SOME THERMODYNAMIC PROPERTIES OF AQUEOUS FERROUS CHLORIDE OR FERRIC CHLORIDE-HYDROCHLORIC ACID SOLUTIONS

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CHAPTER I

INTRODUCTION

Purpose and Scope of Investigation.

This research forms a part of a program of study of the thermodynamic properties of the iron series of transition metal chlorides in hydrochloric acid solution at high concentrations of both salt and acid. The program grew out of a general study of the factors affecting the solvent extraction and separation of transition metal salts (84).

Work by Garwin and Hixson (37) disclosed the preferential promotion of the extraction of $CoCl_2$ from aqueous solutions of $CoCl_2$ and $NiCl_2$ by 2-octanol on the addition of concentrated HCl or $CaCl_2$. Gootman (42) subsequently investigated the activities of all the components of the systems $CoCl_2$-HCl-H_2O and $NiCl_2$-HCl-H_2O at several different concentrations of HCl for the purpose of correlating the extractibility of the salts with their activities in the aqueous phase.

Upon the extension of the solvent extraction studies to the system $MnCl_2$-HCl-H_2O by Moore and Brown (83), Burtch (15) studied the activity relationships in this system. Subsequently Miller (81) investigated the activity relationships in the system $CuCl_2$-HCl-H_2O. This investigation of the activity relationships in the system $FeCl_2$-HCl-H_2O thus complements these previous investigations and completes the studies of the iron series of transition metal chlorides in aqueous hydrochloric acid.

Three series of solutions of $FeCl_2$ in aqueous HCl and one series of solutions of $FeCl_3$ in aqueous HCl were investigated at 25°. The HCl concentration was kept constant in each of the series studied while the salt concentration was varied.

The equilibrium vapor pressures, and consequently the activities, of H_2O and HCl in the ternary solutions were determined experimentally. Salt activities were calculated by integration of the Gibbs-Duhem equation.

An attempt has been made to interpret the data for the $FeCl_2$-HCl-H_2O system in terms of the ionic hydration theory of Stokes and Robinson. The applicability of the empirical Harned's rule (50) to the system $FeCl_2$-HCl-H_2O has been tested.

The data provided by this research should be of value in such areas as liquid-liquid extraction (84) and ion exchange (51). Aside from its applicability to such chemical problems, an investigation of this type is important in that it makes a contribution to the knowledge of concentrated electrolyte solutions, which is, at present, limited.

Literature Survey.

Ferrous Chloride. Investigations comparable to the present one have been made by Moore, Gootman, and Yates (85) and Moore, Burtch, and Miller (86). Moore, Gootman, and

Yates investigated the termodynamic properties of the systems $NiCl_2$-HCl-H_2O and $CoCl_2$-HCl-H_2O, while Moore, Burtch, and Miller studied the systems $MnCl_2$-HCl-H_2O and $CuCl_2$-HCl-H_2O. The activity data of these investigations were interpreted with a fair degree of success in terms of hydration and complex formation. Due to the fact that the $CuCl_2$-HCl-H_2O system shows greater complex formation than the other systems, it was treated in a more empirical manner than were the other systems.

Carter and Megson (23) studied complex formation by $FeCl_2$ and $FeCl_3$ in HCl solutions by utilizing the elevation of the critical solution temperature. These investigators determined the elevation of the critical solution temperature for HCl, $FeCl_2$, and $FeCl_3$ in the isobutyric acid-water system. They found that considerable complex formation occurred between HCl and $FeCl_3$, but none between $FeCl_2$ and HCl. The concentrations of the salts involved were small.

The catalytic oxidation of ferrous chloride in HCl solutions was investigated by Thomas and Williams (142) who measured the rate of absorption of oxygen at atmospheric pressure after shaking solutions of ferrous chloride with HCl, oxygen and nitrogen monoxide.

Audubert (6) studied the oxidation of ferrous salts and reduction of ferric salts under the influence of light.

Agde and Schimmel (3) showed proof for the existence of ferrous chloride hexahydrate.

It was determined by Weiss (146) that the photochemical oxidation of the ferrous ion in solution containing H_2SO_4 in the absence of oxygen takes place in ultraviolet light with the evolution of hydrogen.

Ipatieff, Komerov, and Kurmanaev (55) found that ferrous chloride was oxidized by oxygen at 35^o to 175^o and at pressures of 10 to 40 atmospheres. The velocity of the reaction was found to be a function of the hydrogen ion concentration. An increase in hydrogen ion concentration at low temperature is accompanied by an increase in reaction rate, while at high temperatures the rate decreases with an increase in hydrogen ion concentration. Above 150^o ferric chloride was found to decompose to ferrous chloride.

The oxidation of solutions of ferrous chloride in alcohols was studied by Pound (105). He reported that alcohol solutions of ferrous chloride are oxidized by air much more rapidly than are aqueous solutions. The reaction was reported to be bimolecular with respect to ferrous ion concentration, and the rate increased with the molecular weight of the alcohol used as solvent. Water and acids decreased the speed of oxidation. Pound also found that the rate of oxidation was influenced by the presence of light, mercury, and acids. Electrical conductivity increased during oxidation.

Schwarz (133) investigated the radiation chemistry of ferrous chloride solutions. He induced oxidation of ferrous ions in air-saturated 0.4 M HCl and in 0.4 M H_2SO_4 by radiation. Ferric ion production was found to be linear in the H_2SO_4 and non-linear in the HCl with dose. Kintics studies indicated that the difference was due to the complexing of the ferric ion by the chloride ion.

In studying the effect of ultraviolet radiation on iron salts in aqueous solutions of H_2SO_4, Ivanitskaya and Nanobashvili (56) found that maximum oxidation was obtained in dilute solutions with high pH. The solutions studied were 0.014 M $FeSO_4$ in 0.8 N H_2SO_4, 0.0014 M $FeSO_4$ in 0.08 N H_2SO_4, and 0.0012 M $FeSO_4$ in 0.8 N H_2SO_4.

Randall and Frandsen (113) determined the standard electrode potential of iron and the activity coefficient of ferrous chloride by use of the cell

$$Fe(s),\ FeCl_2(0.1\ M),\ HgCl(s),\ Hg(l).$$

By use of the dialysis method, Brintzinger and Ratanarat (19) determined the number of water molecules in the aquocomplex and the hydration of the ferrous and ferric ion. They reported the number of water molecules in the aquocomplex ion of ferrous and ferric ions to be 6 and 18, respectively, and the additional number of water molecules bound as water of hydration of the aquo-metal ions as 18.7 and 41, respectively. Bockris (16), in a review of ionic solvation, discussed the various methods of determining the hydration number. He divided hydration into "primary" and "secondary" solvation. Brintzinger's dialysis method yields high values for the primary solvation number, and, consequently, measures at least a part of the secondary solvation.

Extinction coefficients for the ferrous and ferric ions in aqueous solutions for wave lengths down to 2200 Å were measured by Potterill, Walker, and Weiss (104). These investigators determined the quantum efficiency for the formation of the ferric ion upon irradiation at wave lengths below 2900 Å. Reactions involved were

$$Fe^{++} + HOH + h\nu = Fe^{+++} + H + OH^{-},$$

followed by the recombination of the hydrogen atoms in competition with the reverse reaction

$$Fe^{+++} + H = Fe^{++} + H^{+}.$$

The activation energy of the latter reaction was reported as 7 cal.

Furlani (33) has studied the absorption spectra of electrostatic complexes of the ferrous ion. He has reported the principal absorption maxima in cm^{-1} as 10,500 and 8,600, respectively, for the hexaaquo and hexachloro complexes. The molar extinction coefficients were 0.204 for the hexaaquo complex and 0.197 for the hexachloro complex.

Several investigators have reported values for the heat of solution of ferrous chloride in aqueous solutions (70, 100). Yatsimirskii and Kharitonov (150) give the heat of solution of ferrous chloride in 6.24 M HCl as 11.0 kcal per mole at 25°.

Gayer and Wootner (38) investigated the hydrolysis of ferrous chloride at 25°. They found that for the reaction

$$Fe^{++} + H_2O = FeOH^{+} + H^{+}$$

$K_1 = 1.20 \times 10^{-8}$ and $\Delta G^{\circ} = 11.0$ kcal., and for the reaction

$$FeOH^{+} = Fe^{++} + OH^{-},$$

$K_{1,2} = 8.3 \times 10^{-7}$, and $\Delta G^{o} = 8.3$ kcal.

From their research on the thermochemistry of the ferrous halides and their carbonyl compounds, Hieber and Woerner (52) determined the heat of formation of ferrous chloride to be 8.93 cal/ mole.

By measuring the appropriate heats of solution and reaction in HCl, Koehler and Coughlin (61) determined the heats of formation of a crystalline product from crystalline metal and gaseous Cl_2 of anhydrous $FeCl_2$ and $FeCl_3$. The following values were obtained: $FeCl_2$, -81.86; $FeCl_3$, -95.7 kcal./ mole at 298.15° K.

Allen (5) has calculated the bond energy and valence bond energy of transition metal halides from experimental data. He calculated the following values in kcal./mole for the bond energy and valence bond energy: $FeCl_2$, 95.4, 95.4; $FeCl_3$, 81.3, 81.3.

Gal and Ruvaroe (34) have investigated the extraction of ferric and ferrous chloride from hydrochloric acid solutions with tributyl phosphate.

The water vapor pressure of the various hydrates of ferrous chloride was determined by Schäfer (126). In addition to the vapor pressure of water, Schäfer also reported that, at 20°, HCl depresses the solubility of ferrous chloride from 3.04 moles of $FeCl_2$ per kilogram of solution at zero per cent HCl to 0.20 moles per kilogram of solution at 37 per cent HCl. He also reported that the solid phase is the tetrahydrate, $FeCl_2 \cdot 4H_2O$, up to 30.9 per cent HCl. Above this concentration in HCl the solid phase was found to be $FeCl_2 \cdot 2H_2O$. The solutions investigated contained about 1 % Fe_2O_3.

Schimmel (131) studied the ternary systems of $FeCl_2$-HCl-H_2O and $FeCl_3$-$FeCl_2$-H_2O. He established the 0, 20, 40, 60, and 100° isotherms of the system $FeCl_2$-HCl-H_2O and the composition of the solid phases.

Stokes and Robinson (139) determined the activity coefficient of ferrous chloride in aqueous solutions by use of the isopiestic method. The values of the activity coefficient from this research were later included by Stokes (138) in a review of the activity and osmotic coefficients of 2:1 and 1:2 electrolytes at 25°. Guggenheim and Stokes (44) have recently revised the values of the activity coefficients of 2:1 and 1:2 electrolytes. They include factors by which the previously determined coefficients should be multiplied. Robinson and Stokes (122) have included these corrections in the second edition of their text, "Electrolyte Solutions."

In discussing the results of these measurements of activity and osmotic coefficients, Stokes (138) points out that the main factor governing the relative behavior of the 2:1 and 1:2 electrolytes is ion size, through its effect on cation hydration and ion-pair formation. Ferrous chloride appeared to behave normally, having practically the same behavior as $CaCl_2$, up to 2 M concentration.

Ferric Chloride. A wide variety of work has been done on the system $FeCl_3$-HCl-H_2O. Much of this work has, however, involved extraction studies with various organic solvents. Laran (68) has reviewed the more important extraction research on ferric chloride up to 1953. Only the more important papers on extraction studies which pertain to the composition and structure of the extracted species need be considered in this literature survey. However, the structure and composition of the complex ion formed in hydrochloric acid medium by ferric chloride is of great importance in the interpretation of both extraction data and the thermodynamic data obtained in this investigation.

Houben and Fischer (53) found that $FeCl_3$ in absolute di-ethyl ether, saturated with HCl, yields the compound $FeCl_3 \cdot HCl \cdot 2(C_2H_5)_2O$. The compound is green and very hygroscopic.

Kato and Isii (57) reported that spectra studies indicated that the compound extracted by diethyl ether from aqueous solutions of $FeCl_3$ and HCl had the formula $FeCl_3 \cdot HCl \cdot 3H_2O$. They suggested a tetrahedral structure for the iron in the compound.

From extraction studies of ferric chloride from aqueous hydrochloric acid solutions by dichloroethyl ether, Axelrod and Swift (8) concluded that, if polymerization and the possible presence of ether in the molecule of the extracted compound were disregarded, the empirical formula for the extracted species was $HFeCl_4 \cdot 4\text{-}5H_2O$.

Nekrasov and Ovayankina (95) investigated the system $FeCl_3\text{-}HCl\text{-}H_2O\text{-}(C_2H_5)_2O$. They supposed the following equilibria for both the aqueous and ether layer when there is a considerable excess of HCl:

$$[FeCl_4(H_2O)_2]^{-} + 2Cl^{-} = [FeCl_5H_2O]^{=} + Cl^{-} = [FeCl_6]^{\equiv} + 2H_2O.$$

They also found that in the absence of excess HCl or for a considerable excess of $FeCl_3$ in the initial solution the ratio Cl^{-}/Fe^{+++} for the ether layer is close to 3.5. This they suggest is due to a simultaneous extraction of both $H[FeCl_4(H_2O)_2]$ and $[FeCl_3(H_2O)_3]$, the latter in the form of the aquo acid $H[FeCl_3(OH)(H_2O)_2]$. They reported that the following equilibria are present in concentrated aqueous solutions of $FeCl_3$:

$$2[FeCl_3(H_2O)_3] = [FeCl_2(OH)(H_2O)_3] + H[FeCl_4(H_2O)_2]$$
$$3[FeCl_3(H_2O)_3] = [FeCl(OH)_2(H_2O)_3] + 2H[FeCl_4(H_2O)_2]$$
$$4[FeCl_3(H_2O)_3] = [Fe(OH)_3(H_2O)_3] + 3H[FeCl_4(H_2O)_2].$$

Nachtrieb and Conway (91) reported the empirical formula for the iron compound extracted from aqueous $FeCl_3$ solutions which do not exceed 8 M in HCl to be $HFeCl_4$. For aqueous HCl solutions exceeding 8 M in HCl they found the mole ratio of HCl to $FeCl_3$ to exceed 1:1 in the extracted species. In their earlier work, Nekrasov and Ovayankina (95) had reported that the ratio of Cl^{-}/Fe^{+++} was 5.38 at 10 moles of HCl and 1 mole of $FeCl_3$ per liter of solution. Nachtrieb and Conway also compared the absorption spectra of the ether-extracted complex, anhydrous $FeCl_3$ in isopropyl ether, aqueous $FeCl_3$, and an HCl solution of $FeCl_3$.

Nachtrieb and Fryxell (92) presented data to support the hypothesis that a salting-out effect may explain the variations in the distribution of $FeCl_3$ between aqueous HCl and iso-propyl ether. They pointed out that a final decision regarding the status of proposed iron polymers (8) in the ether phase would have to await activity measurements of the complex in the ether phase and $FeCl_3$ in HCl solution.

Nachtrieb and Fryxell (93) subsequently determined the stoichiometric activity coefficients of $FeCl_3$ in 5 M HCl saturated with $FeCl_2 \cdot 4H_2O$ by electromotive force measurements. On the basis of these measurements they concluded that the abnormal extraction of $FeCl_3$ by isopropyl ether is the result of the low activity coefficient for the salt in the ether phase.

The distribution of ferric iron between hydrochloric acid and isopropyl ether solutions was studied by Myers, Metzler, and Swift (89). They established the formula of the iron complex extracted with respect to associated chloride, hydrogen and water. They found that the dependence of the distribution ratio upon the aqueous iron concentration could be qualitatively accounted for in terms of polymerization of the ethereal iron. The variation of the number of associated water molecules with the variation of the ethereal iron concentration also indicated association of the ethereal iron.

In further extraction studies, Myers and Metzler (78, 90) evaluated the effective polymerization of the ethereal iron and studied the variation of the distribution constant with the acid concentration and the effect of the acid concentration on the apparent polymerization of the ethereal iron. They further made spectral, isopiestic, and magnetic susceptibility studies (78) of the iron in the ether layer. The ultraviolet spectra of HCl solutions of ferric chloride and anhydrous $FeCl_3$ in isopropyl ether were measured and compared. A great similarity between the spectrum of a concentrated HCl solution of $FeCl_3$ and that of the iron complex in isopropyl ether was observed. Isopiestic measurements indicated that there was polymerization of the extracted iron, but magnetic susceptibility measurements showed a value of 5.95 Bohr magnetons for the magnetic moment of the ethereal iron. This is close to the spin-only value. The authors concluded that the highest complex formed in quantity is $FeCl_4^-$. Werbel, Dibeler, and Vosburgh (147) earlier had found that the magnetic moment of ferric iron has the normal value of 5.92 Bohr magnetons in aqueous hydrochloric acid with concentrations ranging from 1 to 4.8 M in HCl.

Friedman (33) has studied the spectrum of $KFeCl_4$. His interpretation of the structure of chloroferric acid extracted from aqueous hydrochloric acid solutions of $FeCl_3$

by organic solvents is interesting in that he postulates that $HFeCl_4$ is really the ion pair $H_3O^+ FeCl_4^-$.

Chalkley and Williams (24) believe that the distribution of $FeCl_3$ between aqueous HCl solutions and nonaqueous solvents is partly dependent on the equilibrium

$$FeCl_3 + HCl = HFeCl_4 = H^+ + FeCl_4^-$$

and partly on changes in the partition coefficient due to changes in activities of the solvents in the two phases.

Laurene, Campbell, Wiberley, and Clark (69) prepared the anhydrous dietherate of $HFeCl_4$ and studied its behavior with water. The hydrated acid was shown by spectrochemical means to be identical with the complex which is extracted by isopropyl ether from hydrochloric acid solutions containing $FeCl_3$.

Campbell, Clark, and Bauer (22) extracted aqueous solutions which were 7 M in HCl and 0.1, 0.2, or 0.4 M in ferric chloride with isopropyl ether and measured the conductivity of the ether layer. They found that the extracted iron complex was ionic and did not depend on the initial conditions of the extraction.

In the extraction of $FeCl_3$ from HCl solutions by 1-5 % tributyl phosphate in benzene, Specker and Cremer (136) found that $HFeCl_4 \cdot 2Bu_3PO_4$ was extracted from 7-9 N HCl and $FeCl_3 \cdot 3Bu_3PO_4$ from 4 N HCl. In extractions from neutral $CaCl_2$ solution, conductometric titration indicated that $Ca(FeCl_4)_2$ was the important species extracted.

Fomin, Zagorets, Morgunov, and Tertishniks (29) used butyl ether-benzene mixtures to extract $FeCl_3$ from 10 M HCl. They reported the formation of the trisolvate $FeCl_3 \cdot xHCl \cdot 3Bu_2O \cdot yH_2O$ in the organic phase.

Good and Bryan (41) studied the distribution of ferric chloride between aqueous HCl and various long chain alkyl amines in organic solvents by tracer techniques. They compared the spectra of the extracted species with the spectra of $KFeCl_4$ in diethyl ether determined by Friedman (33) and from the similarity concluded that the extracted anion is the tetrachloroferrate (III) ion, $FeCl_4^-$.

The distribution of $FeCl_3$ and HCl between diethyl ether and water at 20° was studied by Nikolaev and Mikhailova (96). The acid concentration was varied from 0 - 4.43 M, while the ferric chloride concentration was varied from 0.02 - 4.30 M. The authors reported that the $FeCl_3$ may enter the ether phase as $FeCl_3 \cdot HCl \cdot 6H_2O$. Later, these same investigators (97), by using the concept of an extraction "ray" concluded that $HFeCl_4 \cdot 6H_2O$ is the only prevailing form of iron resulting from the extraction of $FeCl_3$ into the ether phase.

Nakagawa (94) made an investigation of the extraction of both ferrous and ferric iron from hydrochloric acid and sulfuric acid solutions with a kerosene solution of dodecenyl(trialkylmethyl)amine. Ferrous iron could be extracted from hydrochloric acid solution, but not from sulfuric acid solution. Ferric iron could be quantitatively extracted from hydrochloric acid solutions more concentrated than

6 N in HCl.

Ritchie (115) investigated the influence of light on the color of ferric chloride in the system $FeCl_3$-HCl-H_2O. The system was exposed to intense radiation which brought about a photochemical change in the system. The change was reversible and the solutions returned slowly to their initial condition after the light was removed. The change was similar to that produced on heating and was considered to be probably due to hydrolysis.

Prasad and Schoni (110) studied the photoreduction of alcoholic solutions of ferric chloride. They investigated the influence of temperature, light intensity, presence of small quantities of water, and of neutral salt electrolytes upon the process. They reported that the reduction of ferric ion appeared to reach a steady state in each of the anhydrous solutions and that although small quantities of water increase the initial rate of photochemical reduction, they later seemed to decrease the total amount of ferric ion reduced. Small quantities of $MgCl_2$, LiCl, KCl, or NaCl strongly inhibited the photochemical reduction.

The quantum efficiency of the photoreduction of alcoholic solutions of ferric chloride was determined by Prasad and Limaye (107). They reported that ferrous chloride and chlorine were formed, and that, apparently, no other side reactions occurred during the first two hours after the reaction had started. This corroborates the earlier work by Puxeddu (111), who studied the photochemical reduction of ferric chloride in diethyl ether solutions. Prasad further investigated the photoreduction of ferric chloride in various media with various co-workers (106, 108, 109).

The oxidation-reduction potential of the ferric-ferrous electrode was determined by Popoff and Kunz (103) by use of the cell

$$\text{Pt, H}_2\text{, HCl, HCl} + \text{FeCl}_3 + \text{FeCl}_2\text{, Pt.}$$

The normal oxidation-reduction potential of the ferric-ferrous electrode was found to be -0.7476 v. ± 0.5 mv.

Bezier (15) studied the variations in the oxidation-reduction potential of ferric iron at constant pH caused by the addition of Cl^-, $SO_4^=$, CNS^-, and $C_2O_4^=$ ions to the solution.

Badoz-Lambling (10) determined the dissociation constant of the $FeCl^{++}$ complex by emf means. For

$$K = [Fe^{+++}]\,[Cl^-]\;/\;[FeCl^{++}]$$

he calculated $K = 1 \times 10^{-4.5}$.

Various investigators have studied the hydrolysis of ferric chloride. Katsuri (58) found that $BaCl_2$ and $NaCl$ retard the hydrolysis of ferric chloride in that the temperature at which hydrolysis is complete is raised by the addition of these salts to the ferric chloride solution. The effect of aluminum chloride is negligible. Bray and Hershey (18) investigated the hydrolysis of the ferric ion, the standard potential of the ferric-ferrous electrode at 25 °, and the equilibrium $Fe^{+++} + Cl^- = FeCl^{++}$. Others who have investigated the hydrolysis of ferric chloride include Aumeras and Mounic (7), Lamb and Jacques (66, 67), and Guiter (45).

Milburn (79) made a spectrophotometric study of the hydrolysis of the ferric ion. He assumed the following reactions in interpreting his data:

$$Fe^{+++} + H_2O = FeOH^{++} + H^{+}$$

$$2\ FeOH^{++} = Fe(OH)_2Fe^{+4}.$$

This was a continuation of previous work by Vosburgh and Milburn (80).

Kiss, Abraham, and Hegedus (59) determined the extinction curves at room temperature with wave lengths from 2000 to 7000 Å for aqueous solutions of $Fe(ClO_4)_3 + HClO_4$, $FeCl_3 + HCl$, $Fe_2(SO_4)_3 + H_2SO_4$, $Fe(SCN)_3 + KSCN$ or NH_4SCN, and other such combinations. The absorption of acid solutions of $Fe(ClO_4)_3$ was attributed to the presence of the hexaaquo complex, $Fe(H_2O)_6^{+++}$. These investigators attributed the extinction curve of $FeCl_3$ in concentrated HCl to the complex ion, $FeCl_6^{---}$. The formation of such a complex, in view of later research, is doubtful. Earlier Abraham (2) reported, from a study of the absorption spectra of ferric salts in concentrated acid and salt solutions, the existence of the unstable $FeCl_6^{---}$ complex and the stable $Fe(H_2O)_6^{+++}$ complex.

An important spectroscopic study of the association of ferric ions with chloride, bromide, and hydroxyl ions was made by Rabinowitch and Stockmayer (112). The absorption curves of $FeCl^{++}$, $FeCl_2^{+}$, and $FeCl_3$ were derived. All these species are yellow, with $FeCl_3$ being the most intensely colored. The complex anions, $FeCl_4^{-}$, etc., were reported to be formed only in very concentrated chloride solutions and were found to be less intensely colored than $FeCl_3$. The equilibrium constants of the formation of $FeCl^{++}$, $FeCl_2^{+}$, and $FeCl_3$ were also determined.

Olerup (98) calculated the association constant

$$K = [FeCl^{++}] / [Fe^{+++}][Cl^-] = 5.7$$

from light-absorption measurements of $FeCl^{++}$. His value is not in very good agreement with that of Badoz-Lambling (10).

Gamlen and Jordan (36) in an important paper have reviewed the literature on the stability constants of the chlorocomplexes of ferric ion, and from a study of the spectra of $Fe(ClO_4)_3 + HCl$ solutions, have fairly well established that the highest complex of ferric ion in HCl is the tetrachloroferrate ion, $FeCl_4^{-}$. They found the formation constants of the higher complexes to be $K_3' = 0.73$, and $K_4' = 0.0105$ at 20° and ionic strength zero, where

$$K_n' = \frac{[FeCl_n^{3-n}]}{[FeCl_{n-1}^{4-n}][Cl^-]} \quad \frac{1}{f_{HCl}} .$$

They report the extinction coefficients for $FeCl_4^-$, $FeCl_3$, $FeCl_2^+$, and Fe^{+++}, and have calculated the distribution of Fe(III) among these species. It is concluded that probably the only species present in solutions with chloride concentration in the range 8 - 11.35 M are $FeCl_3$ and $FeCl_4^-$.

Schlafer (132) studied the ultraviolet electron transfer spectra of a number of halogen complexes of the ferric ion.

Weeds, Gallagher, and King (149) have studied the thermodynamics of the reaction

$$Fe^{+++} + Cl^- = FeCl^{++}$$

by emf, spectrophotometric, and calorimetric methods.

Gutmann and Baaz (46) have compared the spectrum of $FeCl_4^-$ in various solvents with the ultraviolet spectra of dilute solutions of $FeCl_3$ alone and of $FeCl_3$ containing an equivalent amount of $(C_2H_5)_2NCl$ in $POCl_3$. This comparison showed that $FeCl_4^-$ is present in both $POCl_3$ solutions.

Gutmann and Baaz (47) also reported that conductometric, potentiometric, and colorimetric titrations, as well as spectrophotometric and conductimetric measurements, all show that Fe(III) in $POCl_3$ forms the very stable tetracoordinated complex $FeCl_4^-$, which is not significantly dissociated, solvolyzed, solvated, or associated into polyions. They report the radius of $FeCl_4^-$ to be 3.1 Å.

Baaz, Gutmann, and Hubner (9) conclude, from further studies of $FeCl_3$ in $POCl_3$, that the $FeCl_4^-$ complex does not form higher complexes by binding solvent molecules, by forming chloride ion bridging-complexes, or by adding additional Cl^- ions.

Connick and Coppel (26) have studied the kinetics of the formation of the ferric chloride complex, $FeCl^{++}$.

The system Fe_2O_3-$FeCl_3$-H_2O-HCl has been extensively investigated by Schäfer and co-workers (127, 128, 129, 130). Of particular interest in connection with this research are the measurements by Schäfer and Gann (130) of the water-vapor pressures of iron (III) chloride hydrate melts. The vapor pressures of water and HCl over $FeCl_3.nH_2O$ ($n = 2.70$ to 8.30) were measured at 5° intervals from 40 to 70° by entrainment with nitrogen. Measurements were made by a static method at 114° ($n = 1.6$ to 7.0). Inflections at $n = 6$ in the curves obtained by plotting viscosity versus molality and also density versus molality indicate that the hexaaquo species must possess a certain stability, although this was not shown by a plot of the vapor pressure of water versus $\underline{n}$. A plot of the activity of the water versus $n/(n+4)$ showed deviation from Raoult's law. From this the authors conclude that aquo complexing occurs and that it is stronger at lower temperatures.

Linke (71) has studied the systems $FeCl_3$-H_2O and $FeCl_3$-HCl-H_2O below 0°. He reports a decahydrate of $FeCl_3$ not reported by Roozeboom and Schreinmakers (124).

The structure in ferric chloride solutions in the concentration range 1.5 to 5 M has been studied by Brady

(17) by measuring the scattering of X-rays. At the highest concentration studied he concluded that the main species present was the $FeCl_6^{---}$ ion. In light of other research, this finding is doubtful.

Standley and Kruh (137) have made diffraction studies similar to those of Brady (17). They conclude that the species present is probably the $FeCl_4^-$ ion, rather than the $FeCl_6^{-3}$ ion in mixtures with HCl. Kruh (65) further discusses the $FeCl_3$-HCl-H_2O system in a review of diffraction studies of the structure of liquids.

Tsitovich (144) in a study of the state of the elements of the first transition family in hydrochloric acid solutions by the use of ion-exchange methods found that the ferric ion formed anion complexes at concentrations above 8 N HCl.

Marcus (73) has measured the formation constants in the system $FeCl_3$-HCl-H_2O by the anion exchange method. This research showed that at higher HCl concentrations the complexes were $FeCl_2^+$, $FeCl_3$ and $FeCl_4^-$, with successive stepwise formation constants of

$$\log k_2 = -0.7,\ \log k_3 = -1.40 \text{ and } \log k_4 = -1.92.$$

In addition to these species, some undissociated $HFeCl_4$ is also believed formed in concentrated hydrochloric acid. Spectrophotometric measurements in concentrated chloride solutions confirmed these results qualitatively.

Thermodynamics of Concentrated Electrolyte Solutions. Burtch (21) and Miller (81) have reviewed recently most of the pertinent theoretical studies relating to hydration and association phenomena in electrolyte solutions. Only a little new work has been reported on 2:1 electrolytes, especially in mixtures.

A new method of calculation of the chemical potentials of dissolved components in simple ternary solutions of water and salts has been reported by Timefeev (143). The chemical potentials of the dissolved components in the $BaCl_2$-HCl-H_2O system were calculated in good agreement with literature values.

Guggenheim (43) has recently calculated the activity coefficients of typical 2:1 electrolytes in aqueous solution by an accurate solution of the Poisson-Boltzmann equation. He found that the values of the activity coefficients differ from the values obtained by the Debye-Huckel approximation by only about 1 to 2 percent, which corresponds to a shift of about 0.2 Å in the apparent ionic diameter. He concludes that the Debye-Huckel approximation is adequate to about 0.035 mole/kg., and that the existing experimental values of the activity coefficients for 2:1 electrolytes in aqueous solution are reliable to about 1 to 2 percent, but no better.

An important publication pertaining to electrolyte solutions appearing since the reviews of Burtch and Miller is "The Structure of Electrolytic Solutions" (48).

