SOME THERMODYNAMIC PROPERTIES OF AQUEOUS CUPRIC CHLORIDE-HYDROCHLORIC ACID SOLUTIONS

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CHAPTER I

INTRODUCTION

Purpose and Scope of Investigation

This research is a continuation of an extensive study of the thermodynamic properties of concentrated hydrochloric acid solutions containing transition metal chlorides. The program was initiated during the course of an investigation of the factors affecting the solvent extraction and separation of transition metal salts. (75). Preliminary work in this field by Garwin and Hixson (34) has shown that the addition of concentrated HCl or $CaCl_2$ to aqueous solutions of $NiCl_2$ and $CoCl_2$ preferentially promotes the extraction of $CoCl_2$ by the organic phase (2-octanol). Gootman (37) made a comprehensive study of the activity of all of the components in several systems composed of hydrochloric acid-water-cobalt or -nickel chloride at 30° in an effort to correlate the extractibility of the salts from the aqueous phase with their activities in the aqueous solutions.

Extension of solvent extraction studies to manganous chloride-hydrochloric acid mixtures by Moore and Brown (74) led to an investigation of the activity relationships in these mixtures by Burtch (16). Recent expansion of the solvent extraction work to include cupric chloride-hydrochloric acid mixtures is now complemented by the present investigation.

Four series of solutions of $CuCl_2$ in aqueous HCl were studied at 25°. Three of the series consisted of solutions having constant HCl molality and varying amounts of $CuCl_2$, whereas in the fourth series the $CuCl_2$ molality was held constant while the HCl concentration was varied.

The experimental work has involved the determination of the equilibrium partial pressures (and consequently the activities) of HCl and H_2O in the ternary solutions. Activities of $CuCl_2$ were calculated by integration of the Gibbs-Duhem equation. Densities of all solutions were accurately measured, and the solubilities and composition of the equilibrium solid phases were determined for the three constant-acid series.

The interpretation of the data has been largely semi-empirical. Theoretical consideration has been given to both ionic association and ionic hydration based upon the models of Glueckauf (38) and Stokes and Robinson (102). Empirical relations such as Harned's rule (41) and the vapor pressure lowering additivity rule (93), for example, have been tested with regard to their applicability to the $CuCl_2$-HCl-H_2O system.

This research not only provides thermodynamic data which is immediately applicable to various chemical problems, but it also importantly contributes to the fund of knowledge of concentrated electrolyte solutions. Presently there is a marked paucity of quantitative data of this type.

Literature Survey

Researches paralleling the present investigation have been conducted by Moore, Gootman, and Yates (76) and Burtch (16). Moore et al. studied systems of $NiCl_2$ and $CoCl_2$ in aqueous HCl solutions at 30°, and Burtch investigated the properties of $MnCl_2$ and $MnSO_4$ in aqueous HCl solutions at 25°. In both instances the activity data have been interpreted with some success from the standpoint of solvent-solute and solute-solute interactions.

The vapor pressures of aqueous mixtures of various salts with HCl have been the object of considerable study. Lilich and Timofeev (65) have determined the total vapor pressures in the three-phase systems of $ZnCl_2$-HCl-H_2O and $CuCl_2$-HCl-H_2O at 25°. The HCl concentrations, however, were such that the vapor phase was essentially free of hydrogen chloride. More recently, these authors have made similar measurements on three-phase systems of $BaCl_2$-HCl-H_2O. (66). Morozov (77), using the gas transipiration method, measured the partial pressure of hydrogen chloride above three series of aqueous $CuCl_2$ solutions (0.46, 1.17. and 2.56 molal) containing from about 8 to 18 molal HCl. Measurements were also made on comparable aqueous HCl solutions of CuCl, CuCl + NH_4Cl, NH_4Cl, $TiCl_4$, $SnCl_4$, and $SnCl_2$. Additions of CuCl, CuCl + NH_4Cl, or NH_4Cl to aqueous HCl solutions resulted in a lowering of the HCl vapor pressure whereas additions of the other salts increased the vapor pressure of the acid. Morozov proposed that solutions that showed a lowering of HCl activity upon the addition of salt(s) contained uncharged molecules produced by salt-salt and acid-salt association. Yannakis (106) measured the total vapor pressures of ternary systems of CuCl-HCl-H_2O and LiCl-HCl-H_2O at 50° by a static method. The total vapor pressure of these solutions was found to decrease linearly with increased CuCl concentrations and to increase markedly with additions of LiCl.

Robinson and Stokes (93) have used the isopiestic technique to determine the H_2O vapor pressure of aqueous mixtures of KCl and $CuCl_2$ having a constant Cl/Cu ratio of 4. Brown (15) made similar measurements on aqueous mixtures of 2LiCl + $CuCl_2$ and $CaCl_2$ + $CuCl_2$ over limited concentration ranges. However, the activity of the water alone could be obtained from these measurements.

