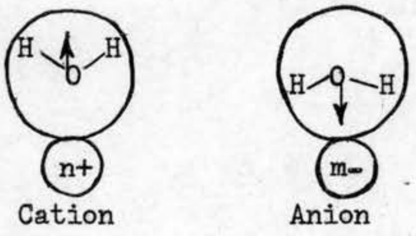


Figure 3. Orientation of Water Molecules near an Ion

Azzam (4,5,8) has calculated the maximum solvation numbers (excluding hydrodynamical solvation) of a series of monovalent and bivalent monatomic ions in water. Some of his results are listed in the following table:

TABLE I

CALCULATED SOLVATION NUMBER OF IONS

Ion	Li^+	Na^+	Cl^-	I^-	Co^{+2}	Ni^{+2}	Cu^{+2}
Solvation Number	29	21	11	6	59	61	60

Following the same statistical-mechanical method of analysis, Azzam has applied his theory to the calculation of heats of solution (6,7). Briefly speaking, his heat of solution is the sum of the heats of interaction of an ion with its four concentric regions of water molecules. He has taken into account the effects of dielectric saturation and electrostrition by using Webb's theory in his calculations (51). When his calculated ionic values are added up for the corresponding salts and compared with the most reliable experimental results, good agreement has been found.

Quite recently, Noyes (40) has investigated the dielectric saturation effect in the vicinity of ions. Effective dielectric constants are given. His semi-empirical thermodynamic calculations lead to the free energies, enthalpies, and entropies of hydration of gaseous ions which are tabulated by Harvey and Porter (23). More recently, Noyes (41) has included the effects of surface free energy, but this has rather little influence on his previous values of ionic contributions to entropy and enthalpy.

For comparison, the enthalpies of hydration of some gaseous bivalent cations are tabulated in the following table. These values are those calculated by Azzam (7), Noyes (23), and other earlier workers (through reference 7).

TABLE II

ENTHALPIES OF HYDRATION OF GASEOUS BIVALENT CATIONS

Ion	Noyes	Azzam	Evans	Latimer	GuaGliano
Zn^{+2}	530	524	485	485	491
Co^{+2}	505	506	488	-	497
Ni^{+2}	520	519	499	-	507
Cu^{+2}	516	524	526	499	507
Fe^{+2}	463	497	485	-	468
Mn^{+2}	455	476	438	438	445
Ca^{+2}	395	385	428	-	395
Sr^{+2}	354	356	381	-	355
Ba^{+2}	326	321	347	-	305

(in unit of minus Kcal per mole)

Ion Association - Bjerrum type ion-association (or ion-pair formation) has been accepted as an important factor causing deviations from both the Debye-Hückel and the Born theories at finite concentrations. In contrast to Debye and Hückel, who assumed ions in solution to be completely free of each other, Bjerrum (10) proposed that when ions of opposite sign get sufficiently close together within a certain critical distance of separation, they would be bound together by their mutual electrostatic forces, losing their thermodynamic independence, and the ion-pairs formed would be in equilibrium with the rest of the ions in solution. According to this theory, higher ionic charges and smaller dielectric constants will favor ion-association.

The terms 'ion-pair' and 'complex' have been used by different workers to distinguish between different types of association, and sometimes with different meanings. A distinction proposed by Smithson and Williams (48) is that the former involves solvent interposed between the ions, $M^{n+}(H_2O)X^{m-}$, as distinct from $MX^{(n-m)+}$. For transition metals they suggest that ion-pair formation, unlike complex formation, will be expected to have very little effect on the low intensity absorption bands in the visible spectrum. Such bands are due to forbidden d-d transitions, the wavelength depending upon the separation of the d-states which in turn is a function of the degree of polarization of the cation by the associating anion as well as the symmetry of the polarizing field. Ion-pair formation will be expected to have very little effect on the d-d splitting because of the large separation of M^{n+} and X^{m-}.

The thermodynamics of ion-association in aqueous solutions has been reviewed recently by Nancollas (39). Extensive treatments of ion-association in general can be found in Davies book (13). Based on many experimental evidences, Nancollas (39) has pointed out that, in most cases where ion-pair formation between cations and anions results in a reduction in the number of ions in solution and a partial neutralization of charge, there is an entropy change favoring ion-pair formation. Frank and Evans (17) have suggested, however, that the ions in solution order water molecules around them to form an 'ice-berg' structure and the decreased orientation of solvent molecules leads to a positive entropy change. Nevertheless, this is not always the case, for one also must take into account, with polyatomic ions, the loss in configurational and rotational entropy which accompanies the association (29). Entropy of ion-association can be calculated in several ways

(12,39). A method which has been adopted by Austin et al (12) for calculating the entropy changes for the formation of ion-pairs $CdCl^+$, $CdBr^+$, $PbCl^+$, etc., from original free ions in water has lead to agreement with experimental data that is all that can be expected.

The degree of ion-association of an electrolyte is best measured by the conductance method. With symmetrical electrolytes the problem is relatively simple. However, this is by no means true when one is dealing with unsymmetrical electrolytes. A simple though semiempirical method has been described by Monk (34). Measured conductance of an unsymmetric electrolyte is compared with Onsager's limiting equation (46) and the decrease of electrical conductance is ascribed to the association of a metal ion with an anion (assumed to be the case in dilute solutions), assuming that the limiting conductance of the ion-pair to be about 0.40 of that of the metal ion. This method is certainly not valid in any case except that of extreme dilution. For, as the concentration electrolyte increases, the limiting equation is no longer theoretically applicable. Quite recently (1957), this limiting equation has been extended by Onsager and Fuoss (13,46) to provide a conductance equation accurate to within experimental error over a range of finite concentrations. Unfortunately this new theory is applicable only to symmetrical electrolytes. Unsymmetrical electrolytes are not included in the treatment, partly because the underlying theory is less exact for these electrolytes and partly because the numerical calculations become impracticably tedious. This is discouraging. However, it is still possible to make use of an empirical equation derived many years ago by Davies and Righellato (13) for uni-bivalent salts. Instead of using the Onsager limiting law these authors compare the conductance of some partially dissociating electrolytes with that of comparatively stronger electrolytes. Although relatively simple, the method has been used extensively by Davies and his students to estimate the degree of dissociation of ion-pairs from limiting ionic conductances.

Liquid-Liquid Extraction - In a recent review by Marcus (33) of solvent extraction two different mechanisms for the extraction of transition metal salts are considered. In the case of extraction of aqueous solutions by TBP (tri-n-butyl phosphate) in kerosene, TBP solvation numbers are found experimentally to be the difference between the maximum coordination number of the cation and the ionic charge. Thus, the extracted species is most likely a definite solvate of a neutral species. By contrast, the extraction of the same salts by the higher alcohols is found to involve the salting-in of water into the alcoholic phase in addition to specific hydration of the cations involved. This leads to non-integral apparent hydration numbers which are generally higher than the characteristic coordination numbers for the cations (52). Indeed, the hydration numbers obtained this way are probably best classified as permanant + primary + some secondary.

The extraction systems consisting of nickel(II) (or copper(II)) perchlorate, water and 1-butanol have been recently studied by Swartz (49). Nearly identical distribution isotherms for the two salt were obtained. The slope of the distribution coefficient curve is discussed qualitatively in terms of Owen's medium effects (22) and the Debye-Hückel theory.

At distribution equilibrium the partial molal free energy of transfer $\Delta\bar{G}_t = 0$; therefore, $\Delta\bar{H}_t = T\Delta\bar{S}_t$, and $\Delta\bar{H}_t$ is simply the difference in the partial molal heats of solution of the distributed anhydrous salt in the two phases. Since it is generally not possible to prepare anhydrous perchlorates of the transition metals, Swartz proposed a thermodynamic cycle from which the enthalpy of transfer could be obtained (49). Thus, with pyridine as a complexing ligand to obtain the anhydrous crystalline compound $M(ClO_4)_2 \cdot 6Py$, the cycle is

$$\begin{tikzcd}
M(ClO_4)_2\ (s) & +\ 1000/m\ \text{gm. solvent} \arrow[r, "\Delta H_s"] & M(ClO_4)_2\ (m) \\
+ & & + \\
6\ Py\ (l) \arrow[d, "\Delta H_x"] & & 6\ Py\ (l) \arrow[d, "\Delta H_r"] \\
M(ClO_4)_2 \cdot 6Py\ (s) & +\ 1000/m\ \text{gm. solvent} \arrow[r, "\Delta H_s^*"] & M(ClO_4)_2 \cdot 6Py\ (m)
\end{tikzcd}$$

Figure 4. Thermodynamical Cycle

where ΔH_r, ΔH_s^* are experimentally measurable quantities. From the above cycle applied to each equilibrium solvent mixture, it follows that

$$\Delta H_t = (\Delta H_s^* - \Delta H_r)_{org} - (\Delta H_s^* - \Delta H_r)_{aq} , \tag{2.5}$$

since the ΔH_x's disappear upon subtraction.

Because of technical difficulties, Swartz could obtain data for ΔH_t for $Ni(ClO_4)_2$ at one concentration only and none for $Cu(ClO_4)_2$. The ΔH_t value obtained was actually the integral heat of transfer. Since the salt molality was small (aqueous phase 0.023 m, and organic phase 0.0013 m), the integral value was assumed to be equal to the partial molal heat of transfer. A value of -13.7±1.6 kcal/mole was obtained for ΔH_t with a corresponding entropy change of -46.0±5.3 e.u. per mole.

Physical Properties of Solvated Perchlorates in Solution - Perchlorates of transition metals are highly dissociated in aqueous solutions. However recent evidence shows that there is a small degree of ion-association in concentrated solutions. Ross (47) found that nickel perchlorate solutions have absorption maxima at 393 and 720 $m\mu$, and on addition of $HClO_4$ the absorptions intensify.

Goodrich (20) has studied the interaction of water with cobalt(II), copper(II), and nickel(II) perchlorates in 1-butanol. The shape and position of the absorption bands in the visible and near infrared regions of the spectrum are completely in agreement with an octahedral ligand field for all three ions in the anhydrous solvent. Addition of small amounts of water shifts the bands slightly without altering their shapes significantly. The shift is only of the order of 10-15 $m\mu$ or less and indicates strongly that replacement of butanol molecules by water molecules is occurring in the coordination sphere of the nickel or copper ions. The magnitude of the shift further suggests that the perchlorate ions are separated from the metal ions in the ion pairs by at least one solvent molecule (12). Saturation of thephase with water yields spectra almost identical to those obtained in aqueous solutions.

Hester and Plane (25) have studied aqueous solutions of nitrates (Cu^{+2}, Zn^{+2}, etc.) sulfates (Cu^{+2}, Zn^{+2}, etc.), and perchlorates (Cu^{+2}, Mg^{+2}, etc.)by Raman spectroscopy. They found that all bivalent ions except Cu^{+2} gave lines in the region 360-400 cm^{-1}, consistent with the formation of hexacoordinated complexes. The non-conformity for copper complexes has been attributed to the Jahn-Teller effect.

Andreeva et al (1) examined the spectra of dilute aqueous solutions of Co(II) perchlorate, chloride and sulfate. The found the presence of absorption maxima at 8100, 16000, 19450, 20650 and 21400 cm^{-1}. This was verified by investigating the absorption of $Co(ClO_4)_2 \cdot 6H_2O$ in a series of alcohols and ketones. The results were interpreted as indicating a deformed octahedral structure for the $Co(H_2O)_6^{+2}$ and $Co(OR_1R_2)_6^{+2}$ complexes (OR_1R_2 represents a ketone).

Pasternack and Plane (42) spectrophotometrically studied the stepwise substitution of two water molecules from the hydration sphere of Cu(II), Ni(II), and Co(II) perchlorates by ethanol and acetone. They suggest that trans-substitution is favored, and that the nature of the substitution does not depend markedly on the identity of the metal ion. If this is true, the binding energy of two of the six water molecules would be relatively small compared with that for the other two pairs. This result appears to confirm to some extent the calculation of Katzin and Ferraro (28), who found that the binding energy of the last pair of water molecules is the least in the stepwise (two at a time) formation of $CoCl_2 \cdot 6H_2O$ starting from the anhydrous compound. This is even more pronounced in the case of the hexapyridinates of cobaltous chlorides. However, it is not possible to consider the two hydration processes on a comparable basis.

CHAPTER III

EXPERIMENTAL METHOD AND PROCEDURE

Distribution Equilibria - The distribution experiments were carried out by mixing the hexahydrates with equal volumes of water and 1-butanol. The mixtures were shaken vigorously for 1 hour; they were then transferred quickly into separatory funnels and allowed to stand in a water bath at 25° ± 0.2°. The standing time was at least three weeks, and often more for mixtures containing very small amounts of salts. In case of copper perchlorate, a month or longer was apparently necessary to reach complete phase equilibrium. The phases were then separated carefully.

The separate phases were analyzed for the metal ion by standard EDTA titration. Results of the determinations are reported in Table 4 as moles of anhydrous salt per 1,000 grams of mixed solvent. Reproducibilities were all better than 0.5%.

Water in the organic phases was determined by standard Karl Fisher direct titration, employing a dead-stop endpoint measurement with a Beckman Expanded Scale pH meter. Results are tabulated in Table 6. Reproducibilities were always better than 0.5%.

Since butanol and water form a minimum boiling azeotrope (b.p.95°), the quantity of 1-butanol in the aqueous phases was determined by measuring the densities at 25.0° of the distillates of the aqueous phase solutions. These were distilled under atmospheric pressure at about 95°

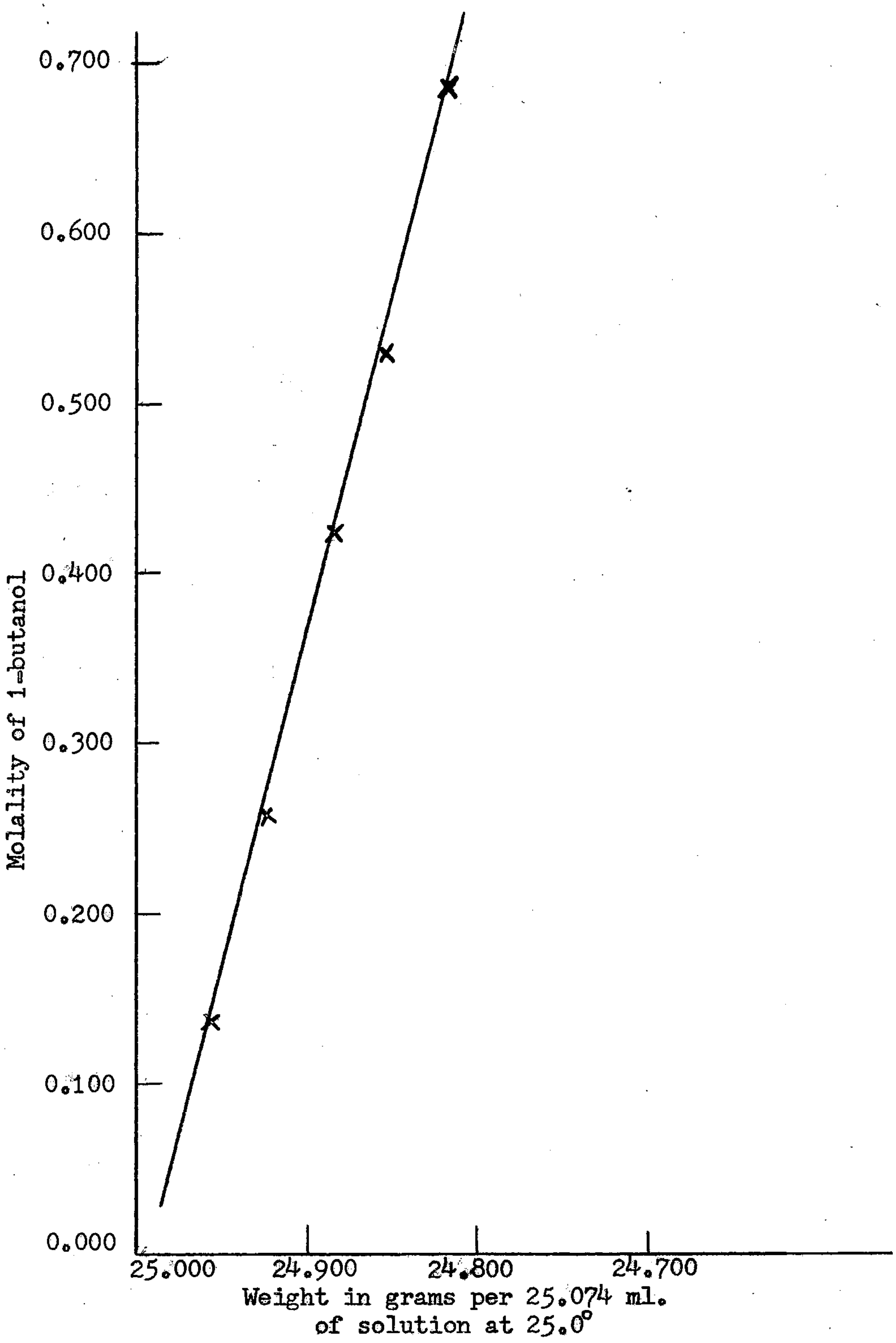


Figure 5. Standard Curve for 1-Butanol-Water Mixture

until about 3/4 of the original solutions had been removed. Water was added to dissolve all the butanol and the density of the distillate was compared with a standard curve obtained before-hand (Figure 5). Results are shown in Table 5. Reproducibilities were better than 1%.

Thermodynamics of Transfer - Since solid hexapyridinates had been found experimentally unsuitable for general use with the thermochemical cycle described on page 17, work was first directed toward finding other solid complexes which might take the place of the pyridinates. The solid compounds sought had to be easily soluble in both the organic and aqueous phase solvents, and at the same time the rate of dissolution had to be reasonably rapid. The compounds should be capable also of being prepared in a pure state and should be stable. Different types of compounds were considered, and several were prepared and tested. These included organic solvates, such as alcoholates, as well as coordination complexes with amines similar to the pyridine compounds. None of the compounds examined were satisfactory.