Bell (13) has pointed out that the concept of a fixed primary hydration number is a useful first approximation in dealing with various properties of ions, but for a more complete understanding of the problem the peculiar associated structure of water must be considered, as well as the effect of ions on the surrounding water outside the region of primary hydration.

CHAPTER II

EXPERIMENTAL

Apparatus.

The apparatus used in this research was essentially identical to that used by Miller (81). Since the author was closely associated with Miller and his work during much of this investigation, frequent reference will be made to Miller's Dissertation (81) where details of most of the experimental techniques can be found. The apparatus was a modification of that described by Smith, Combs, and Googin (134). Among the modifications was an enlargement of the diameters of the rotating drums of the saturators from 25 mm. to 28 mm., and of the solution cells, from 38 mm. to 42 mm. The components for the drying cycle were omitted. Miller had also introduced surface-flow type presaturators through which the carrier gas (nitrogen) was conducted before being passed over the rotating-drum saturators. These changes were also incorporated into the apparatus used for this research.

The gas-flow and pressure-control portion of the apparatus was essentially that described by Bechtold and Newton (12). The flowmeter and its accessories were not used after the first few runs. Miller (81) had also found them unnecessary. The flow of nitrogen was found to be adequately controlled by placing a needle valve between the gas pressure regulator and the safety valve.

During the determinations of the vapor pressures of the $FeCl_2$-HCl-H_2O systems chromous sulfate dissolved in sulfuric acid was used to reduce any oxygen which might be present in the nitrogen used as the carrier gas. The chromous sulfate was kept in gas-scrub bottles over zinc amalgam. It was found that when Linde laboratory grade nitrogen was used the solution in the first scrubber bottle never completely changed to the green color, indicative that the chromous sulfate had been expended. Full details of the method of preparation of the scrubbers is given by Moran (87). After the nitrogen had passed through the chromous sulfate, it was bubbled through concentrated sulfuric acid before it was allowed to pass through the needle valve that controlled the rate of flow.

Procedures.

Vapor Pressure Measurements. The procedure was essentially that followed by Miller (81). Before the run was begun, the saturators and presaturators were cleaned with hot chromic acid and then rinsed thoroughly with distilled water. This was followed by a rinse with acetone. The saturators and presaturators were then dried, rinsed with a small amount of the solution to be used in the run, and finally filled to the proper level with the solution. The saturators and presaturators were placed in a water bath maintained at a temperature of $25.00 \pm 0.01^{\circ}C$. During the first part of the investigation an air bath, having a light bulb as the heating element, was used to maintain the absorbers at a temperature above that of the water bath. During the latter part of the investigation this practice was discontinued since the room temperature remained constant at about 30°C. Whereas Miller allowed the apparatus to remain in the water bath overnight to come to thermal equilibrium, in this investigation the time allowed was less, but it was always at least 4 hours before the measurement actually began.

The absorbers were packed in the manner described by Miller. They were first wiped with a damp lintless cotton cloth, then with a chamois skin and finally placed in a covered container until used. Before being used, they were placed in the balance case for approximately one hour prior to weighing. After having been weighed, the absorbers were placed in the air bath and connected into the flow system.

The apparatus was tested for leaks before an experiment was begun.

The carrier gas was allowed to run through the dummy absorbers for approximately one hour before the weighed absorbers were placed into the system by means of appropriate stopcocks. Upon completion of the experiment the absorbers were removed and reweighed in the manner described earlier. The measurement was usually repeated immediately.

Analytical Methods.

I. Analysis for Chloride in the Absorbers. The chloride content of the sodium hydroxide-asbestos absorbers was analyzed by essentially the same method used by Miller. The only significant difference was that the pH was adjusted to 7 by use of Hydrion paper rather than to the phenolpthalein endpoint. The potentiometric titration apparatus was also that used by Miller, except that a dry cell was used for the working emf during part of the investigation in place of a mercury cell.

II. Analysis for the Chloride Ion. In addition to the potentiometric method used for the absorbers, solutions having relatively high chloride content were analyzed for chloride gravimetrically as silver chloride by the method described by Koltholf and Sandell (62).

III. Analysis for Iron. Iron was determined volumetrically by titration with ceric sulfate solution to the ferrous ortho-phenanthroline endpoint by the method described by Koltholf and Sandell (64).

IV. Analysis for Sulfuric Acid. The sulfuric acid concentration was determined by acid-base titration with standard carbonate-free sodium hydroxide (63) to the phenolphthalein endpoint. Potassium acid phthalate was used as the primary standard in the standardization of the sodium hydroxide.

V. *Analysis of Solid Phases*. The composition of the solid phases in equilibrium with the saturated ternary solutions was determined by use of Schreinmaker's wet residue method (74).

Preparation and Standardization of the Solutions.

I. *Hydrochloric Acid Solutions*. The hydrochloric acid solutions were prepared by mixing concentrated hydrochloric acid and water in proportions calculated to give an approximate molality somewhat above that desired. The concentration was then determined gravimetrically. If the concentration of a solution was greater than that required, the solution was diluted to the required concentration by adding the required weight of water. The solution was then analyzed again to check the concentration.

II. *Ternary Solutions*. Ternary solutions of ferric chloride in hydrochloric acid were prepared by weight from stock solutions. These were diluted with hydrochloric acid of the proper concentration. The weighing was done on a large capacity solution balance with an accuracy generally better than ± 0.005 percent. Before the stock solutions were standardized, they were first filtered through a fritted glass funnel to remove as much as possible of any residue insoluble in hydrochloric acid. The stock solutions were then allowed to set for a day or so in order to allow any remaining insoluble residue to settle to the bottom.

Hydrochloric acid solutions of ferrous chloride were prepared in the same manner as those containing ferric chloride, except that no filtration was necessary. The solutions were kept in the dark as much as possible. The 9.00 m HCl series of solutions were prepared and used as soon as possible (within a period of one or two days). Each time the bottles were opened for any reason they were flushed out with nitrogen. In spite of all precautions, the 9.00 m HCl series changed color from green to yellowish green, indicating that some oxidation had occurred. By reduction with stannous chloride and subsequent titration with ceric sulfate, it was determined that the solutions at the time of the vapor pressure measurements contained about 1 percent ferric chloride. Very possibly the 4.7 m HCl series contained somewhat more ferric chloride, since the color of these solutions was darker. The ferric chloride in these solutions was estimated to be not more than 2 percent at the time the vapor pressure determinations were made.

III. Saturated Solutions. The saturated ternary solution of ferric chloride in hydrochloric acid was prepared by adding small quantities of anhydrous ferric chloride to a concentrated stock solution of ferric chloride in 7.00 m acid. The solution was kept in a 25° water bath for about a week or more with periodic agitation. The liquid phase was analyzed volumetrically with ceric sulfate for iron and gravimetrically for chloride.

Procedures used in the preparation of the saturated ferrous chloride solutions in hydrochloric acid were modified somewhat from those employed with ferric chloride because there was no anhydrous ferrous chloride. A stock solution was saturated with the tetrahydrate at a temperature somewhat above 25°, analyzed to adjust the HCl to the proper concentration, and placed in the water bath at 25° for several days. The liquid phase was then adjusted to the proper HCl concentration and the solution again placed in the water bath for several days. It was then analyzed a second time. Repetitions of this procedure eventually led to saturated solutions of the proper acid concentration. Throughout, the solutions were wrapped to prevent as much light as possible from entering.

IV. Preparation of Sodium Hydroxide-Asbestos Mixture. A mixture of sodium hydroxide and asbestos was prepared by drying a slurry of Gooch-filter quality asbestos in a solution of approximately 5 m sodium hydroxide in an oven at 110°. The dried mixture was ground in a Waring Blendor.

Density Determinations. A Leach-type specific gravity bottle of 50 ml capacity was used to determine the densities of the solutions investigated. The bottle was first calibrated with freshly boiled distilled water at 25°C. Previously chilled solution was added to the bottle until full. The cap containing a thermometer was then inserted into the bottle and the bottle placed in the water bath maintained at 25°. Excess solution drained away through the capillary side arm as the solution warmed slowly to 25°. When the bottle and its contents reached 25° and drainage had ceased, the bottle was capped, dried, and weighed.

Chemicals. The specifications and manufacturers of the chemicals used in this research are as follows:

Sulfuric Acid: Mallinckrodt Chemical Works, analytical reagent grade.

Hydrochloric Acid: Baker and Adamson, C. p. reagent grade; Fisher Scientific Co., reagent grade.

Magnesium Perchlorate: The G. Frederick Smith Chemical Co. This material gave a negative test for chloride with silver nitrate.

Perchloric Acid: Mallinckrodt Chemical Works, analytical reagent grade, listing an assay of not more than 0.001% chloride.

Mercuric Iodide: Eimer and Amend, E. & A. tested purity reagent grade.

Di-n-butyl Phthalate: The Matheson Company, Inc. This chemical was distilled before it was used.

Sodium Hydroxide; Potassium Acid Phthalate; Silver Nitrate; Ammonium Nitrate; Potassium Chloride: Merck and Co., Inc., reagent grade.

Asbestos: Powhatan Mining Co., Gooch acid-washed grade. The washings from this asbestos gave a negative test for chloride when tested with silver nitrate.

Nitrogen: Linde Company and The Air Reduction Co., Inc., water pumped.

Ferrous Chloride ($FeCl_2 \cdot 4H_2O$): Fisher Scientific Co., Fisher certified reagent.

Ferric Chloride: Fisher Scientific Co., anhydrous resublimed.

Distilled water or demineralized distilled water were used throughout this investigation and referred to simply as "water."

Ceric Ammonium Sulfate: The G. Frederic Smith Chemical Co.

CHAPTER III

DETERMINATION OF ACTIVITIES

Methods applicable to the determination of the activities of all of the components of the $FeCl_3$-HCl-H_2O system or the $FeCl_2$-HCl-H_2O system are limited. For example, the HCl activity might be determined by an emf measurement, but this would still leave the salt and water activities undetermined. The salt activity cannot be determined by an emf method partly because of the hydrochloric acid which reacts irreversibly with iron, and partly because iron electrodes are themselves irreversible. Since the systems all contain two volatile components, HCl and water, it was decided that the gas transpiration method would be the most suitable for use. By this method the water and HCl activities can be measured in the same experiment and the salt activity then calculated.

Gas-Transpiration Method.

The gas-transpiration method is quite simple in principle and permits a simultaneous measurement of both water and HCl vapor pressures.

In this method a known amount of carrier gas is saturated with the volatile components of the solution. The volatile components are collected in the sodium hydroxide-asbestos and magnesium perchlorate absorbers.

Analysis of the absorbers gives the mole fractions in the gas phase, from which the partial pressures may be calculated by application of Dalton's law

$$P_i = X_i P \tag{1}$$

where P_i = partial pressure of component i
X_i = mole fraction of component i
P = total pressure.

The activities of the volatile components may then be calculated by assuming that the partial pressures of the volatile components may be substituted for the fugacities,

$$a_i = f_i/f_i^o = P_i/P_i^o , \tag{2}$$

where f_i = fugacity of component i
f_i^o = fugacity of component i in the standard state
P_i^o = partial pressure of component i in the standard state.

Once the activities of the two volatile components are known, the activity of the third component may be calculated by use of the Gibbs-Duhem equation.

The Gibbs-Duhem Equation.

Darken (27) and McKay (76) have discussed the application of the Gibbs-Duhem equation to multicomponent systems. Gootman (42), Burtch (21), and Miller (81) have covered the application of this equation to ternary systems similar to the present ones. The equation in its form extended to three components may be used to calculate the activity of a third component from the known activities of the other two components if the mole ratios of any two of the components are kept constant.

For a three-component system at constant temperature and pressure the Gibbs-Duhem equation for the partial molal Gibbs free energies may be written

$$n_1\ d\bar{G}_1 + n_2\ d\bar{G}_2 + n_3\ d\bar{G}_3 = 0, \qquad (3)$$

where n_1 = moles of component 1

n_2 = moles of component 2

n_3 = moles of component 3

$\bar{G}_1$ = partial molal free energy of component 1

$\bar{G}_2$ = partial molal free energy of component 2

$\bar{G}_3$ = partial molal free energy of component 3.

The definition of the activity ai of the *i*th component may be taken as

$$\bar{G}_i = \bar{G}_i^o + RT \ln a_i, \qquad (4)$$

where $\bar{G}_1^o$ represents the partial molal free energy of component i in the standard state. Differentiation of equation (4) with respect to n_3 at constant n_1 and n_2 yields

$$d\bar{G}_i = RT\ (\partial a_i/\partial n_3)_{n_1,\ n_2}\ d\ n_3. \qquad (5)$$

Substitution of equation (5) in equation (3) gives

$$n_1\,(\partial \ln a_1/\partial n_3)_{n_1,\,n_2}\,dn_3 + n_2(\partial \ln a_2/\partial n_3)_{n_1,\,n_2}\,dn_3$$
$$+ n_3(\partial \ln a_3/\partial n_3)_{n_1,\,n_2}\,dn_3 = 0\,. \qquad (6)$$

After dividing equation (6) by n_3, one has finally

$$(n_1/n_3)\,(\partial \ln a_1/\partial n_3)_{n_1,\,n_2}\,dn_3$$
$$+ (n_2/n_3)\,(\partial \ln a_2/\partial n_3)_{n_1,\,n_2}\,dn_3$$
$$+ (\partial \ln a_3/\partial n_3)_{n_1,\,n_2}\,dn_3 = 0. \qquad (7)$$

On the molal concentration scale equation (7) reduces to

$$(55.51/m_3)\,(\partial \ln a_1/\partial m_3)\,dm_3$$
$$+ (m_2/m_3)\,(\partial \ln a_2/\partial m_3)\,dm_3$$
$$+ (\partial \ln a_3/\partial m_3)\,dm_3 = 0 \qquad (8)$$

with the concentration of component 2 held constant. Integration and rearrangement of equation (8) yields

$$\ln\left(\frac{a_3}{a_3^*}\right) = m_1\int_{m_3}^{m^*_3}\frac{d\ln a_1}{m_3} + m_2\int_{m_3}^{m^*_3}\frac{d\ln a_2}{m_3}, \qquad (9)$$

where asterisk superscripts refer to the upper limit of the integration. Letting the subscript 3 refer to the salt, the subscript 1 refer to the water, and the subscript 2 refer to the acid, equation (9) may be used to calculate the activity of the salt in the ternary solution.

The integration may be carried out graphically by plotting ln a_1 versus $1/m_3$ and ln a_2 versus $1/m_3$ and adding squares in the usual manner, as was done in the case of the $FeCl_3$-HCl-H_2O system. If empirical expressions relating the logarithms of the water and HCl activities to the salt molality are known, these functions may be integrated by equation (9) to yield the logarithm of the salt activity as a function of the salt molality. This was the procedure followed in the $FeCl_2$-HCl-H_2O systems where the data could be expressed by power series in the salt concentration.

CHAPTER IV

DATA AND CALCULATIONS

Preliminary measurements of the vapor pressures of some sulfuric acid solutions and hydrochloric acid solutions were made to determine the accuracy with which the activities of water and HCl could be found by the method used in this investigation. The results of the sulfuric acid measurements are recorded in Table I, where they are compared with the values of Stokes (138) which are accepted as isopiestic standards. The partial pressure of SO_3 in the vapor phase was not included in the calculations, since it may be considered negligible (1, 72).

The results of the measurements on the hydrochloric acid solutions are tabulated in Table II, Figure 2 shows a graphical comparison of the values for the partial pressure of HCl with those determined by Bates and Kirschman (11). The partial pressures of water obtained experimentally are compared in Figure 3 with those obtained by Randall and Young (114) and also with those listed by Zeisberg (151).

All measurements were made at 25°. In all tables, the last digit in any column marked with an asterisk was retained for computational purposes only, unless stated otherwise.

Vapor Pressure Measurements.

Ternary Systems. Vapor pressure measurements were made on three series of ferrous chloride in hydrochloric acid. The HCl molal concentration, and consequently the mole ratio of HCl to H_2O, was kept constant throughout any given series. The concentration of the salt was varied from zero to saturation. The results of these measurements are recorded in Tables III, IV, and V.

In addition to the ferrous chloride hydrochloric acid series, a series of solutions of ferric chloride in hydrochloric acid was also studied. The concentration of the ferric chloride varied from zero to saturation. The results of vapor pressure measurements on this series are tabulated in Table VI.

Calculation of Partial Pressures. It was pointed out in the previous chapter that the principle upon which the gas-transpiration method depends is Dalton's law. In order to calculate the partial pressures of HCl and H_2O in the gas phase, the number of moles of the carrier gas, nitrogen, must be determined. This is done by use of the following equation

$$n_x = n_w(P_1/P_1^o) - n_w \qquad (1)$$

where P_1 = total pressure in the reference saturator,

P_1^o = vapor pressure of pure water at 25°,

n_w = moles of water collected in reference absorber,

n_x = moles of nitrogen gas passed through system.

The amount of HCl in the absorber following the solution saturator was determined by a potentiometric chloride titration. The weight of water taken up by the absorber was then determined from the weight increase of the absorber and the weight of the absorbed HCl. From the weights of the water and HCl the moles of water and HCl in the saturated gas were calculated. The vapor pressure of the water in the solution was then found from the equation

$$P_{H_2O} = (n_1/n_x + n_1 + n_2)\ P_2 \qquad (2)$$

where P_{H_2O} = vapor pressure of the water in the solution,

P_2 = total pressure in the solution saturator,

n_1 = moles of water vapor collected in second absorber,

n_2 = moles of HCl collected in second absorber,

n_x = moles of carrier gas passed through the system.

Partial pressures of HCl in the solutions were calculated similarly.

Calculation of Activities.

Since the activity is a measure of the difference in partial molal free energies in a given state and in a standard reference state, the standard states for the solution components water, HCl, and salt must be defined.

Standard State of Water. The usual convention was followed in defining the standard state of the solvent; i.e., pure liquid water at 25° and 1 atmosphere pressure. Since the vapor pressure of water at 25° is 23.756 mm. Hg (121), the activity of the water in the solutions was calculated by use of the following equation

$$a_1 = P_1/23.756 \ , \qquad (3)$$

where $\underline{P}_1$ and $\underline{a}_1$ represent the vapor pressure and activity, respectively.

<u>Standard State of Hydrochloric Acid</u>. Since the following relation defines the activity, when the pressures are substituted for fugacities,

$$a_2 = P_2/P_2^o \ , \qquad (4)$$

where $a_2 =$ activity of HCl,

$P_2 =$ vapor pressure HCl in a given solution,

$P_2^o =$ vapor pressure HCl in standard state,

and since $$(1/P_2^o) = (a_2/P_2) = k \qquad (5)$$

then $$a_2 = k\ P_2. \qquad (6)$$

Thus, equation (6) may be used to calculate the activity of HCl in any given solution provided the constant, $\underline{k}$, is known. The average value of $\underline{k}$ was determined by comparison of the vapor pressures of HCl in binary colutions from Table II with the activities of HCl determined by Randall and Young (114) by electromotive force measurements. The value of $\underline{k}$ was found to be $(2.55 \pm 0.01) \times 10^3$ mm^{-1}. Thus, equation (6) may be rewritten as

$$a_2 = 2550\ P_2. \qquad (7)$$

Equation (7) was used to calculate the activities of HCl in the solutions investigated. Since the activities calculated from the electromotive force measurements are relative to a hypothetical ideal one molal binary solution of hydrochloric acid, equation (7) refers to the same state.

The results from the experimental vapor pressure measurements together with calculated activities are given in Tables III, IV, V and VI.

Standard States of the Salts. The saturated solution of ferrous chloride in each constant molality acid series was chosen as a reference state for solutions in the series, and the activity of the ferrous chloride in each of the reference solutions was then related to the activity of ferrous chloride in a 4.7 m HCl solution saturated with ferrous chloride. A word of explanation seems in order at this point.

The necessary binary solution data were not available for relating the activities of $FeCl_2$ in ternary $FeCl_2$-HCl-H_2O mixtures to the conventional, hypothetical one molal solution. Stokes and Robinson (122, 123) record activity data for the binary water solutions only up to 2 molal in $FeCl_2$. Therefore, activity of $FeCl_2$ in 4.70 m HCl solution in equilibrium with $FeCl_2 \cdot 4H_2O$ was arbitrarily set equal to unity. Since the tetrahydrate, $FeCl_2 \cdot 4H_2O$ is also the solid phase in equilibrium with the saturated solutions in all three series (131), the $FeCl_2$ activities in each of these can be related. It may readily be shown that

TABLE I

VAPOR PRESSURE DATA FOR THE SYSTEM H_2SO_4-H_2O

		Experimental Values			Literature Values	
Molality H_2SO_4	Run Number	P_{H_2O} (mm)	$\bar{P}_{H_2O}$ (mm)	Activity H_2O	$\bar{P}_{H_2O}$	Activity H_2O
3.824	1-4	18.83	18.84	0.7931	18.84	0.7931
	1-5	18.84				
5.298	1-1	16.14	16.16	0.6802	16.17	0.6807
	1-3	16.18				
8.039	1-1	11.31	11.31	0.4761	11.37	0.4786
	1-2	11.30				
	1-3	11.33				
	1-4	11.32				
	1-5	11.31				
	1-6	11.31				

TABLE II

VAPOR PRESSURE DATA FOR THE SYSTEM $HCl-H_2O$

Molality HCl	Run Number	P_{HCl}* (mm)	$\overline{P}_{HCl}$* (mm)	$a_{2\,HCl}$* (Lit.)	P_{H_2O} (mm)	$\overline{P}_{H_2O}$ (mm)	$a_{1\,H_2O}$
4.70	1-2	0.0435			18.02		
	1-3	0.0455	0.0441	113.1	18.03	18.02	0.7585
	1-4	0.0434			18.00		
7.00	1-1	0.366			14.28		
	1-2	0.372	0.367	937.0	14.24	14.24	0.5994
	2-1	0.366			14.22		
	2-2	0.362			14.24		
8.18	2-1	1.018	1.024	2625	12.47	12.46	0.5245
	2-2	1.030			12.44		
8.59	1-2	1.439			11.77		
	2-1	---	1.442	3660	11.82	11.77	0.4955
	2-3	1.444			11.71		
9.00	1-1	2.010	2.011	5112	11.14	11.14	0.4689
	1-3	2.011			11.14		
9.16	1-1	2.265			10.93		
	1-2	2.265	2.263	5790	10.93	10.93	0.4601
	1-3	2.258			10.94		
10.21	1-3	5.017	5.026	12800	9.563	9.572	0.4030
	2-2	5.034			9.582		

TABLE III

VAPOR PRESSURE DATA FOR THE $FeCl_2$-HCl-H_2O SYSTEM

4.7 MOLAL HYDROCHLORIC ACID SERIES

Molality $FeCl_2$	Run Number	P_{HCl} (mm)	$\overline{P}_{HCl}$ (mm)	a_{2}^{*} HCl	P_{H_2O} (mm)	$\overline{P}_{H_2O}$ (mm)	a_1 H_2O
0.2046	1-1	0.0564			17.45		
	1-2	0.0583	0.0568	144.8	17.48	17.52	0.7375
	1-3	0.0558			17.62		
0.4000	1-1	0.0846			17.06		
	1-2	0.0869	0.0857	218.5	17.04	17.05	0.7177
	1-3	0.0855			17.05		
0.5934	1-1	0.0924			---		
	1-2	0.0954	0.0909	231.8	16.72	16.72	0.7038
	1-3	0.0849			16.71		
0.8534	1-1	0.1295			16.08		
	1-2	---	0.1287	328.2	16.00	16.03	0.6748
	1-3	0.1278			16.02		
1.000	1-1	0.1404			15.77		
	1-2	0.1396	0.1412	360.1	15.63	15.70	0.6609
	1-3	0.1436			---		
1.200	1-1	0.187			---		
	1-2	0.185	0.185	471.8	15.14	15.16	0.6382
	1-3	0.183			15.19		
1.400	1-1	0.236			14.59		
	1-2	0.246	0.244	622.2	14.50	14.55	0.6125
	1-3	0.251			---		
1.548	1-1	0.2817			14.33		
	1-2	0.2775	0.2807	715.8	14.32	14.32	0.6028
	1-3	0.2830			14.30		
1.900	1-1	0.3880			13.63		
	1-2	0.3869	0.3859	984.0	13.63	13.63	0.5737
	1-3	0.3849			13.64		
	1-4	0.3839			13.62		

TABLE III (Continued)

Molality $FeCl_2$	Run Number	P_{HCl} (mm)	P_{HCl} (mm)	$a_{2\,HCl}$*	P_{H_2O} (mm)	P_{H_2O} (mm)	$a_{1\,H_2O}$
2.200	1-1	0.5304	0.5255	1340	13.03	13.06	0.5498
	1-3	0.5240			13.11		
	1-4	0.5221			13.05		
2.300	1-1	0.5685	0.5633	1436	12.96	12.91	0.5434
	1-2	0.5555			12.90		
	1-3	0.5659			12.87		
2.400	1-1	0.6296	0.6341	1617	12.64	12.62	0.5312
	1-2	0.6360			12.61		
	1-4	0.6367			12.62		
2.547	1-1	0.8157	0.8161	2081	12.19	12.17	0.5123
	1-2	0.8150			12.15		
	1-3	0.8176			12.16		

TABLE IV

VAPOR PRESSURE DATA FOR THE $FeCl_2$-HCl-H_2O SYSTEM

7.0 MOLAL HYDROCHLORIC ACID SERIES

Molality $FeCl_2$	Run Number	P_{HCl} (mm)	$\bar{P}_{HCl}$ (mm)	$a_{2\,HCl}$*	P_{H_2O} (mm)	$\bar{P}_{H_2O}$ (mm)	$a_{1\,H_2O}$
0.4000	1-2	0.5873	0.5839	1489	13.39	13.37	0.5628
	1-3	0.5805			13.34		
0.6000	1-1	0.7247	0.7231	1844	12.92	12.88	0.5422
	1-3	0.7214			12.83		
0.8000	2-1	0.8674	0.8661	2209	12.53	12.51	0.5266
	2-2	0.8647			12.51		
	2-3	---			12.50		
1.000	1-1	1.061	1.058	2698	12.13	12.16	0.5119
	1-2	1.054			12.18		
1.166	2-1	1.244	1.235	3149	11.98	11.97	0.5039
	2-2	1.225			11.95		
1.300	1-1	1.406	1.404	3580	11.51	11.51	0.4845
	1-2	1.401			11.51		
1.400	2-1	1.513	1.515	3863	11.36	11.36	0.4778
	2-2	1.517			11.35		
1.500	1-1	1.677	1.676	4274	---	11.32	0.4765
	1-2	1.674			11.29		
	1-3	---			11.24		
1.600	1-1	1.869	1.867	4761	11.03	11.02	0.4639
	1-2	1.864			11.00		

TABLE V

VAPOR PRESSURE DATA FOR THE $FeCl_2$-HCl-H_2O SYSTEM

9.0 MOLAL HYDROCHLORIC ACID SERIES

Molality $FeCl_2$	Run Number	P_{HCl} (mm)	$\overline{P}_{HCl}$ (mm)	a_2 HCl*	P_{H_2O} (mm)	$\overline{P}_{H_2O}$ (mm)	a_1 H_2O*
0.0500	1-1	2.133	2.132	5436	10.99	11.01	0.4635
	1-2	2.134			11.01		
	1-3	2.127			11.04		
0.1500	1-2	2.261	2.263	5771	10.86	10.84	0.4563
	1-3	2.264			10.81		
0.2153	1-1	2.523	2.519	6423	10.64	10.69	0.4500
	1-2	---			10.73		
	1-3	2.515			10.69		
0.3500	1-1	2.757	2.760	7038	10.47	10.44	0.4395
	1-2	2.763			10.42		
	1-3	2.759			10.42		
0.4500	1-1	3.039	3.022	7706	10.27	10.31	0.4340
	1-2	3.018			10.34		
	1-3	3.008			10.31		
0.5500	1-1	3.299	3.292	8395	10.13	10.12	0.4260
	1-2	3.300			10.09		
	1-3	3.278			10.13		
0.6000	2-1	3.448	3.451	8800	9.984	10.01	0.4214
	2-2	3.454			10.04		
0.7000	2-2	3.752	3.763	9596	---		
	2-3	3.774			---		
0.7500	1-1	3.871	3.872	9874	9.772	9.762	0.4109
	1-2	3.869			9.751		
	1-3	3.877			---		
0.8000	2-1	4.013	3.991	10180	9.641	9.66	0.4066
	2-2	3.976			9.647		
	2-3	3.983			9.696		

TABLE V (Continued)

Molality $FeCl_2$	Run Number	P_{HCl} (mm)	$\bar{P}_{HCl}$ (mm)	a_2 HCl*	P_{H_2O} (mm)	$\bar{P}_{H_2O}$ (mm)	a_1 H_2O*
0.8500	1-1	4.293	4.26	10860	9.521	9.55	0.4020
	1-2	4.231			9.576		
	1-3	4.133			---		
0.9000	2-1	4.331	4.33	11040	---		
	2-2	4.309			---		
	2-3	4.344			---		
0.9384	1-1	4.479	4.48	11420	9.421	9.42	0.3965
	1-3	4.488			9.410		

TABLE VI

VAPOR PRESSURE DATA FOR THE $FeCl_3$-HCl-H_2O SYSTEM

(Molality HCl = 7.00)

Molality $FeCl_3$	Run Number	P_{HCl} (mm)	$\bar{P}_{HCl}$ (mm)	$a_{2\,HCl}^{*}$	P_{H_2O} (mm)	$\bar{P}_{H_2O}$ (mm)	$a_{1\,H_2O}^{*}$
0.6928	1-1	0.764	0.763	1946	13.74	12.67	0.5333
	1-2	0.763			13.70		
	1-3	0.763			13.57		
1.314	1-1	1.279	1.282	3269	11.64	11.61	0.4887
	1-2	1.285			11.61		
	1-3	1.282			11.58		
1.858	1-1	1.854	1.854	4728	10.81	10.79	0.4542
	1-3	1.854			10.77		
2.499	1-1	---	2.740	6987	9.919	9.909	0.4171
	1-2	2.740			9.911		
	1-3	2.740			9.899		
3.190	1-1	3.792	3.790	9665	9.088	9.081	0.3823
	1-3	3.788			9.074		
3.847	1-2	4.649	4.650	11860	8.449	8.479	0.3569
	1-3	4.651			8.509		
4.630	1-1	5.067	5.071	12930	7.988	8.025	0.3378
	1-2	5.075			8.031		
	1-3	5.072			8.057		
5.301	1-1	5.285	5.283	13470	7.699	7.686	0.3235
	1-2	5.270			7.687		
	1-4	5.295			7.673		
5.963	1-1	5.198	5.195	13250	7.539	7.487	0.3152
	1-2	5.192			7.507		
	1-3	5.228			7.455		
	1-4	5.200			7.480		
	2-1	5.180			7.449		
	2-2	5.184			7.506		
	2-3	5.180			7.476		

TABLE VI (Continued)

Molality $FeCl_3$	Run Number	P_{HCl} (mm)	$\overline{P}_{HCl}$ (mm)	a_{2} HCl*	P_{H_2O} (mm)	$\overline{P}_{H_2O}$* (mm)	a_{1} H_2O*
6.626	1-1	4.960	4.973	12680	7.315	7.319	0.3081
	1-2	4.990			---		
	1-3	4.990			7.319		
	1-4	4.951			7.322		
7.289	1-1	4.710	4.687	11950	7.111	7.009	0.2950
	1-2	4.626			---		
	1-3	4.720			6.918		
	2-1	4.695			7.010		
	2-2	4.673			6.959		
	2-3	4.687			7.042		
	2-4	4.701			7.017		
7.951	1-1	4.394	4.390	11190	6.721	6.667	0.2806
	1-2	4.385			6.635		
	1-3	4.392			6.645		
8.586	1-1	4.088	4.088	10420	6.434	6.438	0.2710
	1-2	4.088			6.451		
	1-3	4.089			6.428		
9.276	1-2	---	3.672	9364	5.958	5.992	0.2522
	1-3	3.656			6.041		
	2-1	3.673			6.034		
	2-3	3.679			5.954		
10.57	1-1	3.256	3.260	8313	---	4.894	0.2060
	1-2	3.261			---		
	1-3	---			4.877		
	2-1	3.261			4.904		
	2-2	3.268			4.899		
	2-3	3.256			4.898		
11.93	2-1	3.143	3.151	8035	3.761	3.741	0.1575
	2-2	3.166			3.732		
	2-3	3.147			3.736		
	2-4	3.149			3.733		
12.59	1-2	3.226	3.219	8208	3.169	3.167	0.1333
	1-3	3.212			3.166		

TABLE VI (Continued)

Molality $FeCl_3$	Run Number	P_{HCl} (mm)	$\bar{P}_{HCl}$ (mm)	a_2 HCl*	P_{H_2O} (mm)	$\bar{P}_{H_2O}$ (mm)	a_1 H_2O*
13.25	2-1	3.332	3.346	8532	2.729	2.688	0.1132
	2-2	3.348			2.692		
	2-3	3.366			2.700		
	2-4	3.338			2.634		
13.91	1-2	---	3.571	9106	2.226	2.219	0.09341
	2-1	3.582			2.251		
	2-3	3.577			2.220		
	2-4	3.555			2.169		
	1-3	---			2.230		
14.58	1-1	3.729	3.730	9512	---	1.840	0.07745
	1-2	3.737			1.836		
	1-3	3.731			1.861		
	1-4	3.733			1.815		
	1-5	3.730			1.843		
	1-6	3.722			1.844		
15.20	1-1	4.436	4.430	11300	1.286	1.256	0.05287
	1-2	4.410			1.243		
	1-3	4.443			1.238		
15.80	1-1	4.796	4.794	12220	1.037	1.051	0.04424
	1-2	4.787			1.026		
	1-3	4.814			1.068		
	1-4	4.790			1.098		
	1-5	4.783			1.024		
16.40	1-2	5.116	5.116	13050	0.997	1.011	0.04256
	1-3	5.115			1.024		
16.90	1-1	5.564	5.576	14220	0.763	0.749	0.03153
	1-2	5.577			0.743		
	1-3	5.585			0.821		
	2-2	5.598			0.729		
17.00	1-1	5.715	5.724	14600	0.718	0.718	0.03022
	1-2	5.730			0.705		
	1-3	5.727			0.732		

$$a_3^1 = (a_1/a_1^1)^4 , \qquad (8)$$

where a_3^1 = activity of $FeCl_2$ at saturation in 7.0 mHCl or in 9.0 m HCl solution,

a_1 = activity of water at saturation in 4.7m HCl solution,

a_1^1 = activity of water at saturation in 7.0 m HCl or in 9.0 m HCl solution.