Holland and Bonner (46) have recently determined ratios of the activity coefficients of the solutes in systems composed of H_2SO_4-$CuSO_4$ and

$HClO_4$-$Cu(ClO_4)_2$ from electromotive force measurements with cells having glass and copper electrodes. In the solutions studied the acid/salt molality ratio was varied from about 0.4 to 8 at an ionic strength of unity. Attempts to obtain similar data on the HNO_3-$Cu(NO_3)_2$ and HCl-$CuCl_2$ systems were unsuccessful. In the nitrate system the spongy copper electrode was attacked by the dilute HNO_3, and in the chloride system the cupric ion in the presence of the copper electrode was reduced irreversibly to cuprous chloride.

The activity coefficients of $CuCl_2$ in aqueous solutions (0.1 to 2.8 molal) have been evaluated at 25° from isopiestic data by Robinson and Stokes (92). Later, Stokes (101) extended the data up to 6 molal $CuCl_2$. In the first paper Robinson and Stokes suggested that the abnormally low activity coefficient found for $CuCl_2$ in its aqueous solutions may be due to its less extensive hydration as compared to other transition metal chlorides such as those of Mn (II), Co (II), and Ni (II). Stokes (101), however, attributed the low values for the $CuCl_2$ activity coefficient to complex ion formation.

The evidence for chlorocomplex formation in solutions containing copper (II) ions and chloride ions is convincing. Interfacial tension measurements on aqueous solutions of $CuCl_2$ also containing KCl (50), NH_4Cl (51), NaCl, and LiCl (52) against n-butyl acetate showed maxima at 3:1, 2:1, 1:1, 1:2 MCl/$CuCl_2$ mole ratios. In solutions of higher total salt concentration the maxima at mole ratios of 2:1 and 1:1, corresponding to $CuCl_4^{--}$ and $CuCl_3^-$ formation, respectively, were favored.

The researches of Donnan and Bassett (25) led these authors to the conclusion that the change in color observed in concentrated cupric, cobaltous, and ferric chloride solutions relative to the colors of dilute solutions is due to the formation of complex ions or undissociated molecules. Sidgwick and Tizard (99) also suggested that the color changes observed in cupric chloride solutions with changes in concentration are due to the formation of various complexes. Getman (35) concluded from spectrometric studies that the $CuCl_4^{--}$ ion is present only in extremely concentrated mixtures of $CuCl_2$ with HCl, KCl, LiCl, $CaCl_2$, $AlCl_3$, and $ZnCl_2$ but that intermediate chlorocomplexes are present in less concentrated solutions. Bjerrum (8) considered the possibility of identifying the individual species in concentrated cupric chloride solutions by optical methods and reached the conclusion that, in general, direct information regarding the number of complexes present could not be expected. Later, Bjerrum (9) conducted optical studies on both aqueous cupric chloride solutions and on mixtures of $CuCl_2$ with HCl, LiCl, $MgCl_2$, and $CaCl_2$. The cupric chloride concentration in these solutions was varied from 0.001 N to 0.1 N while the normality of the added salt was varied from 3 N to 14 N. Although only orders of magnitude for the stability constants of the complex ions could be estimated from the results, the values so obtained indicate extensive formation of $CuCl_3^-$ and $CuCl_4^{--}$ ions. Moeller (73) has made similar optical absorption studies on mixtures of 1 molar $Cu(NO_3)_2$ with varying amounts of NaCl and LiCl. The results clearly indicate the presence of $CuCl_4^{--}$ ions in the solutions but provide no information relative to the presence or absence of other complexes. Equilibria between hydrated copper (II) ions and the relatively unstable tetrachlorocuprate (II) ion account for color changes in such systems, but the color changes produced by concentrating aqueous cupric chloride solutions are due to the appearance of $CuCl_4^{--}$ ions arising from autocomplexing. Hemholz and Kruh (42) found that all but a small percent of copper (II) ions in solutions having Cl/Cu mole ratios of 10^5 was in the form of $CuCl_4^{--}$ ions.

McConnell and Davidson (69) have determined the stability constant of the monochlorocopper (II) ion and the cupric chloride molecule in concentrated HCl-$HClO_4$ solutions. Their values are of the same order as those estimated by Bjerrum; i.e., $K_1 = 1.30 \pm 0.03$ and $K_2 = 0.23 \pm 0.15$. Kiseleva (53) has determined the stability constant for the tetrachlorocuprate (II) ion in approximately 1 molal $CuCl_2$; his value also agrees with the approximate value given by Bjerrum. Näsänen (78, 79), however, has concluded from optical measurements that the monochlorocopper (II) ion is the only complex present to any appreciable extent in dilute aqueous solutions of $CuCl_2$ and also in dilute mixtures of $CuCl_2$ with $Cu(ClO_4)_2$. The apparent lack of agreement between Näsänen's (78) and McConnell's and Davidson's (69) values for the stability constant of the monochlorocomplex has been shown by Kruh (63) to be due to the neglect of the undissociated molecule, $CuCl_2$. Näsänen (78) had previously reported that higher complexes interfered when the chloride ion concentration exceeded 0.25 molal. On the other hand, Brown (15) showed from absorbency measurements on dilute cupric chloride solutions (5×10^{-4} molar) containing varying large amounts of chloride ions that the only stability constant exhibiting any degree of constancy was that for the formation of the monochlorocopper (II) ion. Several other investigators have also investigated the absorption spectra of cupric chloride in aqueous mixtures with other chlorides. (10, 23, 49).