Consideration of the thermochemical cycles involved indicated, however, that the heat mixing of a reference solution of definite composition could be substituted in the cycle in place of the heat of solution of a solid compound. Further consideration suggested the use of concentrated aqueous perchlorate solutions in the case of the butanol extractions. Such solutions were found to be completely miscible with the equilibrium solvents of both the aqueous and the organic phases at the temperature of experiment, and they have been found satisfactory for use over the entire range of concentrations with each of the metal salts.

The modified thermochemical cycle is now shown in Figure 6. From this one sees that the partial molal enthalpy of solution $\Delta\overline{H}_s$ of one

$$\begin{tikzcd}
M(ClO_4)_2\ (s)\ +\ \text{an infinitely large quantity of equilibrium phase solution (molality m)} \arrow[r, "\Delta\overline{H}_s"] & M(ClO_4)_2\ (m) \\
+ & + \\
xH_2O \arrow[d, "\Delta H_x"] & xH_2O \arrow[d, "\Delta\overline{H}_r"] \\
M(ClO_4)_2\cdot(xH_2O)+\ \text{an infinitely large quantity of equilibrium phase solution (molality m)} \arrow[r, "\Delta\overline{H}_s^*"] & M(ClO_4)_2\cdot(xH_2O)\ (m)
\end{tikzcd}$$

Figure 6. Modified Thermochemical Cycle

mole of salt in an infinitely large quantity of equilibrium phase solution of salt molality m is thermodynamically equivalent to the sum of the following enthalpy changes

(a) $\Delta\overline{H}_s^*$ - the partial molal enthalpy change for dissolving 1 mole of the "reference solution" in an infinitely large quantity of equilibrium phase solution of salt molality m,

(b) ΔH_x - the enthalpy change for the process of dissolving the hypothetical anhydrous perchlorate salt in x moles of water to form a reference solution, $M(ClO_4)_2\cdot(xH_2O)$,

(c) $\Delta\overline{H}_r$ - the partial molal enthalpy change for the process of dissolving x moles of water in an infinitely large quantity of the equilibrium phase solution of salt molality m.

Thus, $\Delta\overline{H}_s = \Delta H_x + (\Delta\overline{H}_s^* - \Delta\overline{H}_r)$.

The partial molal enthalpy of transfer of the perchlorate from the aqueous phase to the organic phase is represented by $\Delta\overline{H}_t = (\Delta\overline{H}_s)_{org} - (\Delta\overline{H}_s)_{aq}$, the right hand side of which is equal to $(\Delta\overline{H}_s^* - \Delta\overline{H}_r)_{org} - (\Delta\overline{H}_s^* - \Delta\overline{H}_r)_{aq}$, since ΔH_x disappears on subtraction.

In order to transfer the salt from one phase to the other without disturbing extraction equilibrium, it is necessary that the amount transferred be infinitesimally small. Since there is equilibrium, the partial molal free energy change upon transfer is equal to zero, and $\Delta\overline{H}_t = T\,\Delta\overline{S}_t$, where $T=298.15^\circ$ K, $\Delta\overline{H}_t$ and $\Delta\overline{S}_t$ are the partial molal enthalpy change and entropy change respectively, for the transfer. From the considerations presented above, the partial molal enthalpy of transfer is given by the sum of the differences in the experimental values of the partial molal heats of solution of water and the reference solution in the equilibrium phase mixtures.

Heats of solution were measured directly in a calorimeter at 26.5° and practically at constant atmospheric pressure (so that heat of solution = enthalpy of solution). The calorimeter used will be described later. To get a value of $\Delta\overline{H}_s^*$ at a salt concentration corresponding to the extraction equilibrium, an aqueous reference solution of about 3 molar salt concentration was added incrementally from a micrometer syringe to 125 grams of solvent in the calorimeter. The solvent consisted of a butanol-water mixture of the same composition as in the equilibrium phase solutions. Additions were continued until the concentration of salt in the calorimeter was a little greater than the equilibrium value. Although each increment of reference solution resulted in the simultaneous addition of water and hence a small alteration in the solvent composition, calculation shows that the total effect upon the water/salt ratio at the equilibrium composition is only about 1% while the effect upon the salt concentration is less than 0.1%. Furthermore, the thermal effect of the additional water is exactly compensated for in the thermochemical cycle by the method of finding $\Delta\overline{H}_r$.

The integral heat of mixing was plotted against the number of moles of salt added and the slope evaluated graphically at the equilibrium composition to obtain the partial molal quantity, $\Delta\overline{H}_s^*$. It should be pointed out that plotting the data against the number of moles of salt is equivalent to plotting against the number of moles of reference "compound", since a mole of reference "compound" can be defined as the quantity of reference solution having one mole of salt and x moles of water.

Values of $\Delta\overline{H}_r$ were obtained in a manner similar to that for $\Delta\overline{H}_s^*$. Water was added incrementally to the equilibrium phase solution (125 g. + required amount of salt) by a micrometer syringe, and the integral heat of mixing was plotted against the number of moles of water added. Since x moles of water were added for each mole of reference solution in the thermochemical cycle, the values of partial molal heat of solution of water, obtained (again) graphically from the slopes, were multiplied by x to find $\Delta\overline{H}_r$.

In the preparation of the reference solution in the case of $Cu(ClO_4)_2$, a small amount of a white precipitate was observed; this was filtered from the solution. The filtered reference solution was tested and found to be acidic toward blue litmus paper. The acidity and precipitate were very probably due to hydrolysis of the Cu(II) ion. No effort was made to analyze for the nature and quantity of the hydrolytic product. However, the amount of H^+ present arising from the hydrolysis was estimated from the calibration experiment described in the next section. The small amount of hydrolysis was found to have negligible effect on the enthalpy of transfer and the distribution equilibrium. For the other two salts, no such hydrolysis occurred.

Thermochemical data are tabulated in Table 7. Except for the first four cycles in the case of $Ni(ClO_4)_2$, for which the additions of reagents were made with a Menisco-Matic buret, it was found that $(\Delta\overline{H}_r)_{org}$ values were practically zero. This is reasonable since the organic solutions were already saturated with water, and the addition of a minute amount of water should not cause significant change of enthalpy. All values are recorded as the averages of duplicates. Deviations of the duplicates from their averages are incorporated in the table.

The Calorimeter - The calorimeter used was essentially the same as that employed by Fielder (15).

A sketch of the calorimeter assembly is whown in Figure 7. The calorimeter vessel consisted of a 150 ml. capacity dewar flask (R) suspended in an air bath whose temperature was closely regulated (±.05) with a Yellow Springs Instrument Co. thermister temperature controller. The outer jacket (G) of the calorimeter was made of insulating bakelite material with a heater (P) and fan (L) mounted inside to insure a uniform environment for the dewar flask and its contents.

The silvered dewar (R), which composed the bottom half of the calorimeter vessel, was coupled by a ground flange (H) to a glass solvent-tight lid (F). The lid was secured by a bakelite ring (C) and suspended from a bakelite disc (B) forming part of the top of the calorimeter jacket. The dewar flask was fastened to the lid by a bakelite ring (I) during experiment. Through ports in the glass top were inserted the liquid reagent delivery needle (E), thermistors (J,K) for temperature detection, and the leads from the internal heater (O). The heater itself was made from 40 gauge platinum wire, 30 ohms of which was wound on a 3/4-inch high cylindrical open glass form. The platinum wire was connected to the heavy copper leads through a mercury junction.

Two Veco (#32A30) 2000-ohm thermistors were calibrated and used to-

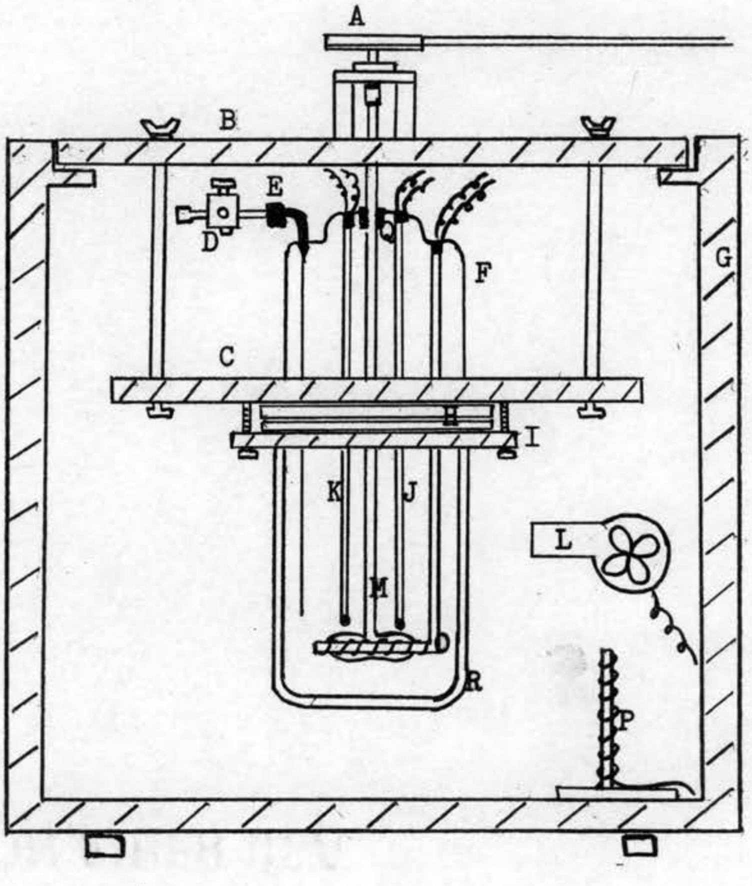


Figure 7. The Calorimeter

gether with a Rubicon Co. (catalog #3403HH) galvanometer (0.0051μa mm.$^{-1}$) in a shielded dc Wheatstone-bridge arrangement to monitor the temperature of the solution in the calorimeter and also that of solution in the buret. The third thermistor (J) was a Veco (#51 A1) 10^5-ohm probe constituting one arm of a shielded dc Wheatstone-bridge. The bridge voltage was provided by a Willard low-discharge 6-volt battery. This circuit had as the detector of unbalanced current on the Wheatstone-bridge a Sargent Model SR recording potentiometer. The recorder,through interchangeable range-plugs, had several available sensitivity settings. A compromise could be reached whereby the stirrer noise was minimized and at the same time the high sensitivity of the 10^5-ohm thermistor fully utilized.

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

A diagram of the circuit for the calibration heater is shown in Gigure 8. The platinum heating element was completely immersed and exposed to the solution in the dewar. By doing this thermal lags were made negligible. The mercury connection and copper leads from the calorimeter were made 12 gauge in order to insure that any resistance in leads outside the calorimeter would be very small compared to the resistance of the platinum heater. The heater circuit was powered by an isolated 6-volt storage battery, which provided a constant current over the 60-second intervals used in measuring the heat capacity of the solu-

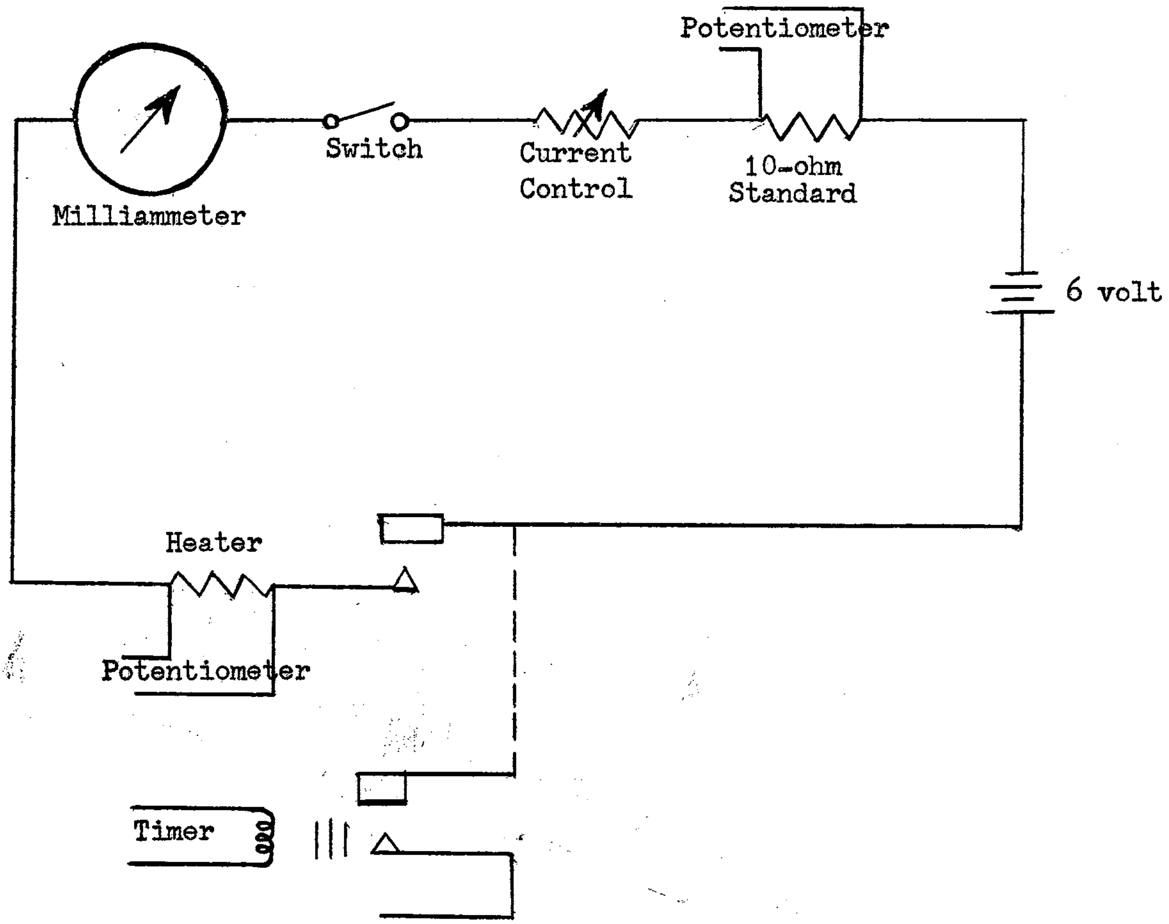


Figure 8. The Calorimeter Internal Heater Electrical Circuit

tion in the calorimeter.

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

The current used in the measurement of the heat capacity of the solution in the dewar was approximately 50 milliamperes. This value of the current was chosen in order that the same potentiometer (Rubicon Instrument Co., Model 2730) could be used to measure, by switching, both the voltage drop across the heater and across a General Radio (Series 500) secondary laboratory standard 10-ohm (±0.05%) resistor in series with the heater. This resistor had a resistance of 10.002 ohms when compared with a Leeds and Northrup Co. (Cat. #4025-B) standard 10.000-ohm resistor.

Liquid reagent was added through a stainless steel needle; throughout the addition of reagent the end of the needle was kept beneath the level of liquid in the dewar. The needle was connected to the buret by a 3-way stopcock (D in fig. 7). This allowed an unlimited amount of liquid to be delivered conveniently. For the measurements of Nickel(II) perchlorate, an American Instrument Co. Menisco-Matic buret delivered the reagent into the calorimeter. It was found, however, that the speed of addition and the accuracy were not completely satisfactory; also leakage with this instrument was a frequent problem. For later measurements, a manually operated 2-ml. Gilmont micrometer syringe having a slight modification in length for proper insertion into the calorimeter jacket was used. By calibration with water at 26.5° , it was found that actual volume delivered from the syringe was 1.0047 of the volume shown on the digital dial. However, this correction factor was found applicable to every 0.1000 milliliter portion delivered.

A calibration of the two 2000-ohm thermistors gave a linear 0.014 deg. ohm^{-1} relationship over the 25°-27° range. The individual runs made with the calorimeter were carried out within this temperature span. A calculation of the quantity of heat to be added or subtracted as a correction for any difference in temperature of the buret and the solution in the calorimeter showed that no correction was necessary for temperature differences up to 0.1° because of the small increments of titrant.

The 10^5-ohm thermistor used to measure the heats of reaction had a temperature coefficient of resistance of 4.6% deg.$^{-1}$. This is equivalent to -4600 ohm deg.$^{-1}$ at 25°. When the one millivolt range-plug was used in the recorder, the sensitivity of the calorimeter was 0.0630 cal. cm.$^{-1}$ of recorder pen movement for 1-butanol solutions and 0.0885 to 0.0925 cal. cm.$^{-1}$ for aqueous solutions, depending on the amount of reagent delivered. The pen travel could easily be read to better than ± 0.5 mm.

A 6-volt potential was impressed across the thermistors at all times to assure stability and uniformity of reponse (38).

The values of current, potential across the heater, and time were measured to four significant figures. The timer had 0.01 second divisions and the heating runs were about 60 seconds duration. The method used in calculating the heat capacity of the calorimeter was to find the values of <u>h</u> from

$$h = EIt/ 4.186d$$

where I = current, amps
E = potential across internal heater, volts
t = time, seconds
d = recorder deflection, cm.
4.186 = Joules per calorie.

This gave a value of h in calories cm.^{-1} at a given temperature. Any single measurement of the heat capacity raised the temperature of the solution less than 0.014°, and usually 2 or 3 successive measurements could be made without increasing the temperature more than this. When corresponding calibrations were compared, the results were always within about 1% of each other.

The performance of the calorimeter has been recently tested by Fielder (15). He measured the heat of neutralization of the reaction in dilute solution:

$$HCl + NaOH \longrightarrow NaCl + H_2O \qquad (27.7^{\circ}).$$

The value of -13.19 ± 0.05 kcal. mole^{-1} found experimentally compares favorably with the liturature value of -13.21 kcal. mole^{-1}.

The calorimeter was designed to measure experimental heats of reaction of the order of one calorie and less with an accuracy of 1% or better. This seems to have been achieved. Furthermore, the calorimeter was designed to permit very small successive metered additions of reagent to be made, and the overall accuracy of 1% includes also any errors in the volumetric addition of reagent.

<u>Conductance in Equilibrium Phases</u> - On the basis of the calculated relative dielectric constants of the aqueous-phase solvent (98 mole percent H_2O), and the organic-phase solvent (50 mole percent H_2O), the Bjerrum ion-association theory predicts that even the transition metal perchlorates will associate in the organic phases. This is believed to be important in relation to the thermodynamics of transfer, and hence

to the distribution equilibrium. A study of the electrical conductance of the solutions in both equilibrium phases was made, therefore, to obtain an estimate of the degree of association of the ions and the association constant.