Equation (8) takes the form shown because of the arbitrary selection of the state of unit activity of the salt to be the saturated solution in 4.70 m HCl. Thus, the activities of the salt in each constant acid series were first calculated with reference to the saturated solution in the series. The activities of $FeCl_2$ in the reference solutions of the two series of higher acid concentration were then related to the activity of $FeCl_2$ in the saturated solution in 4.70 m HCl by equation (8). In this manner, comparison of the activities in the three series can be made. This should also facilitate the calculation of the ternary solution activities when the requisite binary solution data become available.

The standard state of $FeCl_3$ in the $FeCl_3$-HCl-H_2O system was also arbitrarily chosen by setting the activity of the salt in the saturated solution in 7.00 m HCl equal to unity. This solution is in equilibrium with $Fe_2Cl_6 \cdot 5H_2O$ (125). Here again, the requisite binary solution data were not available and activities could not be referred to the conventional standard state.

The activities of the various reference states are recorded in Table VII.

TABLE VII

ACTIVITIES OF THE SALTS IN THE REFERENCE STATES

State	a_3(salt)
4.7 m HCl Solution Sat'd with $FeCl_2$	1.00
7.0 m HCl Solution Sat'd with $FeCl_2$	2.81
9.0 m HCl Solution Sat'd with $FeCl_2$	7.56
7.0 m HCl Solution Sat'd with $FeCl_3$	1.00

<u>Treatment of the Data</u>. The experimental values of the water and HCl activities given in Tables III, IV, and V were first fitted to the following empirical function by the method of least squares with the aid of an IBM 650 Computer.

$$\log a = A + Bm_3 + Cm_3^2 + Dm_3^3 + \ldots. \qquad (9)$$

The Gibbs-Duhem equation was then integrated after substitution of the analytical expressions for the logarithms of the activities of water and HCl given by equation (9). The reference state for the salt in each constant acid series was as described in the preceding section, the saturated solution. The saturated solution in each of the two higher series was then related to the saturated 4.7 m HCl series by use of equation (8). The final equations for the salt activity have the form

$$\log a = A + B \log m_3 + Cm_3^2 + Dm_3^3 + \ldots. \qquad (10)$$

Coefficients for equation (9) and equation (10) are recorded in Table VIII.

TABLE VIII

$FeCl_2$-HCl-H_2O SYSTEM AT 25° C.

(Coefficients of Empirical Equations)

Molality HCl	Coefficients of Equation (9)				Range m_3	S.E.E.
	A	B	C	D		
			log a_1			
4.70	-0.1193	-0.06009	-0.002177		0 - 2.55	0.0029
7.00	-0.2221	-0.06927			0 - 1.60	0.0032
9.00	-0.3298	-0.07615			0 - 0.938	0.0009
			log a_2			
4.70	2.0509	0.6331	-0.1205	0.02515	0 - 2.55	0.026
7.00	2.9704	0.5819	-0.1983	0.07298	0 - 1.60	0.0093
9.00	3.7116	0.4120	-0.04597		0 - 0.938	0.0050

Molality HCl	Coefficients of Equation (10)				Range m_3
	A	B	C	D	
4.70	-2.688	0.8282	1.374	-0.1774	0 - 2.55
7.00	-1.927	-0.5253	2.777	-0.766	0 - 1.60
9.00	0.1354	1.196	0.827		0 - 0.938

The activities of the components in the $FeCl_2$-HCl-H_2O systems are recorded in Tables IX, X, and XI.

The activity of $FeCl_3$ in the $FeCl_3$-HCl-H_2O system was also obtained from the Gibbs-Duhem equation. Large-scale plots of $1/m_3$ versus log a_1 and $1/m_3$ versus log a_2 were made and the integration was done graphically. The standard state was again chosen to be the saturated solution with an arbitrarily chosen activity of $FeCl_3$ of unity. Smoothed values of the logarithms of the activities of the components in this system are given in Table XII A. In Table XII B are listed the corresponding values of the activities.

Analysis of Saturated Solutions and Solid Phases

Results of the analyses of the liquid phases and the wet-solids obtained from the saturated ternary solutions are given in Tables XIII and XIV. Literature values listed for the solubility of $FeCl_2$ in the ternary solutions were determined by graphical interpolation of data given by Schimmel (131). The literature value shown for the solubility of $FeCl_3$ was taken from the data of Roozeboom and Schreinmakers (125) given in Seidell (135). This value was also determined by graphical interpolation.

The composition of the solid phase in equilibrium with 7.0 m HCl was not experimentally determined because of insufficient solid for analysis. There is no reason to believe, however, that the solid phase would be different from that in equilibrium at higher and lower acid concentrations. This was found by Schreinaker's wet residue method (74) to be $FeCl_2 \cdot 4H_2O$. Schimmel (131) also reports the solid phase to be $FeCl_2 \cdot 4H_2O$ for all three series.

The results from the analysis of the saturated ternary solution of $FeCl_3$ in 7.00 m HCl are recorded in Table XIII also. Unfortunately, the solid phase in this system could not be analyzed either because of insufficient solid. Roozeboom and Schreinmaker (125) report, however, that it is $Fe_2Cl_6 \cdot 5H_2O$.

TABLE IX

ACTIVITY DATE FOR THE $FeCl_2$-HCl-H_2O SYSTEM

4.7 MOLAL HYDROCHLORIC ACID SERIES

Molality $FeCl_2$	a_1 H_2O	a_2 HCl*	$\gamma_\pm$ HCl	a_3 $FeCl_2$*	$\gamma_\pm$ $FeCl_2$*
0.1	0.7493	129.8	2.37	0.000420	0.0155
0.2	0.7390	148.9	2.49	0.00100	0.0202
0.3	0.7286	170.1	2.61	0.00188	0.0243
0.4	0.7185	193.4	2.74	0.00319	0.0282
0.5	0.7081	219.0	2.86	0.00509	0.0322
0.6	0.6979	247.0	2.99	0.00774	0.0362
0.7	0.6880	277.7	3.11	0.0114	0.0403
0.8	0.6767	311.2	3.24	0.0165	0.0446
0.9	0.6681	347.9	3.37	0.0233	0.0490
1.0	0.6583	387.9	3.53	0.0323	0.0535
1.1	0.6486	431.5	3.65	0.0440	0.0581
1.2	0.6390	479.3	3.79	0.0590	0.0629
1.3	0.6294	531.6	3.94	0.0781	0.0678
1.4	0.6199	589.0	4.08	0.102	0.0728
1.5	0.6105	652.1	4.25	0.132	0.0779
1.6	0.6011	721.8	4.41	0.168	0.0831
1.7	0.5919	798.9	4.58	0.212	0.0882
1.8	0.5826	884.5	4.76	0.264	0.0934
1.9	0.5737	980.1	4.95	0.326	0.0986
2.0	0.5647	1087	5.16	0.398	0.104
2.1	0.5558	1208	5.37	0.481	0.109
2.2	0.5470	1344	5.61	0.575	0.114
2.3	0.5383	1498	5.86	0.681	0.119
2.4	0.5296	1675	6.12	0.799	0.124
2.5	0.5210	1877	6.42	0.929	0.128
2.55	0.5167	1990	6.57	1.00	0.130

TABLE X

ACTIVITY DATE FOR THE $FeCl_2$-H_2O-HCl SYSTEM

7.0 MOLAL HYDROCHLORIC ACID SERIES

Molality $FeCl_2$	a_1 H_2O	a_2 HCl*	$\gamma_\pm$ HCl	a_3 $FeCl_2$*	$\gamma_\pm$ $FeCl_2$
0.1	0.5902	1066	4.60	0.00657	0.0193
0.2	0.5808	1201	4.82	0.0170	0.0354
0.3	0.5716	1346	5.03	0.0365	0.0449
0.4	0.5626	1500	5.24	0.0712	0.0551
0.5	0.5537	1663	5.45	0.129	0.0661
0.6	0.5449	1836	5.66	0.222	0.0779
0.7	0.5363	2021	5.86	0.363	0.0903
0.8	0.5279	2220	6.07	0.567	0.103
0.9	0.5195	2436	6.29	0.847	0.116
1.0	0.5112	2673	6.52	1.21	0.129
1.1	0.5032	2935	6.75	1.51	0.137
1.2	0.4952	3230	7.01	1.82	0.143
1.3	0.4873	3566	7.29	2.13	0.149
1.4	0.4797	3951	7.59	2.41	0.153
1.5	0.4721	4399	7.93	2.65	0.156
1.6	0.4646	4928	8.31	2.81	0.157

TABLE XI

ACTIVITY DATA FOR THE $FeCl_2$-H_2O-HCl SYSTEM

9.0 MOLAL HYDROCHLORIC ACID SERIES

Molality $FeCl_2$	a_1 H_2O*	a_2 HCl*	$\gamma_\pm$ HCl	a_3 $FeCl_2$*	$\gamma_\pm$ $FeCl_2$*
0.1	0.4598	5,653	8.26	0.105	0.0513
0.2	0.4519	6,197	8.56	0.292	0.0716
0.3	0.4440	6,778	8.86	0.573	0.0884
0.4	0.4362	7,396	9.16	0.978	0.104
0.5	0.4287	8,056	9.46	1.55	0.120
0.6	0.4212	8,756	9.77	2.32	0.135
0.7	0.4139	9,495	10.1	3.38	0.151
0.8	0.4067	10,280	10.4	4.80	0.168
0.9	0.3997	11,100	10.7	6.68	0.185
0.938	0.3970	11,420	10.8	7.56	0.192

TABLE XII

ACTIVITY DATA FOR THE SYSTEM $FeCl_3$-HCl-H_2O

(HCl molality = 7.00)

PART A

Salt Molality	-log a_1 (H_2O)	log a_2 (HCl)	-log a_3 ($FeCl_3$)
0	0.223	2.970	---
1	0.293	3.411	6.728
2	0.355	3.701	5.978
3	0.406	3.957	5.387
4	0.450	4.085	5.009
5	0.485	4.128	4.712
6	0.503	4.121	4.461
7	0.522	4.090	4.240
8	0.550	4.046	3.998
9	0.592	3.991	3.649
10	0.650	3.935	3.280
11	0.725	3.908	2.851
12	0.816	3.905	2.396
13	0.923	3.920	1.974
14	1.047	3.957	1.506
15	1.197	4.023	0.992
16	1.367	4.097	0.420
17	1.513	4.162	0.000

TABLE XII (Continued)

PART B

Salt Molality	a_1 (H_2O)	a_2 (HCl)	a_3 ($FeCl_3$)
0	0.598	933	------
1	0.509	2580	0.000000187
2	0.442	5020	0.00000105
3	0.393	9060	0.00000410
4	0.355	12200	0.00000980
5	0.327	13400	0.0000194
6	0.314	13200	0.0000346
7	0.301	12300	0.0000575
8	0.282	11100	0.000105
9	0.256	9800	0.000224
10	0.224	8610	0.000525
11	0.188	8090	0.00141
12	0.153	8040	0.00402
13	0.119	8320	0.0106
14	0.0897	9060	0.0312
15	0.0635	10500	0.102
16	0.0430	12500	0.380
17	0.0307	14500	1.00

TABLE XIII

COMPOSITION OF SATURATED SOLUTIONS

	% Salt		% H_2O	% HCl	% Salt Lit. Value
4.70	21.61	($FeCl_2$)	66.81	11.59	21.16
7.00	13.46	($FeCl_2$)	68.89	17.65	13.91
9.00	8.220	($FeCl_2$)	69.10	22.68	8.673
7.00	68.72	($FeCl_3$)	24.92	6.354	68.84

<u>Densities</u>.

The densities of all the ternary mixtures investigated in this research were determined at 25°. The estimated accuracy of these measurements is ± 0.02 percent. The values are recorded in Table XV for the $FeCl_2$-HCl-H_2O system and in Table XVI for the $FeCl_3$-HCl-H_2O system.

TABLE XIV

COMPOSITIONS OF THE WET SOLID PHASES

m_2 (HCl)	% $FeCl_2$	% H_2O	% HCl
4.70	60.97	38.01	1.02
9.00	61.53	37.68	0.79

In Figure 1 there is shown the variation of the densities in the latter system with salt concentration. These density values were used to calculate the apparent molal volumes, and the partial molal volumes of the salt in the solutions.

TABLE XV

DENSITY DATA FOR THE $FeCl_2$-HCl-H_2O SYSTEM AT 25° C.

4.7 Molal HCl		7.0 Molal HCl		9.0 Molal HCl	
$m_3(FeCl_2)$	Density (g./cc.)	$m_3(FeCl_2)$	Density (g./cc.)	$m_3(FeCl_2)$	Density (g./cc.)
0.0000	1.0684	0.0000	1.0969	0.0000	1.1192
0.2046	1.0821	0.2000	1.1144	0.1000	1.1280
0.4000	1.0992	0.4000	1.1318	0.2000	1.1369
0.5934	1.1188	0.6000	1.1491	0.4000	1.1526
0.8534	1.1463	0.8000	1.1661	0.5000	1.1610
1.000	1.1639	1.000	1.1841	0.6000	1.1689
1.200	1.1770	1.166	1.1969	0.7000	1.1767
1.400	1.1975	1.300	1.2088	0.8000	1.1855
1.548	1.2070	1.400	1.2173	0.9000	1.1937
1.900	1.2434	1.500	1.2254	0.9384	1.1965
2.200	1.2662	1.600	1.2266		
2.300	1.2663				
2.400	1.2747				
2.547	1.2995				

TABLE XVI

DENSITY DATA FOR THE $FeCl_3$-HCl-H_2O SYSTEM AT 25° C.

(Molality HCl = 7.00)

Molality $FeCl_3$	Density (g./cc.)
0.0000	1.0964
0.6928	1.1606
1.314	1.2133
1.858	1.2572
2.499	1.3008
3.190	1.3475
3.847	1.3798
4.630	1.4130
5.301	1.4357
5.963	1.4547
6.626	1.4717
7.289	1.4875
7.951	1.5032
8.586	1.5171
9.276	1.5354
10.57	1.5693
11.26	1.5880
11.93	1.6057
12.23	1.6125
12.59	1.6232
13.25	1.6402
13.91	1.6547
14.58	1.6720
15.80	1.7207
16.40	1.7330
17.00	1.7447

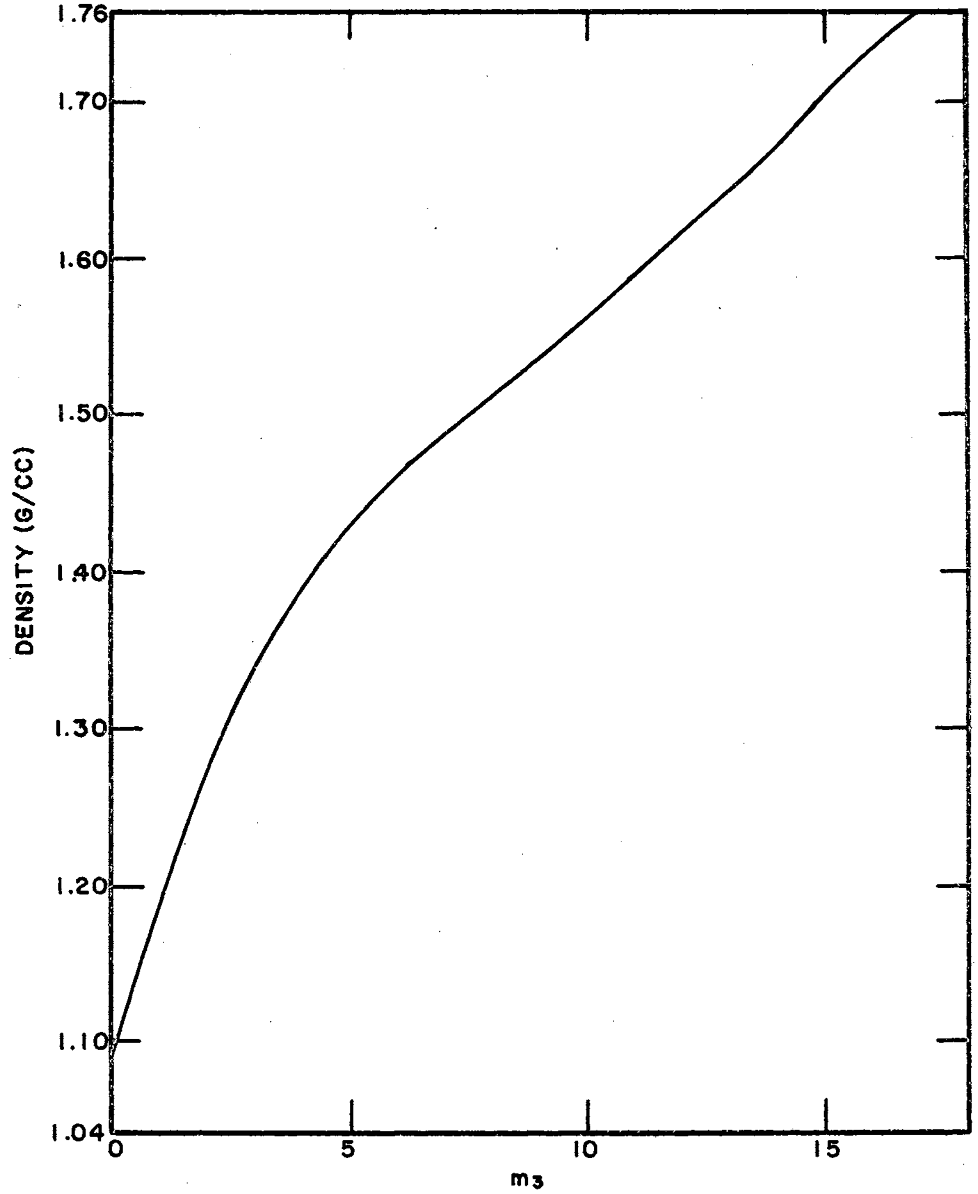

FIGURE I. DENSITIES OF THE $FeCl_3-HCl-H_2O$ SYSTEM (MOLALITY HCl = 7.00)

TABLE V

ACCURACY AND PRECISION

Binary Systems.

Sulfuric Acid-Water. In Table I are recorded the measured activities of water in three sulfuric acid solutions together with the activities calculated from the osmotic coefficients reported by Stokes (138). A comparison of the latter values with the experimental values shows that the literature values are on the average 0.2% higher. The average precision of the vapor pressure measurements for these solutions was slightly better than ± 0.1%, however.

Hydrochloric Acid-Water. The values of the activities of water and HCl in seven solutions of hydrochloric acid are recorded in Table II along with the corresponding experimentally determined vapor pressures. The activities of HCl listed in this table were calculated from the activity coefficients given by Stokes and Robinson (123) based upon the data of Randall and Young (114). The activities of water listed in Table II are experimental values. In Figure 2 there is shown graphically a comparison of the experimental results and the values reported by Bates and Kirschman (11) for the partial pressure of HCl in binary solutions with water. The experimental values are approximately 2 percent higher than those of Bates and Kirschman (11). The deviations from the data of Bates and

Kirschman become greater above 8 molal in HCl. Figure 3 presents a comparison of the experimental values of the partial pressure of water with those reported by Randall and Young (114) and Zeisberg (151). As may be seen, the experimental values fall between Randall's and Young's and Zeisberg's values. The greatest deviation from the values of Randall and Young occurs at about 6.0 molal in HCl and is about 0.2 mm. Hg.

Ternary Systems.

Water and Hydrochloric Acid. The average precision with which the vapor pressures of water and HCl were measured in the four series varied from series to series. The average precision of the vapor pressure measurements in each series is recorded in Table XVII, where the average precision, p, is defined by the expression

$$p = \frac{1}{n} \sum \frac{P}{\overline{P}} \times 100. \qquad (1)$$

where n = number of concentrations measured,
P = average deviation of pressure from average pressure at each concentration,
$\overline{P}$ = average pressure.

In Table VIII are included the standard errors of estimate for the fitting of the experimental activity data to the assumed analytical functions. The standard error of estimate is defined by the expression

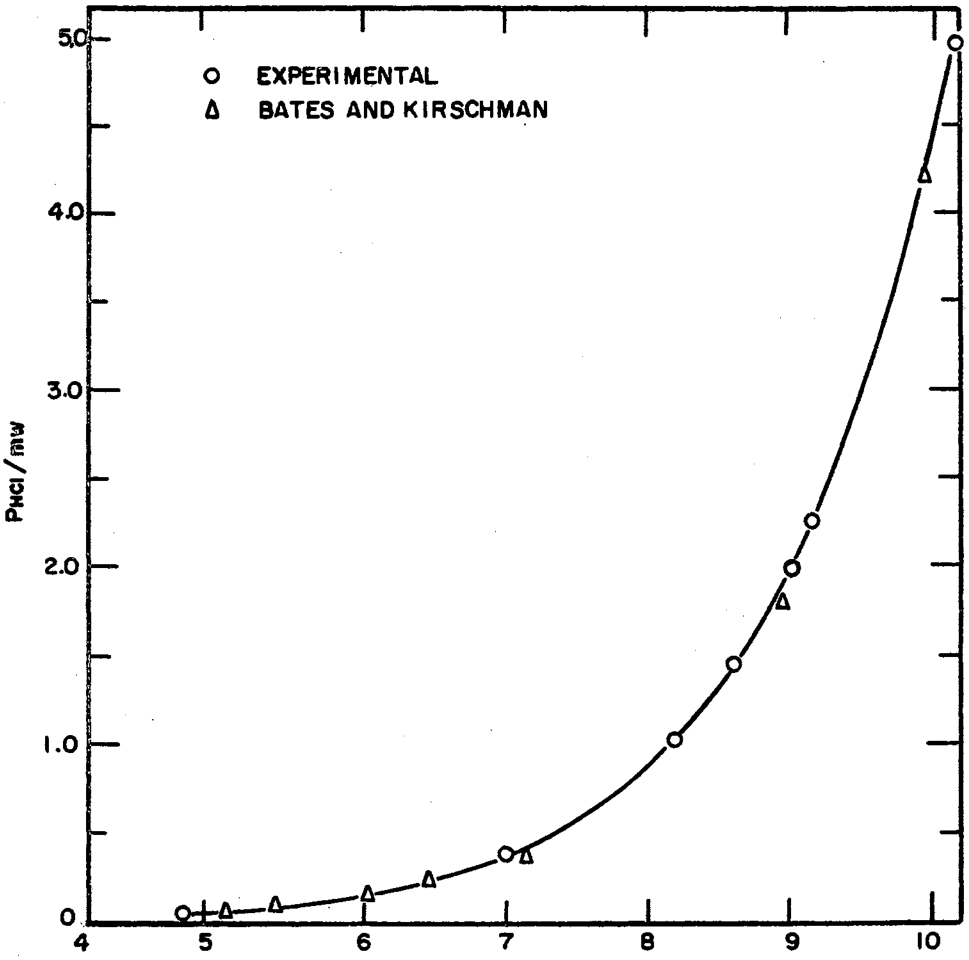

FIGURE 2. VAPOR PRESSURE OF HCl IN AQUEOUS HYDROCHLORIC ACID SOLUTIONS

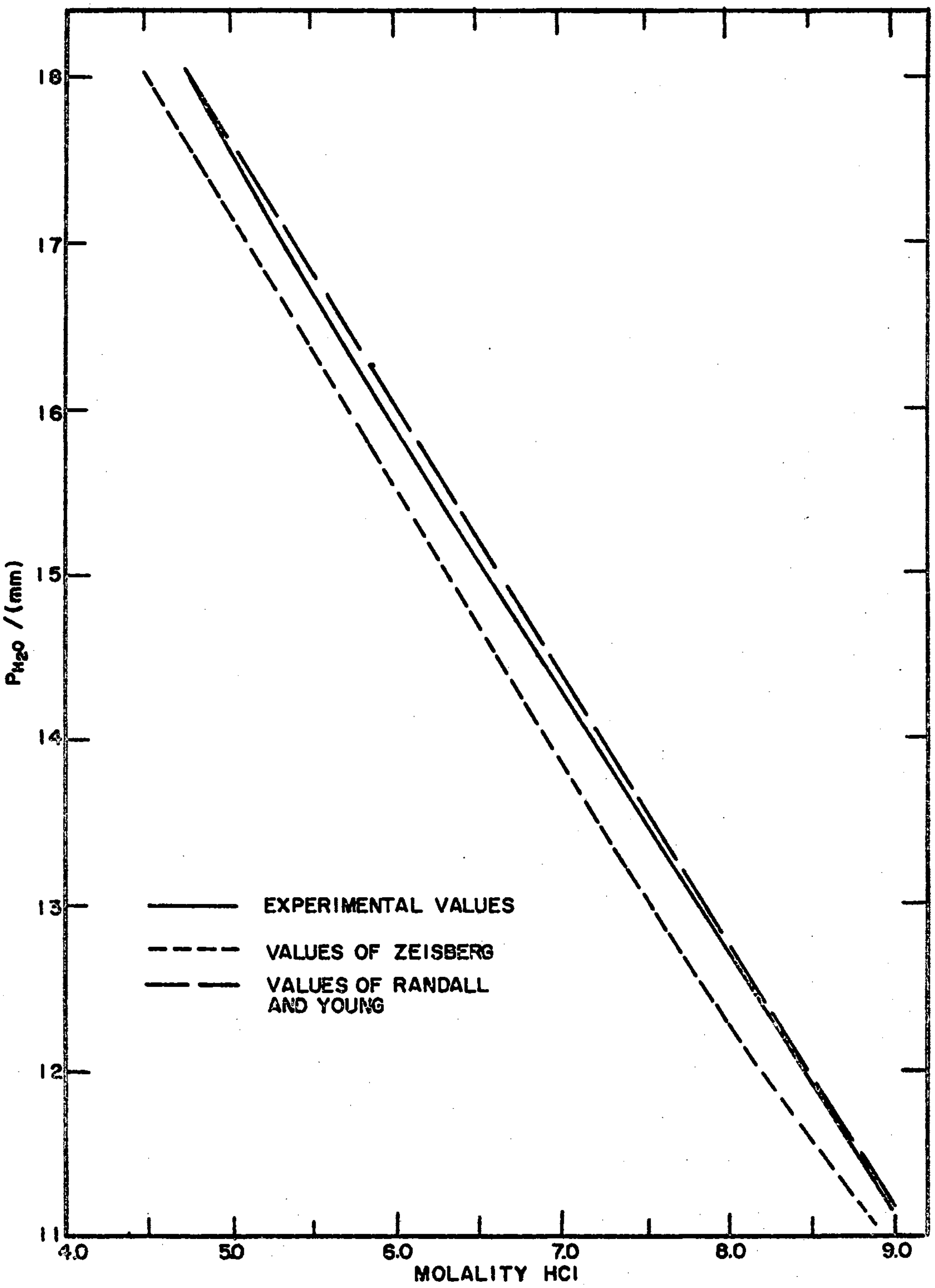

FIGURE 3. VAPOR PRESSURE OF WATER IN AQUEOUS HCl SOLUTIONS

$$\text{S.E.E.} = \sqrt{\frac{(Y - y)^2}{n - (N + 1)}} \qquad (2)$$

where Y = log a (experimental),

y = log a (from equations),

n = number of experimental points,

N = number of terms in equation.

In Table XVIII are shown the average differences between the experimentally observed activities and those calculated by use of the analytical functions obtained by the method of least squares. In the case of the $FeCl_3$-HCl-H_2O system, the Gibbs-Duhem equation was graphically integrated; consequently, no analytical functions were found for the activities in this system.

The Ferrous and Ferric Chloride. The total uncertainty in the values of the activities of water and hydrochloric acid calculated from the empirical equations was considered to be the sum of the uncertainties arising from both experimental measurements and curve fitting. The uncertainties, Δa_3, in the value of the activity of the ferrous chloride were calculated from the Gibbs-Duhem equation

$$- \text{dln } a_3 = (m_1/m_3) (\text{dln } a_1 + (m_2/m_3) (\text{dln } a_2) \qquad (3)$$

or, expressed in increments,

$$\pm \Delta a_3/a_3 = \pm(m_1/m_3) (\Delta a_1/a_1) \pm (m_2/m_3) (\Delta a_2/a_2). \qquad (4)$$

In estimating the error in $\underline{a}_3$ by equation (4) it was assumed that the deviations in $\underline{a}_1$ and $\underline{a}_2$ were additive. While there is an uncertainty in the concentrations, especially in view of the oxidation of the ferrous ion mentioned earlier, still, since the uncertainties have been assumed additive, it would seem that the estimates by equation (4) are of the order of the <u>maximum</u> uncertainty in $\underline{a}_3$. The uncertainties in the calculated values of a_3 are included in Table XVIII along with the uncertainties in the water and HCl activities.

No such estimates are available for the error in the $FeCl_3$ activities in the $FeCl_3$-HCl-H_2O system. It is estimated, however, that the graphical integration is accurate to about 0.5%.

TABLE XVII

PRECISION OF VAPOR PRESSURE MEASUREMENTS

System	n_{HCl}	p_{HCl}	n_{H_2O}	p_{H_2O}
4.70 m HCl + $FeCl_2$	14	1.23	14	0.18
7.00 m HCl + $FeCl_2$	10	0.34	10	0.15
9.00 m HCl + $FeCl_2$	14	0.29	12	0.21
7.00 m HCl + $FeCl_3$	26	0.18	26	0.69

The uncertainty in the calculated values of a_3 given in Table XVIII were calculated at 1.00 molal $FeCl_2$ concentration for the 7.00 m HCl and 4.70 m HCl series and at 0.80 molal $FeCl_2$ for the 9.00 m HCl series.

TABLE XVIII

UNCERTAINTY IN CALCULATED ACTIVITIES

System	% a_1 (H_2O)	% a_2 (HCl)	% ($FeCl_2$)
4.7 m HCl + $FeCl_2$	± 0.45	± 3.78	± 42.7
7.0 m HCl + $FeCl_2$	± 0.37	± 1.07	± 28.0
9.0 m HCl + $FeCl_2$	± 0.14	± 0.83	± 19.1

While the estimated uncertainties in the values of a_3 obtained by integration of the Gibbs-Duhem equation are large, it should be pointed out that the $FeCl_2$ activity increases 200 fold over the concentration range of from 0.5 m to 2.55 m in the 4.7 m HCl series. Correspondingly large variations in $FeCl_2$ activity occur in the other series. In the absence of a direct determination of the salt activity, however, the only method available for finding the activity of a transition metal salt is through the Gibbs-Duhem relation. Examination of equation (4) shows that with experimental uncertainties in the measurement of a_1 and a_2 of the order of tenths of a percent, there will always be an uncertainty in a_3 one to two magnitudes greater.

CHAPTER VI

DISCUSSIONS OF RESULTS

The Debye-Hückel theory of electrolyte solutions at infinite dilution has proved successful as a limiting law (49, 117). At greater, though still moderate concentrations of from 0 to about 0.5 molal, the rigorous theory of thermodynamic properties of electrolyte solutions proposed by Mayer (75) and extended by Poirer (101, 102) shows promise. At still higher concentrations, however, it would appear that no really convincing rigorous theories comparable to the Debye-Hückel theory have been devised although there have been several attempts made (39, 140). This is understandable in view of the large deviations from the ideal state of solution at infinite dilution. Even less progress has been made in the theory of electrolyte mixtures. Glueckauf (39) and others (116) have pointed out that there are many factors which must be taken into account at high concentrations of strong electrolytes which can be ignored at very low concentrations. But, as Moriyama (88) has emphasized, the predominant effect which must be taken into consideration in the treatment of activity coefficients of concentrated electrolyte solutions which do not show association is the hydration effect. This effect and other factors will be discussed in more detail in the following sections where an attempt will be made to apply the concept of ionic hydration in an interpretation of the data from the $FeCl_2$-HCl-H_2O systems.

A. Ferrous Chloride-Hydrochloric Acid Mixtures.

Water Activities and Hydration Theory. In Figure 4, there is shown the variation of the water activities with salt concentration in the three series of ferrous chloride solutions in hydrochloric acid. As may be seen, the activity of water in the 4.70 m. HCl - $FeCl_2$ series decreases more rapidly with increase in $FeCl_2$ concentration than in either of the other two higher acid concentration series. The rate of decrease of water activity in the two higher acid concentration series is nearly equal. As Figure 4 also clearly indicates, the variation in all three acid concentrations is not linear, except perhaps as a first approximation. Also it is obvious from a comparison of Figures 4 and 5 that the rate of decrease in water activity in binary solutions of $FeCl_2$ in water is much less than in even the 9.0 m. HCl series; the water activity is much less in all of the HCl-$FeCl_2$ mixtures than in binary solutions, however. The decrease in water activity in any given series at constant acid concentration with increase in salt concentration can probably best be ascribed to the hydration of the ions of the salt in solution decreasing the amount of "free" water.

By way of comparison, Figure 6 shows the variation of water activity with salt molality for approximately corresponding series of other iron-family transition metal

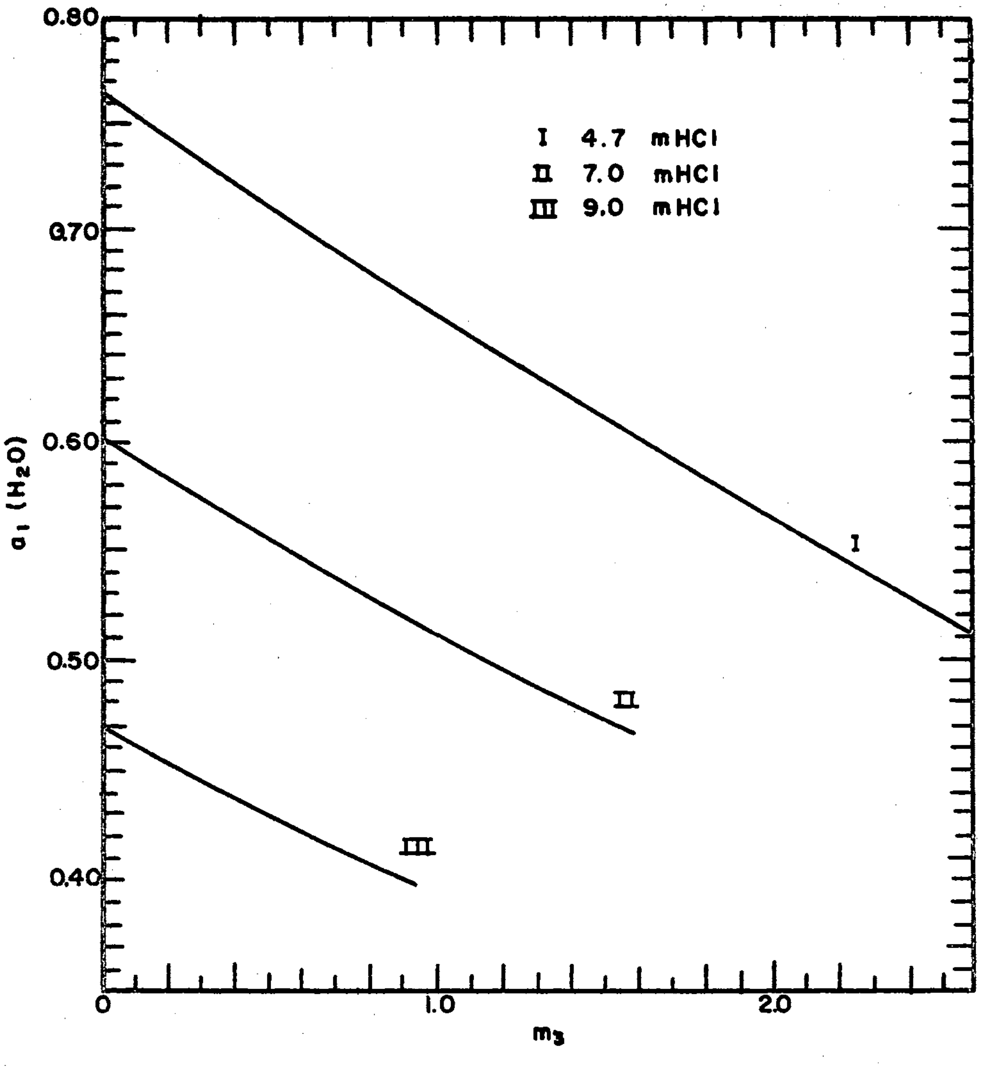

FIGURE 4. ACTIVITIES OF WATER IN THE THREE $FeCl_2$ - HCl - H_2O SERIES

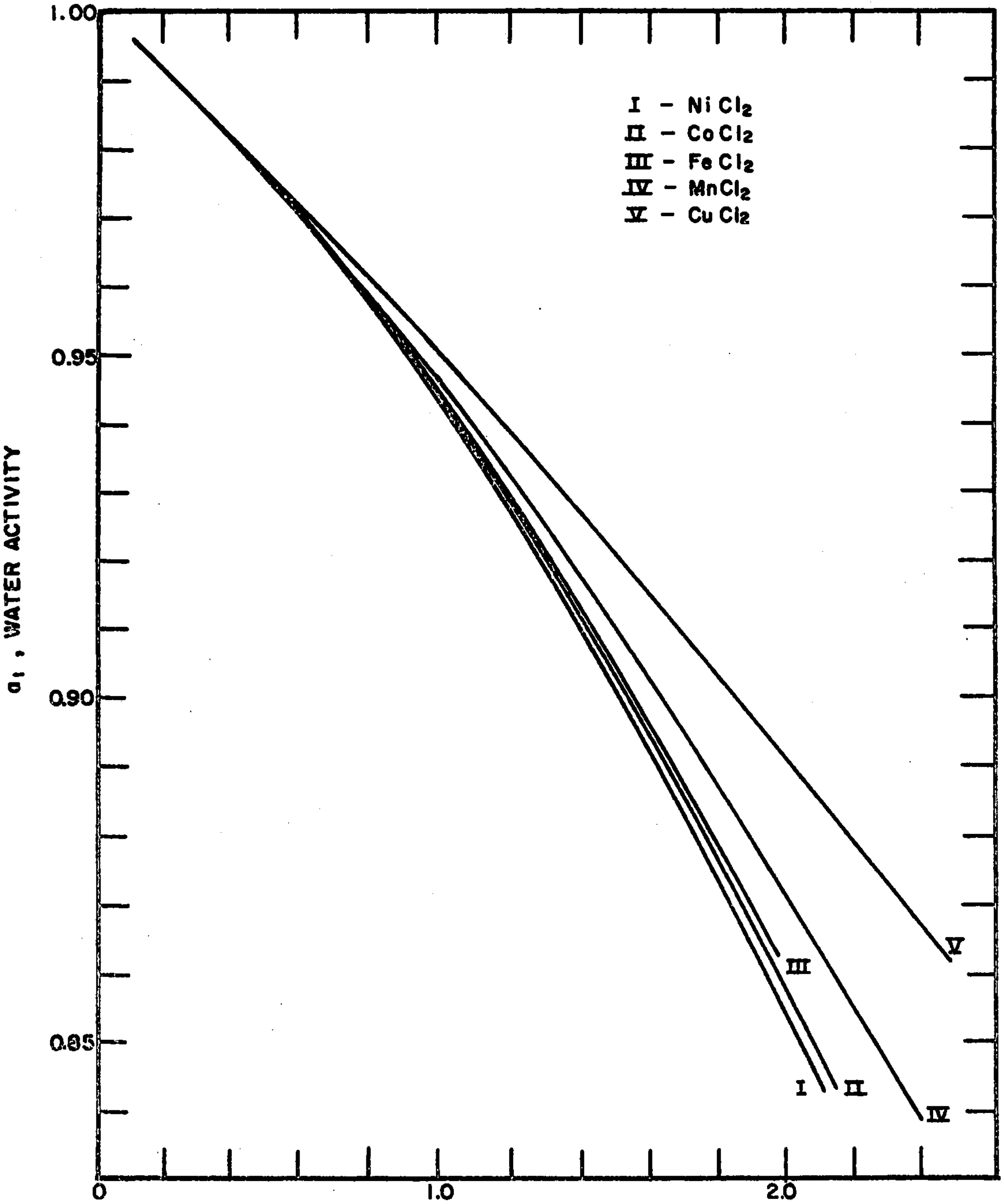

FIGURE 5 WATER ACTIVITY IN BINARY AQUEOUS SOLUTIONS OF SOME TRANSITION METAL CHLORIDES [FROM STOKES AND ROBINSON (122)]

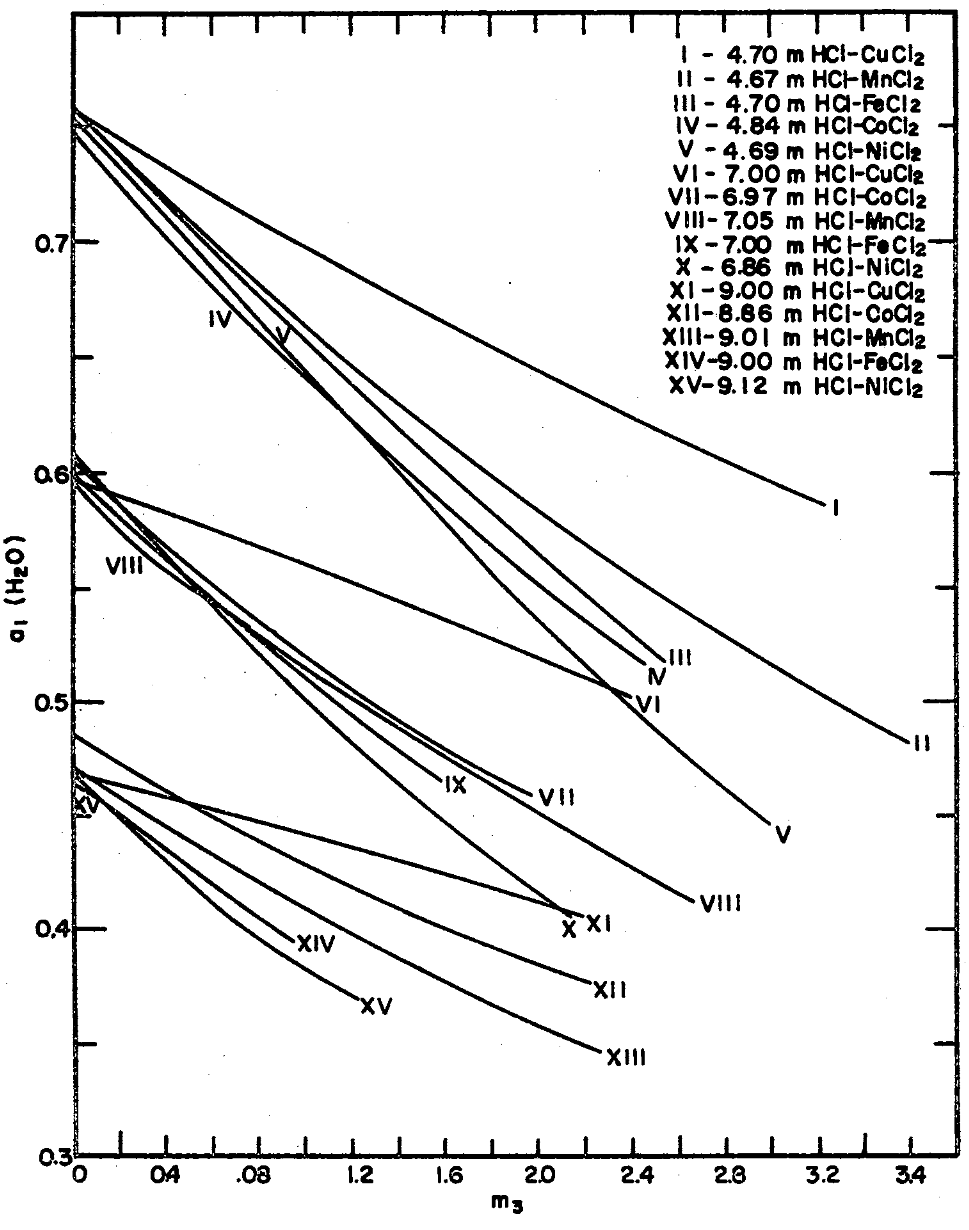

FIGURE 6. VARIATION OF WATER ACTIVITIES IN SOME TERNARY SOLUTIONS OF TRANSITION METAL CHLORIDES IN HYDROCHLORIC ACID

chlorides in hydrochloric acid. Comparison of Figures 5 and 6 shows that the order of the water activity lowering with respect to the metal is the same in the 4.7 molal HCl series as in the binary solutions. It is significant that the order of increasing ionic radius of the bare ion is $Cu < Ni < Co < Fe < Mn$ for the bi-valent ions (99) while the order of water activity lowering in the 4.7 m HCl series is $Cu < Mn < Fe < Co < Ni$. In light of the well-known complexing of the Cu^{++} with Cl^- ion it is not too surprising that Cu^{++} is the only ion out of order when ionic size is correlated with water activity. The order of water activity lowering in the 7.0 m. HCl series and the 9.0 m. HCl series is $Cu < Mn < Co < Fe < Ni$. The order of Mn^{++} and Co^{++} might possibly be reversed, but otherwise the order given above is correct (as nearly as can be determined since the $CoCl_2$ series are 6.97 m. and 8.86 m. in HCl, while the corresponding $MnCl_2$ series are 7.05 m and 9.01 m in HCl). Differences in HCl concentration make exact comparisons difficult. Furthermore, the observed change in order may well be due to greater degrees of complexing of Co^{++} and Mn^{++} at higher acid concentrations. Complex ion formation by Co^{++} and Cl^- is well known (42) and Burtch (21) has observed changes in color of $MnCl_2$ solutions with increasing HCl concentration indicating probable complex ion formation. Stokes (138) pointed out that the activity coefficient curve for aqueous solutions of $MnCl_2$ indicate the possible formation of a complex or at least the presence of an undissociated molecule of low stability. Stokes (138) also noted that $CoCl_2$ exhibits anamalous behavior in binary solutions at higher concentrations. In the case of $FeCl_2$ and $NiCl_2$, both of which were considered "normal" by Stokes (138), the order of water activity lowering is the same both in binary solutions and in ternary solutions at all three acid concentrations at which comparison is possible. Moore, et al (85) concluded from activity measurements that $NiCl_2$ and $MnCl_2$ showed no association appreciably greater in concentrated HCl solutions up to 9.12 m HCl than in aqueous solutions. From the effect that $FeCl_2$ has on the activity of water and by comparison with other systems of 2:1 transition metal chlorides in aqueous HCl, it would appear that $FeCl_2$ behaves in a normal manner in concentrated HCl solutions, much as does $NiCl_2$. Thus, it would seem that ionic hydration is the principal factor causing the large water activity lowering in the system $FeCl_2$-HCl-H_2O, and that the ionic radius is consequently just as important a factor in ternary solutions through its effect on hydration as it is in binary solutions (138). But, for those transition metal ions which have chloro-complexing tendencies, ionic association becomes a factor of greater effect as the concentration of HCl increases than it is in binary solutions.

The hydration theory of Stokes and Robinson (140) has met with considerable success in empirically correlating the activity coefficients of electrolytes in binary solutions with ionic hydration. The theory is essentially an extension of the Debye-Hückel theory, based upon mole fraction statistics, which takes into consideration the fact that the conventional activity coefficient disregards hydration and, therefore, differs from the rational activity coefficient of the hydrated solute. The equation for the activity coefficient in the Stokes and Robinson theory contains two adjustable parameters. These two parameters are a, the distance of closest approach of cation and anion, and n, the effective hydration number of the solute. The parameter, n, according to the authors of the theory, "is not the same thing as the conventional number of water molecules in the first layer round the ion. It is rather a number introduced to allow for the average effect of all ion-solvent interactions where these are large compared to kT, and may therefore very well contain contributions from solvent molecules outside the first layer." (140) By use of an "idealized" radius for the hydrated cation, it is possible to eliminate a from the equation, leaving only n as the adjustable parameter (82).

In commenting upon the theory, Moelwyn-Hughes points out that it is neither necessary, nor, as the authors appreciate, likely, that n should be independent of concentration; in very concentrated solutions a molecule of water is often shared by two ions. More precisely defined values of n will doubtless emerge when the complex problem of its variation with concentration is solved, and when a more precise estimate can be made of its relation to the critical ionic distance. In the meantime, the theory is able, by incorporating only one adjustable parameter, to extend the concentration range from 1 millimole per liter to about 5 moles per liter (82).

Subsequently Stokes and Robinson (141) have proposed a method of relating the parameter a to the hydration parameter n by use of a random close-packing model.

Gleuckauf (39), using volume fraction statistics instead of mole fraction statistics and the Debye-Hückel expression for the electrostatic contribution to the Gibbs function instead of the chemical potential, has derived an expression for the activity coefficient of the electrolyte in which the hydration parameters do not exhibit certain anomalies which were shown by the Stokes and Robinson theory. But as Burtch has observed (21), "unfortunately, however, lack of knowledge of the proper volumes to use with the model makes the use of volume fractions probably no more nearly correct than the use of mole fractions."

Moore, Gootman, and Yates (85) have applied Stokes' and Robinson's equation to mixtures of two strong electrolytes in water. In principle, the equation of Stokes and Robinson is applicable to systems containing any number of electrolytes, provided the hydration parameters are constants (85). More recently, Moore, Burtch, and Miller (86) have assumed the hydration parameter for HCl to be constant and the parameter for the salt to be variable.

Following Glueckauf (40) the Gibbs function for the $FeCl_2$-HCl-H_2O mixtures can be written as

$$G = N_1\overline{G}_1^o + m_2\overline{G}_2^o + m_3\overline{G}_3^o + G^{el} + G^s \qquad (1)$$

where N_1 represents the moles of "free" water per 1000 g. of total water and may be written as

$$\begin{aligned} N_1 &= 55.51 - b \\ &= 55.51 - h_2m_2 - h_3m_3. \qquad (2) \end{aligned}$$

The significance of the other symbols used in equations (1) and (2) are

m_2 = moles of component 2, HCl, per 1000 g. of total water in the solution.

m_3 = moles of component 3, $FeCl_2$, per 1000 g. of total water in the solution.

b = moles of "bound" water per 1000 g. of total water in the solution.

$\overline{G}_1^o$ = chemical potential of "free" water in the standard state.

$\overline{G}_2^o$ = chemical potential of hydrated HCl in the standard state.

$\overline{G}_3^o$ = chemical potential of hydrated salt, $FeCl_2$, in the standard state.

G^{el} = the electrostatic contribution to the Gibbs function.

G^s = entropy contribution to the Gibbs function.

h_2 = average number of moles of water bound to a mole of HCl.

h_3 = average number of moles of water bound to a mole of salt, $FeCl_2$.

The chemical potential of the "free" water may be determined by differentiating equation (1) with respect to N_1 at constant m_2 and m_3. Hence

$$\bar{G}_1 = \bar{G}_1^o + \left(\frac{\partial G^{el}}{\partial N_1}\right)_{m_2,m_3} + \left(\frac{\partial G^s}{\partial N_1}\right)_{m_2,m_3} . \tag{3}$$

If the basis for the calculation of the entropy contribution to the Gibbs function is considered to be derived from the mixing of ideal particles (31), mole fraction statistics is used and

$$G^s = \sum n_i \ln(n_i/D) \tag{4}$$

where $D = \sum n_i = N_1 + 2\ m_2 + 3\ m_3.$ (5)

Thus, for the $FeCl_2$-HCl-H_2O system

$$G^s = RT\left[N_1 \ln(N_1/D) + (m_2 + 2m_3)\ln\left[(m_2 + 2m_3)/D\right] + m_3 \ln(m_3/D) + m_2 \ln(m_2/D)\right] \tag{6}$$

$$G^s = RT\left[N_1 \ln N_1 + (m_2 + 2m_3)\ln(m_2 + 2m_3) + m_3 \ln m_3 + m_2 \ln m_2 - D \ln D\right] . \tag{7}$$

Thus, the entropy contribution to the chemical potential of the "free" water is

$$\left(\frac{\partial G^s}{\partial N_1}\right)_{m_2,m_3} = RT\ \ln(N_1/D). \tag{8}$$

This treatment of the statistical term does not take into consideration the co-volume entropy effect; it ignores the fact that the ions have a finite size. Glueckauf (39) has attempted to deal with the effect of ionic size on the entropy contribution to the Gibbs function by the use of volume fraction statistics. This treatment will be considered in more detail later.

Fowler and Guggenheim (32) have shown that the electrostatic contribution to the Gibbs function is (for dilute solutions, at any rate) given by the expression

$$G^{el} = - \frac{\sum s_i z_i^2 e^2}{3\varepsilon} k \tau (ka) \tag{9}$$

where s_i = the number of i-ions in the system of total volume V.

z_i = charge on the ith ion.

e = electronic charge

a = distance of closest approach of ions

ε = dielectric constant of medium (water).

k is given by Debye-Hückel theory at 25°

$$k = \left[\frac{4\pi e^2 \sum s_i z_i^2}{\varepsilon kTV} \right]^{\frac{1}{2}} = b(I)^{\frac{1}{2}} = 0.3286(I)^{\frac{1}{2}} \tag{10}$$

Here I is the volume ionic strength $I = (\tfrac{1}{2}/V) \sum_i s_i z_i^2$

and τ (Ka) is defined by the function

$$\tau(x) = (3/x^3) \left[\ln(1+x) - x + (x^2/2) \right] . \tag{11}$$

For the "free" water, which has no charge,

$$\left(\frac{\partial G^{el}}{\partial N_1} \right)_{m_2, m_3} = \frac{RT k^3 \sigma (ka)}{24} \bar{V}_1 \tag{12}$$

where $\bar{V}_1$ represents the partial molal volume of the "free" water, and σ(ka) is defined by the function

$$\sigma(x) = \frac{3}{x^3}\left[1 + x - \frac{1}{1 + x} - 2\ln(1 + x)\right] \tag{13}$$

The electrostatic term is insignificant at values of ka small compared to unity, for then σ (ka) is approximately equal to unity and $(ka)^3$ is very small. At high concentrations, however, it is doubtful whether the theory is valid (118).

Combining equations (3), (7), and (12),

$$\bar{G}_1 = \bar{G}_1^o + RT\ln(N_1/D) + RT\left[\frac{k^3\sigma(ka)}{24\pi}\bar{V}_1\right] \tag{14}$$

By the usual definition of the activity

$$\bar{G}_i = (\partial G/\partial n_i)_{m_j} = \mu_i = \mu_i^o + RT\ln a_i, \tag{15}$$

and substitution of equation (15) into equation (14)

$$\ln a_1 = \ln(N_1/D) + \frac{k^3\sigma(ka)}{24\pi}\bar{V}_1 \tag{16}$$

$$\ln a_1 = \ln x_1 + B^{el} \tag{17}$$

where

$X_1 = N_1/D$ = mole fraction of "free" water.

$B^{el} = \frac{k^3\sigma(ka)}{24\pi}\bar{V}$ = the electrostatic term.

Reference to equation (17) shows that the electrostatic term, B^{el}, represents the whole of the deviation of the solvent activity from ideality, when mole fraction statistics are used (118). Moore, et al (86) found that equation (17), (2), and equation (40) on page 110 very satisfactorily accounted for the concentration dependence of the activity coefficient of HCl in 4.7 m. HCl-$MnCl_2$ mixtures. The series of higher acid concentration showed somewhat more deviation but the calculated activity coefficients still checked within about 1.5% with experimental values.

Combination of equations (2) and (17) gives

$$\frac{a_1\ (2m_2 + 3m_3)}{a_1 - e^{B^{el}}} + 55.51 = h_2m_2 + h_3m_3. \qquad (18)$$

If h_2 and h_3 are concentration independent, a plot of b versus m_3 should result in a straight line with slope h_3 and intercept h_2m_2, provided that B^{el} is essentially constant, or negligibly small. Figure 7 shows the variation of b with m_3 if the electrostatic term is neglected. Glueckauf (40) considers all electrostatic contributions to the logarithm of the activity coefficient of the electrolyte, except the Debye-Hückel expression, to be negligible. Moore, et al (86) considered B^{el} to be negligibly small. As Glueckauf (40) has pointed out, neglect of all electrostatic terms except the Debye-Hückel expression is compensated for by a change in the hydration parameters of the order of only 1 to 2% for binary solutions. As Figure 7 clearly indicates, b does not vary linearly with m_3 for the systems of $FeCl_2$ in hydrochloric acid investigated, although in the 9.0 m HCl-$FeCl_2$ series it does to a first approximation.