As the concentration of salt in the aqueous phase increases, the compositions of the solvents change, since water is being salted-in by the metal perchlorate into the organic phase, and butanol is being salted-out of the aqueous phase. However, as an approximation, it was assumed that the compositions of the solvents were fixed, being equal to those of the solvents at zero salt concentration. This assumption is justified since the conductances were measured at low salt concentrations.

A precision Leeds and Northrup Jones type conductivity bridge was used at 1,000 cps for the measurements in conjunction with a dilution cell. Conductance water was prepared by redistilling the deionized water from the tap, first with a little potassium permanganate present and then with a little potassium hydroxide present. Solvent 1-butanol was purified by distilling reagent grade 1-butanol. All parts of the distillation apparatus were aged and were made of pyrex. Solvents were then prepared from these purified reagents.

Fifty milliliters of solvent was pipetted into the cell, which was immersed in an oil-bath at $25.00^\circ \pm 0.05^\circ$. A standard reference solution of perchlorate salt (about 3-molar) was added incrementally to the solvent; resistance readings were taken after each successive addition and thorough mixing. For very low concentrations, the solutions were accurately made up in advance.

From the cell constant obtained for the conductance cell by calibration using a decimolal solution of potassium chloride in water (46) the conductance at various salt concentrations were calculated according to the equation: $\Lambda = (1,000)(0.4143)/C_e \cdot R$.

Here Λ is the equivalent conductance, 0.4143 the cell constant, C_e the equivalent concentration, and R, the resistance of the solution. Since the specific conductivities of the solvents were extremely low (less than $2x10^{-6}$ $ohm^{-1}cm^{-1}$ for the aqueous phase and less than $2x10^{-7}$ ohm^{-1} cm^{-1} for the organic phase), the conductance contributions from the solvents could be ignored.

Experimental precision was checked by measuring the limiting conductances of each of the metal perchlorates in aqueous (containing no butanol) solutions at 25.0° (Figure 9). The values compare with literature values (calculated using the limiting ionic conductances of the component ions listed in the appendix of reference 46) as follows

TABLE III LIMITING CONDUCTANCE IN WATER AT 25.0°

Salt	Limiting Conductances	
	Lit.	Exp.
$Ni(ClO_4)_2$	--	122
$Co(ClO_4)_2$	122	122
$Cu(ClO_4)_2$	121	126

(cm^2 $ohm^{-1}equiv.^{-1}$)

It can be seen that the agreement between experiment and literature is excellent for $Co(ClO_4)_2$. Although there is no literature value for $Ni(ClO_4)_2$ the experimental value found is assumed to be correct, basing this on the assumption that Ni(II) and Co(II) ions in solution are closely similar (this will be clarified in later chapters).

The less satisfactory agreement found for $Cu(ClO_4)_2$ could be

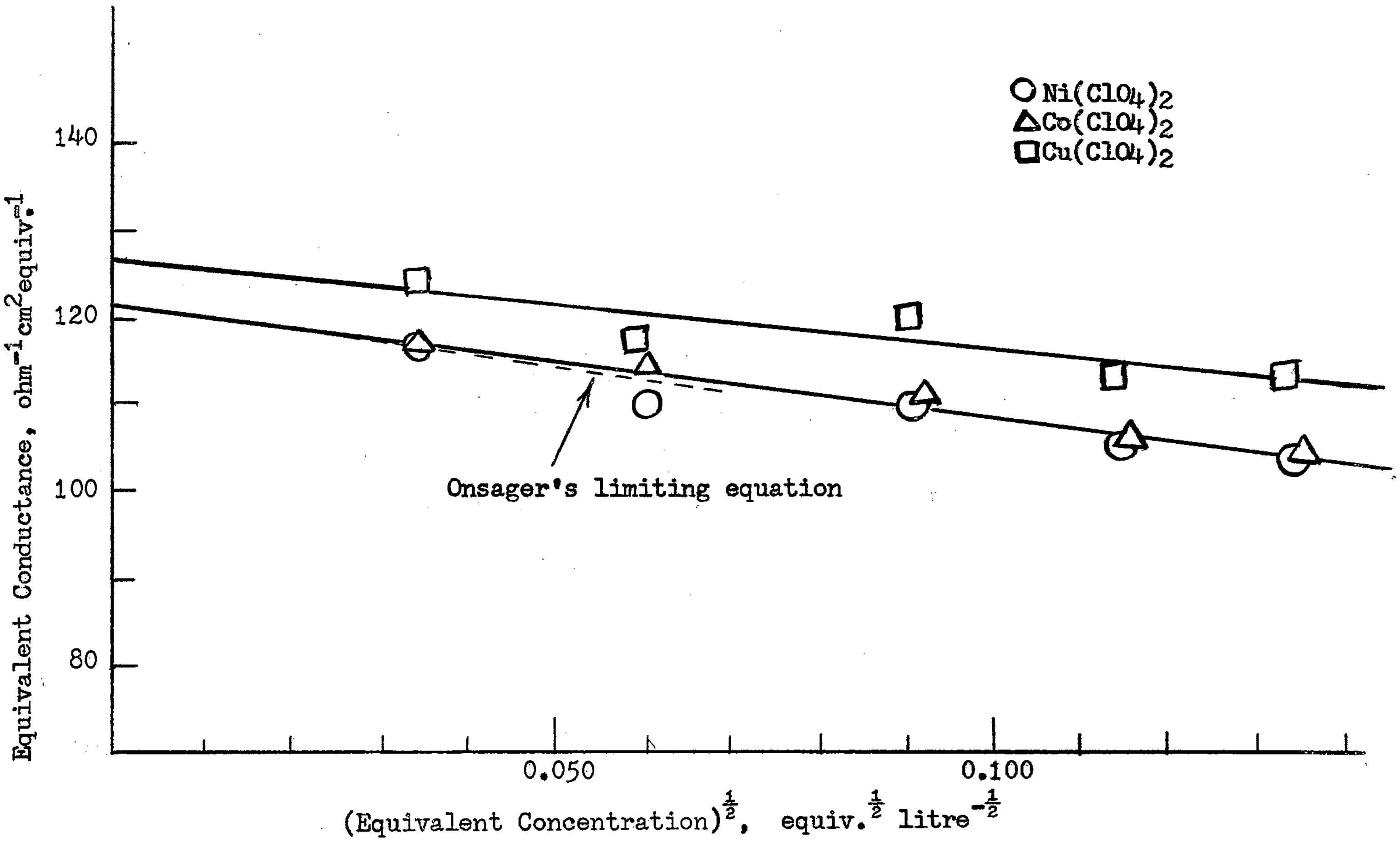


Figure 9. Conductance in Aqueous Solutions at 25.0°

ascribed to the presence of the acid from the hydrolysis mentioned in the previous section. The complete hydrolysis of a mole of cupric ion generates two moles of H^+, and since the limiting conductance of H^+ is 350 $cm^2 ohm^{-1} equiv.^{-1}$, the net increase of conductance per mole would be 700 - that of Cu^{+2} =646 $cm^2 ohm^{-1} equiv.^{-1}$. Since the limiting conductance found experimentally was higher than the true value (assumed to be the literature value) by 5 units, then the amount of H^+ present for every mole of copper(II) perchlorate would be about 0.7%, corresponding to about 0.35% of the cupric ion hydrolyzed on a mole basis.

Conductance results are tabulated in Tables 9 and 10. The data for $Cu(ClO_4)_2$ have been corrected for the presence of traces of acid and viscosity differences by subtracting $5\eta_{H2O}/\eta_{aq} = 4$ from the conductance in the aqueous phase and $5\eta_{H_2O}/\eta_{org} = 2$ from the conductance in the organic phase, where the η's are viscosities.

Viscosity of Equilibrium Phases - Viscosities of equilibrium phases were measured in order to study the structure-alteration effect of the perchlorates on the aqueous and the organic solvents. Solutions were prepared from purified 1-butanol and conductance water. Measurements were made with a simple Ostwald-type viscosimeter immersed in a water bath at 25.0° . Agreement between duplicate measurements was always better than 0.5%. A Gilmont falling-ball type viscosimeter was tried initially, but agreements for duplicates were usually poorer than 5%. The precision of the falling-ball instrument is thus by far inferior to that of the Ostwald-type, although the latter instrument is much cheaper and easier to use. Densities of the solutions were measured at 25.0° with a pycnometer. Viscosities were calculated from the equation

$$\underset{\text{(centi-poise)}}{\text{Viscosity in liq.}} = \frac{\text{(density of liq.)(time ,fall of liq.)(0.8937)}}{\text{(0.99704)(time, fall of water)}}$$

where 0.8937 is the viscosity of water in centi-poise and at 25.0°, and 0.99704 is the density of water at 25.0° in g. cc.$^{-1}$. Results are shown in Figure 16.

Chemicals - The chemicals used in this research were as follows:

Cobalt(II), Nickel(II) and Copper(II) perchlorate hexahydrates: The G. Frederick Smith Chemical Co., Reagent. These chemicals were used without further purification.

1-Butanol: J. T. Baker Chemical Co., "Baker analyzed" reagent. Lot No. 25238. This compound was used without further purification for the distribution and calorimetric experiments. For conductance experiments, it was purified by distillation through a water-cool condenser at about 118°. Only the middle portion of the distillate was collected.

Deionized water was used throughout all but the conductance experiments. The method of preparing conductance water for conductance experiments has be described earlier.

Disodium (ethylenedinitrilo)tetraacetic (EDTA): Eastman Organic Chemicals. Distillation Products Industries. This material was used without further purification. All EDTA titrations were made with Murexide as an indicater.

Karl Fisher Reagent: Eastman Organic Chemicals, Reagent. The reagent was diluted with three parts by volume of absolute methanol per part of reagent before using.

CHAPTER IV

EXPERIMENTAL RESULTS AND DISCUSSION

Distribution Isotherms - The distribution data for $Ni(ClO_4)_2$, $Co(ClO_4)_2$, and $Cu(ClO_4)_2$ are tabulated in Table IV. Figure 10 shows the distribution isotherm for the three salts at 25.0°. Although the data for all three salts do not fall exactly on a common curve, the isotherms are quite close together. The logarithm of the distribution coefficients (organic phase salt molality/aqueous phase salt molality) for the three perchlorates are shown plotted against the square root of the aqueous phase molality of the salts in Figure 11. It can be seen there that the concentration dependence of the logarithm of the distribution coefficients in each case is linear with respect to the square root of the molality of salt. The slopes of the lines are the same for all three salts, and to a close approximation the lines can be replaced by a single line. This result points up the strong probability of a common basis for the extractions.

Table V shows the content of 1-butanol in the aqueous phase. The molality of 1-butanol has been plotted in Figure 12 as a function of the aqueous phase salt molality. Again the relation is linear for all three salts. Also, the data for the three salts fall on a common line. This means that 1-butanol is salted-out of the aqueous phase by the three salts at corresponding concentrations to the same degrees, or that the salting-out coefficient is independent of the chemical nature of the anc ter

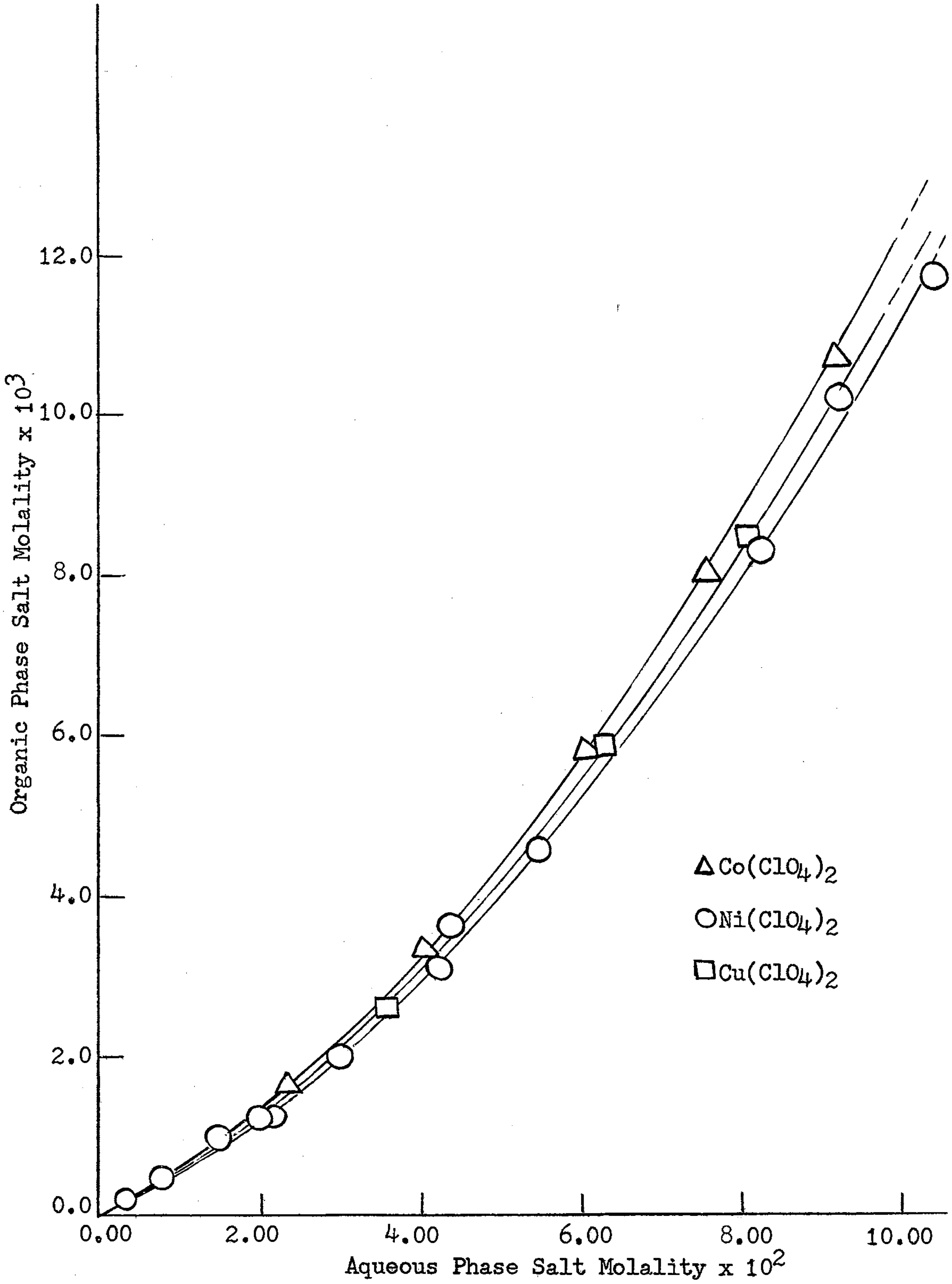


Figure 10. Distribution of Perchlorates at 25.0

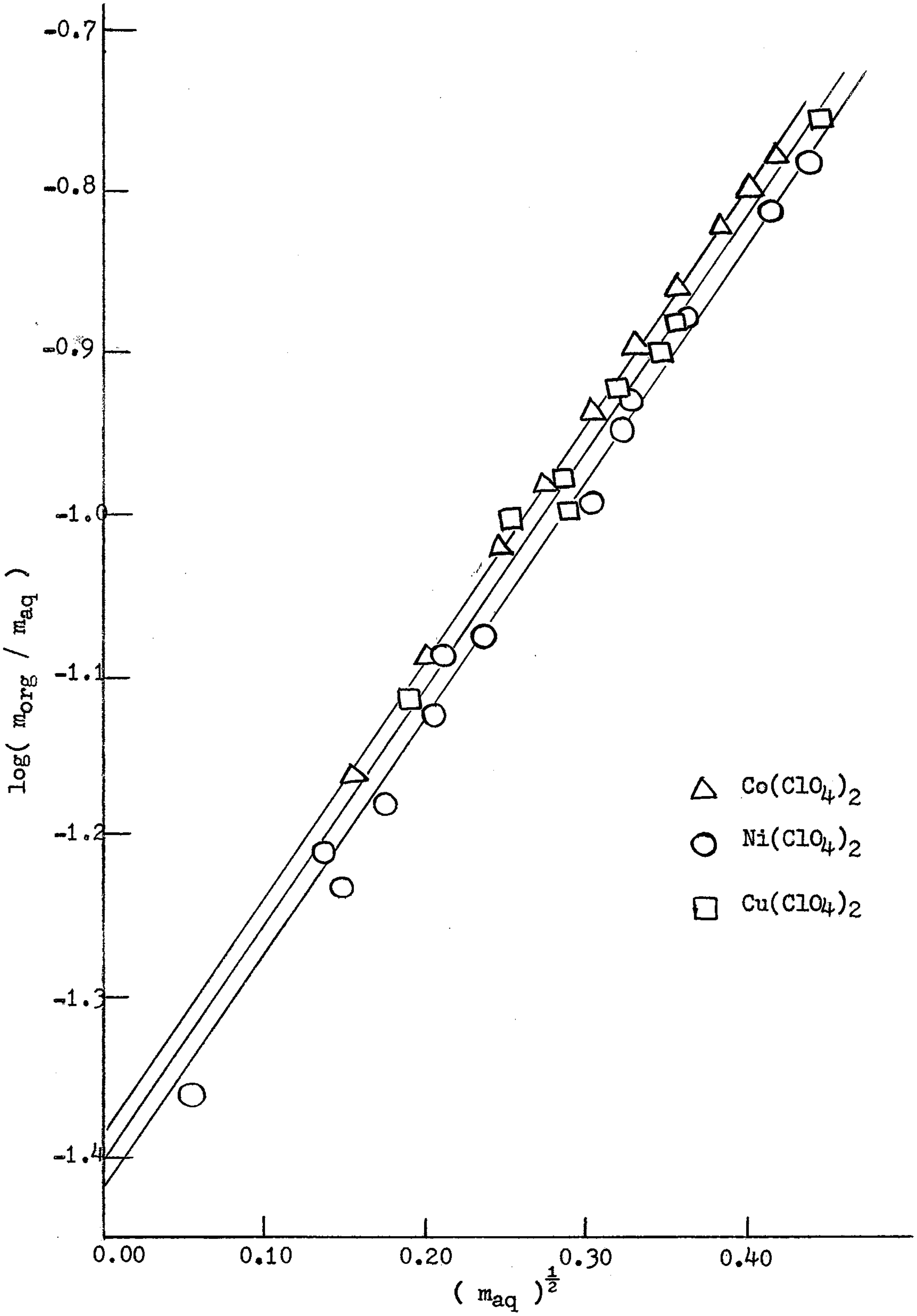


Figure 11. Rectified Distribution Data

TABLE V

CONTENT OF 1-BUTANOL IN AQUEOUS PHASES AT 25.0°

$Ni(ClO_4)_2$		$Co(ClO_4)_2$		$Cu(ClO_4)_2$	
$m_{aq} \times 10^2$	BuOH Molality *	$m_{aq} \times 10^2$	BuOH Molality	$m_{aq} \times 10^2$	BuOH Molality
0.30	1.071	2.32	1.056	1.15	1.050
0.74	1.063	4.08	1.062	2.35	1.051
1.43	1.056	6.07	1.033	3.71	1.045
2.11	1.052	7.59	1.043	5.49	1.042
2.97	1.042	9.19	1.032	7.22	1.031
4.12	1.059	10.97	1.023	8.81	1.023
4.35	1.033	12.77	1.034	10.05	1.013
5.44	1.042	14.71	0.974	11.43	1.037
8.22	1.026	15.35	1.011	12.80	1.014
10.59	1.013	17.56	0.971	14.76	1.023
12.86	1.011			15.04	0.981
17.67	0.990				
19.31	0.970				

* moles kg^{-1} H_2O + salt

TABLE VI

CONTENT OF WATER IN ORGANIC PHASES AT 25.0°

$Ni(ClO_4)_2$		$Co(ClO_4)_2$		$Cu(ClO_4)_2$	
$m_{org} \times 10^3$	H_2O Molality *	$m_{org} \times 10^3$	H_2O Molality	$m_{org} \times 10^3$	H_2O Molality
0.13	13.60	1.59	13.83	1.67	13.85
0.45	13.60	3.32	13.79	3.33	13.95
0.96	13.72	5.80	13.86	5.21	14.08
1.23	13.70	7.94	13.97	7.34	14.24
1.93	13.77	10.66	14.01	11.65	14.45
4.52	13.88	13.96	14.12	13.92	14.66
11.64	14.16	17.65	14.31	18.23	14.92
12.19	13.99	22.18	14.44	18.30	14.76
16.73	14.28	25.64	14.60	23.49	15.14
17.61	14.16	29.09	14.65	34.74	15.72
26.11	14.55				
31.25	14.60				

* moles kg^{-1} 1-BuOH + salt

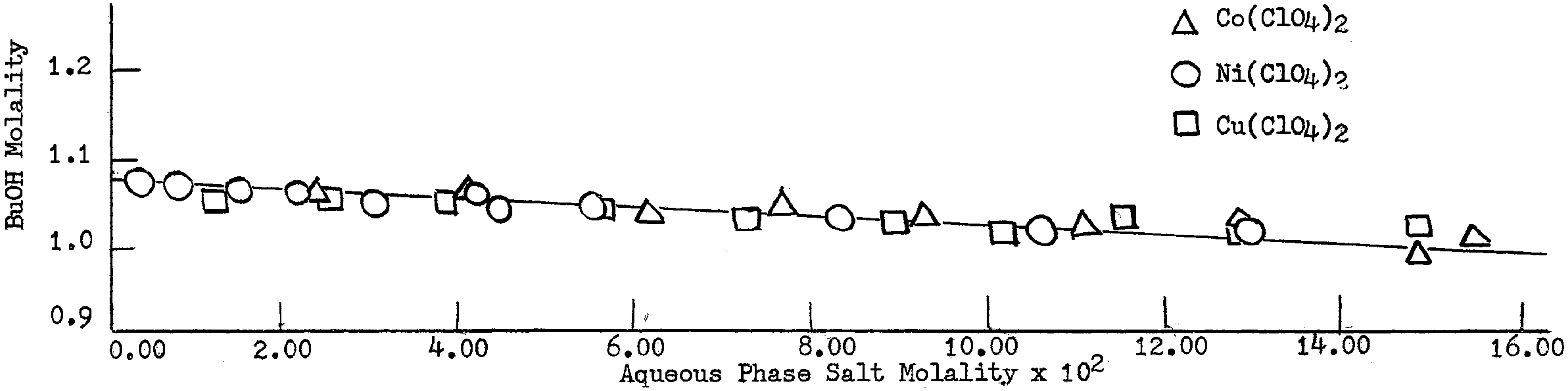


Figure 12. Content of 1-Butanol in Aqueous Phases at 25.0°

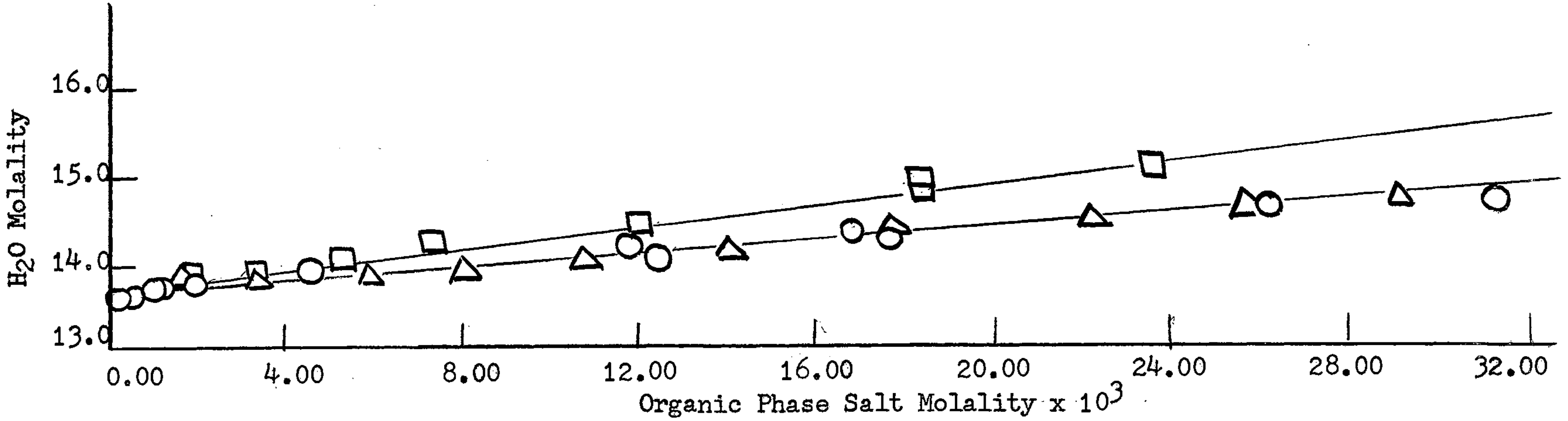


Figure 13. Content of Water in Organic Phases at 25.0°

cation.

Hydration Numbers - The content of water in the 1-butanol phase is tabulated in Table VI. Figure 13 shows also the distribution of water in the organic phase as a function of the salt concentration in that phase. Again one can see clearly the degree of similarity between the extraction behavior of $Co(ClO_4)_2$ and $Ni(ClO_4)_2$, for the data for both salts fall on a common curve. In contrast, the data for $Cu(ClO_4)_2$ are significantly different from those for the other two salts. From the slopes of the straight lines apparent hydration numbers, excess moles H_2O per mole of extracted salt, of the order of 30 for $Ni(ClO_4)_2$, $Co(ClO_4)_2$ and 50 for $Cu(ClO_4)_2$ can be calculated. According to a recent and thorough analysis of hydration numbers (in aqueous solutions) by Azzam (8), hydration numbers of the order 60 are to be expected when one considers both the primary and secondary hydration, in addition to the permanant hydration, for Co^{+2}, Ni^{+2}, and Cu^{+2} ions. In any event, the butanol phases correspond to 1:1 mole ratio butanol-water solvent with ample water for complete hydration of ions in the organic phase.

Based on the above hydration numbers and the fact that water is a stronger ligand than 1-butanol (37), one can visualize that the immediate solvation sheaths around the cations in both aqueous and organic phases are occupied almost entirely by water molecules, the hydration numbers for the three salts being of the order of 50 in both phases. Because of the fact that the organic phase contains adequate water for complete hydration, one can further presume that the nature of solvation in the vicinity of the cations is similar in the two phases. A still more accurate picture is provided by the results of the studies of the thermodynamics of transfer.

Enthalpy of Transfer - Partial molal enthalpies of transfer, $\Delta\overline{H}_t$, have been determined from the thermochemical cycle described in the previous chapter (Figure 6). Thermal quantities for the cycle are listed in Table VII. Measurements have been made for the range of aqueous salt concentrations between 0.02 molal and 0.12 molal, for which the composition of the solvents can be considered to be practically constant and which does not go beyond the limitation of accuracy of the calorimeter.

Values of $\Delta\overline{H}_t$ and $\Delta\overline{S}_t$ shown plotted in Figures 14 and 15 as a function of aqueous salt molality. Surprisingly, the relation between the two is approximately linear, and the lines for the three perchlorates have about the same slope. The absolute magnitudes of $\Delta\overline{H}_t$ for the three salts follow the order $Cu^{+2} > Ni^{+2} > Co^{+2}$. This is reasonable, since the relative ionic radii are in the order $Cu^{+2} < Ni^{+2} < Co^{+2}$, and a simple Born's model would predict such a trend. It is significant that the data for $Ni(ClO_4)_2$ and $Co(ClO_4)_2$ can be represented approximately by a common line. This again indicates the close similarity of the two salts. The values for $Cu(ClO_4)_2$ are about 1.5 kcal.mole^{-1} more negative than those of the other two salts. This may be associated with a distortion from octahedral symmetry in the copper ion. Nevertheless, 1.5 kcal. mole^{-1} is only a small difference compared with the heats of solution (hydration of gaseous ions), which should be at least two hundred times larger in magnitude. One, therefore , should be cautious in concluding that the nature of extraction for $Cu(ClO_4)_2$ is fundamentally different from that of $Co(ClO_4)_2$ and $Ni(ClO_4)_2$.

The values of $\Delta\overline{H}_t$ and $\Delta\overline{S}_t$ are all negative (Figure 14, 15). Extrapolation of the enthalpy curves to zero concentration gives approximately

TABLE VII

HEAT VALUES FOR STEPS IN THE THERMOCHEMICAL CYCLE

$m_{aq} \times 10^2$ / $m_{org} \times 10^3$	$(\Delta \bar{H}_s^*)_{org}$ kcal/mole	$(\Delta \bar{H}_r)_{org}$ kcal/mole	$(\Delta \bar{H}_s)_{org}$ kcal/mole	$(\Delta \bar{H}_s^*)_{aq}$ kcal/mole	$(\Delta \bar{H}_r)_{aq}$ kcal/mole	$(\Delta \bar{H}_s)_{aq}$ kcal/mole	$(\Delta \bar{H}_t)$ kcal/mole	$(\Delta \bar{S}_t)$ e.u./mole
$Ni(ClO_4)_2$								
1.94/1.19	-9.18±0.17	-0.00±0.00	-9.18±0.17	-0.99±0.01	-0.29±0.03	-0.70±0.04	-8.48±0.21	-28.4±0.7
2.11/1.23	-9.10±0.03	-0.155±0.005	-9.255±0.035	-1.035±0.015	-0.26±0.01	-0.775±0.025	-8.46±0.06	-28.4±0.2
2.97/1.93	-9.49±0.02	-0.28±0.03	-9.21±0.05	-1.01±0.03	-0.35±0.04	-0.66±0.07	-8.55±0.12	-28.7±0.6
3.50/2.50	-9.17±0.01	-0.17±0.02	-9.00±0.03	-0.96±0.00	-0.28±0.03	-0.68±0.03	-8.32±0.06	-27.9±0.2
4.35/3.40	-8.51±0.02	+0.01±0.03	-8.52±0.05	-0.91±0.05	-0.23±0.00	-0.68±0.05	-7.84±0.10	-26.3±0.3
5.44/4.63	-8.31±0.00	+0.07±0.03	-8.38±0.03	-0.74±0.01	-0.21±0.02	-0.53±0.03	-7.85±0.06	-26.3±0.2
6.50/6.00	-8.46±0.05	-0.00±0.00	-8.46±0.05	-0.77±0.00	-0.18±0.00	-0.59±0.02	-7.87±0.07	-26.4±0.3
7.00/6.65	-7.98±0.01	+0.06±0.02	-8.04±0.03	-0.77±0.01	-0.17±0.02	-0.60±0.03	-7.44±0.06	-25.0±0.2
$Co(ClO_4)_2$								
2.00/1.33	-9.37±0.05	-0.00±0.02	-9.37±0.05	-1.19±0.02	-0.40±0.00	-0.79±0.02	-8.58±0.07	-28.8±0.3
4.00/3.17	-8.45±0.07	-0.00±0.00	-8.45±0.07	-1.07±0.02	-0.31±0.03	-0.66±0.05	-7.79±0.12	-26.1±0.4
6.00/5.62	-8.05±0.01	-0.00±0.00	-8.05±0.01	-1.00±0.00	-0.17±0.01	-0.83±0.01	-7.22±0.02	-24.2±0.1

TABLE VII (Continued)

8.00/ 8.61	-7.70±0.03	-0.00±0.00	-7.70±0.04	-1.08±0.02	-0.18+0.02	-0.80±0.04	-6.90±0.08	-23.1±0.3
10.00/12.04	-7.10±0.05	-0.00±0.01	-7.10±0.06	-0.98±0.01	-0.16±0.01	-0.82±0.02	-6.28±0.08	-21.1±0.2
$Cu(ClO_4)_2$								
3.00/ 2.20	-10.03±0.03	-0.00±0.00	-10.03±0.03	-0.46±0.01	-0.39±0.02	-0.07±0.03	-9.96±0.06	-33.4±0.2
5.00/ 3.95	-9.52±0.01	-0.00±0.00	-9.52±0.01	-0.42±0.03	-0.35±0.03	-0.07±0.06	-9.45±0.07	-31.7±0.2
7.00/ 6.88	-9.02±0.02	-0.00±0.00	-9.02±0.02	-0.35±0.01	-0.25±0.00	-0.10±0.01	-8.92±0.03	-29.9±0.1
9.00/10.00	-8.25±0.05	-0.00±0.00	-8.25±0.05	-0.33±0.01	-0.20±0.01	-0.13±0.02	-8.12±0.07	-27.2±0.2
11.00/13.50	-7.90±0.07	-0.00±0.00	-7.90±0.07	-0.31±0.00	-0.21±0.02	-0.10±0.02	-7.80±0.09	-26.2±0.3

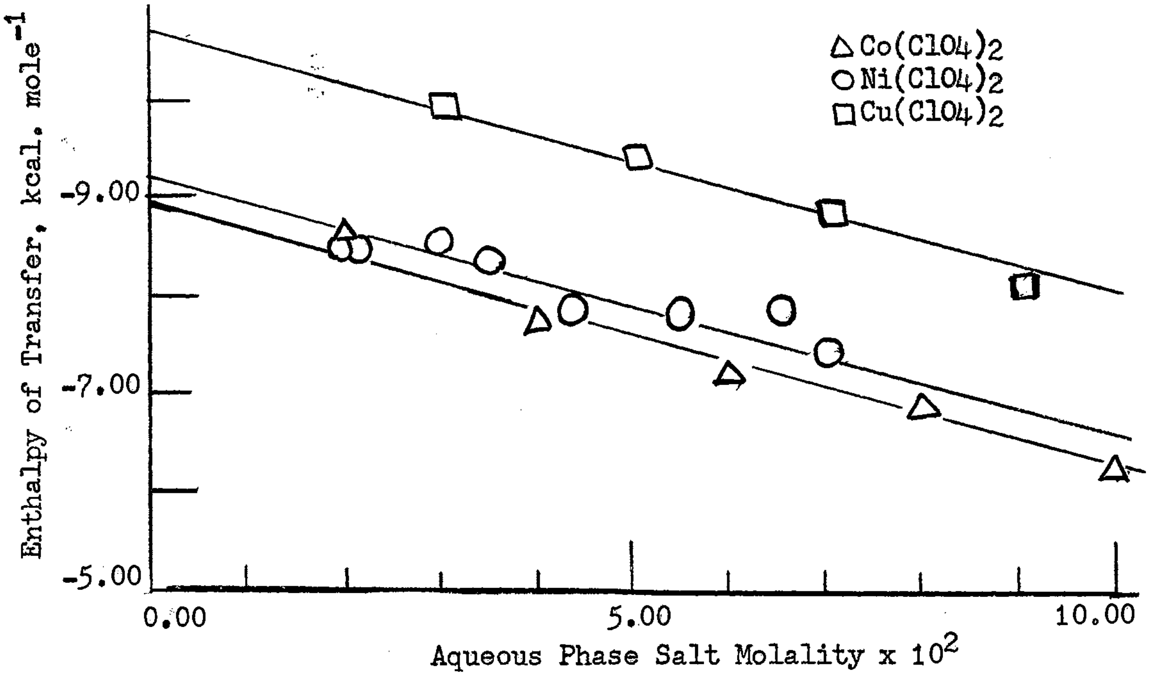


Figure 14. Enthalpy of Transfer at Equilibrium at 25.0°

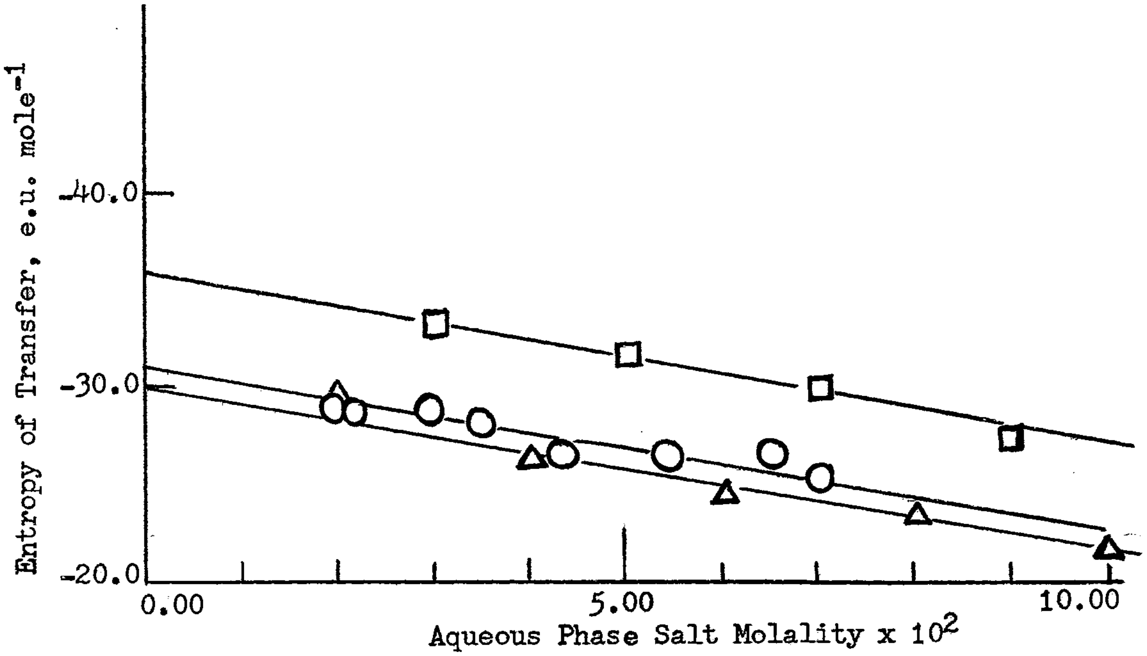


Figure 15. Entropy of Transfer at Equilibrium at 25.0°

$\Delta\overline{H}_t^{\circ}$ = -9 kcal.mole^{-1} for the cobalt and nickel salts and about -10.5 kcal.mole^{-1} for copper perchlorate (Figure 14).