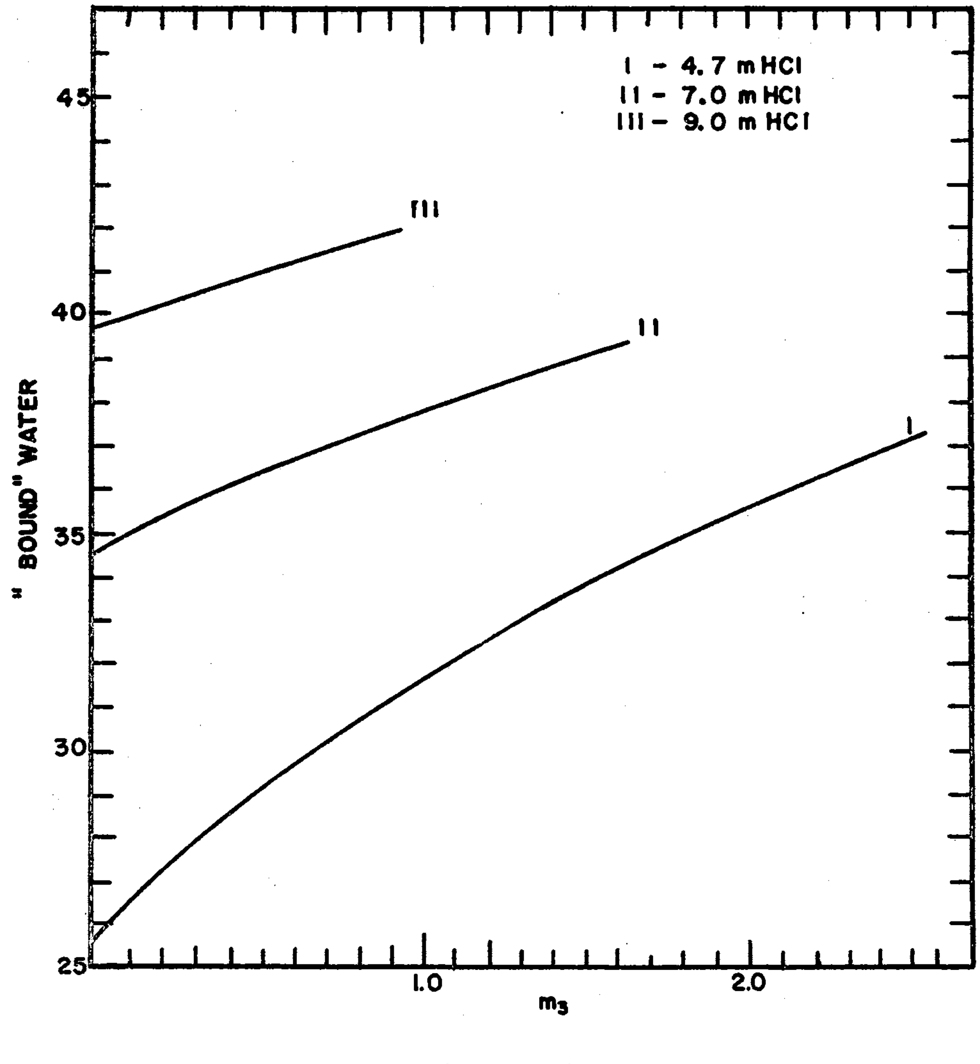

FIGURE 7. VARIATION OF "BOUND" WATER WITH SALT MOLALITY FOR THREE $FeCl_2$-HCl-H_2O SYSTEMS. (B^{el} NEGLIGIBLE)

In light of the previously quoted statement of Moelwyn-Hughes (82), this can probably best be accounted for in terms of a variation in the hydration parameters with concentration.

There are two difficulties connected with the determination of B^{el}. These are (1) the determination of $\overline{V}_1$, the partial molal volume of the "free" water, and (2) the determination of a, the distance of closest approach of the hydrated cation and anion.

Strictly speaking

$$V = N_1\overline{V}_1 + m_2\overline{V}_2 + m_3\overline{V}_3 \tag{19}$$

where

V = total volume of the solution,
$\overline{V}_1$ = partial molal volume of the "free" water,
$\overline{V}_2$ = partial molal volume of the hydrated acid,
and $\overline{V}_3$ = partial molal volume of the hydrated salt.

Thus the problem of calculating $\overline{V}_1$ is dependent upon a knowledge of the partial molal volumes of the hydrated acid and salt. Since

$$\overline{V}_1 = (\partial V/\partial N_1)_{m_2,\, m_3} \tag{20}$$

$$\overline{V}_2 = (\partial V/\partial m_2)_{N_1,\, m_3} \tag{21}$$

$$\overline{V}_3 = (\partial V/\partial m_3)_{N_1,\, m_2} \tag{22}$$

the required partial molal volumes cannot be evaluated from data at constant m_2 and total water without making simplifying assumptions.

Burtch (21) and Miller (81), for the purpose of estimating B^{el}, assumed

$$V = 55.51\,\overline{V}_w + m_2\overline{V}_2 + m_3\overline{V}_3 \qquad (23)$$

i.e., $\overline{V}_1 = \overline{V}_w$, where $\overline{V}_w$ represents the partial molal volume of total water in the solution. They further assumed that $\overline{V}_w$ is constant (concentration independent) for a given series of solutions having constant hydrochloric acid concentration. In addition, they also assumed an arbitrary value for a of 4.8 Å. These assumptions are not entirely satisfactory, for a depends upon the hydration parameters and one would expect greater electrostrictive effects for the bound water, which is included in the total water, than for the "free" water. But, as Miller (81) has observed, the choice of values of a and $\overline{V}_1$ are not critical, for if B^{el} is neglected entirely, the error introduced in the final value of the "free" water is only about 3 percent over the entire range of values covered by the three $CuCl_2$-HCl-H_2O systems that he investigated.

B^{el} may be estimated in a different manner. Certain factors are to be considered. The value of a would be expected to decrease with increasing concentration. This decrease in a would lead to an increase in B^{el}. The value of a also would be expected to be dependent upon the hydration numbers of the hydrated ions. Stokes and Robinson (141) have proposed a method whereby a may be calculated from a knowledge of the crystal radius of the bare ion and the hydration number of the ion in solution based upon the "random close-packed volume" for a system of spherical particles derived by Alder (4). For spherical ions which dissolve without significant electrostriction of surrounding water molecules, the molar volume for such ions randomly close packed should be

$$\bar{V}^{o} = \frac{4\ N\ r^{3}}{3 \times 0.58} = 4.35 \times 10^{24} r^{3} \text{ cc/mole.} \qquad (24)$$

If an ion contains h molecules of water of hydration, its volume is

$$\bar{V}_{h} = (\bar{V}^{o} + 18h) \text{ cc/mole,} \qquad (25)$$

and if it obeys equation (24) its radius may be calculated as

$$r_{h} = \left[(V^{o} + 18h)/4.35 \times 10^{24} \right]^{1/3}. \qquad (26)$$

The Debye-Hückel parameter a should then be given by

$$a = r_{h+} + r_{h-}\ . \qquad (27)$$

Stokes and Robinson (141) give a table in which they have determined $\bar{V}^{o}$ for several cations and anions taking into consideration electrostriction; as a consequence most of the cations considered have negative limiting molar volumes ($\bar{V}^{o}$). The authors point out that since a and h are interrelated, it may be necessary to use a value of h somewhat different from that given by Glueckauf (39), but of the same magnitude.

If, following Moore, et al (86), h_2 can be assumed constant in any given constant acid series, a method of successive approximations might be employed to estimate a, $\bar{V}_1$, h_3, N_1, and B^{el} since these quantities are all interrelated. As a first approximation B^{el} may be assumed negligible and N_1 calculated for the various values of m_3. From the values of N_1 may be calculated h_2^o, the value of h_2 at $m_3 = 0$, and the values of h_3 at the various salt concentrations. These values of h_2 and h_3 may then be used to calculate the values of the partial molal volumes of acid and salt if, following Bernal and Fowler (14), the assumption is made that the Cl^- ion is not hydrated. If the partial molal volumes of salt and acid and N_1 are known, the partial molal volume of the "free" water, $\overline{V}_1$, may be readily calculated. From an estimate of a̲ based upon the radii of the hydrated metallic cation and the hydrated hydronium ion B^{el} may be approximated. This in turn leads to a new estimation of N_1, and so on, until successive approximations of B^{el} differ only slightly, if at all. An attempt was made using this method of successive approximations to estimate the value of B^{el} for the three series of solutions of $FeCl_2$ in hydrochloric acid studied in this research. The results of this attempt yielded values of B^{el} from 0.01 to 0.02 over the entire range of concentrations covered by the three series. The significance of a̲ becomes somewhat indefinite for mixtures of electrolytes (120). The value of a̲ used in the calculations cited above was determined by weighting the a̲ for HCl and the a̲ for $FeCl_2$, on a mole basis.

Burtch (21) found that the values of B^{el} vary only from 0.01 to 0.02 over the entire range of concentrations covered by three series of solutions of $MnCl_2$ in hydrochloric acid comparable to the $FeCl_2$-HCl mixtures of this work. Thus the values of B^{el} obtained by successive approximations are comparable in magnitude to those calculated by Burtch; this should not be surprising in light of the previous discussion, however.

It would seem, for the purpose of making comparisons between similar series of salt-HCl-H_2O mixtures at least, that B^{el} may be ignored. It must be remembered, however, that in so doing the assumption is made that there is no deviation in the activity of the free water from ideality (118). In Figure 8, there is shown the variation in b, the moles of "bound" water per 1000 g. of total water, with salt molality, m_3, for several transition metal chlorides in hydrochloric acid solution. It should be noted that the data for $NiCl_2$-HCl-H_2O and $CoCl_2$-HCl-H_2O given by Moore, Gootman, and Yates (85) are at 30° while the data for $MnCl_2$-HCl-H_2O and $CuCl_2$-HCl-H_2O are given by Moore, Burtch, and Miller (86) at 25°. The data for $MnSO_4$-HCl-H_2O given by Burtch (21) are for 25°. As may be seen, the order of decreasing values of b in 4.7 m HCl is $NiCl_2 > CoCl_2 > FeCl_2 > MnCl_2 > CuCl_2$ while the order of decreasing b in the two higher HCl series is the same, $NiCl_2 > FeCl_2 > MnCl_2 > CoCl_2 > CuCl_2$. Again, the change in order in the two higher acid series from the order of b in the lowest acid series may be attributed to complex formation. It is significant that the $CoCl_2$ curve in the 4.7 series begins to flatten out at higher

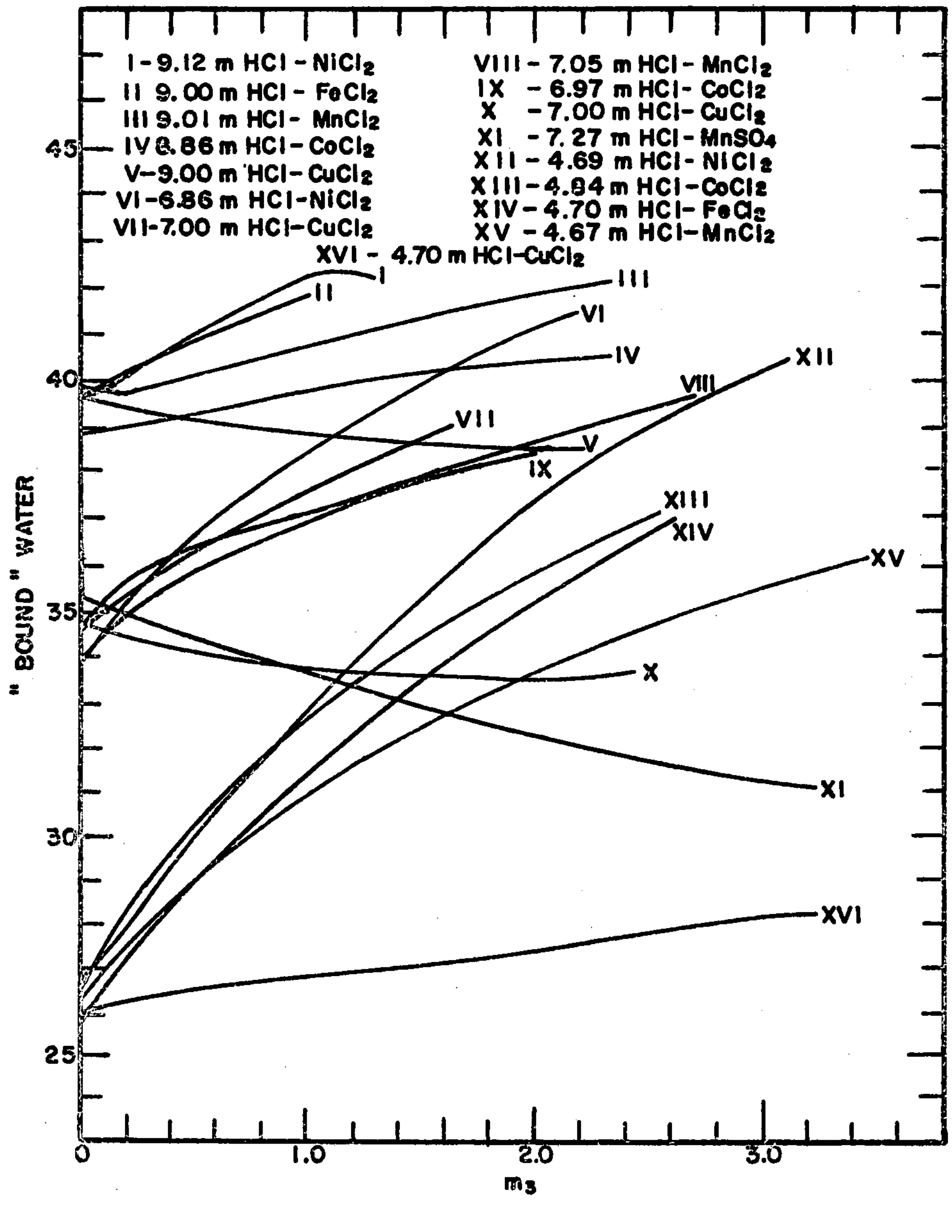

FIGURE 8. "BOUND" WATER FOR SOME TERNARY SOLUTIONS OF SOME TRANSITION METAL CHLORIDES IN HYDROCHLORIC ACID B^{01} NEGLIGIBLE

concentrations, very possibly indicating greater complex formation. Also the decrease of the "bound" water in the two higher acid series of $CuCl_2$ can be attributed to complex formation. The 7 m HCl-$MnSO_4$ series has been included for comparison purposes. Here again, the decrease in *b* may be attributed to either chloro complex formation or ion-pairing, or both.

It is also of interest that there is much greater rate of increase in b in the 4.7 m HCl series for any given transition metal relative to the rate of increase in *b* for the same transition metal in the two series of higher acid concentration. This can very likely be attributed to the greater amount of water already bound by the HCl in the higher acid series. A greater interpenetration of the water sheath surrounding the ions at the higher HCl concentrations would be expected to bind the water more tightly than the larger metal cations, thus effectively decreasing the hydrating ability of the metal cations. Thus, the theory qualitatively accounts for the trends found for the water activities in ternary solutions.

The hydration parameters for the salt, h_3, in the $FeCl_2$-HCl-H_2O system were calculated on the basis that B^{el} may be neglected by use of the equation

$$h_3 = \frac{b - \overset{o}{h}_2 m_2}{m_3} \tag{32}$$

where h_2^o represents the value of h_2 at $m_3=0$. In Figure 9 is shown the variation of h_3 with m_3 for some transition metal chlorides in HCl. All of the hydration parameters were calculated on the same basis. The hydration parameter for the 4.7 m HCl-$FeCl_2$ system shows greater variation with concentration than does h_3 for the two higher acid series, while h_3 for the 9.0 m HCl-$FeCl_2$ series stays relatively constant, varying only from about 2.5 to 2.3. As would be expected, the value of h_3 for the $NiCl_2$-HCl-H_2O system at a given concentration of HCl is greater than the corresponding value of h_3 for the $FeCl_2$-HCl-H_2O system. On the whole, however, little additional insight can be gotten from Figure 9 over that which could be deduced from the water activity curves for the systems. Undoubtedly the assumption of constant h_2 begins to break down at higher concentrations of salt. Strictly speaking, the only systems which can be described in terms of the theory are the $NiCl_2$-HCl-H_2O and the $FeCl_2$-HCl-H_2O systems, for the others show complex formation or ion-pairing, even in their binary solutions.

Glueckauf (40) following Flory (29) and Huggins (54) has expressed the entropy contribution to the Gibbs function in terms of volume fraction statistics; thus

$$G^S = RT \sum n_i \ln(n_i V_i / V) \qquad (33)$$

which, for the system $FeCl_2$-HCl-H_2O, may be written

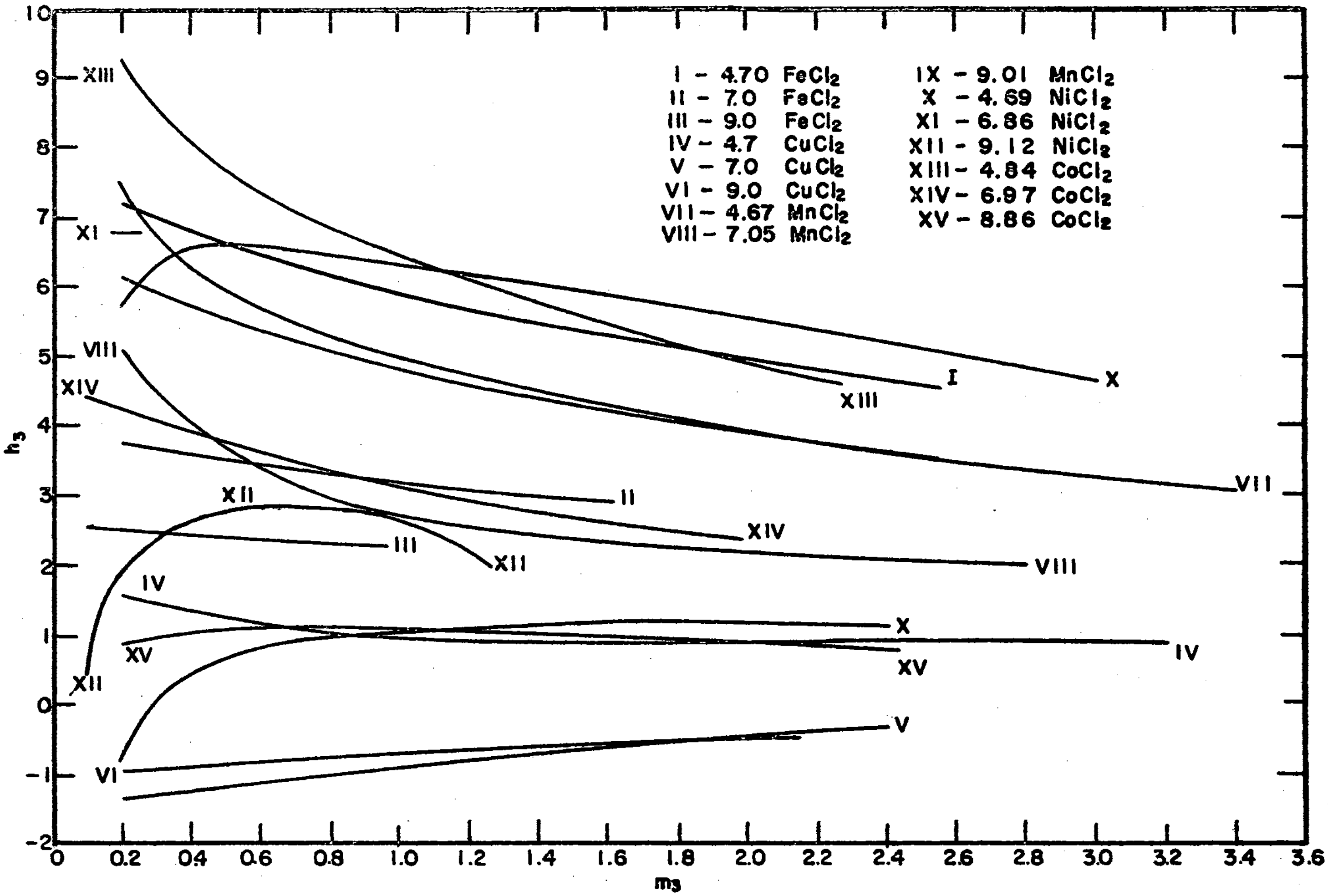

FIGURE 9 h_3 FOR SOME TRANSITION METAL CHLORIDES IN TERNARY HCl SOLUTIONS

$$G^s = RT\Big\{ N_1 \ln(N_1\bar{V}_1/V) + (m_2 + 2m_3)\ln\Big[(m_2 + 2m_3)\bar{V}_{Cl^-}\ V\Big] + m_3 \ln(m_3\bar{V}_{Fe^{++}}/V) + m_2 \ln(m_2\bar{V}_{H^+}/V)\Big\}. \qquad (34)$$

Differentiation of equation (34) with respect to N_1 at constant m_2 and m_3 and combination with equations (3) and (12) yields the equation first used by Burtch (21) and subsequently by Miller (81) to estimate the free water on the basis of volume fraction statistics.

$$2.303(\log X) - X = 2.303(\log a_1) - (B^{el} + 1) + (\bar{V}_1/V)\ (2m_2 + 3m_3). \qquad (35)$$

In deriving equation (35) it was assumed that the $\bar{V}$'s are concentration independent. In equation (35), $X = N_1\bar{V}_1/V$, and and B^{el} has the same significance as in equation (17). In the calculation of N by equation (35), B^{el} was considered negligible.

As a first approximation Burtch (21) and Miller (81) following Glueckauf (39) assumed the $\bar{V}$'s to be concentration independent. Gleuckauf (39) justified this assumption by pointing out that most of the apparent partial molar volumes of common electrolytes in aqueous solutions vary less than 10% between 1 and 4 N. In this research and in the previous investigations (42, 21, 81), however, ternary solutions are being considered in which the smallest concentration of HCl is greater than 4 molal. The treatment by volume fraction statistics thus suffers from assumptions which very possibly yield values for the hydration parameters which are little, if any, better than those obtained from mole fraction statistics for the solutions investigated in this research.

Volume fraction statistics also suffers from being more mathematically cumbrous for the calculation of N_1. Moore, et al (86) using mole fraction statistics and assuming h_2 constant and h_3 variable, found that h_3 for $MnCl_2$ in 4.7 m HCl varied from 5.5 to 3.2, in the range of m_3 from 0.5 to 3.0 m. According to the packing concept of Stokes and Robinson (141) this would correspond to a change of $\overline{V}_{Mn^{++}}$ of from about 90.6 to 57.6 cc/mole, a variation of greater than 30%. For $\overline{V}_{MnCl_2}$, assuming that Cl^- does not hydrate, the variation would be from about 141 to 108 cc/mole. Since the size of the hydrated ion is so strongly dependent on the hydration number of the ion, it would seem that possibly any theoretical advantage of fraction statistics over that of mole fraction statistics is negated by the uncertainties in the molal volumes.

Values of $\overline{V}_1$ also are dependent on hydration, although not as sensitive to change in salt molality as the partial molal volume of the cation. This does not imply that the volume effect does not make a considerable contribution to the entropy term in solutions of transition metal chlorides in hydrochloric acid, but until the concentration dependence of the $\overline{V}$'s can be taken into consideration, there seems little to recommend the use of volume fraction statistics over mole fraction statistics in any theoretical treatment of the properties of the concentrated ternary solutions dealt with in this research.

In spite of the acknowledged limitations in the use of volume fraction statistics, an attempt was made to apply the theory to the $FeCl_2$-HCl-H_2O system. $\overline{V}_1$ was approximated by considering it equal to $\overline{V}_w$ and using equation (25). $\overline{V}_2$ was estimated at a salt concentration of 0.8 m from a plot of total volume V against m_2 for each of the three series of solutions. Unfortunately, only three experimental points were available, one from each of the series, for the determination of $\overline{V}_2$. The partial molal volume $\overline{V}_3$ was was evaluated in a manner which will be discussed in more detail later. $\overline{V}_w$ was considered to remain constant for a given series. The value of $\overline{V}_1$ used in the calculations was 18.0 cc/mole in each series.

Plots of "bound" water, b, versus salt molality are smooth curves for each of the three iron (II) series of solutions. This is shown in Figure 10. The results in terms of h_2^o, the value of h_2 at $m_3 = 0$, and h_3 are also recorded in Table XIX along with values of the same parameters calculated by other methods.

In view of the fact that the hydration parameters determined from volume fraction statistics in binary solutions are usually smaller than those determined from mole fraction statistics, it is interesting to observe that whereas the values of h_2^o are uniformly lower for the volume fraction statistics, the values of h_3 are higher, except at the lower salt concentrations. Burtch (21) found that

TABLE XIX

HYDRATION PARAMETERS

	4.7 m HCl		7.0 m HCl		9.0 m HCl	
Method of Evaluation	h_2	h_3	h_2	h_3	h_2	h_3
Mole-Fraction Statistics B^{el} Neglected	5.5	$7.2(m_3=0.2)$ to $4.5(m_3=2.55)$	4.9	$3.8(m_3=0.2)$ to $2.9(m_3=1.6)$	4.4	$3.5(m_3=0.1)$ to $2.3(m_3=.938)$
Mole-Fraction Statistics B^{el} Estimated	5.7	$7.0(m_3=0.2)$ to $4.4(m_3=2.55)$	5.0	$3.7(m_3=0.2)$ to $2.8(m_3=1.6)$	4.5	$2.5(m_3=0.1)$ to $2.2(m_3=0.938)$
Volume-Fraction Statistics B^{el} Neglected	4.2	$6.4(m_3=0.2)$ to $5.1(m_3=2.55)$	4.1	$4.7(m_3=0.2)$ to $3.9(m_3=1.6)$	4.1	$3.6(m_3=0.1)$ to $3.2(m_3=.938)$
$A_1 = N_1/55.51$	2.8	$5.8(m_3=0.2)$ to $5.3(m_3=2.55)$	3.2	$5.3(m_3=0.2)$ to $4.7(m_3=1.6)$	3.3	$4.6(m_3=0.1)$ to $4.2(m_3=.938)$

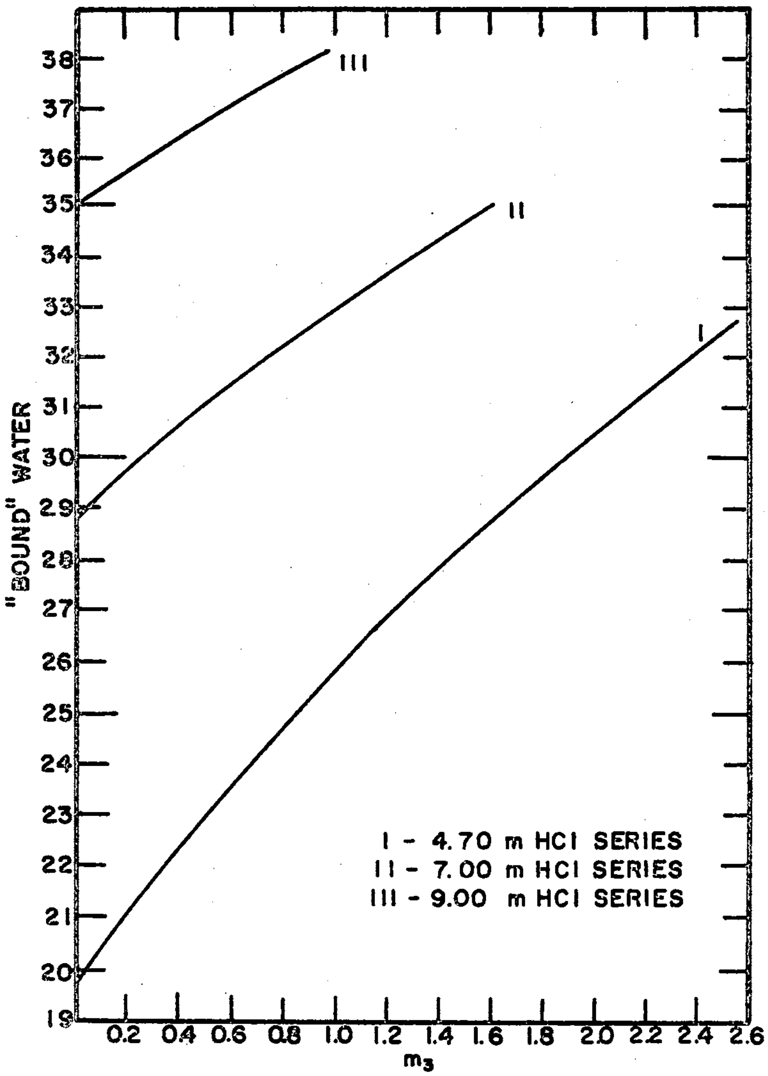

FIGURE 10. VARIATION OF "BOUND" WATER, FROM VOLUME-FRACTION STATISTICS, WITH SALT MOLALITY FOR THE THREE $FeCl_2$-HCl - H_2O SERIES

the values of N_1 were impossibly high when volume fraction statistics were applied to the $MnCl_2$-HCl-H_2O system, exceeding even the 55.51 moles of total water present. Miller (81) found the values of the hydration parameters calculated by use of volume fraction statistics to be lower for $CuCl_2$ in HCl, however. No great significance can be attached to the values of hydration parameters for this system, though, because of the tendency toward the chlorocomplex formation by the cupric ion.

Neglect of the electrostatic term should lead to values of N_1 about 2 to 3 percent low. Thus, the values given in Table XIX for the hydration parameters obtained by use of volume fraction statistics are approximately 2 to 3 percent high. Even with this correction, however, the values for the hydration parameters calculated from volume fraction statistics are higher than those based upon mole fraction statistics. The values obtained by the two methods are comparable, however, differing by about 1.5 moles or less when B^{el} is neglected.

Moore, Gootman, and Yates (85) have proposed a simple method of correlating hydration and water activities, which was subsequently also tested by Miller (81). Even though the method is strictly empirical, it does yield hydration parameters which are in relatively good agreement with those calculated by other methods.

Assuming that the vapor pressure of water is directly proportional to the moles of "free" water per 1000 grams of total water in the solution, there is obtained

$$P = k\ N_1 \qquad (35)$$

For 1000 grams of pure water in the standard state N_1 is equal to 55.51 and P is equal to P^o. Hence,

$$a_1 = N_1/55.51. \qquad (36)$$

Substituting equation (2) into equation (36) yields

$$(1 - a_1) = (h_2m_2/55.51) + (h_3/55.51)\ m_3. \qquad (37)$$

If the hydration parameters are constants, a plot of $(1-a_1)$ versus m_3 should be linear with a slope of $(h_3/55.51)$ and an intercept of $(h_2m_2/55.51)$. Figure 11 shows such plots for the ferrous chloride system. It can be seen from the figure that none of the series exhibits linearity, although curve for the 9.0 m HCl-$FeCl_2$ series does approximate linearity.