According to the Born model of ion transfer, $\Delta\overline{H}_t^{\circ}$ is given ideally by the equation (Appendix F)

$$\Delta\overline{H}_t^{\circ} = -4313 \left(\sum_{\alpha} \nu_{\alpha} z_{\alpha}^2 \; / \; r_{\alpha}\right) \qquad (4.1)$$

where r_{α} is the radius of ion α in Å. The other symbols are defined in Appendix F. When ionic charges and Pauling radii are substutited into equation (4.1), the following results can calculated

$\Delta\overline{H}_t^{\circ}$ for $Ni(ClO_4)_2$ = -27.7 kcal. mole^{-1}

$\Delta\overline{H}_t^{\circ}$ for $Co(ClO_4)_2$ = -27.1 kcal. mole^{-1}

$\Delta\overline{H}_t^{\circ}$ for $Cu(ClO_4)_2$ = -28.8 kcal. mole^{-1} .

Although the equation predicts correctly the sign and the relative order of the salts, the absolute magnitudes are three times too large. From among the various possible causes, probably the most important are (a) neglect of dielectric saturation and electrostriction and (b) failure to account for the detailed structure of solvation. When these are taken into proper consideration, much better agreement can be achieved (next chapter).

It was reported that there was an estimated 0.7% of free acid from hydrolysis for every mole of $Cu(ClO_4)_2$ present. Since the value of $\Delta\overline{H}_t$ for the acid impurity should be much less than 9 kcal. mole^{-1} (absolute magnitude), then a small quantity of impurity would contribute much less than 0.06 kcal. to the partial molal enthalpies of transfer of the salt. The effect, therefore, should be negligible. Based on this arguement, one would not expect the presence of a such a small amount of acid impurity to affect the viscosity of the solutions, nor to affect the distribution equilibria significantly.

Entropy of Transfer - The extrapolation of the entropy curves to zero salt concentration yields approximately $\Delta\bar{S}_t^{\circ} = -30$ e.u. mole^{-1} for the cobalt and nickel salts, and about -35 e.u. mole^{-1} for copper perchlorate (Figure 15).

The negative sign of the entropy change can be easily accounted for. The non-organic solvent contains only a small amount of alcohol, and is essentially aqueous. According to Franks and Ives (Chapter II) water is able to act as host to a small number of molecules, which , although alien, have a certain affinity for water. Therefore, the order of the water structure is more or less preserved. On the other hand, for the organic solvent, which is a 1:1 mole ratio alcohol-water mixture, the structure would be expected to be less ordered than that of pure water, since both linear polymerization of the alcohol and the tetrahedral clustering of water would be mutually interfered with. Franks and Ives described this as "with increasingly extensive invasion by the foreign species, however, rather sudden co-operative failure of structure retention is to be expected - the sooner, the more 'foreign' the invader". Consequently, the effect of strongly structure-ordering ions such as the bivalent metal cations would be enhanced in the butanol-rich phases while that of ordinarily structure-breaking anions (perchlorate) would be diminished. A negative entropy of transfer will be found in such cases.

Viscosity of Solution - Figure 16 shows the results of viscosity measurements. In agreement with the idea of an enhancement of structure-making by the cation and a decrease in structure-breaking by the anion in the organic phase, there is observed in the organic phase a more rapid increase in the viscosity with increase in concentration of

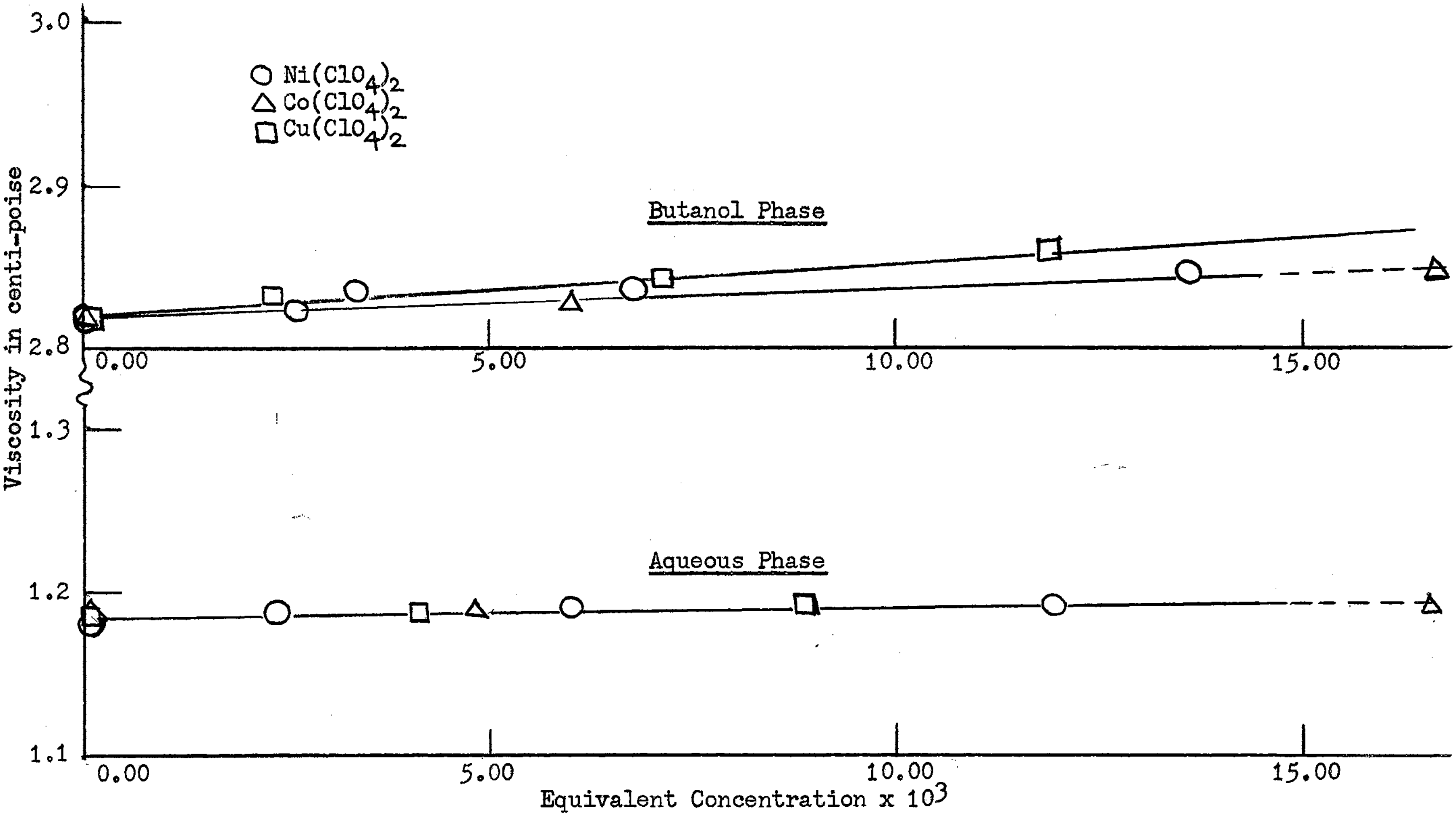


Figure 16. Viscosity of Extraction Phases at 25.0°

salt than in the aqueous phase. Significantly, copper solutions show the most marked effects while those for cobalt and nickel solutions remain closely similar.

Electrical Conductances - Reference to Figure 15 again shows that with increasing concentration there is a linear increase in the values of $\Delta\bar{S}_t$ with increase in concentration of salt. In a solvent of bulk dielectric constant of approximately 27, a high degree of ionic association is probable, and since $\Delta\bar{S}^{\circ}$ values for ion-association reactions are usually positive, an increase in entropy with increasing concentration is expected. Such is the case (Figure 15).

A study of the electrical conductance of the solutions in both equilibrium phases was made to obtain an estimate of the degree of first order association. Results are given in Tables IX and X. The equivalent conductance is plotted against the square root of the equivalent concentration in the conventional manner (Figures 17 and 18). Also shown in this figure are the dash lines calculated from the Onsager limiting equation (Appendix C). From Figures 17 and 18 it can be seen that all three salts have practically the same conductance in both phases. This again signifies that the solvation of the three salts in the extraction phases are essentially identical.

Since Walden's rule was found to be followed fairly closely (Table VIII) in the aqueous phases, it was assumed that the rule could be applied to the organic phase solutions to obtain the limiting conductance (38.7 $cm.^2$ ohm^{-1} $equiv.^{-1}$ for all three salts). The experimental values of the conductance for aqueous solutions can be seen (Figure 17) to be all higher than predicted by the limiting law. This, in general, signifies that the salts are behaving as nonassociated electrolytes.

TABLE VIII

WALDEN'S RULE AND THE LIMITING CONDUCTANCES OF THE PERCHLORATES IN AQUEOUS AND BUTANOL PHASES AT 25.0°

Limiting Equivalent Conductance cm.^{2}ohm^{-1} equiv.$^{-1}$	$Co(ClO_4)_2$	$Ni(ClO_4)_2$	$Cu(ClO_4)_2$
Λ°(water)	122	122	121
Λ°(aqueous phase)	94	94	94
Λ°(aqueous phase, calculated)	92	92	91
Λ°(organic phase, calculated)	38.7	38.7	38.7

Viscosity: of water = 0.8937 centi-poise

of aqueous phase = 1.184 centi-poise

of organic phase = 2.816 centi-poise

TABLE IX

CONDUCTANCE OF EQUILIBRIUM AQUEOUS PHASES AT 25.0°

$Ni(ClO_4)_2$		$Co(ClO_4)_2$		$Cu(ClO_4)_2$	
$(C_e)^{\frac{1}{2}} \times 10^2$	Λ	$(C_e)^{\frac{1}{2}} \times 10^2$	Λ	$(C_e)^{\frac{1}{2}} \times 10^2$	Λ
3.66	91.27	6.00	87.94	5.96	90.23
6.00	86.47	9.16	86.81	9.11	88.38
7.76	87.50	12.00	82.55	11.92	85.32
9.18	86.14	14.41	79.32	14.13	83.32
10.79	84.04	16.24	79.33	16.10	82.23
11.50	84.67	17.97	77.72	17.83	80.44
12.50	84.19	21.00	75.31	20.84	78.20
13.42	82.42	25.01	71.67	25.82	75.00
14.30	82.07	33.81	66.85	33.61	70.41
15.20	81.80	40.10	62.74	39.80	66.86
16.61	80.54				

C_e = Equivalent concentration

Λ = Equivalent conductance, cm.^{2} ohm^{-1} equiv.$^{-1}$

TABLE X

CONDUCTANCE OF EQUILIBRIUM 1-BUTANOL PHASE AT 25.0°

$Ni(ClO_4)_2$		$Co(ClO_4)_2$		$Cu(ClO_4)_2$	
$(C_e)^{\frac{1}{2}} \times 10^2$	Λ	$(C_e)^{\frac{1}{2}} \times 10^2$	Λ	$(C_e)^{\frac{1}{2}} \times 10^2$	Λ
4.90	15.67	3.46	17.63	3.44	16.82
6.94	14.98	4.89	15.85	4.87	15.32
8.50	13.73	6.92	14.91	6.88	13.96
9.81	13.42	9.15	13.94	8.43	12.99
10.97	13.13	10.93	13.03	10.34	12.01
12.98	12.59	12.46	12.81	11.93	11.67
13.87	12.37	13.81	12.37	13.31	11.13
14.71	12.26	15.04	12.13	15.77	10.77
15.50	12.10	16.20	12.01		
16.25	11.96	17.24	11.80		
16.98	11.85				

C_e = Equivalent concentration

Λ = Equivalent conductance, cm.^{2} ohm^{-1} equiv.$^{-1}$

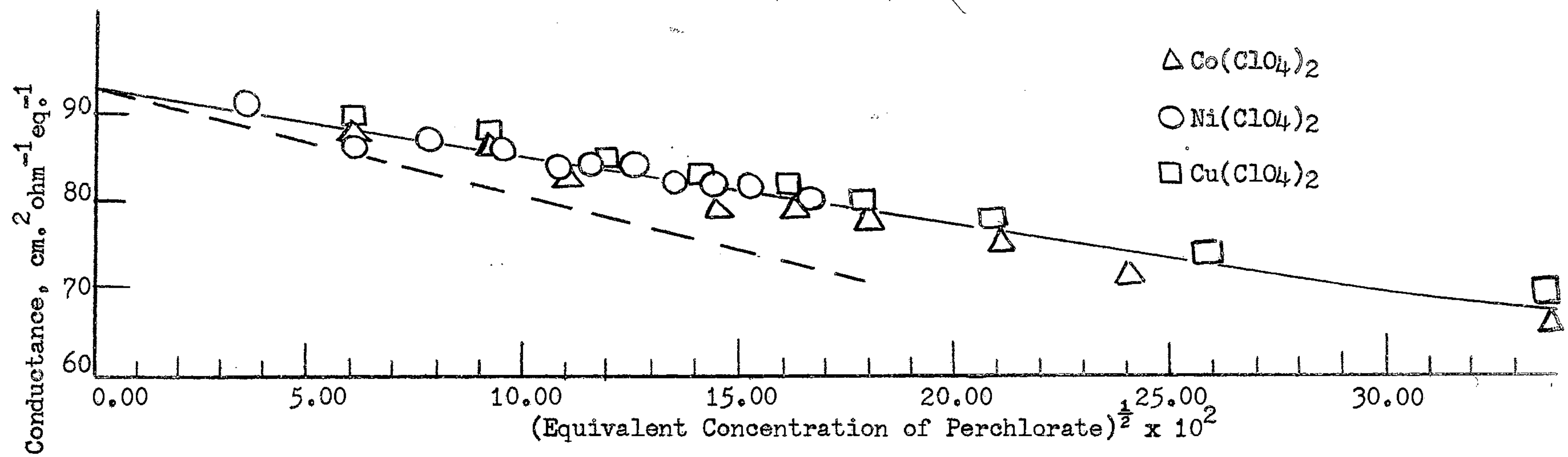


Figure 17. Conductance of the Equilibrium Aqueous Phase at 25.0°

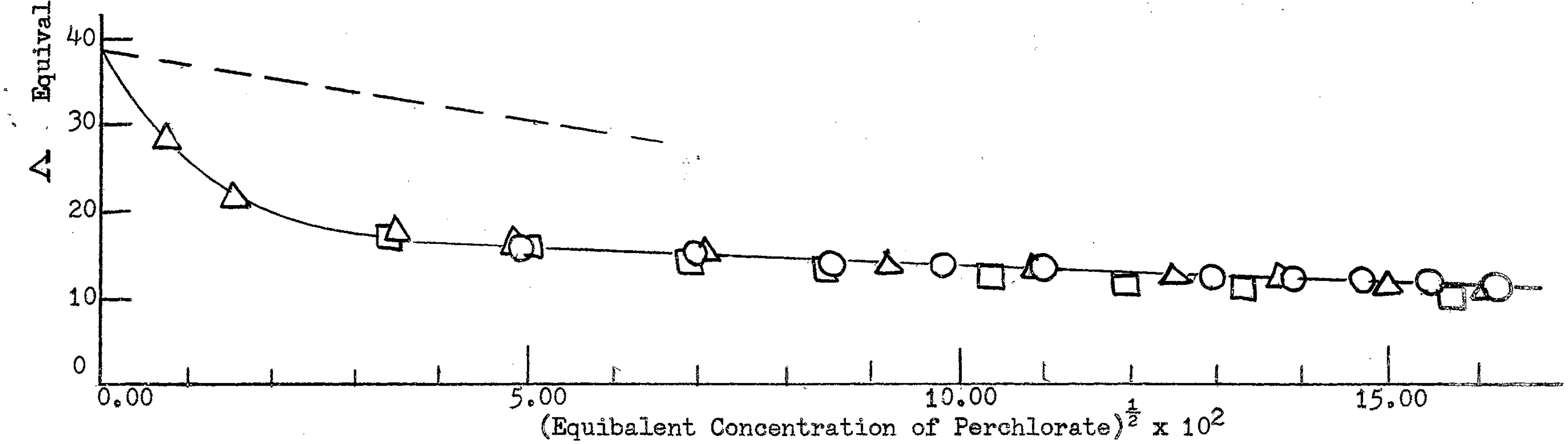


Figure 18. Conductance of the Equilibrium 1-Butanol Phase at 25.0°

For the organic solutions, however, the experimental conductances are much lower than predicted (Figure 18). This is an indication of large degree of ionic association, possibly as $Ni(ClO_4)^+$ at lower concentrations, and at higher concentrations as neutral $Ni(ClO_4)_2$. Similar species are assumed for the other salts.