Figure 12 shows the variation in b calculated by the simple empirical method discussed above with m_3 for some transition metal chlorides in hydrochloric acid solution. As may be seen, the shapes of the curves obtained by this method are very similar to those obtained by mole fraction statistics, but the values of b are seen to be uniformly lower by about 10 to 12 moles compared with the values in Figure 8. Examination of Table XIX shows that the values of h_2^o by this method are also lower. The values of h_2^o

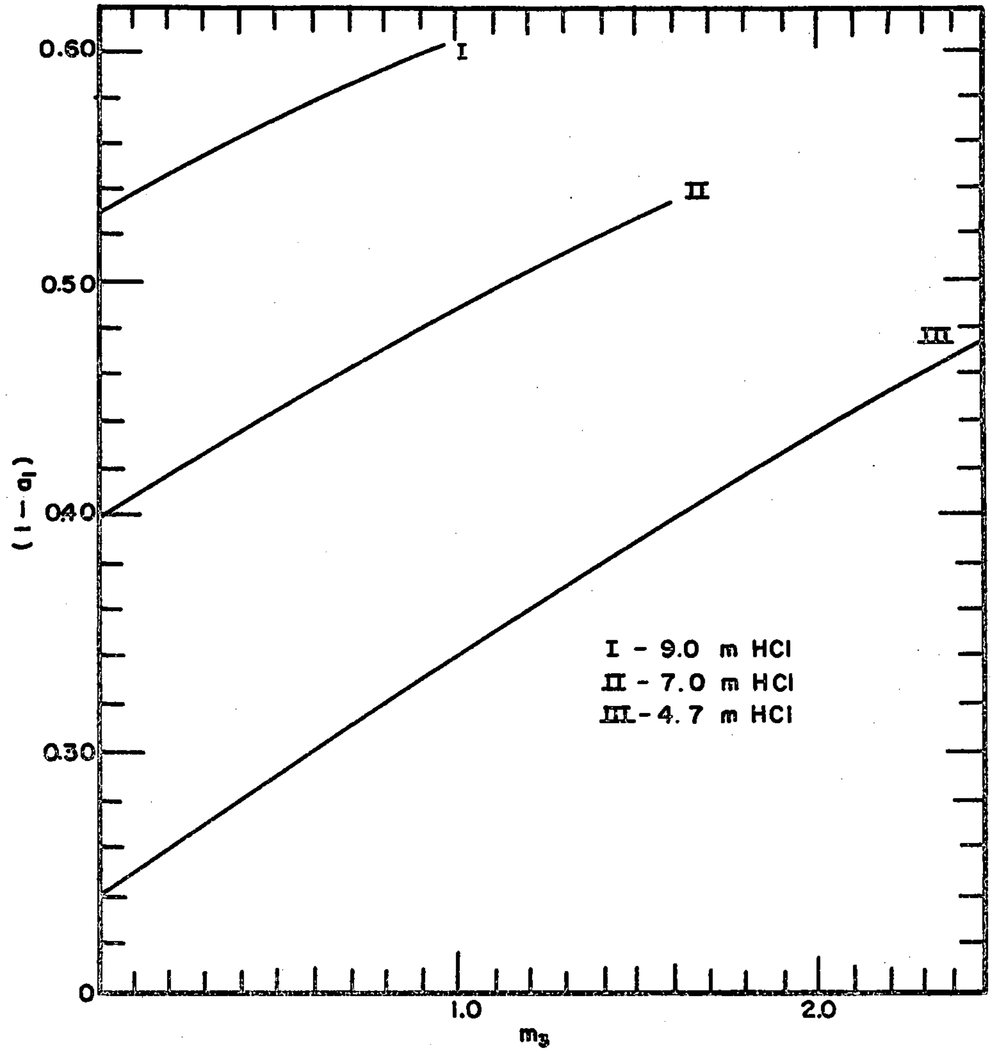

FIGURE 11. VARIATION OF $(1-a_1)$ VERSUS m_3 FOR THE THREE $FeCl_2$-HCl-H_2O SERIES

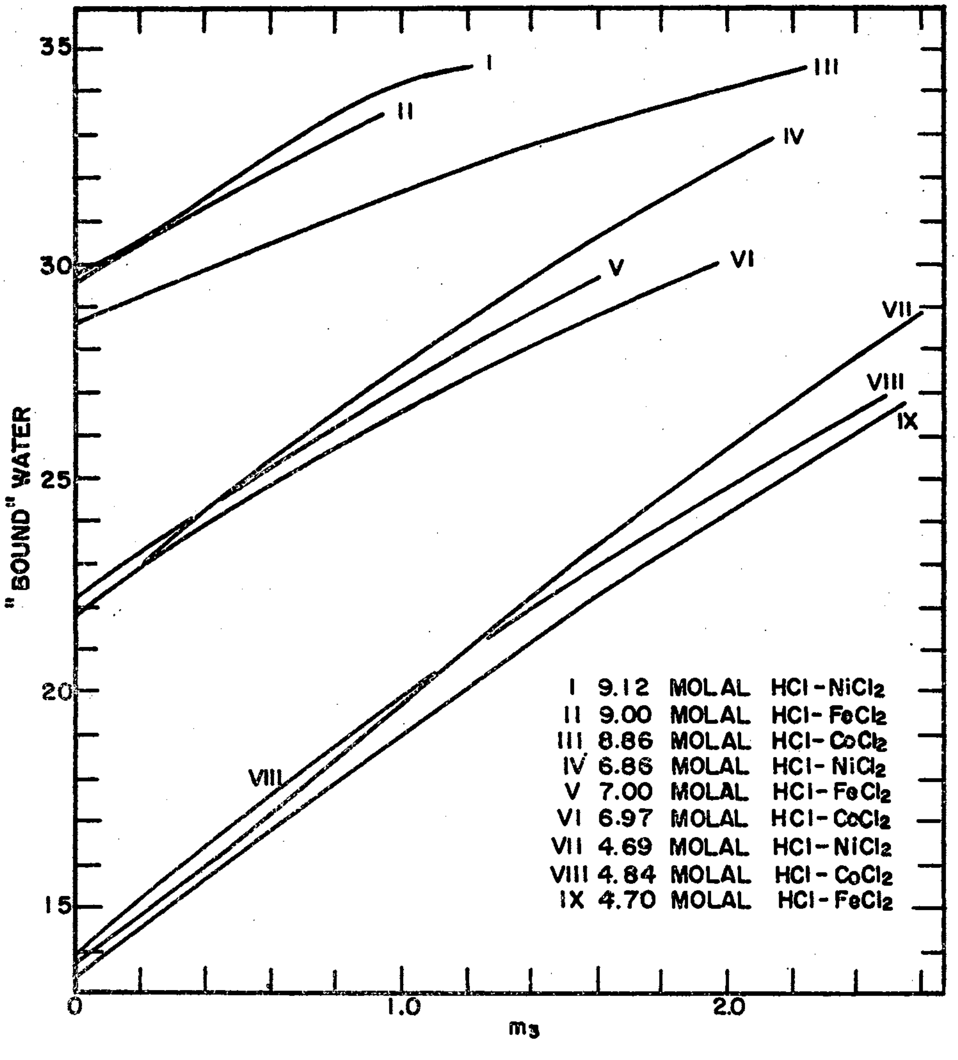

FIGURE 12. VARIATION OF "BOUND" WATER WITH SALT CONCENTRATION FOR SOME TRANSITION METAL CHLORIDES IN TERNARY HYDROCHLORIC ACID CALCULATED FROM

$a_1 = N_1/55.51$

seem somewhat low and especially so in light of evidence that the coordination number of the hydrogen ion in aqueous solution is 4 (28, 145). Thus, it would seem that although the simple empirical method might be used for comparison purposes, it would only be a first approximation to the true values of the hydration parameters.

Hydrochloric Acid and Ferrous Chloride Activities. As an inspection of the curves in Figure 13 clearly indicates, the addition of ferrous chloride to a hydrochloric acid solution greatly increases the activity of the HCl. For example, the activity of the HCl in the 9.0 m $HCl-FeCl_2$ series more than doubles in going from the binary HCl solution ($m_3 = 0$) to the saturated solution. The relative changes produced in the other two series are even more noticeable. Such large changes in the activity of the HCl may be qualitatively accounted for by use of Brönsted's principle of the specific interaction of ions (20) and the "salting-out" effect caused by the hydration discussed in the preceding section. The relatively small percent in activity increase in the 9.0 m $HCl-FeCl_2$ series would be expected because of the smaller percent increase in the chloride ion. The reverse would hold for the 4.7 m $HCl-FeCl_2$ series.

Figure 14 shows the variation of HCl activities for some comparable solutions of other transition metal chlorides in hydrochloric acid solution. Such a plot clearly shows the effect of hydration on the "salting-out" of HCl. Comparison of Figures 6 and 14 shows that the order of decreasing water activity is the same as the order of increasing HCl activity for a given series at constant HCl concentration. As can be seen from Figures 9 and 16, the activity coefficients of HCl vary in what may be considered a normal manner in the $FeCl_2$-HCl-H_2O system.

Figure 18 shows the variation of the salt activity with concentration for some transition metal chlorides in binary aqueous solution (138). It may be seen there that the order of the salt activities is $NiCl_2 > CoCl_2 > FeCl_2 > MnCl_2 > CuCl_2$ which is the same as the order of water activities in the solutions. Unfortunately, a similar comparison cannot be made for the same group of transition metal chlorides in aqueous hydrochloric acid solution because of the necessary choice of a different standard state for $FeCl_2$ in the solutions. Figure 19 shows the variation in the logarithm of the salt activity with the salt molality, while Figure 20 shows the variation of the activity coefficient of the salt with concentration. The observed increase in salt activity with increasing salt concentration can be largely attributed to hydration and to the high chloride concentration in the solutions. It is apparent that the activity coefficient curves show no peculiarities such as maxima or minima similar to those found for $MnCl_2$(21). It thus appears that $FeCl_2$ behaves in the manner to be expected for a non-associated electrolyte in hydrochloric acid solution.

The hydration theories discussed in the preceding section of this chapter were tested by applying them to the problem of calculating the concentration dependence of the activity coefficient of HCl in the solutions, under the assumption that the hydration parameter of HCl remained constant at constant concentrations of acid. A similar calculation of the variation in the salt activity coefficient could not be made because of variation in h_3.

The determination of the hydration parameters for HCl used in the calculations has been described. In order to relate the parameters to the activity coefficient, the extension of Stokes' and Robinson's equation (140) by Moore, et al (85, 86) was used. For hydrochloric acid the equation takes the form

$$\log \gamma_{\pm 2} = -(h_2^o/2) \log a_1 - \log D - \frac{0.509\, I^{\frac{1}{2}}}{1 + 0.329\, \mathring{a}\, I^{\frac{1}{2}}} + C_2 \qquad (40)$$

where $D = N_1 + 2m_2 + 3m_3$. In equation (40) I represents the ionic strength and $\underline{C}_2$ is a constant whose value is determined at some reference concentration.

The distance parameter $\mathring{a}$ was estimated by the method suggested by Stokes and Robinson (141). The results of the calculations are illustrated by Figure 17 for the cases where B^{el} was estimated by successive approximations and where B^{el} was neglected but its effects incorporated into the hydration parameters. As the figure shows, there is little difference

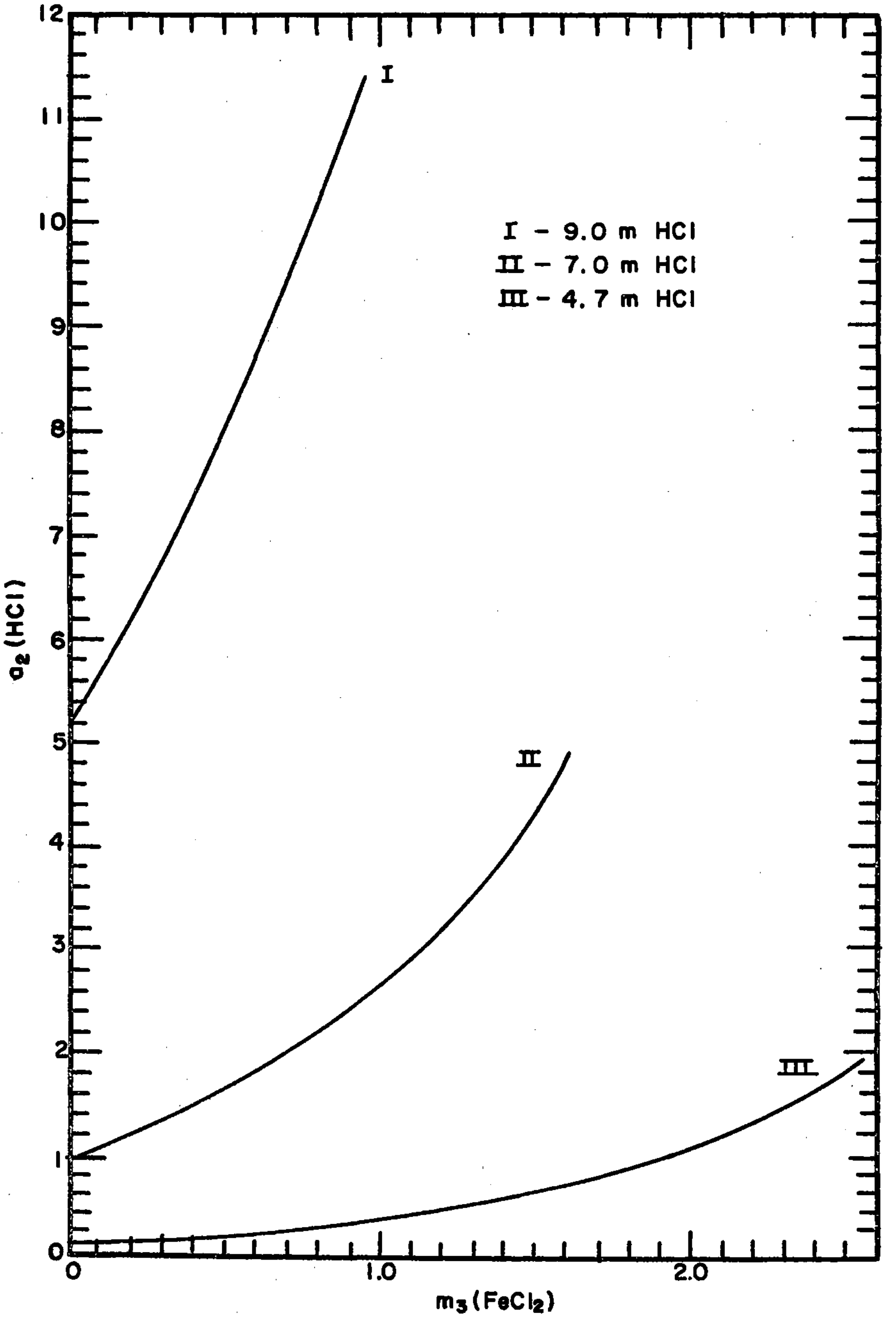

FIGURE 13. HCl ACTIVITY OF THE THREE $FeCl_2-HCl-H_2O$ SERIES

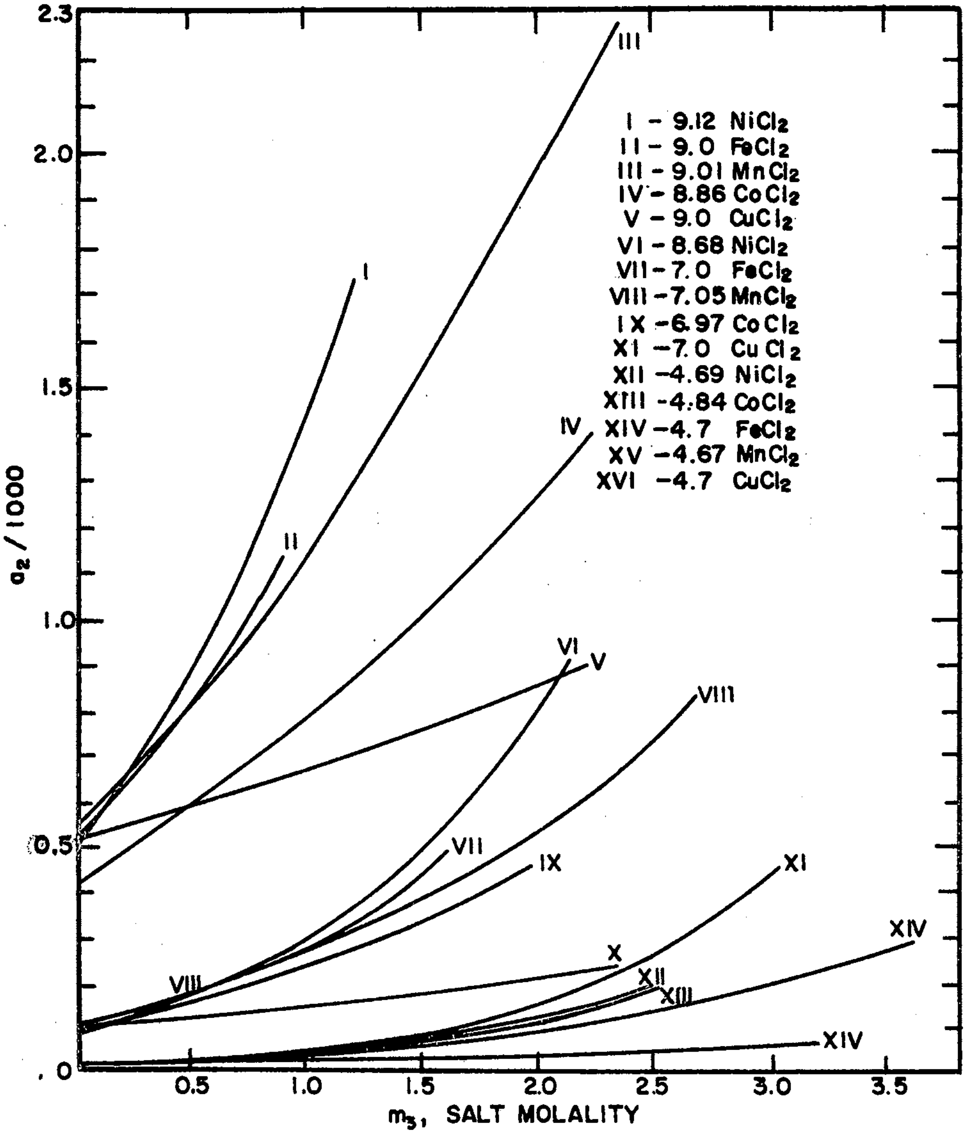

FIGURE 14. ACTIVITIES OF HCl IN SOME TERNARY SOLUTIONS WITH SOME TRANSITION METAL CHLORIDES

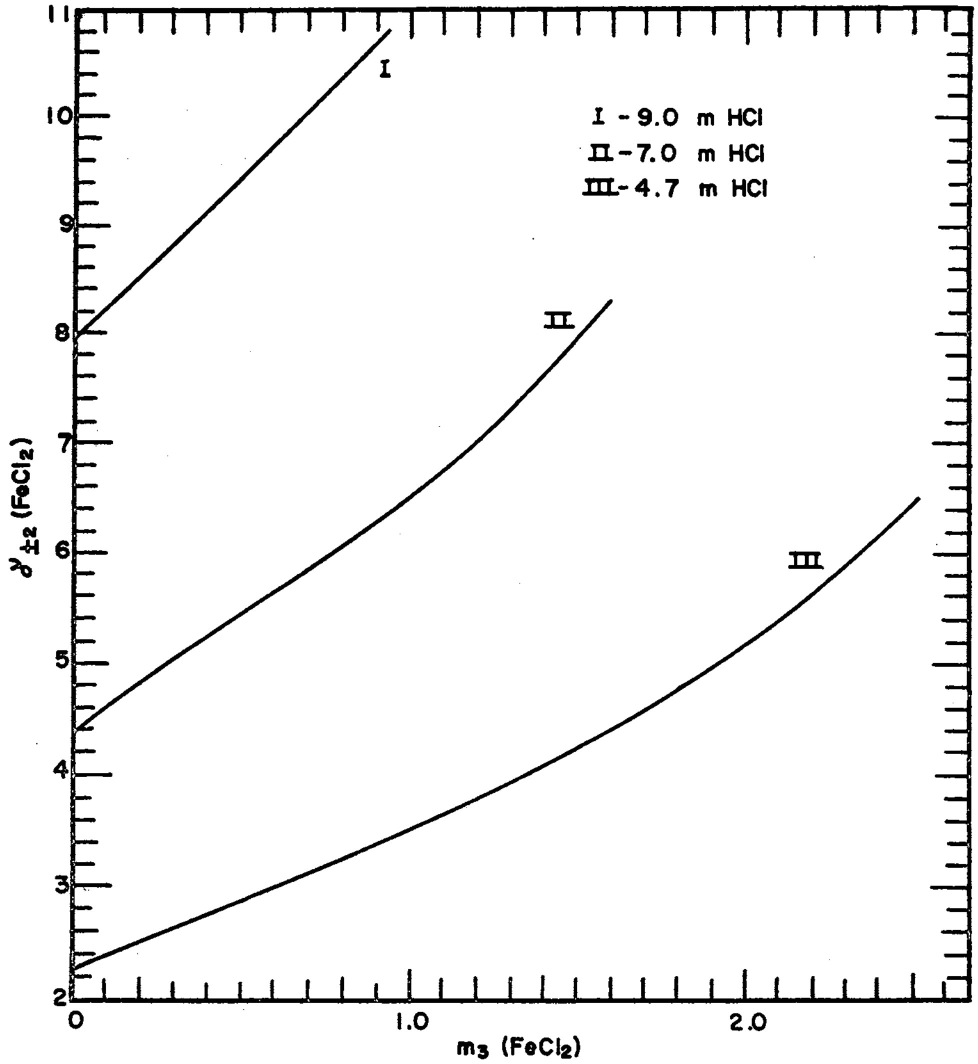

FIGURE 15. VARIATION OF THE ACTIVITY COEFFICIENT OF HCl IN THE THREE $FeCl_2$-HCl-H_2O SERIES

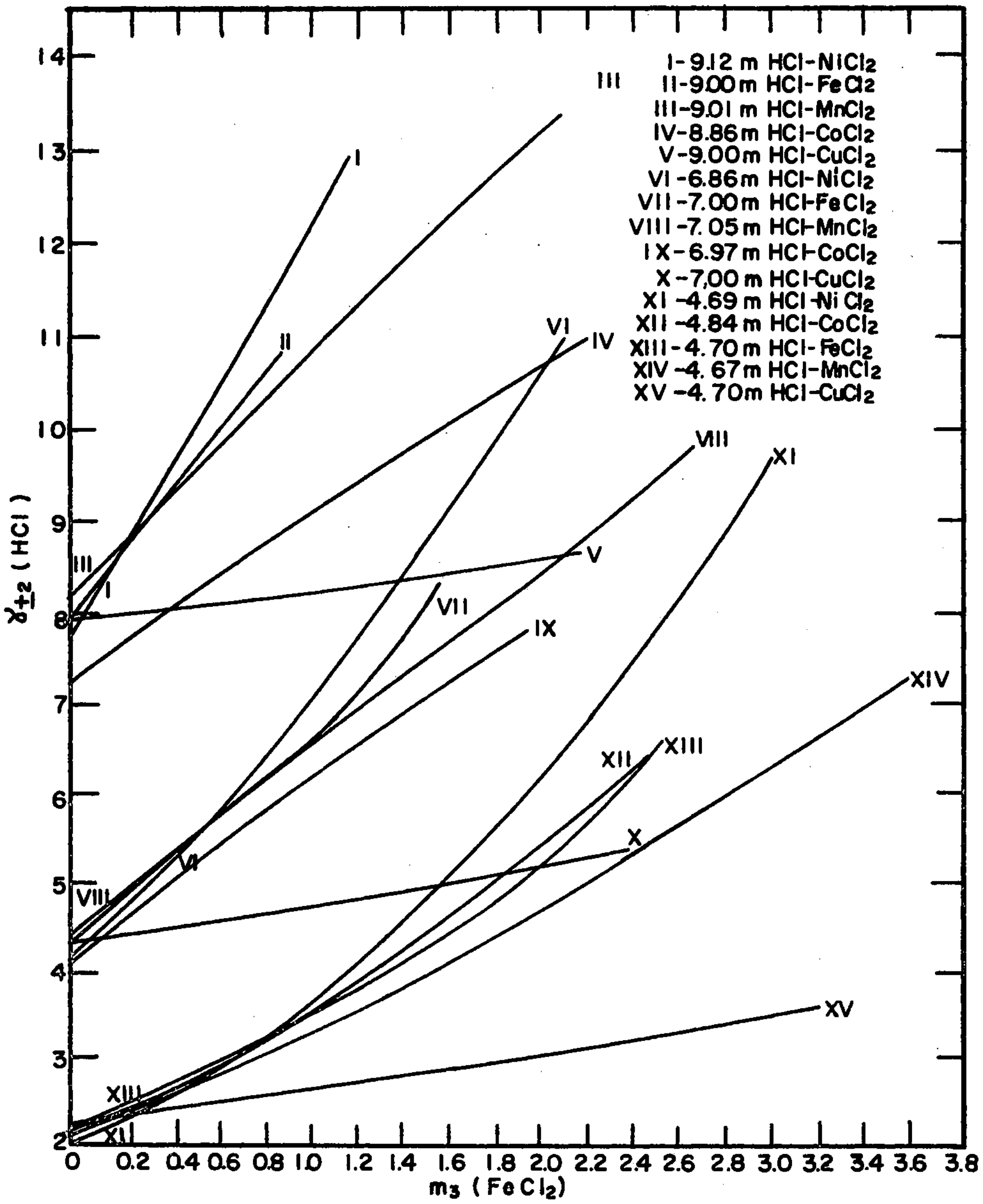

FIGURE 16. VARIATION OF THE ACTIVITY COEFFICIENT OF HCl IN TERNARY SOLUTION WITH SOME TRANSITION METAL CHLORIDES

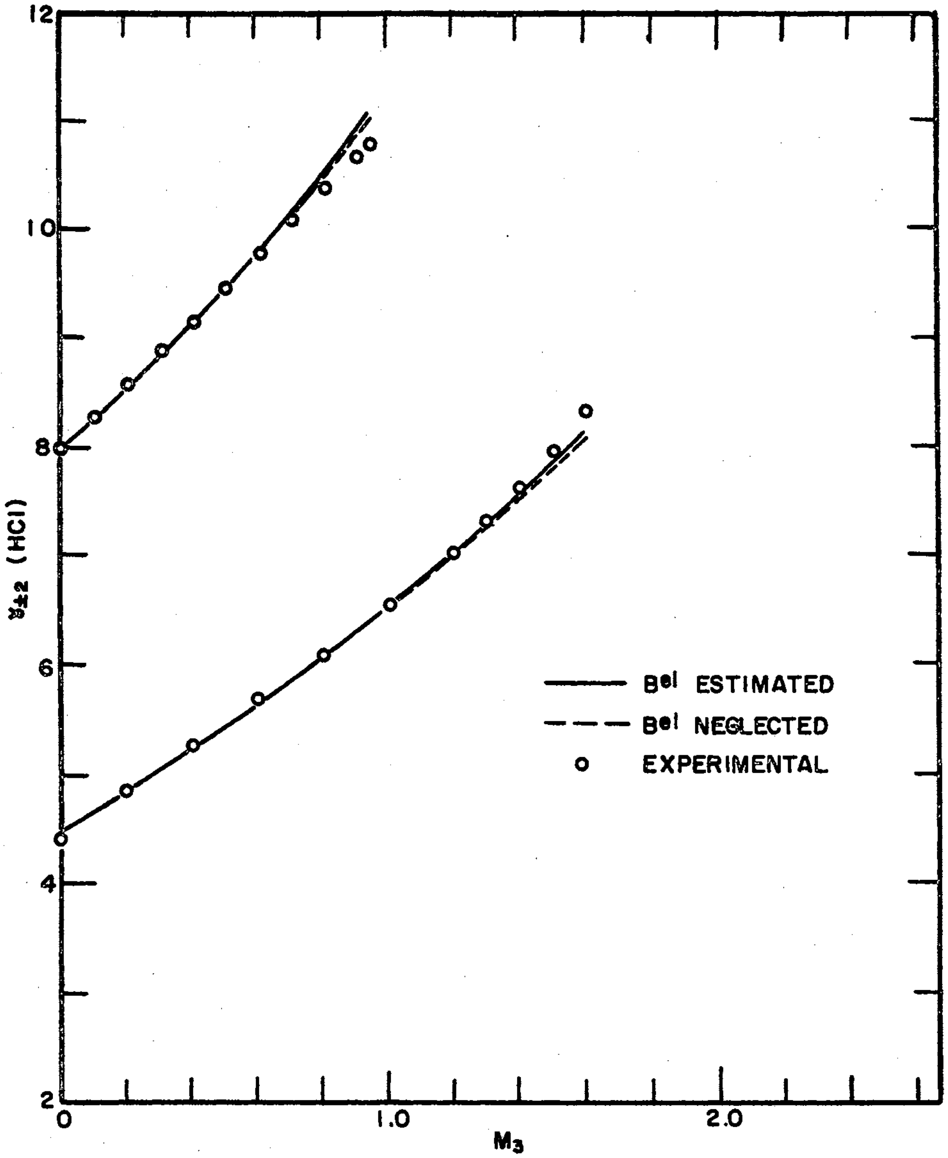

FIGURE 17. COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF THE ACTIVITY COEFFICIENTS OF HCl, $\gamma_{\pm 2}$ IN THE TERNARY $FeCl_2$-HCl-H_2O SYSTEM

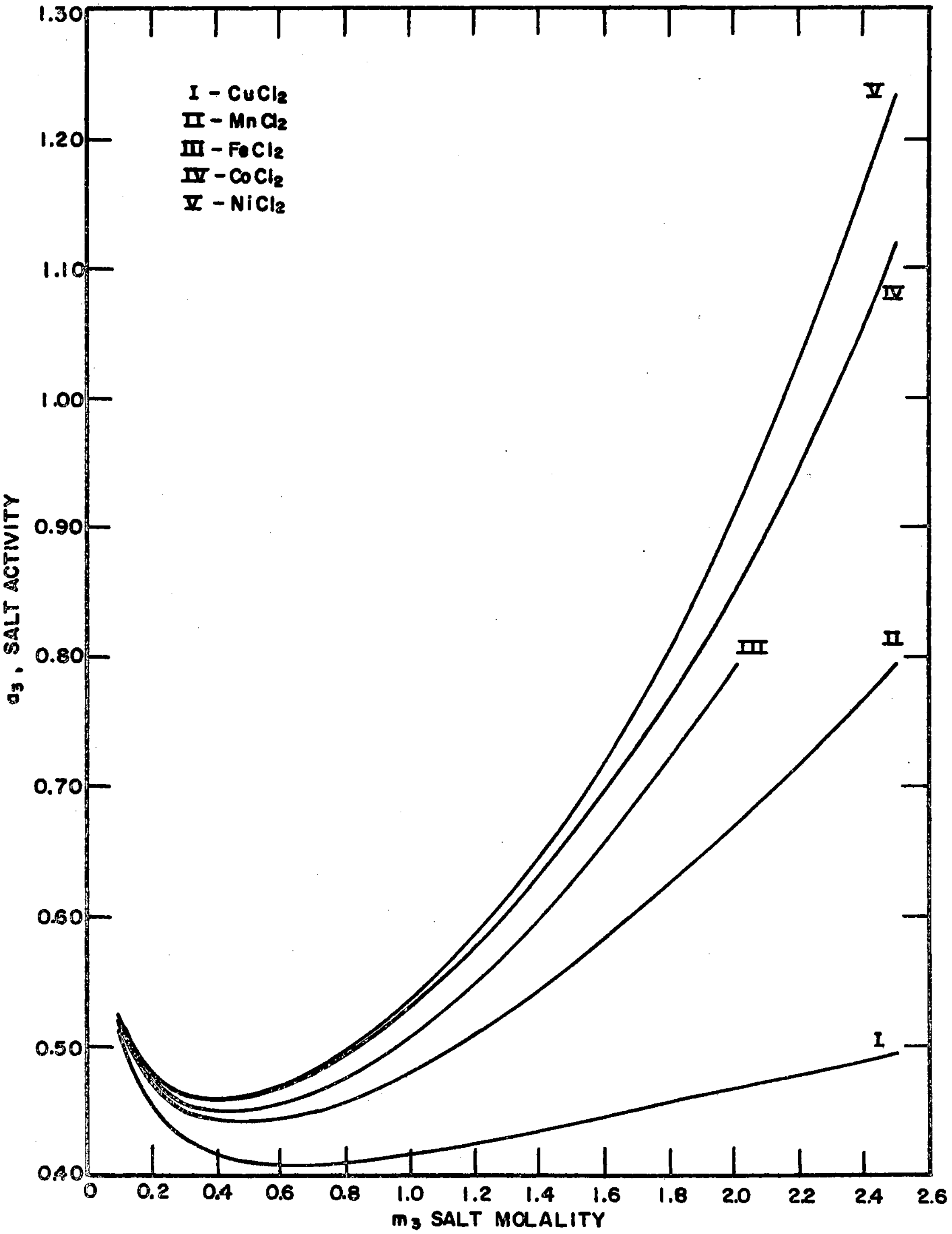

FIGURE 18. VARIATION OF SALT ACTIVITY WITH MOLALITY OF SOME TRANSITION METAL CHLORIDES IN BINARY AQUEOUS SOLUTIONS. [FROM ROBINSON AND STOKES (123)]