To form an estimate of the degree of ion-association in butanol phases, the following equation (Appendix D) was applied to the data.

$$\Lambda_{obs.} = (37.8 - 92.4\Gamma^{\frac{1}{2}})(1-\alpha) - \alpha(24.4 - 69.1\Gamma^{\frac{1}{2}}) \qquad (4.2)$$

where Γ = ionic strength = $3C_e - 4C_e\alpha$

α = fraction of perchlorate ions associated

C_e = equivalent concentration salt .

Following Monk (34) the contribution to the limiting conductance from the ion-pair $Ni(ClO_4)^+$ has been estimated to be ca. $0.4\Lambda^\circ$ for Ni^{+2}. The results (Table XI), notwithstanding the uncertainties in extrapolation to the limiting conductance and in the proper value for the conductance of the ion-pair, lead to the conclusion that over the entire concentration range for which the transfer experiments were made the salts are extensively associated into ion-pairs and neutral species. This is further expressed by the large value of the first association constant of ca. 10^4 liter $mole^{-1}$.

At least qualitatively, therefore, the observed increase in the entropy of transfer with increasing concentration can be accounted for in terms of a positive entropy of ion-association (39). This, at least in the case of the systems investigated, is believed to be caused not so much by the displacement of water molecules in the permanent hydration sheath around the cations upon ion-association but rather by a gain in freedom of the water molecules surrounding the ions which

TABLE XI

CALCULATED DEGREE OF FIRST ORDER ION ASSOCIATION OF THE THREE PERCHLORATES IN EQUILIBRIUM BUTANOL PHASES FROM CONDUCTANCE AT 25.0°

$\sqrt{C_e} \times 10^3$	Fraction of metal associated, 2α
1	0.10
3	0.18
5	0.24
7	0.30
10	0.38
20	0.52
30	0.60
50	0.64

TABLE XII

CALCULATED DEGREE OF SECOND ORDER ION ASSOCIATION OF THE THREE PERCHLORATES IN EQUILIBRIUM BUTANOL PHASES FROM CONDUCTANCE AT 25.0°

$\sqrt{C_e} \times 10^3$	Fraction of metal associated, β
50	0.59
70	0.61

(C_e = Equivalent concentration)

arises from the reduction in the electric field accompanying ionic association. This should be especially true for those molecules outside the permanent hydration sheath.

It should be noted that the conductance calculated using equation (4.2) which is based on the limiting equation is a little too low, and the difference increases as the concentration of salt increases (page 11 of reference 13). Therefore, the actual degree of association should be even greater than indicated in Table XI, particularly at higher concentrations.

According to Table XI, it is evident that even at $C_e = 1x10^{-4}$, there is already extensive first order ion-association in the organic phase. At higher concentrations, it is probable that second order ion-association (formation of neutral $Ni(ClO_4)_2$) will be important. An approximation of second order association can be calculated using the equation (Appendix E)

$$\Lambda_{obs.} = (1-\beta)\left[38.7 - 160\sqrt{(1-\beta)\, C_e}\,\right] \qquad (4.3)$$

where β is the fraction of metal ions associated (or perchlorate ions associated). Here it is assumed that there is no first order association. Results are shown in Table XII.

According to Table XII, the second order association constant at 25.0° is calculated roughly to be ca. 10^7 liter^{2}mole^{-2}. This, however, is not very meaningful, for the association is most certainly stepwise; i.e.,

$$M^{+2} + ClO_4^- \rightleftharpoons MClO_4^+ \qquad (4.4)$$

$$MClO_4^+ + ClO_4^- \rightleftharpoons M(ClO_4)_2 \qquad (4.5)$$

CHAPTER V

THEORETICAL MODELS

Solvation Models - In chapter IV, the general picture of the solvation of all of the salts studied has been developed. The salts are all visualized as being fully solvated by water molecules in both the aqueous and organic phases. This is evidenced by their all having large apparent hydration numbers and the fact that the organic-phase solvent contains ample water for complete solvation. Also, the apparent validity of Walden's rule is further evidence that in the transference from aqueous to butanol phases, the salts suffer no significant change in their hydration sheaths. On the other hand, similarities in distribution equilibria, nearly equal enthalpies and entropies of transfer - all suggest that the nature of the extraction of the three salts is basically the same.

Since all three salts in the equilibrium butanol phases have visisble absorption spectra which are indistinguisable from their aqueous solutions, the first coordination sites of the cations must be approximately octahedrally symmetric and occupied by water molecules (37). In other words, six-coordinately hydrated cations can be regarded as the "effective" cationic species in both the aqueous phase and the 1-butanol phase.

At infinite dilution, the solvation of the perchlorates is visualized as in Figure 19. Where the innermost circle around the metal

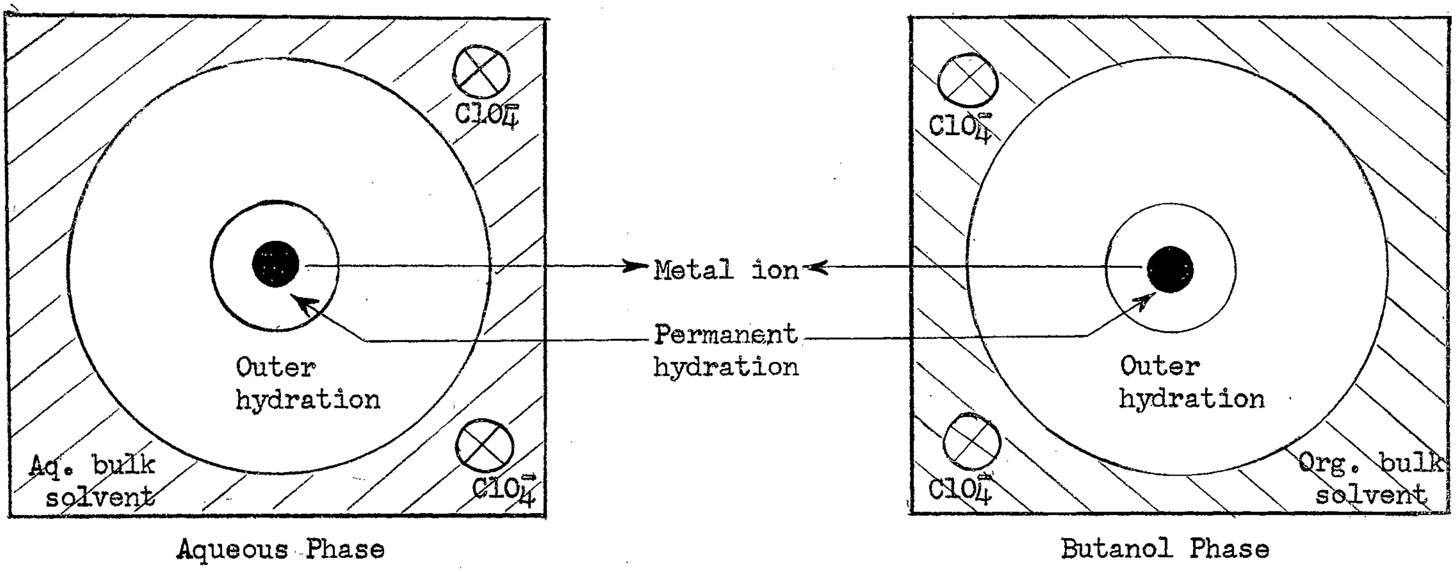
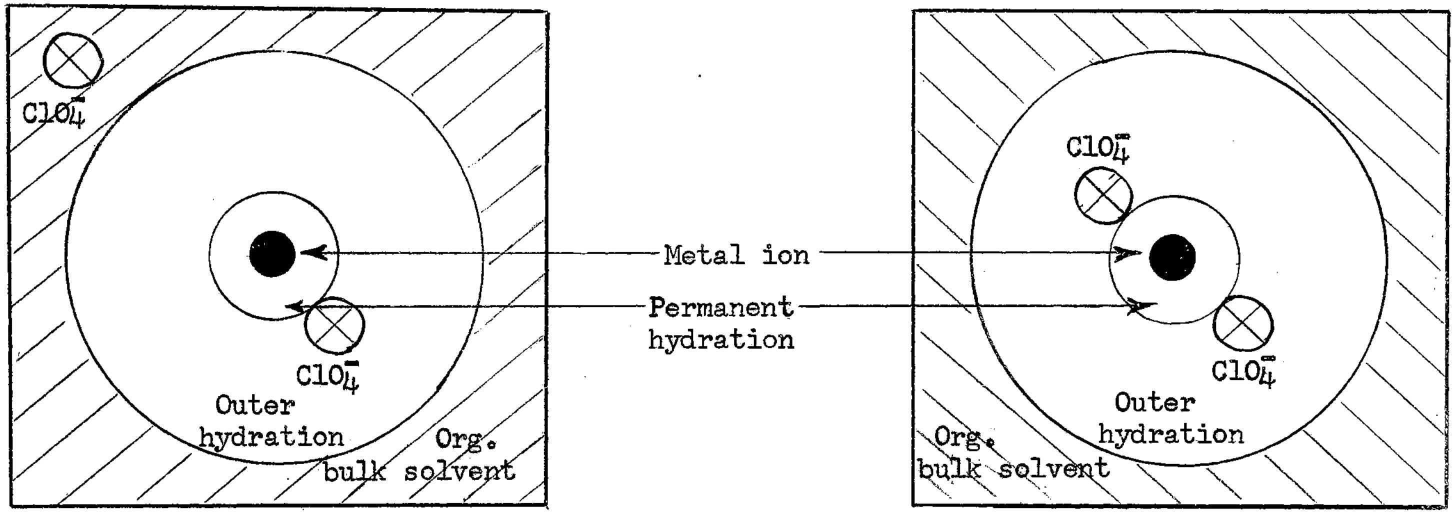


Figure 19. Solvation Model at Infinite Dilution



(a)First Order Association (b)Second Order Association

Figure 20. Solvation Model of Organic Phase at Finite Salt Concentrations

ion represents the outer boundary of the permanent hydration sheath, occupied by six water molecules. Outside this circle, there is a outer hydration sheath, assumed occupied mostly by water molecules, especially in the rigion immediately next to the permanent hydration sheath. It is assumed that the dielectric constant of the extraction solvent (Appendix B) is effective immediately outside the permanent hydration sheath, which means one regards the octahedrally-hydrated cation as the "effective cation". Perchlorate ions are not considered hydrated, and are pictured as bare ions in contact with bulk solvents.

At finite concentrations of salt, extensive ionic association in the organic phases has been found (Tables XI and XII). Ion-association can take place with a water molecule (or water molecules) separating the cation and anion (Chapter II). This is probably the case here as evidenced by the spectra of the salts in the organic phases. Thus the organic phase at finite salt concentrations can be pictured by Figure 19 and either Figure 20(a) or 20(b), or by all three.

Figure 20(a) represents first order ion-association, and 20(b) second order ion-association, with relative positions of the perchlorate anions unspecified (will be specified later).

In summary, at finite concentrationsthe transfer of the salts is to be considered as the transfer of fully hydrated ions with subsequent association into hydrated ion aggregates in hydrous butanol.

<u>Enthalpy of Transfer</u> - It has been shown (Chapter IV) that the simple Born model predicts $\Delta\bar{H}_t^\circ$ values which are almost three times more negative than the experimental values. However, the model does predict the right sign and the right trend among the salts expected on the basis of ionic radii; therefore, the model may be considered as essen-

tially correct.

Figure 19 is pictorily a modified Born model. It is this model which is to be examined here. As shown in Appendix F, $\Delta\overline{H}_t^\circ$ at 25.0° is given on the basis of the Born model by the equation

$$\Delta\overline{H}_t^\circ = -(4.313)\ (\sum_\alpha \nu_\alpha Z_\alpha^2\ /\ r_\alpha\ ), \qquad (5.1)$$

where $\Delta\overline{H}_t^\circ$ is in kcal. mole^{-1} if r_α is in Å. Using the model described in Figure 19, the values of r_α for the cations should now be replaced by the effective radii, i.e., r_{cation} = Pauling radius + 2.72 Å (p. 51 of reference 21). Thus,

$r_{Ni^{+2}} = 0.72 + 2.72$ Å

$r_{Co^{+2}} = 0.74 + 2.72$ Å

$r_{Cu^{+2}} = 0.69 + 2.72$ Å, where 2.72 is the diameter of H_2O.

Since ClO_4^- is not considered to be hydrated, $r_{ClO_4^-} = 2.28$ Å (see Appendix F). Upon substitution of the above values of r_α and ionic charges into equation (5.1), one gets

$\Delta\overline{H}_t^\circ$ for $Ni(ClO_4)_2$ = -8.8 kcal. mole^{-1}

$\Delta\overline{H}_t^\circ$ for $Co(ClO_4)_2$ = -8.8 kcal. mole^{-1}

$\Delta\overline{H}_t^\circ$ for $Cu(ClO_4)_2$ = -8.8 kcal. mole^{-1} .

Therefore, the modified Born model predicts $\Delta\overline{H}_t^\circ$ to be about -9 kcal mole^{-1} for all three salts. The corresponding entropy change is about -30 e.u. mole^{-1}. These agree very well with the experimental values of about -8.9 to -10.7 kcal. mole^{-1} for the enthalpy of transfer and about -30 to -36 e.u. mole^{-1} for the entropy of transfer. In view of the simplicity of the electrostatic model and the uncertainties involved in the physical quantities needed for calculation, the agreement is better than normally could be expected.

The addition of the diameter of a water molecule to the Pauling radii of the metal ions neglects the interaction between the permanent hydration (water) with the metal ions. Fortunately, the same interaction is present in both the aqueous phase and the 1-butanol phase, and therefore, cancellation results when $\Delta\overline{H}_t^\circ$ is calculated. On the other hand, the use of effective radii avoids the catastrophe of dielectric saturation and electrostriction, which, together with ignorance of the detailed solvation structure, cause the failure of the simple Born model.

The fact that $\Delta\overline{H}_t^\circ$ for $Cu(ClO_4)_2$ was found experimentally more negative by 1.5 kcal. mole^{-1} than the cobalt and nickel salts can be ascribed possibly to the distortion of the octahedral symmetry about the Cu^{+2} ion. This has not been taken into account in the calculation.

Entropy of Ion Association - In view of the gratifying success of the "effective cation" concept in the calculation of $\Delta\overline{H}_t^\circ$, the calculation of entropy of ion-associations based on the same model will be now considered. The modified Born equation again will be used where applicable. The method is, therefore, essentically identical to that described by Austin and Matheson (chapter 24 of reference 12).

First Order Ion-Association

Based upon the association model described in Figure 20 (a) (relative sizes of ions and water molecules are shown in Figure 22), an analysis of the ion association by the Evans-Nancollous entropy cycle (39) leads to to the following

$$\begin{tikzcd}
M(H_2O)_n^{2+}(g) & + X^-(g) \arrow[r, "\Delta S_2^\circ"] & M(H_2O)_{n-2}X^+(g) \arrow[d, "\Delta S_3^\circ"] & + 2H_2O(g) \arrow[d, "\Delta S_4^\circ"] \\
M(H_2O)_n^{2+}(Aq) \arrow[u, "\Delta S_1^{\circ +}"] & + X^-(Aq) \arrow[u, "\Delta S_1^{\circ -}"] & M(H_2O)_{n-2}X^+(Aq) \arrow[l, "\Delta S_5^\circ"'] & + 2H_2O(g)
\end{tikzcd}$$

Figure 21. The Entropy Cycle, First Order Ion Association

Here, $M(H_2O)_n^{2+}$ represents the hydrated cation of Figure 19. The extent of the hydration needs not be specified. Nevertheless, the very large hydration numbers determined experimentally indicate that n should be of the order of 30-50. Because of the larger size of the perchlorate ion relative to the water molecule, it is assumed that first order ion-association takes place when a perchlorate ion displaces two molecules of H_2O from the hydration sheath immediately surrounding the "effective cation" (Figure 20 (a)).

Since the major contributing factor to the change of entropy upon ion-association in the present system is due to the change in the order of water molecules in the solvent, the process can be approximated as taking place in purely aqueous solution. It should be pointed out here that "Aq" is used to denote "aqueous solution", as distinguished from "aq" which represents "aqueous <u>phase</u> solution".

From Figure 21 it follows that the entropy change of first order ion-association at infinite dilution, $(\Delta S^\circ_{ass})_{1st}$, can be represented by

$$(\Delta S^\circ_{ass})_{1st} = -\Delta S^\circ_5 = \Delta S^{\circ+}_1 + \Delta S^{\circ-}_1 + \Delta S^\circ_2 + \Delta S^\circ_3 + \Delta S^\circ_4 \ . \qquad (5.2)$$

Both $\Delta S^{\circ+}_1$ and ΔS°_3 can be calculated approximately using Born's equation and Gibbs-Helmholtz equation $((\partial \Delta G^\circ / \partial T)_p = -\Delta S^\circ)$, assuming that the radii of all hydrated cations and ion-pairs are 2.72 Å greater than the crystal radii (r^+) of the metal ion (so that the Born expressions differ only in the charge). Thus,

$$\Delta S^{\circ+}_1 = -\frac{Z_1^2\, e^2}{2(r^+ + 2r_{H_2O})} \left(\frac{1}{D^2}\right) \left(\frac{dD}{dT}\right)$$

$$\Delta S^\circ_3 = \frac{Z_2^2\, e^2}{2(r^+ + 2r_{H_2O})} \left(\frac{1}{D^2}\right) \left(\frac{dD}{dT}\right) \ . \qquad (5.3)$$

Where Z_1, Z_3 are the valences on M^{+2} and the ion-pair, D is the dielectric constant of water.

Since

$$\Delta S_1^{\circ -} = S^\circ_{X^-(g)} - S^\circ_{X^-(Aq)} \qquad (5.4)$$

$$\Delta S_4^\circ = 2\left[S^\circ_{H_2O(Aq)} - S^\circ_{H_2O(g)}\right] \qquad (5.5)$$

$$\Delta S_2^\circ = S^\circ_{\text{ion-pair}(g)} + 2S^\circ_{H_2O(g)} - S^\circ_{M(H_2O)_n^{2+}} - S^\circ_{X^-(g)}. \qquad (5.6)$$

on substitution into equation (5.2), one has

$$(\Delta S^\circ_{ass})_{1st} = \left(\frac{-dD/dT}{D^2}\right)(N_0 e^2)\left|\frac{Z_1^2 - Z_2^2}{2(r^+ + 2r_{H_2O})}\right| + 2\,S^\circ_{H_2O(Aq)} - S^\circ_{X^-(Aq)}$$

$$+ \left[S^\circ_{\text{ion-pair}(g)} - S^\circ_{M(H_2O)_n^{2+}(g)}\right] \quad . \qquad (5.7)$$

The value of the square bracket is essentially a rotational entropy change, which is assumed to be not much different from 2.5 e.u. mole^{-1} — a value estimated by Austin and Matheson for a similar entropy change, using a slightly different ion-association model (ch. 24 of ref. 12). Upon substitution of the above and the appropriate physical constants, one has

$$(\Delta S^\circ_{ass})_{1st} = 19.4\left|\frac{3}{2(r^+ + 2r_{H_2O})}\right| + 2S^\circ_{H_2O(Aq)} - S^\circ_{ClO_4^-(Aq)}$$

$$+ 2.5 \qquad (5.8)$$

$$= \text{e.u. mole}^{-1} \text{ if radius is in } \text{Å} .$$

Setting $r^+ + 2r_{H_2O} = 3.4$ Å for all three metal ions, and since $S^\circ_{H_2O(Aq)} = 16.7$ e.u. mole^{-1} and $S^\circ_{ClO_4^-} = 43.5$ e.u. mole^{-1},

$(\Delta S^\circ_{ass})_{1st} = 8.6 + 33.4 + 2.5 - 43.5 = 1.0$ e.u. mole^{-1} for all three salts and at 25.0°.

It is assumed that the solutions are sufficiently dilute so that $(\Delta S^\circ_{ass})_{1st} \cong (\Delta S_{ass})_{1st}$ in the organic phase. When $C_e^{\frac{1}{2}} = 1 \times 10^{-2}$ in the organic phase, the salt molality of the organic solution is 5×10^{-5}, and the corresponding concentration in the aqueous phase is

1×10^{-3} molal. At this concentration the fraction of metal ion associated is about 0.4 (Table XI). Therefore, the contribution to $\Delta\overline{S}_t$ is about 0.4 e.u. mole^{-1} based on the model shown in Figures 20(a) and 22.

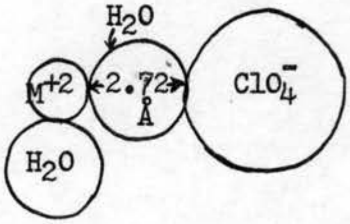


Figure 22. Orientation of ClO_4^- around the Effective Cation

The experimental value of $\Delta\overline{S}_t - \Delta\overline{S}_t^\circ$ is about 0.3 e.u. mole^{-1}(Figure 15).

Second Order Ion-Association

Although $(\Delta S_{ass})_{1st}$ is positive, it is too small to account for large increases in the entropy of transfer at higher salt concentrations. As disscussed previously, second order ion-association becomes important at high concentrations. The model for this ion-association is shown in Figure 20(b). In order for $2ClO_4^-$ ions to come in contact with the effective cation (hexahydrated metal ion) four water molecules must be liberated from the hydration sheath immediately surrounding the "effective cation". However, owing to very effective reduction of ionic charge in the present case, more than four water molecules are likely to be released. In order to allow for this possibility, it is assumed that m, an integer parameter greater than 4 but relatively small compared with n, water molecules are released from the hydration sheath mentioned. The association process accordingly can be represented by the following entropy cycle:

$$\begin{tikzcd}
M(H_2O)_n^{2+}(g) & +\ 2X^-(g) \arrow[r, "\Delta S_2^\circ"] & M(H_2O)_{n-m}X_2(g) \arrow[d, "\Delta S_3^\circ"] & +\ mH_2O(g) \arrow[d, "\Delta S_4^\circ"] \\
M(H_2O)_n^{2+}(Aq) \arrow[u, "\Delta S_1^{\circ+}"] & +\ 2X^-(Aq) \arrow[u, "\Delta S_1^{\circ-}"] & M(H_2O)_{n-m}X_2(Aq) \arrow[l, "\Delta S_5^\circ"'] & +\ mH_2O(Aq)
\end{tikzcd}$$

Figure 23. The Entropy Cycle, Second Order Ion Association

from which

$$(\Delta S^\circ_{ass})_{2nd} = -\Delta S_5^\circ = \Delta S_1^{\circ+} + \Delta S_1^{\circ-} + \Delta S_3^\circ + \Delta S_4^\circ + \Delta S_2^\circ. \quad (5.9)$$

As before, $\Delta S_1^{\circ+} = -\dfrac{2^2e^2}{2(r^+ + 2r_{H_2O})}\left(\dfrac{1}{D^2}\right)\left(\dfrac{dD}{dT}\right).$ (5.10)

The quantity ΔS_3° now represents the entropy change for transferring a fully hydrated neutral ion-triplet from its gaseous state to its aqueous solution. Because of the electric neutrality of the ion-triplet, entropy loss for the process should be much smaller than for the process $M(H_2O)_{n-2}X^+(g) \longrightarrow M(H_2O)_{n-2}X^-(Aq)$, for which entropy change is calculated to be only 2.8 e.u. mole^{-1} using Born's equation and Gibbs-Helmholtz equation. Therefore, in the present case, it can be assumed that $\Delta S_3^\circ = 0$. Since

$$\Delta S_1^{\circ-} = 2\left[S^\circ_{X^-(g)} - S^\circ_{X^-(Aq)}\right], \quad (5.11)$$

$$\Delta S_2^\circ = S^\circ_{M(H_2O)_{n-m}X_2(g)} + mS^\circ_{H_2O(g)} - S^\circ_{M(H_2O)_n^{2+}}(g) - 2S^\circ_{X^-(g)}, \quad (5.12)$$

$$\Delta S_4^\circ = m\left[S^\circ_{H_2O(Aq)} - S^\circ_{H_2O(g)}\right], \quad (5.13)$$

$$\therefore\ (\Delta S^\circ_{ass})_{2nd} = 19.4\left[\frac{4}{2(r^+ + 2r_{H_2O})}\right] + mS^\circ_{H_2O(Aq)} - 2S^\circ_{X^-(Aq)} + \left[S^\circ_{M(H_2O)_{n-m}X_2(g)} - S^\circ_{M(H_2O)_n^{2+}(g)}\right]. \quad (5.14)$$

Assuming the value of the term in the last square bracket to be 2 x 2.5 = 5 e.u. mole^{-1}, and $r^+ + 2r_{H_2O} = 3.4$ Å for all three salts, then

$(\Delta S^{\circ}_{ass})_{2nd} = 16.7m - 71.$

In order that $(\Delta S^{\circ}_{ass})_{2nd}$ be positive, m must be equal or greater than 5. When m=5, $(\Delta S^{\circ}_{ass})_{2nd} = 12$ e.u. mole^{-1}. From Table XII, at $C_e = 49 \times 10^{-3}$ equiv. liter^{-1} (organic salt molality is 2.9×10^{-3} molal, and the corresponding salt molality in the aqueous phase is about 3.8×10^{-2} molal) the fraction of metal ions involved in the 2nd order ion-association (assuming there is no first order ion-association) is about 0.6. It is further assumed that $(\Delta S^{\circ}_{ass})_{2nd} = (\Delta S_{ass})_{2nd}$. Then the entropy contribution to the partial molal entropy of transfer will be $(0.6)(12) = 7$ e.u. mole^{-1}. From Figure 15, the experimental value is seen to be about 3.5 e.u. mole^{-1}.

Although the agreement here is not good, it is all can be expected, considering the highly approximate nature of the calculation. Moreover, first order ion-association can be expected to occur to a comparable extent. If, for example, there is 30% first order ion-association and 30% second order ion-association, then $(\Delta S_{ass})_{total} = 3.9$ e.u. mole^{-1}, which agrees with experiment.

The calculation for second order ion-association based on the model used does not depend on the relative positions of the two perchlorate ions in an ion-triplet (Figure 20(b)). However, in order to minimize ionic repulsion and steric hindrance, the perchlorates ions would be expected to take the axial positions in the octahedral symmetry of the effective cation.

At higher concentrations, first order ion-association becomes relatively less and less important, and according to Figure 15 all salts would exist in the organic phase almost entirely as fully hydrated ion-triplets (Figures 20(b) and 22) when the aqueous salt molality is greater than 12 x 10^{-2} molal, because the calculated maximum entropy change due to second ion-association has been reached. This, however, is not predicted by equation (4.3), because Onsager's limiting equation breaks down completely at high salt concentrations in the organic phase, where the dielectric constant is quite small. At the highest experimental concentrations and above, the extent of second order ion-association should approach the maximum (100%), so that the increase in the entropy of transfer should diminish, and the entropy curve should level off gradually. This is hardly seen in Figure 15, which is a useful plot for extrapolation at dilute salt concentrations. When one plots the entropy of transfer vs. the molality of salt in the organic phase (Figure 24), however, one indeed sees the predicted levelling behavior; at concentrations greater than 15 x 10^{-3} molal (corresponding concentration in the equilibrium aqueous phase is about 12 x 10^{-2}molal), the levelling is practically complete.

According to Figure 24, the maximum increase in the entropy of transfer is about 9 e.u. mole^{-1}. This compares favorably with the theorectically calculated value of 12 e.u. mole^{-1}. Therefore, it can be concluded that the model is at least reasonable, though admittedly very rough.

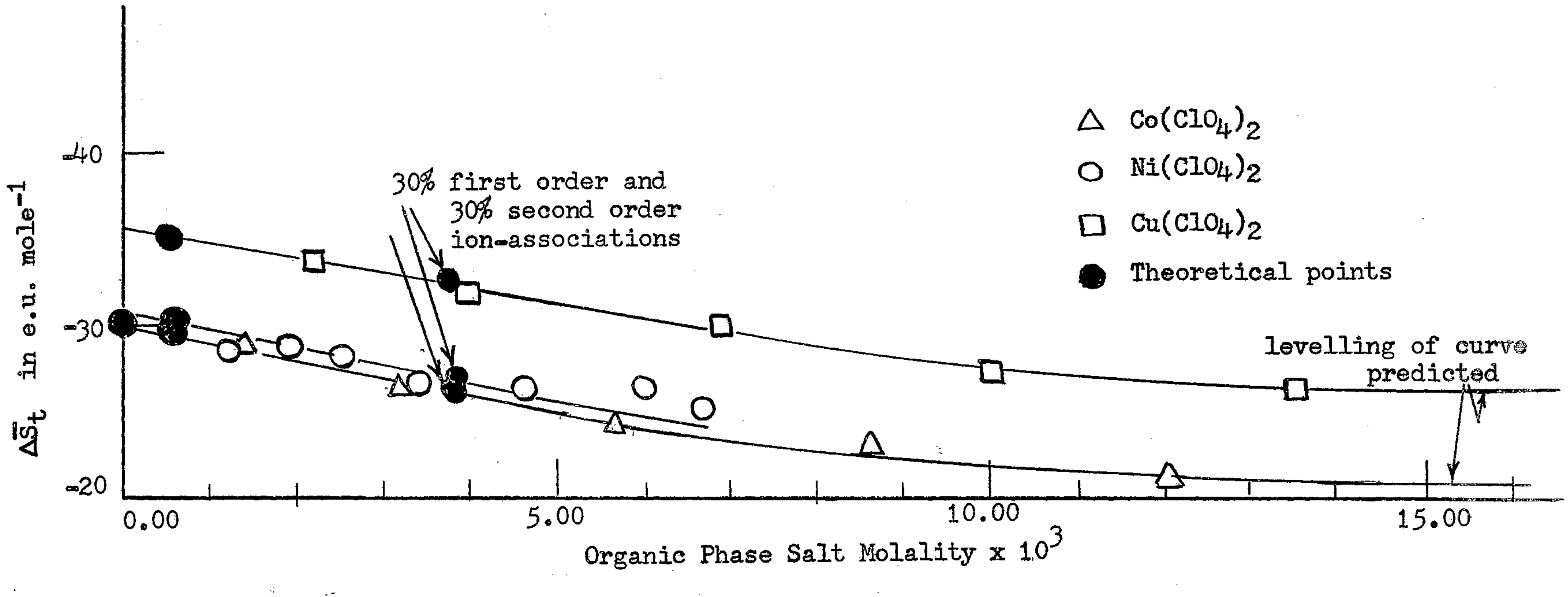


Figure 24. Partial Molal Entropy of Transfer Plotted against Organic Phase Salt Molality

CHAPTER VI

CONCLUSIONS

The high extractibility of $Ni(ClO_4)_2$, $Co(ClO_4)_2$, and $Cu(ClO_4)_2$ is closely related to the fact that they can be fully solvated by water in the 1-butanol phase. All three salts have been found to have many extraction properties in common; therefore, it may be concluded that the nature of extraction is essentially the same for all three salts.

Extraction at very low concentrations appears to be simply the transfer of fully hydrated ions from aqueous to organic phases of high water content. At higher salt concentrations, the hydrated ions associate into hydrated ion-pairs and triplets in hydrous butanol. The ion aggregate is formed as a result of the electrostatic attraction of the hydrated metal ion and one (or both) perchlorate ion (or ions). This liberates water molecules from the primary hydration sheath of the metal ions without disturbing the permanent hydration sheath. As a consequence, the cation and the perchlorate ion (or ions) of the ion aggregate are separated by a layer of very tightly bound water molecules (Figures 20 and 22).

The gratifying success of the modified Born model in predicting the value of $\Delta\overline{H}_t^{\circ}$ lends support to the conclusion that the permanent hydration sheaths of the metal ions are similar in both aqueous and 1-butanol phases, and therefore, the spectra of the two phase solutions should be indistinguishable as is observed (37).

Because of ion-associations in the organic phase, the entropy of transfer increases as the salt concentration increases. This leads to an explanation of the increase in the extractibility of the perchorate salts with increase in concentration. However, the shape of the salt distribution curves in dilute solutions can not be very simply related to the entropy and enthalpy of transfer alone, for the distribution coefficient is not determined by the equilibrium values of $\Delta\overline{H}_t$ or $T\Delta\overline{S}_t$. These, of necessity, are equal to one another.

Figure 25 is the distribution isotherm for $Ni(ClO_4)_2$, which is representative of that for all three salts. Part I of the curve corresponds to that part of the distribution isotherm for which there is extensive first order ion-association (except in the extremely dilute region) and practically no second order ion-association in the organic phase. A positive entropy of ion-association causes an increase in the entropy of transfer; this in turn causes an increase in the extractibility of $Ni(ClO_4)_2$ (same thing for the other salts). Therefore, the distribution curve is concave upward. In region II of the curve, both first order and second order ion-associations are important in the organic phase (except at the lower concentration end where the former is most important, and the upper end where the latter is predominant). Further increases in the entropy of transfer are again found. Correspondingly, the distribution curve continues to be concave upward. In region III, the maximum second ion-association is reached. There is almost no first order ion-association left, and a large percent of all ions exist as hydrated ion-triplets (Figure 20(b) and 22). Further entropy increase is not possible. Consequently, the distribution curve stops concaving upward and approaches linearity (Figure 25).

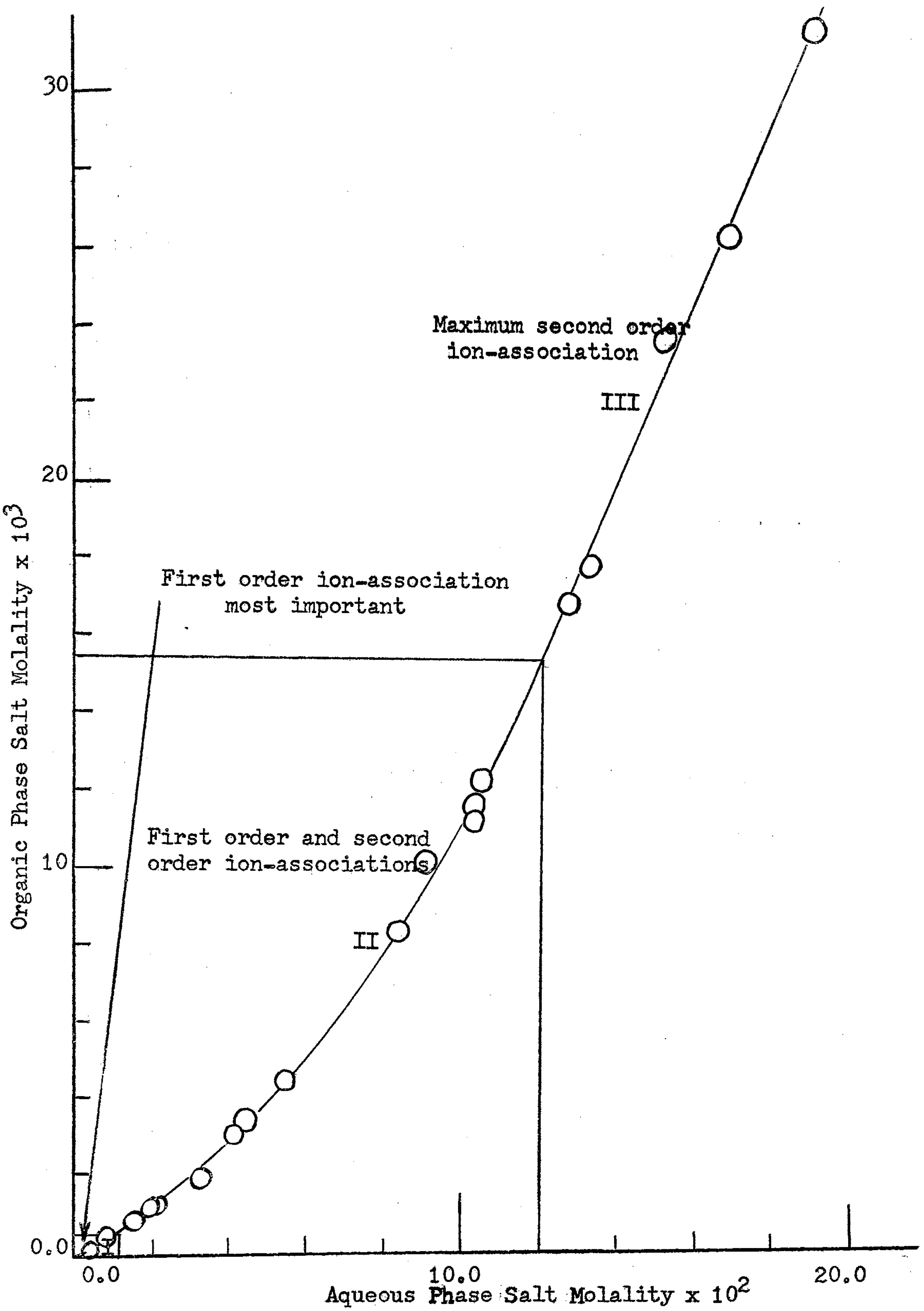


Figure 25. Ion Association and the Distribution Isotherm

At the higher concentrations the isotherms still do not correspond to constant values of the distribution coefficient as demanded by ideal behavior (Nernst distribution law), and this emphasizes again the complexity of even such simple extraction systems as the ones chosen for this study. The study has demonstrated, however, that the thermodynamic behavior of such systems can be approximated by electrostatic models with reasonable success; this is encouraging for future work.