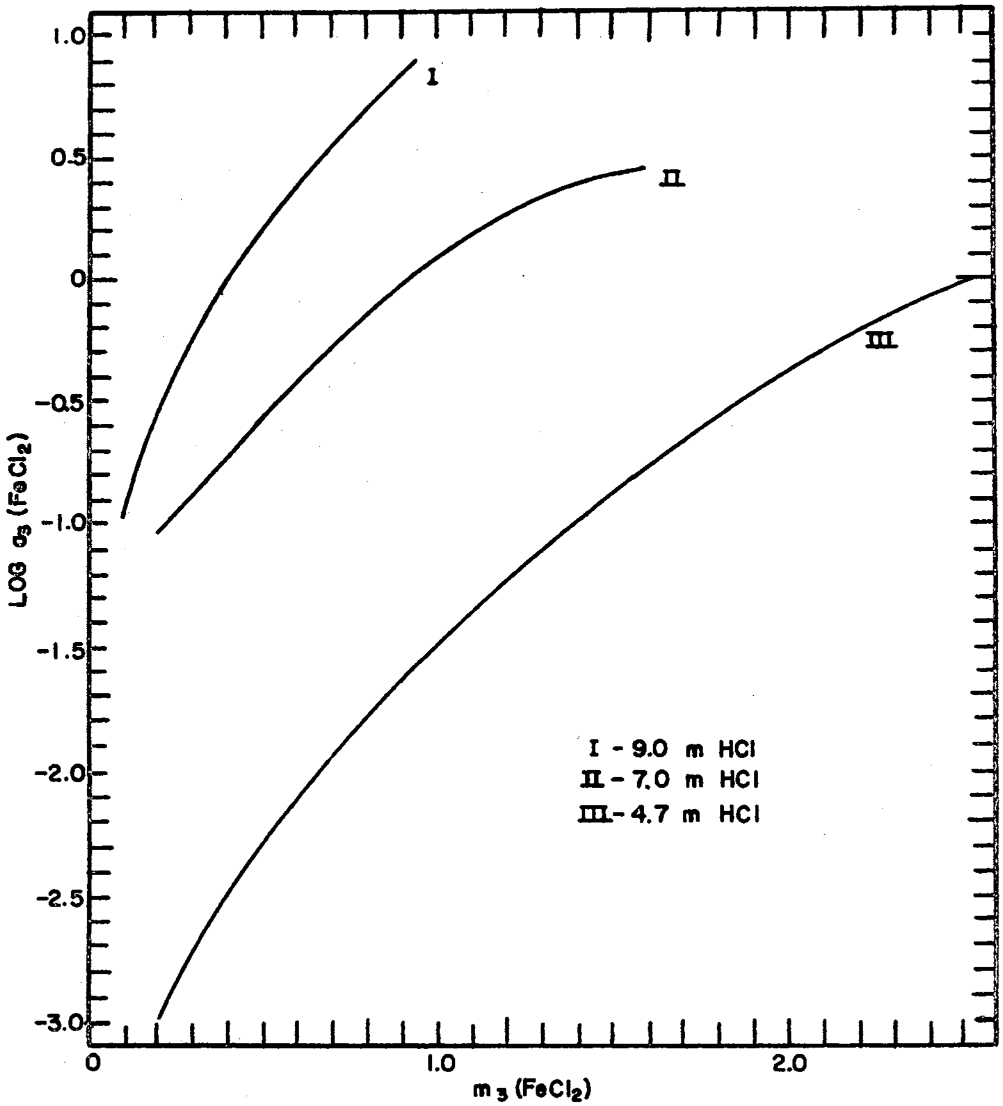

FIGURE 19. LOGARITHM OF SALT ACTIVITY IN THE THREE $FeCl_2$-HCl-H_2O SERIES

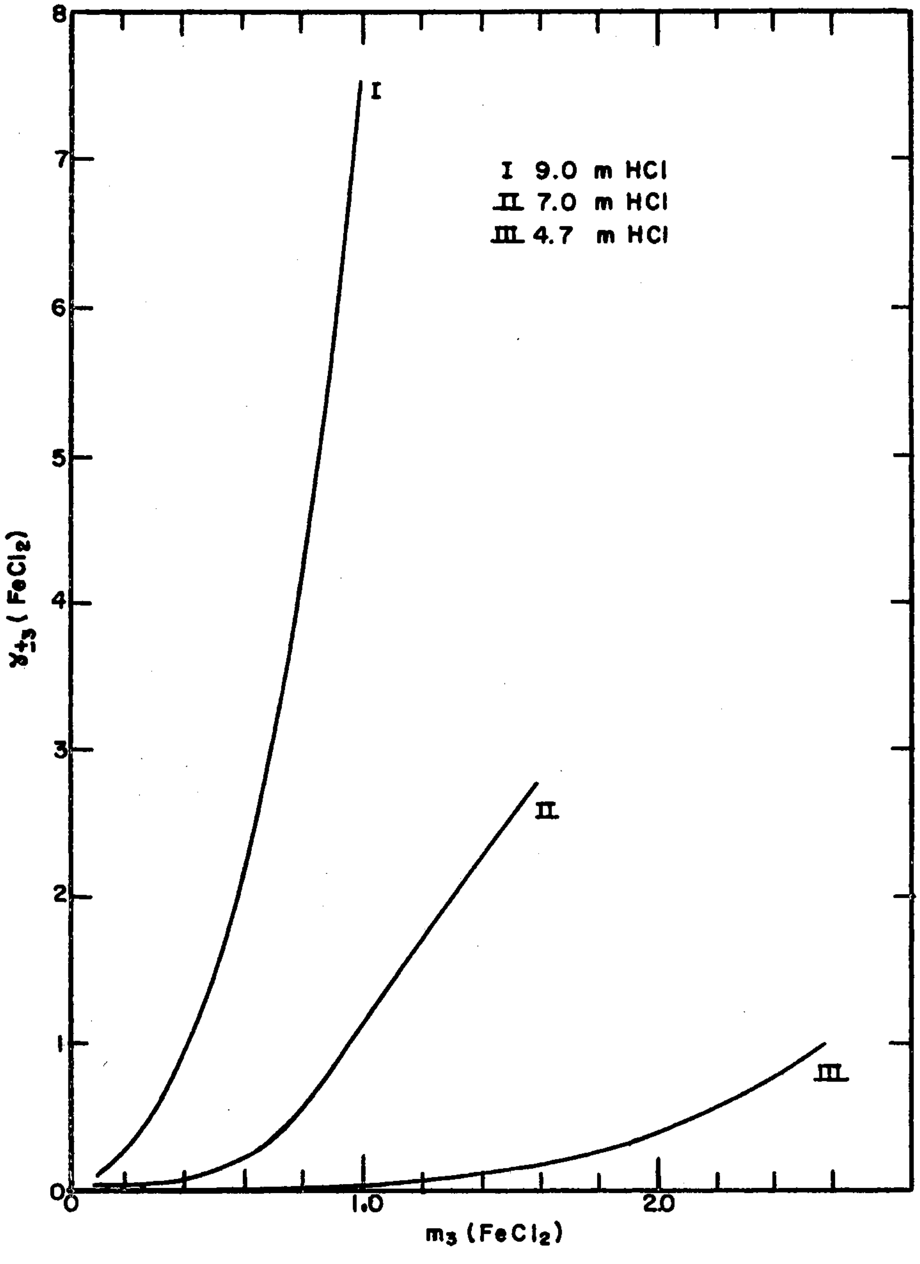

FIGURE 20 ACTIVITY COEFFICIENT OF THE SALT IN THE THREE $FeCl_2 - HCl - H_2O$ SERIES

in the two sets of calculated values. In either case the estimated deviation between experimental and calculated values is 1 percent or less, for the two higher acid series. Furthermore, the deviations in the 9.0 m HCl series are in the direction expected, since a too-large hydration parameter gives high values for the activity coefficients.

All attempts to use the hydration parameters obtained from the volume fraction statistics of Glueckauf (39) in equation (40) were unsuccessful. The calculated values of the acid activity coefficient were lower than the experimental values. Although Glueckauf recommends the use of the Debye-Hückel expression for the electrostatic contribution to the Gibbs function, rather than the chemical potential, he points out that there is little difference in the final values of the electrolyte activity coefficient when such a substitution is made.

Harned's Rule. The logarithm of the activity coefficient of hydrochloric acid in mixtures of constant ionic strength with electrolytes such as the alkali metal halides in which there is no extremely strong ionic interaction of the "chemical" type has been found to vary linearly with the molality of the other electrolyte (50, 119). This follows from Brönsted's principle of specific interionic interactions. The following empirical equation has been found to correlate the data for the $FeCl_2$-HCl-H_2O system at constant molal ionic strength:

TABLE XX

DATA ON HARNED'S RULE

Ionic Strength	m_2(HCL)	m_3($MnCL_2$)	log γ2(CL)	α	β
9.00	4.70	1.43	0.617	-0.215	0.012
9.00	7.00	0.67	0.763		
9.00	9.00	0.00	0.900		
9.00	9.00	0.00	0.900		
9.50	4.70	1.60	0.644	-0.217	0.011
9.50	7.00	0.83	0.788		
9.50	9.00	0.17	0.927		
9.50	9.50	0.00	0.961		
10.00	4.70	1.73	0.667	-0.206	+0.0013
10.00	7.00	1.00	0.814		
10.00	9.00	0.33	0.952		
10.00	9.50	0.00	1.019		
10.50	4.70	1.93	0.701	-0.212	0.0086
10.50	7.00	1.17	0.840		
10.50	9.00	0.50	0.976		
10.50	10.50	0.00	1.077		
11.00	4.70	2.10	0.730	-0.205	0.0065
11.00	7.00	1.33	0.868		
11.00	9.00	0.67	1.000		
11.00	11.00	0.00	1.131		

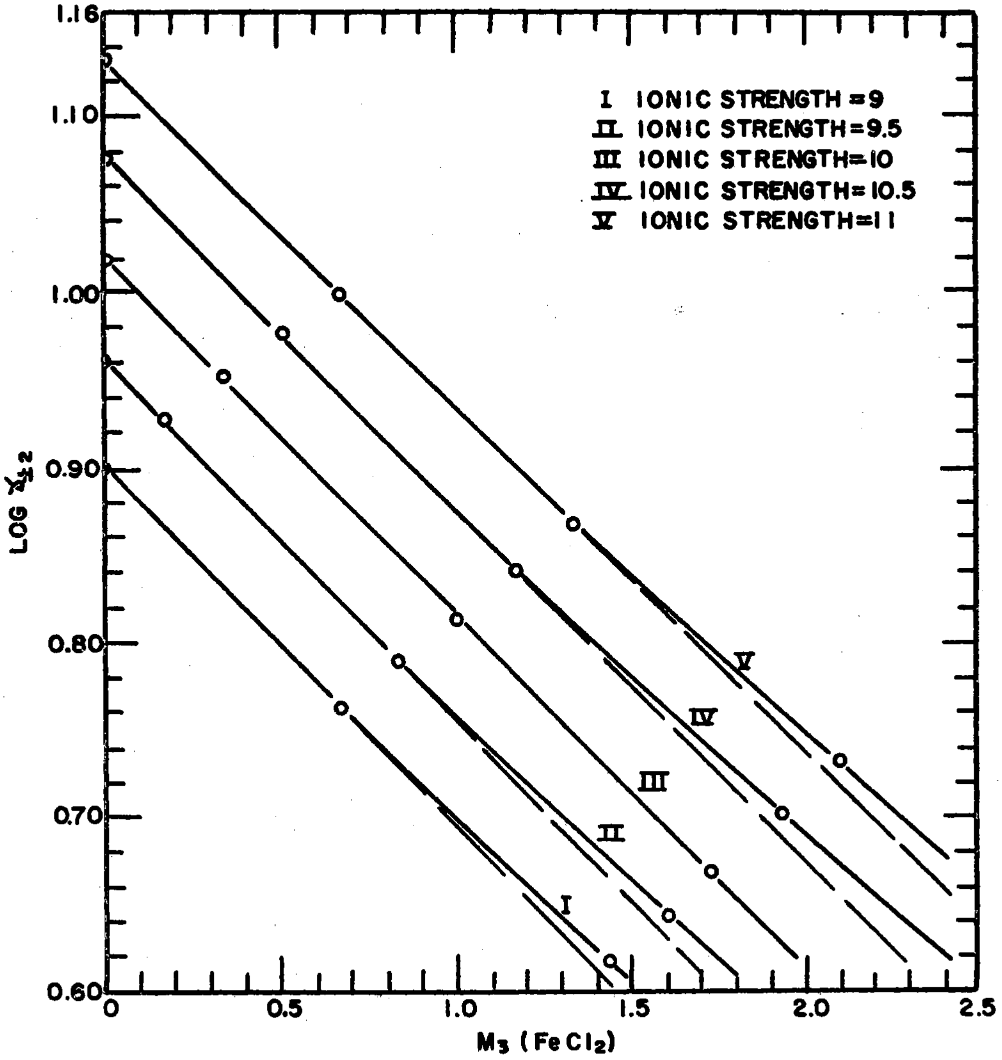

FIGURE 21. VARIATION OF LOG $\gamma_{\pm 2}$ (HCl) WITH FeCl$_2$ MOLALITY AT CONSTANT IONIC STRENGTHS

$$\log \gamma_{\pm 2} = A + \alpha m_3 + \beta m_3^2 . \qquad (41)$$

Burtch (21) found that a similar equation also expressed the HCl activity as a function of salt molality in the system $MnCl_2$-HCl-H_2O. In equation (41) α and β are in general functions of the ionic strength and have the values shown in Table XX. One notes from the table, however, that α is approximately independent of ionic strength and that the deviations from linearity indicated by β are small. The constant A equals $\log \gamma_{\pm 2}$ for pure hydrochloric acid at the same ionic strength as that of the mixtures and m_3 is the molality of the salt. The values of α and β given in Table XX were determined by the method of least squares from the experimental data. It is of interest to note that the values of α listed in Table XX are quite similar to those found by Burtch for the $MnCl_2$-HCl-H_2O system. In view of the findings of McKay (77) it is not too surprising that the $FeCl_2$-HCl-H_2O system does not follow Harned's rule, for as McKay points out, there are probably widespread deviations from Harned's rule. Calculated and experimental values are shown in Figure 21. The activity coefficients at the higher salt concentrations are seen to be predicted by Harned's rule. Miller (81) found that the $CuCl_2$-HCl-H_2O system behaved in a similar manner, although the deviations were somewhat greater in magnitude.

Apparent and Partial Molal Volumes. In order to find the volume ionic strengths and to apply volume-fraction statistics it was necessary to measure the density of the solutions. From the densities the total and apparent molal volumes were calculated. The partial molal volume of $FeCl_2$ was also computed by a method similar to that described by Klotz (60). The total volume of a solution containing 1,000 grams of water is

$$V = \frac{1000 + m_2(W_2) + m_3(W_3)}{d} \qquad (42)$$

where V = total volume of the solution in cc.

m_2 = molality of the hydrochloric acid

m_3 = molality of the salt

W_2 = gram-molecular weight of the acid

W_3 = gram-molecular weight of the salt

d = density of the solution at 25°

From the value of the total volume recorded in Table XXI the apparent molal volumes, ϕ_3, were calculated by the following equation:

$$\phi_3 = \frac{V - V^o}{m_3} \qquad (43)$$

where ϕ_3 = apparent molal volume in cc.

V = total volume of the solution per 1000 g of water

V^o = volume of the solution at zero salt concentration

m_3 = molality of the salt.

The values of the apparent molal volume so obtained are also recorded in Table XXI.

Figure 26 shows the variation of ϕ_3 with concentration for HCl = 7 m. The curve drawn has been smoothed out. The partial molal volume of $FeCl_2$ was determined from the equation:

$$\bar{V}_3 = \left(\frac{\partial V}{\partial m_3}\right)_{m_2} = \phi_3 + \left(\frac{\partial \phi_3}{\partial m_3}\right)_{m_2} m_3 \qquad (44)$$

where $\bar{V}_3$ represents the partial molal volume of the salt. Calculated values of the partial molal volume of $FeCl_2$ in each series are recorded in Table XXII. The molal volumes of $FeCl_2$ are remarkably constant over most of the concentration range in each series. This also is true for the other 2:1 transition metal halides in HCl and is in sharp contrast to the behavior of $FeCl_3$ in HCl.

B. Ferric Chloride-Hydrochloric Acid Mixtures.

Unlike the $FeCl_2$-HCl-H_2O system which might be characterized as a "physical" system in that the predominate interactions are long-range electrostatic and short range ion-solvent (i.e., hydration), the $FeCl_3$-HCl-H_2O system might be classified as a "chemical" system since ionic association or chemical complex formation largely determines the activity relations.

In Figure 22 there is shown the variation in the water activity with $FeCl_3$ molality in 7 m. HCl. The difference

TABLE XXI

TOTAL AND APPARENT MOLAL VOLUMES FOR THE $FeCl_2$-HCl-H_2O SYSTEM AT 25° C.

PART A. 4.70 m HCl SERIES

$m_3(FeCl_2)$	Total Volume (cc.)	ϕ_3 (cc.)
0.0000	1096.4	----
0.2046	1106.5	49.4
0.4000	1111.8	38.5
0.5934	1114.2	30.0
0.8534	1116.3	23.3
1.000	1115.3	23.1
1.200	1124.5	22.8
1.400	1126.4	22.6
1.548	1133.1	22.4
1.900	1135.8	21.9
2.200	1145.4	21.5
2.300	1155.3	21.3
2.400	1147.7	21.2
2.547	1149.9	21.0

PART B. 7.00 m HCl SERIES

$m_3(FeCl_2)$	Total Volume (cc.)	ϕ_3 (cc.)
0.0000	1144.4	----
0.2000	1149.2	23.9
0.4000	1153.8	23.8
0.6000	1158.6	23.8
0.8000	1163.4	23.8
1.000	1167.2	23.7
1.166	1172.3	23.6
1.300	1174.7	23.5
1.400	1177.0	23.4
1.500	1179.5	23.3
1.600	1188.7	23.2

TABLE XXI (Continued)

PART C. 9.00 m HCl SYSTEM

m_3(FeCl$_2$)	Total Volume (cc.)	ϕ_3 (cc.)
0.0000	1186.7	----
0.1000	1188.7	19.8
0.2000	1190.6	19.1
0.4000	1196.3	24.3
0.5000	1198.6	24.3
0.6000	1201.4	24.3
0.7000	1204.1	24.2
0.8000	1205.9	24.1
0.9000	1208.2	23.9
0.9384	1209.5	23.8

TABLE XXII

PARTIAL MOLAL VOLUMES FOR THE $FeCl_2$-HCl-H_2O SYSTEM AT 25° C.

Salt Molality m_3	Partial Molal Volume, V_3 (cc.)		
	4.7 m HCl	7.0 m HCl	9.0 m HCl
0.20	----	23.9	----
0.40	----	23.8	26.1
0.50	----	----	25.6
0.60	----	23.8	24.5
0.70	----	----	23.6
0.80	----	23.2	22.4
0.85	22.7	----	----
0.90	----	----	22.0
0.94	----	----	21.1
1.0	22.4	23.0	
1.2	21.9	22.8	
1.3	----	22.6	
1.4	21.6	22.4	
1.5	----	22.2	
1.55	21.3	----	
1.6	----	22.1	
1.9	20.6		
2.2	19.9		
2.3	19.7		
2.4	19.5		
2.55	19.2		

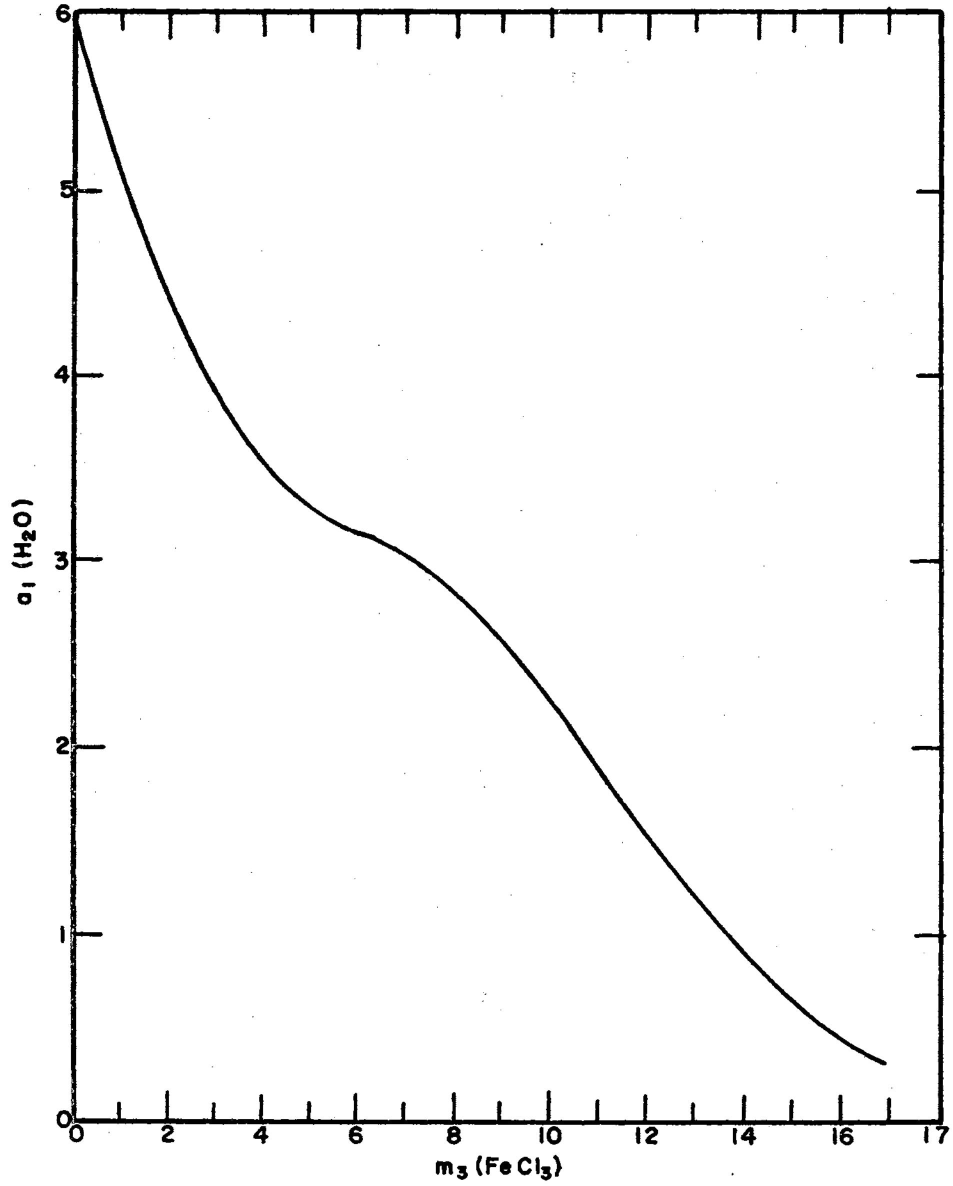

FIGURE 22. ACTIVITY OF WATER IN THE SYSTEM $FeCl_3$-HCl-H_2O (HCl MOLALITY = 7.00)

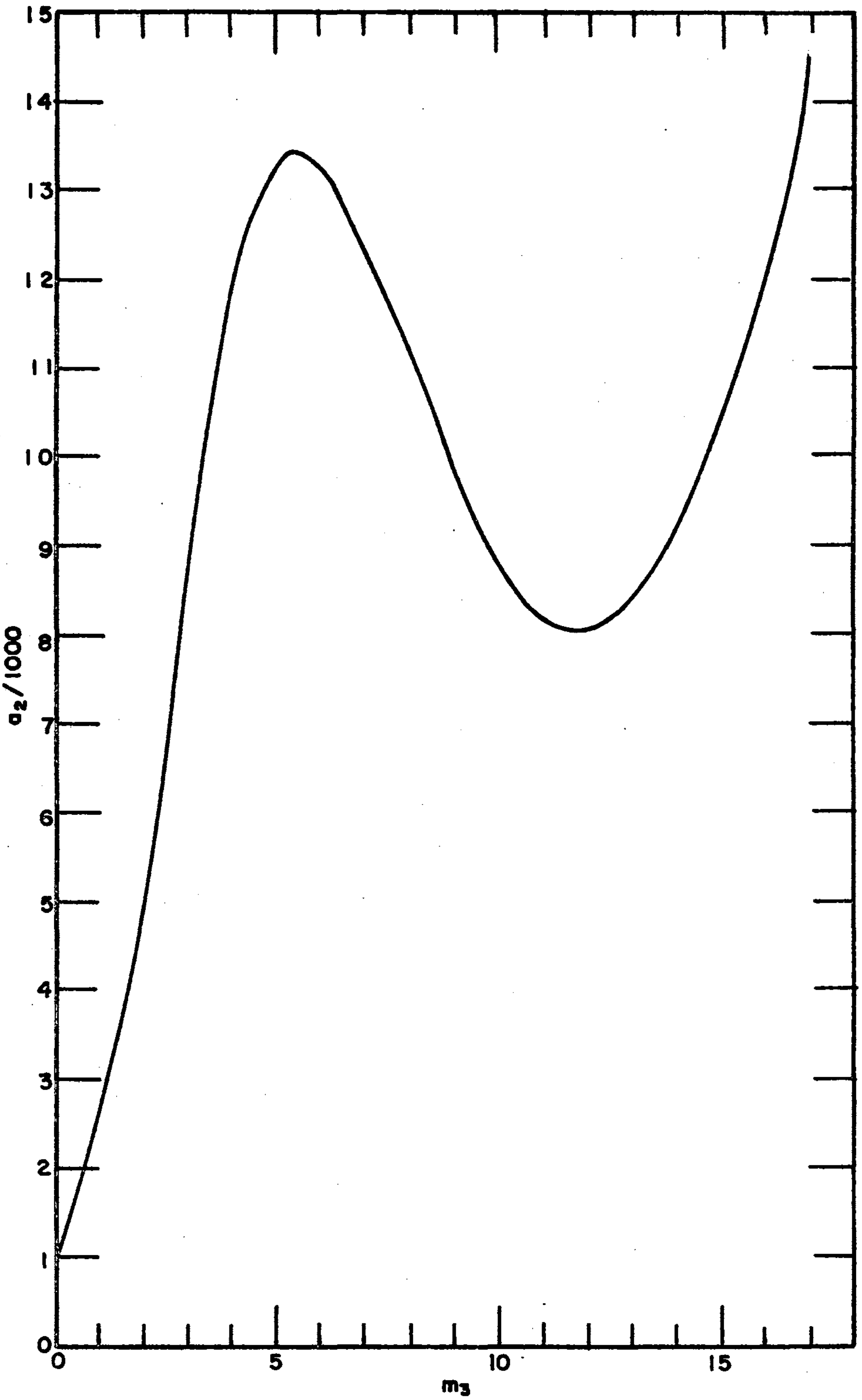

FIGURE 23. THE ACTIVITY OF THE HCl IN THE TERNARY $FeCl_3-HCl-H_2O$ SYSTEM (HCl MOLALITY = 7.00)

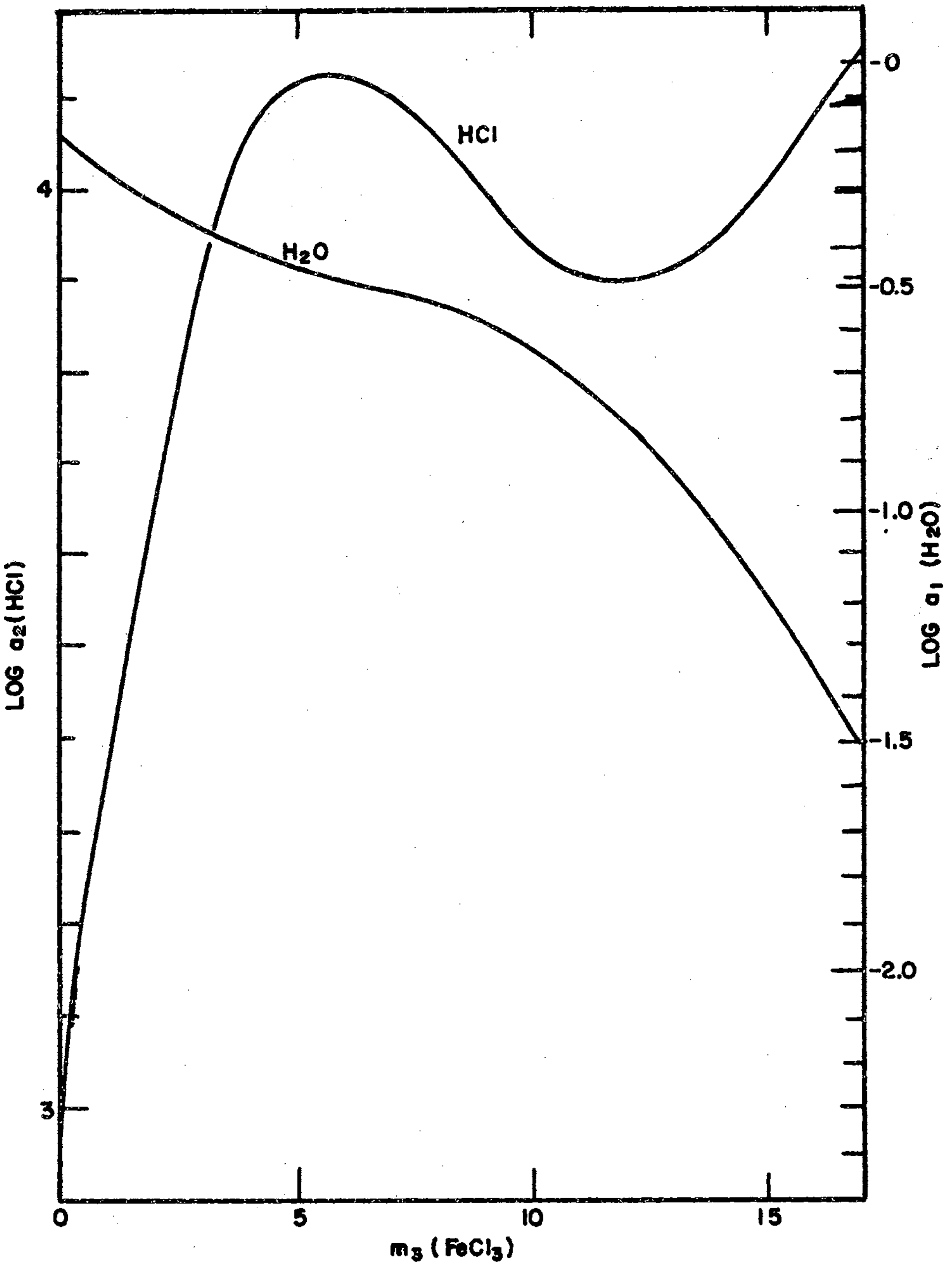

FIGURE 24. VARIATION OF LOG a_2 AND LOG a_1 WITH SALT CONCENTRATION IN THE $FeCl_3-HCl-H_2O$ SYSTEM (MOLALITY HCl = 7.00)

between this and the variation shown by the water activity in the "normal" $FeCl_2$-HCl-H_2O system (Figure 4) is obvious. The change in water activity in going from the binary HCl solution ($m_3 = 0$) to the saturated $FeCl_3$ solution is of course much greater than for any of the 2:1 transition metal halides investigated (21, 42, 81) since the concentration of $FeCl_3$ in the saturated solution is almost 5 times greater than in any other solution studied.

The variation in the activity of HCl with salt molality is shown in Figure 23. The curve is striking, having a maximum in HCl activity at about 5 m $FeCl_3$ and a minimum at about 12 m $FeCl_3$. The logarithm of the HCl activity and the logarithm of the water activity are also shown in Figure 24 for comparison. The pronounced inflection in the curve around 7 molal $FeCl_3$ is significant and will be discussed later.

The variations in the activity of HCl water can be qualitatively accounted for in terms of complex formation. As was brought out clearly in the literature survey, the highest complex formed in this system is undoubtedly the tetrachloroferrate (III) ion, $FeCl_4^-$. Other lower complexes, such as $FeCl^{++}$ and $FeCl_2^+$ (112) may be present in low concentrations in HCl solution, but as the work of Gamlen and Jordan (36) has shown the principal species likely to be present at the high chloride concentrations of this study are $FeCl_3$ and $FeCl_4^-$ (or $HFeCl_4$). Thus, the variations in HCl activity can be qualitatively explained in terms of hydration and

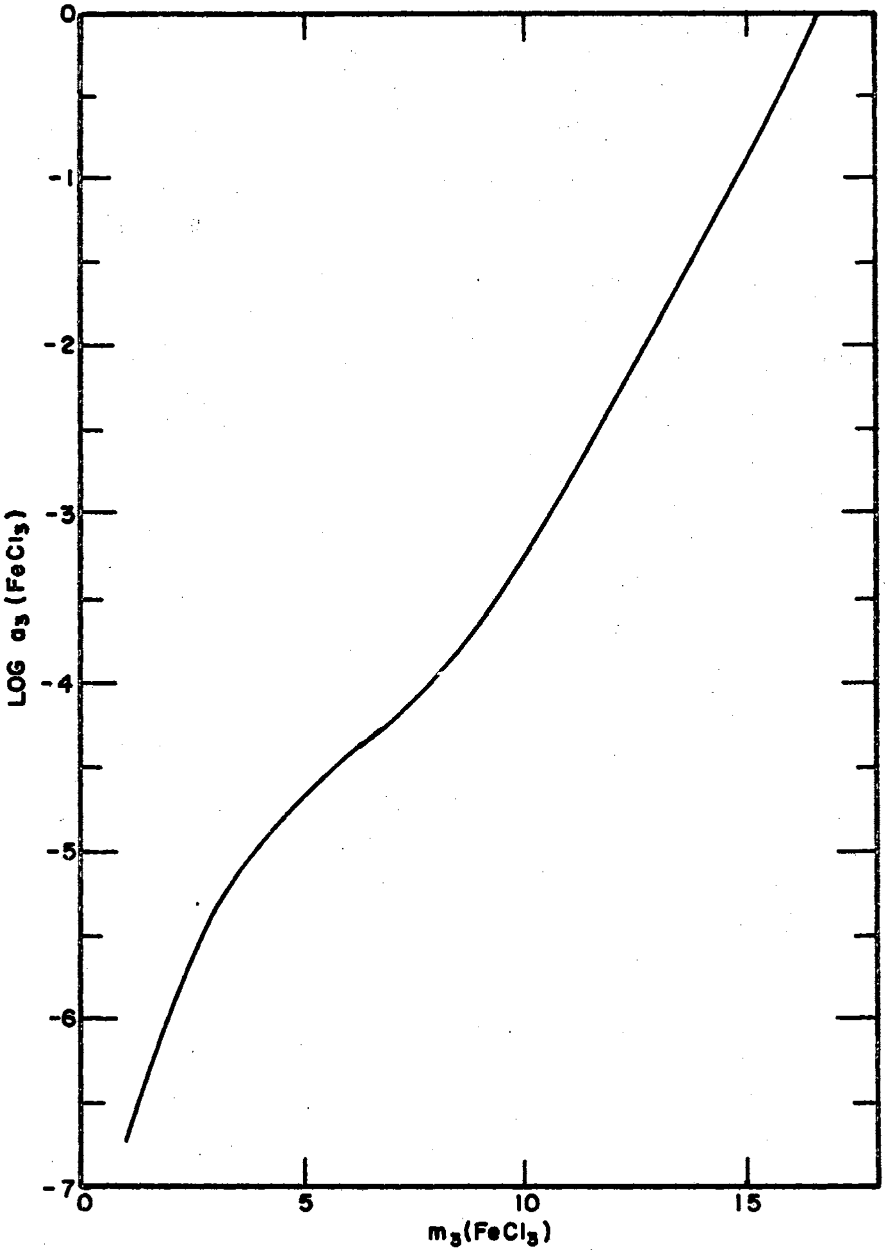

FIGURE 25. VARIATION OF LOG a_3 ($FeCl_3$) WITH SALT MOLALITY IN THE $FeCl_3$-HCl-H_2O SYSTEM (MOLALITY HCl = 7.00)

complex formation in the following manner. At the lower concentrations of $FeCl_3$, up to about 5 molal, the hydration of the salt increases the activity of the acid by the "salting-out" effect discussed in connection with $FeCl_2$-HCl mixtures. Up to about 5 to 7 molal in $FeCl_3$, the hydration effect is dominant. Above 7 molal and up to about 11 molal complex formation causes effectively a decrease in the concentration of HCl present. Again above about 12 molal the hydration effect dominates and the acid activity again increases. The inflection observed in the water activity curve is also consistent with the progressive replacement of water coordinated with the ferric ion by chloride as complex formation occurs.

The variation of the salt activity with salt concentration shown in Figure 25 is in agreement with the above conclusions, the inflection occurring at approximately a 1:1 HCl to $FeCl_3$ ratio. Perhaps the most remarkable feature of the salt activity curve is the enormous increase in the salt activity in going from 1 molal concentration to saturation (17 molal). The salt activity increases over one million times in this concentration range. From Figure 22 it can be seen that the activity curve flattens out somewhat between about 4 and 9 molal but as pointed out above, this can be attributed to tetrachloroferrate formation.

In Figure 1 there is plotted the density of the solutions as a function of salt molality. While the densities of the $FeCl_2$ solution series could be considered, to a first approximation, straight lines, the densities of the $FeCl_3$-HCl-H_2O system can be seen to deviate considerably from a simple linear relationship. The apparent molal volumes illustrated in Figure 26 were calculated and recorded in Table XXIII. It is evident that the apparent molal volumes go through a maximum at about 10 m $FeCl_3$. The curve for the apparent molal volumes was used to calculate the partial molal volumes which are also shown in Figure 26 and recorded in Table XXIII. The partial molal volumes in this system are remarkable, not only because they reach a maximum, but also because of their quite large values. Whereas the apparent molal volumes of the bivalent salts in the other systems studied (81, 21) have been in the range of 20 to 30 cc/mole, the apparent molal volumes in the $FeCl_3$-HCl-H_2O system reach values of the order of 65 to 70 cc/mole. Such high values are due, in all probability, to the formation of $HFeCl_4$, for the maximum in the partial molal volume curve occurs at 7 molal in salt concentration corresponding to the stoichiometric composition.

The partial molal volumes of the water in the system would be of interest here, since as Wirth and Collier (148) have pointed out, the addition of strong electrolytes breaks the open structure of water and causes a decrease in the partial molal volume of water. On the other hand Bernal and Fowler (14) have commented that the evidence from Raman spectra as well as other experimental evidence indicates that

TABLE XXIII

TOTAL, APPARENT, AND PARTIAL MOLAL VOLUMES FOR THE $FeCl_3$-HCl-H_2O SYSTEM AT 25° C.

(Molality HCl = 7.00)

m_3 ($FeCl_3$)	Total Volume (cc.)	ϕ_3 (cc.)	V_3 (cc.)
0.0000	1144.9	----	----
0.6928	1178.4	43.3	45.1
1.314	1210.3	45.1	48.6
1.858	1238.2	45.8	51.7
2.499	1276.6	48.7	56.5
3.190	1315.6	49.8	62.0
3.847	1362.0	53.0	68.9
4.630	1419.9	56.3	75.5
5.301	1473.2	59.1	81.6
5.963	1527.9	61.6	82.3
6.626	1583.3	63.7	84.0
7.289	1638.8	65.4	82.4
7.951	1693.1	66.8	80.5
8.586	1745.5	67.9	78.1
9.276	1797.6	68.4	75.5
10.57	1892.5	68.9	70.5
11.26	1921.8	68.9	68.3
11.93	1987.0	68.9	67.7
12.23	1990.2	69.0	67.7
12.59	2031.5	68.8	67.2
13.25	2075.8	68.7	67.3
13.91	2122.3	68.7	67.2
14.58	2165.3	68.5	67.1
15.80	2219.1	68.2	66.8
16.40	2259.5	68.2	66.7
17.00	2300.1	68.2	66.5

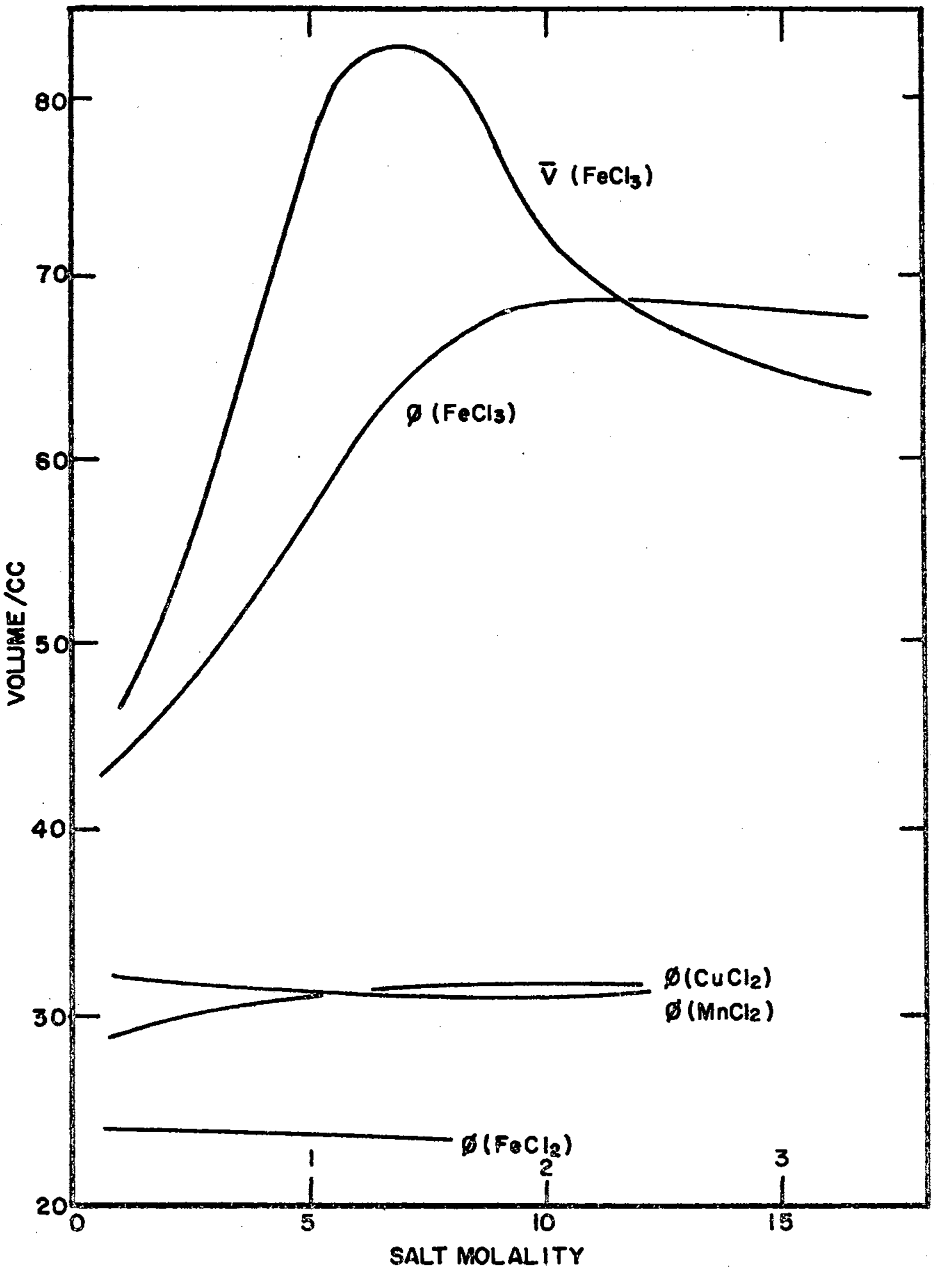

FIGURE 26. APPARENT AND PARTIAL MOLAL VOLUMES OF SOME TRANSITION METAL CHLORIDES IN TERNARY HCl SOLUTION. SALT MOLALITY BELOW LINE REFERS TO FeCl$_3$. SALT MOLALITY ABOVE LINE TO ALL OTHER SALTS

the addition of the hydrogen ion to water apparently causes an increase in the partial molal volume of the water. It may be that the tetrahedral structure of the $FeCl_4^-$ ion fits into the structure of water. Unfortunately, there is not enough data available from this research to make any estimation of the molal volume of water. So many different interactions are involved in a system of this complexity that the individual effects cannot be disentangled, and hence a quantitative interpretation is very difficult, if not impossible.

An attempt was made to apply the simple hydration model discussed for $FeCl_2$ solutions in HCl (equation 18) to the $FeCl_3$-HCl-H_2O system under three extreme assumptions. First it was assumed that the HCl and the $FeCl_3$ dissociate completely. The "bound" water calculated under these assumptions was plotted against the salt molality. The curve (Figure 27) showed a maximum at about 4.5 molal and a minimum at about 7.5 molal. This could be construed to indicate the formation of the complex $FeCl_4^-$, for at the maximum formation of the complex the "bound" water would be expected to be a minimum since in light of the findings of Gutmann and Baaz (47), it is doubtful that the $FeCl_4^-$ complex ion is strongly hydrated. However, the assumption of complete dissociation is admittedly incorrect.

The "bound" water was also calculated by assuming complete formation of the tetrachloro complex, the complex then dissociating completely to H^+ and $FeCl_4^-$. With these assumptions a plot of "bound" water gives the curve shown in Figure 28. It may be seen from the figure that there is a very rapid increase in the "bound" water followed by a slight leveling off from about 5 to 7 molal $FeCl_3$ concentration. The "bound" water passes through an inflection point at about 7 molal and thereafter increases almost linearly to about 13 molal, after which it again begins to level off.

In Figure 29 there is shown the variation of the "bound" water with salt concentration under the assumption that the $HFeCl_4$ formed does not dissociate. The equilibrium constant for the formation reaction of $HFeCl_4$ from $FeCl_3$ and HCl

$$FeCl_3 + HCl = HFeCl_4$$

given by Marcus (73), i.e.

$$K = \frac{[HFeCl_4]}{[FeCl_3]a_{HCl}} = 3.5 \times 10^{-5}, \qquad (45)$$

was used to determine the concentration of the $HFeCl_4$. As Figure 29 shows, the "bound" water exhibits a plateau from 5 to 7 molal in $FeCl_3$. It should be mentioned that although the assumption was made that the only species present were $FeCl_3$ and $HFeCl_4$ in agreement with the conclusions of Gamlen and Jordan (36), it should be remembered that they were working with solutions which contained far less $FeCl_3$ than the solutions studied in this research. The assumption that $HFeCl_4$ is not appreciably dissociated does not conform to the findings of Marcus (73), who concluded from spectrophotometric measurements that there is present some dissociated $HFeCl_4$. It should

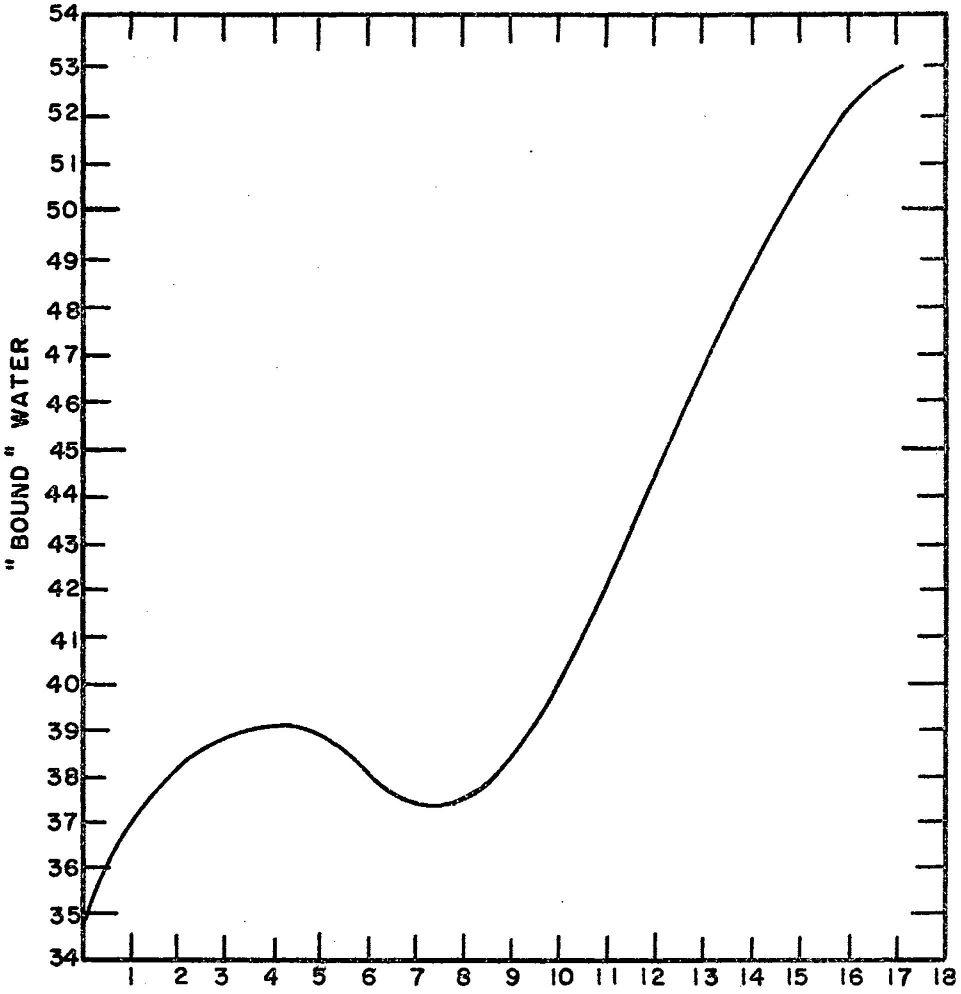

FIGURE 27. "BOUND" WATER FOR THE SYSTEM $FeCl_3$-HCl-H_2O BASED ON COMPLETE DISSOCIATION OF THE $FeCl_3$ AND HCl.

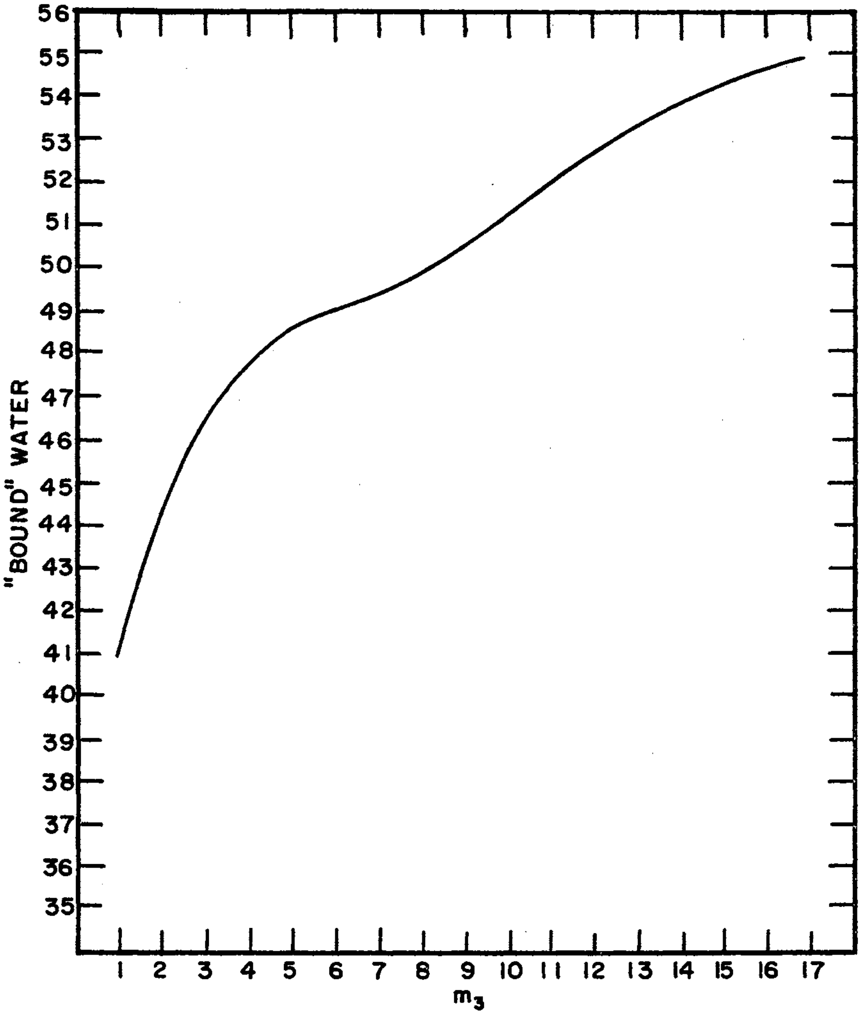

FIGURE 28. "BOUND" WATER FOR THE $FeCl_3$-HCl-H_2O SYSTEM BASED ON COMPLETE ASSOCIATION AND SUBSEQUENT COMPLETE DISSOCIATION TO $H^+ + FeCl_4^-$.

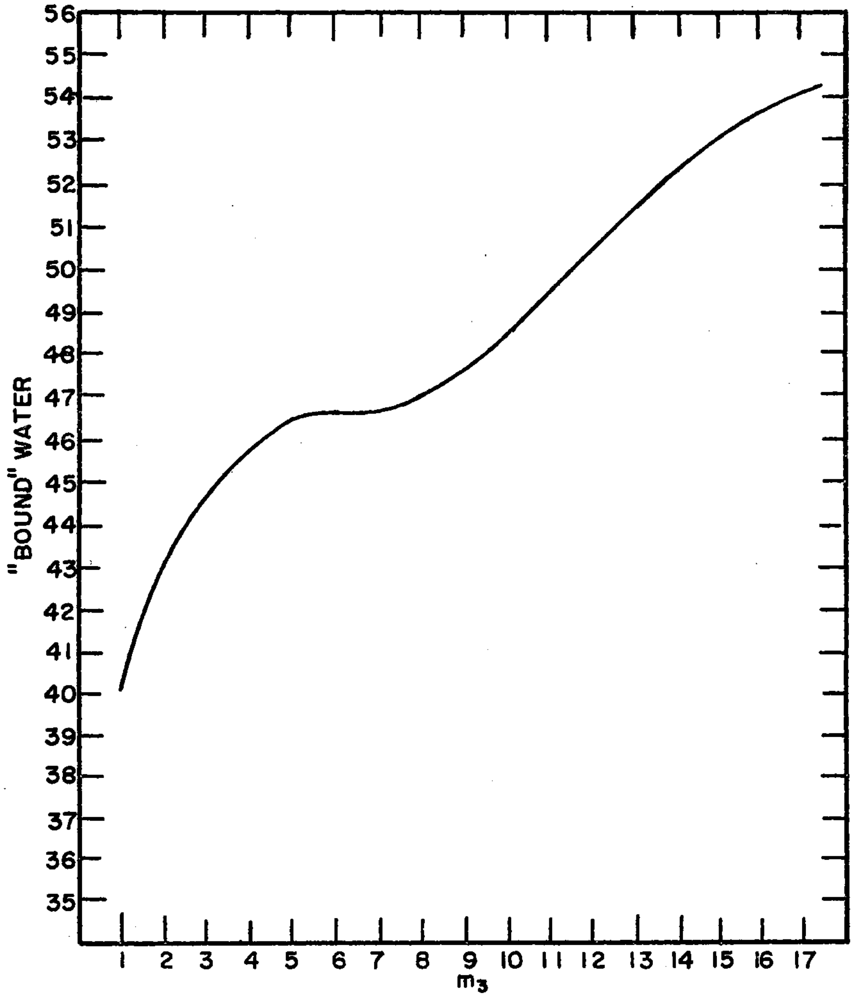

FIGURE 29. "BOUND" WATER FOR THE SYSTEM $FeCl_3$-HCl-H_2O BASED ON ASSUMPTION OF INCOMPLETE ASSOCIATION AND SUBSEQUENT COMPLETE DISASSOCIATION OF $HFeCl_4$ TO $H^+ + FeCl_4^-$

be pointed out that the constant given by equation (45) was determined by assuming that the ratio of activity coefficients of the neutral complexes of $FeCl_3$ and $HFeCl_4$ is unity. It should also be mentioned that the formation constant was determined for relatively dilute solutions of $FeCl_3$ in concentrated HCl. Goll, Nauman, and West (25) have concluded that formation constants are extremely sensitive to changes in the medium, and particularly to changes in the activity of water. As was shown earlier, the water activity in the $FeCl_3$-HCl-H_2O system varies drastically, reaching very low values ($\nleq 0.1$) in the most concentrated solutions. It can only be concluded that the use of the constant given by equation (45) can, at best, give only a first approximation to the ratio of the concentrations of the complexes. Because of its complexity, no very satisfactory quantitative interpretations can be given to this most interesting system.

In conclusion, it can be said that the investigation has provided new thermodynamic information about transition metal chlorides in concentrated hydrochloric acid. While one always seeks to fit his results into a theoretical framework which accounts quantitatively for his experimental findings, this is not always possible when the experiments are conducted on systems of greater complexity. Whereas the $FeCl_2$-HCl-H_2O system fits reasonably satisfactorily into the general pattern established for the other

2:1 iron-family transition metal chlorides, the properties of the $FeCl_3$-HCl-H_2O system seem to be determined to a far greater extent by chemical reaction between the components than for any of the other systems so far studied.

CHAPTER VII

SUMMARY

The vapor pressures of water and hydrochloric acid were measured in four series of solutions at 25° by the comparative gas-transpiration method. Three of the series contained ferrous chloride and hydrochloric acid at constant concentrations of 4.70, 7.00, and 9.00 molal. The fourth series of solutions was composed of ferric chloride in 7.00 molal hydrochloric acid. The salt concentration was varied from zero to saturation in each series. Activities of ferrous chloride and ferric chloride were calculated from the vapor pressure data by integration of the Gibbs-Duhem equation.

The experimentally determined activities of water and hydrochloric acid in each of the three ferrous chloride series were first fitted by empirical equations by the method of least squares, and the equations were then integrated to give the activity of ferrous chloride as a function of concentration.

Densities of all solutions were measured at 25° C. The solubility of ferrous and ferric chlorides in hydrochloric acid solutions of the concentrations given above were also determined at 25° C. The composition of the solid phases in equilibrium with the saturated solutions of ferrous chloride in 4.70 and 9.00 molal hydrochloric acid was found to correspond to $FeCl_2 \cdot 4H_2O$.

Apparent and partial molal volumes of the salts in all of the ternary solutions were calculated from the density measurements.

It was found that the activity coefficient of hydrochloric acid was greater in all of the ternary mixtures with ferrous chloride than in binary aqueous solutions of the same concentration. The activity of ferrous chloride was also found to increase with increase in salt concentration within a series and to increase with hydrochloric acid concentration in different series. This was attributed to solute hydration. The hydration model of Robinson and Stokes was used as a basis for a calculation of the concentration dependence of the hydrochloric acid activity in the ferrous chloride solutions. The agreement between calculated and experimental values of the activity coefficient was of the order of one percent. Mole fraction statistics were used to evaluate the "free" water in the solutions. In comparison with similar solutions of other bivalent transition metal chlorides, ferrous chloride appears normal and nonassociated.

The effect of complex formation was evident in the series of solutions of ferric chloride in 7.00 molal hydrochloric acid. This was clearly indicated not only by the anomalous behavior of the activity of each of the three components, but also by the partial molal volumes of ferric chloride. All of the data are in qualitative agreement with the formation of the relatively weak tetrachloroferrate (III) complex. The activity of ferric chloride was found to increase over a million times in the concentration range of from 1 to 17 molal. The water activity was correspondingly reduced to extremely small values at saturation.

This research represents the first thermodynamic investigation of a trivalent transition metal halide in mixtures with hydrochloric acid, not only at high concentrations of salt and acid but also under conditions where reaction between the electrolytic components occurs.

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