CHAPTER VII

SUMMARY

The extraction systems of nickel(II), cobalt(II), and copper(II) perchlorates in the water-1-butanol solvent pair at 25° have been investigated over the aqueous phase concentration range from 0.01 to 0.18 molal. It was found that the distribution isotherms for all three salts are quite similar, and apparent hydration numbers of the order of 30-50 have been measured.

Partial molal enthalpies of transfer, $\Delta\overline{H}_t$, for all three salts at distribution equilibrium and at 25.0° have been measured over the aqueous phase concentration range from 0.02 to 0.13 molal. Corresponding entropy changes, $\Delta\overline{S}_t$, have also been calculated from the condition that $\Delta\overline{G}_t = 0$ at distribution equilibrium. Both $\Delta\overline{H}_t$ and $\Delta\overline{S}_t$, when plotted against the aqueous phase salt concentration, were found to increase linearly with increasing salt concentration. Extrapolation to infinite dilution for each salt gave $\Delta\overline{H}_t^\circ$ values which are of the order of -9 to -10.5 kcal. mole^{-1} and $\Delta\overline{S}_t^\circ$ values which are of the order of -30 to -36 e.u. mole^{-1}. When $\Delta\overline{S}_t$ is plotted against the organic phase molality, it is found that the curve increases approximately linearly with increasing salt concentration at low concentrations, but levels off at higher salt concentrations. This is attributed to ion-association, since the entropy change for ion-association is usually positive.

Conductances and viscosities for all three salts in both aqueous and organic phases have been measured at 25.0° and at relatively low salt concentrations. Results show that these salts are completely dissociated in the aqueous phase, but that they are extensively associated in the organic phase. The degree of ion-association at several concentrations has been calculated. The order of magnitude of the association constants was also obtained.

A modified Born model has been proposed for the solvation of the three salts in the extraction phases. Values of $\Delta\overline{H}_t^o$ were calculated theoretically and good agreement was achieved with experiment. With this and models for the ion-association, the entropies of the first and second order ion-associations were calculated theoretically, and found to compare favorably with experiment.

First order ion-association is assumed to take place when a perchlorate ion is bound to an octahedrally hydrated metal ion by electrostatic attraction. As the consequence of the positioning of the perchlorate ion adjacent the highly hydrated metal ion, two water molecules are assumed displaced from the primary hydration sheath of the metal ion. Second order ion-association is considered to take place in a similar manner, except that as many as five water molecules are believed to be liberated from the primary hydration sheath of the metal ion. In both cases, the positive increase to the entropy of transfer mentioned above can be accounted for. Moreover, the general shapes of the salt-distribution curves and the entropy curves can qualitatively be explained by the models assumed.

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APPENDIX

A. Glossary

C_e = concentration in equivalents per litre of solution

D = dielectric constant

e = electronic chage

$\Delta G^\circ, \Delta H^\circ, \Delta S^\circ$ = Born's free energy, enthalpy and entropy changes for the transfer of a mole of an ion from vacuum to a medium with dielectric constant D

$\Delta G_t, \Delta H_t, \Delta S_t$ = integral free energy, enthalpy and entropy of transfer of a mole of a salt from aqueous to 1-butanol phases at extraction equilibrium

$\Delta\overline{G}_t^\circ, \Delta\overline{H}_t^\circ, \Delta\overline{S}_t^\circ$ = partial molal free energy, enthalpy and entropy of transfer of a mole of a salt from aqueous to 1-butanol phases at infinite dilution of salt, and at extraction equilibrium

$\Delta\overline{G}_t, \Delta\overline{H}_t, \Delta\overline{S}_t$ = partial molal free energy, enthalpy and entropy of transfer of a mole of a salt from aqueous to 1-butanol phases at extraction equilibrium

I = molar ionic strength

K_{ass} = ion association constant

$N_\circ$ = Avogadro's number

P = pressure

r_α = radius of ion α

$(\Delta S_{ass})_{1st}$ = entropy change upon first order ion association

$(\Delta S_{ass})_{2nd}$ = entropy change upon second order ion association

$(\Delta S^\circ_{ass})_{1st}$ = entropy change upon first order ion association at infinite dilution

$(\Delta S^\circ_{ass})_{2nd}$ = entropy change upon second order ion association at infinite dilution

T = temperature in degrees Kelvin, 298.15° K in most cases

X = volume fraction

Z_α = charge on ion α

Λ = equivalent conductance of salt

Λ° = limiting equivalent conductance

λ = ionic equivalent conductance

λ° = limiting ionic equivalent conductance

Γ = ion concentration = 2I

α = fraction of perchlorate ions associated as ion-pairs

β = fraction of perchlorate ions associated as ion-triplets

η = viscosity

ν_α = number of ions of kind α in molecular formula of salt

density of aqueous solvent at 25.0° = 0.9870 gm. cm.$^{-3}$

density of organic solvent at 25.0° = 0.8344 gm. cm.$^{-3}$

Aq - refers to aqueous solution (no butanol present)

aq - refers to aqueous phase

org - refers to 1-butanol phase

B. Evaluation of Dielectric Constants

Dielectric constants of the equilibrium solvents (at zero salt concentration) at 25.0° can be calculated using the equation (see ref. 22) below

$$D = X_{H_2O}\, D_{H_2O} + X_{BuOH}\, D_{BuOH} \quad , \tag{A.1}$$

where the X's represent volume fractions of the solvent components and the D's the dielectric constants of the solvent components.

At 25.0°

density of H_2O = 0.9970 gm. ml^{-1}

density of BuOH= 0.8058 gm. ml^{-1}

$D_{H_2O} = 78.54$

$D_{BuOH} = 17.1$

The dielectric constants of the two solvents are then calculated to be

$D_{aq} = 73.06$

$D_{org} = 27.31$

The temperature derivatives of the dielectric constants can be evaluated by using equation (A.1) with the D's now replaced by dD/dT's. Since at 25.0°

$(\frac{dD}{dT})_{H_2O} = -0.36175$ per degree Kelvin

$(\frac{dD}{dT})_{BuOH} = -0.13193$ per degree Kelvin

therefore, $(\frac{dD}{dT})_{aq} = -0.3413$ per degree Kelvin

$(\frac{dD}{dT})_{org} = -0.1701$ per degree Kelvin

The reliability of equation (A.1) can be tested by comparing the dielectric constant of a 80% (per cent in weight of ethanol) ethanol-water mixture at 20.0° (from p. 101 International Critical Tables, Vol. VI, McGraw-Hill, N. Y., 1929) and the value calculated using equation (A.1) with the sub-index BuOH being replaced by EtOH:

Calculated value : 35.3

Experimental value : 34.1

It can be seen that the calculated value is slightly larger (by a factor of 1.04). In the calculation of the degree of ion-association in the equilibrium organic phase, the value 1.04 is taken as correction factor, and the value used is $D_{org} = 26.3$. In the calculation of $\Delta\bar{H}_t^\circ$, however, the "uncorrected" dielectric constants are used, since corresponding errors will cancel each other out. In any event, equation (A.1) gives dielectric constant which are satisfactory for the purposes of the calculations mentioned, and any correction used would not change the results significantly.

C. Onsager's Limiting Equations

The general form of the Onsager's limiting equation for the conductance of a salt (46) is

$$\Lambda = \Lambda^\circ - \left[\frac{2.801 \times 10^6 \, |Z_1 Z_2| \, q \, \Lambda^\circ}{(DT)^{3/2} \, (1+q^{1/2})} + \frac{41.25 \, (|Z_1| + |Z_2|)}{\eta (DT)^{1/2}} \right] I^{1/2}, \tag{A.2}$$

where, Z_1 = charge on the cation

Z_2 = charge on the anion

Λ = equivalent conductance of salt

Λ° = limiting equivalent conductance of salt

$$q = \frac{|Z_1 \, Z_2|}{|Z_1| + |Z_2|} \cdot \frac{\lambda^\circ_1 + \lambda^\circ_2}{|Z_2|\lambda^\circ_1 + |Z_1|\lambda^\circ_2}$$

η = viscosity of solvent (0.02816 poise for organic phase and 0.01184 poise for aq. phase)

λ° = limiting ionic conductance (94 cm.^{2} ohm^{-1} equiv.$^{-1}$ for all three cations and 51.6 cm.^{2} ohm^{-1} equiv.$^{-1}$ for ClO_4^- in aqueous phase; 38.7 cm.^{2} ohm^{-1} equiv.$^{-1}$ for the cations and 17.4 cm.^{2} ohm^{-1} equiv.$^{-1}$ for ClO_4^- in organic phase; 55 for Co^{+2} and Ni^{+2} and 67 for ClO_4^- in aqueous solutions containing no butanol; all at 25.0°)

$I^{\frac{1}{2}}$ = (ionic strength)$^{\frac{1}{2}}$ = $(1.5)^{\frac{1}{2}} \, C_e^{\frac{1}{2}}$ for the three perchlorates salts

On substitution of physical constants, the limiting equations are obtained as follows for the three perchlorates:

(a) in aqueous phase at 25.0° (298.15°K)

$$\Lambda = 94 - 130 \, C_e^{\frac{1}{2}} \tag{A.3}$$

(b) in organic phase

$$\Lambda = 38.7 - 160 \, C_e^{\frac{1}{2}} \tag{A.4}$$

(c) in aqueous solutions (no butanol) for $Co(ClO_4)_2$ and $Ni(ClO_4)_2$

88

$$\Lambda = 122 - 172\, C_e^{\frac{1}{2}} \qquad (A.5)$$

$$\Lambda = 122 - 172\, C_e^{\frac{1}{2}} \qquad (A.5)$$

$$\Lambda = 122 - 172\, C_e^{\frac{1}{2}} \qquad (A.5$$

D. First Order Ion Association in Organic Phase at 25.0°

The first order ion association for $Ni(ClO_4)_2$ (b) can be represented by the equation

$$Ni^{+2} + ClO_4^- = NiClO_4^+ \qquad \text{(in solution).}$$

If α is the fraction of perchlorate ions associated (2α is the fraction of metal ions associated), then the observed equivalent conductance Λ_{obs}, is given by ($0 \leqslant \alpha \leqslant 1/2$):

$$\begin{aligned}\Lambda_{obs} &= \lambda_{ClO_4^-}(1-\alpha) + \lambda_{Ni^{+2}}(1-2\alpha) + \lambda_{NiClO_4^+}(\alpha) \\ &= (\lambda_{Ni^{+2}} + \lambda_{ClO_4^-})(1-\alpha) - \alpha(\lambda_{Ni^{+2}} + \lambda_{NiClO_4^+}).\end{aligned} \tag{A.6}$$

Thus, using the equation corresponding to equation 3.78 of Monk's book (34), which is identical with the general equation (A.2) given in Appendix C, except that the Λ's have been replaced by the ionic conductances and Γ is used instead of C_e (Γ = ion concentration = $2I = 3C_e$), one has the following limiting law equations for the equivalent conductance in the organic phase

$$\lambda_{Ni^{+2}} = 17.4 - 49.17\Gamma^{\frac{1}{2}} \tag{A.7}$$

$$\lambda_{ClO_4^-} = 21.3 - 43.26\Gamma^{\frac{1}{2}} \tag{A.8}$$

$$\lambda_{NiClO_4^+} = 6.96 - 19.92\Gamma^{\frac{1}{2}} \tag{A.9}$$

(it is assumed that $\overset{\circ}{\lambda}_{NiClO_4^+} = 0.4\overset{\circ}{\lambda}_{Ni^{+2}}$).

Equation (A.6) then becomes

$$\Lambda_{obs} = (38.7 - 92.4\Gamma^{\frac{1}{2}})(1-\alpha) - \alpha(24.4 - 69.1\Gamma^{\frac{1}{2}}) \tag{A.10}$$

where $\Gamma = 3C_e - 4C_e\alpha$.

The ion-association constant K_{ass} (a), is given in terms of C_e and α by

$$K_{ass} = [NiClO_4^+] \; / \; [Ni^{+2}][ClO_4^-]$$
$$= (C_e\alpha) \; / \; (\tfrac{1}{2}C_e - C_e\alpha)(C_e - C_e\alpha) \text{ litre mole}^{-1} \qquad (A.11)$$

Notes: (a) Since only the order of magnitude is needed, activity coefficients have not been included in the calculation of K_{ass} .

(b) Equations derived are also good for $Co(ClO_4)_2$ and $Cu(ClO_4)_2$ in the organic phase .

E. Second Order Ion Association in Organic Phase at 25°

Second order ion association can be represented by

$$Ni^{+2} \; + \; 2ClO_4^- \; = \; Ni(ClO_4)_2 \quad \text{(in solution)} \qquad (A.12)$$

When there is no ion-association, the equivalent conductance of $Ni(ClO_4)_2$ is given by

$$\Lambda_{Ni(ClO_4)_2} \; = \; 38.7 \; - \; 160C_e^{\frac{1}{2}} \qquad \text{(Appendix C)}$$

When there is second order ion-association only and if β is the fraction of perchlorate ions (or metal ions) associated, then the observed equivalent conductance Λ_{obs} is given by (A.13)

$$\Lambda_{obs} \; = \; (1-\beta)\left[38.7 \; - \; 160\sqrt{(1-\beta)\,C_e}\right]$$

The second order association constant, K_{ass}, is defined by

$$K_{ass} \; = \left[Ni(ClO_4)_2\right] / \left[Ni^{+2}\right]\left[ClO_4^-\right]^2$$

or $$K_{ass} \; = \left[\tfrac{1}{2}C_e\beta\right] / \left[\tfrac{1}{2}C_e\,(1-\beta)\right]\left[\,C_e\,(1-\beta)\right]^2 \qquad (A.14)$$

F. Enthalpy of Transfer, Born's Model

According to Born, the free energy change for the transfer of a mole of an ion of radius r and charge Ze from vacuum to a medium with dielectric constant D, is given by

$$\Delta G^\circ = -\frac{N_0 Z^2 e^2}{2r}(1 - 1/D) \qquad \text{(A.14)}$$

where, N_0 represents the Avogadro's number, and e the electronic charge.

From the Gibbs-Helmholtz equation the corresponding enthalpy change is given by

$$\begin{aligned} \Delta H^\circ &= -T^2 \frac{\partial(\Delta G^\circ/T)_P}{\partial T} \\ &= -T^2 \frac{\partial}{\partial T}\Big[(-N_0 Z^2 e^2/2rT)(1-1/D)\Big] \\ &= -(N_0 Z^2 e^2/2r)\Big\{1 - (1/D)\big[1 + (T/D)(dD/dT)\big]\Big\} \qquad \text{(A.15)} \end{aligned}$$

If the species transferred is a mole of salt, then

$$\Delta H^\circ = (-N_0 e^2/2)\Big(\sum_\alpha \nu_\alpha Z_\alpha^2/r_\alpha\Big)\Big\{1 - (1/D)\big[1 + (T/D)(dD/dT)\big]\Big\} \qquad \text{(A.16)}$$

where, Z_α, r_α represent the charge and radius of ion α, and ν_α number of ions α in the molecular formula of the salt.

The transfer of a mole of salt from the aqueous phase to 1-butanol phase will results in an enthalpy change ΔH_t°, given by

$$\begin{aligned} \Delta H_t^\circ &= (\Delta H^\circ)_{org} - (\Delta H^\circ)_{aq} \\ &= (N_0 e^2/2)\Big(\sum_\alpha \nu_\alpha Z_\alpha^2/r_\alpha\Big)\Big[\Big\{(1/D)\big[1+(T/D)(dD/dT)\big]\Big\}_{org} \\ &\qquad - \Big\{(1/D)\big[1+(T/D)(dD/dT)\big]\Big\}_{aq}\Big] \qquad \text{(A.17)} \end{aligned}$$

Substituting $e = 4.80 \times 10^{-10}$ e.s.u.

$N_0 = 6.02 \times 10^{23}$ mole^{-1}

$\left(\frac{dD}{dT}\right)_{aq} = -0.3413$ per degree Kelvin

$\left(\frac{dD}{dT}\right)_{org} = -0.1701$ per degree Kelvin

$D_{aq} = 73.06$

$D_{org} = 27.3$

$T = 298.15^\circ K$

and after conversions of units

$$(\Delta H_t^\circ) = -4.313 \left(\sum_\alpha \nu_\alpha Z_\alpha^2 / r_\alpha\right) \quad \text{kcal. mole}^{-1} \qquad (A.18)$$

providing r_α is in Å.

Since ΔH_t° refers to infinite dilution of salt,

$\Delta H_t^\circ = \Delta \overline{H}_t^\circ$. (It should be known that $\Delta \overline{H}_t^\circ$ is the partial molal enthalpy of transfer at <u>extraction</u> <u>equilibrium</u>.)

Thus, at 25.0°

$$\Delta \overline{H}_t^\circ = -4.313 \left(\sum_\alpha \nu_\alpha Z_\alpha^2 / r_\alpha\right) \quad \text{kcal. mole}^{-1} \qquad (A.19)$$

The ionic radii to be used are as follows:

$r_{Ni^{+2}} = 0.72$ Å

$r_{Co^{+2}} = 0.74$ Å

$r_{ClO_4^-} \cong 2.28$ Å

$r_{Cu^{+2}} = 0.69$ Å

VITA

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