Dixmier (24), interestingly, has ascribed the decrease in magnetic susceptibility of 0.2 molar $CuCl_2$ in HCl solutions (up to 12 M HCl) to the formation of hexachlorocuprate (II) ions. However, this seems improbable.

Addition of $CuCl_2$ to HCl solutions causes a decrease in the electrical conductivity; the effect is increased by increased HCl concentration and has been attributed to the formation of $CuCl_3^-$ and $CuCl_4^{--}$ ions in the solutions. (94).

Herrera (44) has offered an explanation, based on the formation of the tetrachlorocuprate (II) ion, for the variation of the chloride ion activity coefficient with concentration in cupric chloride solutions. Yajnik and Uberoy (105) similarly based their explanation of the abnormally high viscosity of $CuCl_2$-HCl-H_2O solutions on the assumption of extensive $CuCl_4^{--}$ ion formation.

Important reviews of current theoretical and experimental developments in the field of electrolyte solutions are given in volumes 1 through 6, 8, and 9 of Annual Reviews of Physical Chemistry. Burtch (16) has also reviewed the recent literature relative to the general theory of concentrated electrolyte solutions, and Gootman (37) has considered the problem of the calculation of activities in electrolyte mixtures from the Gibbs-Duhem equation and the cross-differentiation relations proposed by McKay (70).

In a recent paper dealing with the present state of the theory of electrolyte solutions Kraus (62) has commented that an understanding of concentrated electrolyte solutions will only come from greatly expanded knowledge of such factors as

(1) the ion fraction, i.e., the fraction of electrolyte present as ions,

(2) the nature of the ions and their interactions with one another,

(3) the nature of ion-solvent interactions,

(4) the effect of ion-solvent interactions on ion association,

(5) the effect of the ions on the state of the solvent.

The importance of the factors listed above has been recognized by others, notably, Scatchard (97), Robinson and Stokes (89), and Glueckauf (36) in their respective theoretical treatments of the thermodynamic behavior of solutions of completely dissociated electrolytes.

Because ionic association and solvation are the two factors which determine to a large measure the magnitude of the chemical potential in concentrated solutions, a brief résumé of the important developments concerning these effects will be given, and even though it involves some repetition, the reader will find it useful in subsequent discussions.

The concept of ionic solvation was introduced by Bjerrum (89) as early as 1918 to account for the activity coefficients of some 1-1 electrolytes at concentrations of the order of several moles per liter. In a review of ionic solvation, Brockris (13) discuss some of the former concepts of ionic solvation and suggests a more precise definition of this term. Brockris proposes that total solvation be divided into "primary" and "secondary" solvation; i.e., solvent molecules attached to the ions in solution so as to form with the ion a separate entity constitute the "primary" solvation, and all electrostatic interactions which are not included in "primary" solvation make up the "secondary" solvation. His review includes a critical survey of some of the more important experimental methods for determining solvation numbers, from which the conclusion is drawn that those methods which give concordant and rational values of solvation numbers of less than 10 measure "primary" solvation whereas methods giving values greater than 10 probably measure both "primary" and all or part of the "secondary" solvation. Other reviews of recent work on ionic hydration in aqueous solutions have been published by Samoilov (96) and Haase (39).

The principle of specific interaction of ions was postulated by Brönsted (14), who concluded from his solubility studies of slightly soluble electrolytes in mixed salt-solvent systems that ions are uniformly influenced by ions of their own sign and, therefore, specific effects depend chiefly upon the interactions of ions of opposite sign and the salting-out effect of the solvent. This theory may be shown to lead to equations having the same mathematical form as the empirical rule of Harned (41), referred to earlier. The basis for Brönsted's theory of specific interaction of ions has been recently re-examined by Scatchard and Brechenridge (98). These authors give a critique of Brönsted's theory and suggest that a very useful approximation for the activity coefficient, that usually holds up to high concentrations, may be obtained when this theory is paired with the Debye-Hückel term for the electrostatic part of the interactions.

Almost all theoretical treatments of electrolyte mixtures begin with the Debye-Hückel theory (21), introduced in 1923 to account for the electrostatic attractions in very dilute solutions. This has been highly successful in representing the activity coefficient of completely dissociated 1-1 and 2-1 valence-type electrolytes. The complete theoretical expression has been thoroughly tested and found to hold quite well up to an ionic strength of about 0.1, but in its limiting form it is seldom applicable above about 0.01. (84). Guggenheim (38) combined the Debye-Hückel equation with a linear term for expressing Brönsted's concept to derive the theoretical expression applicable to moderately concentrated solutions of mixed electrolytes, and Rysselberghe and Eisenberg (95) have similarly extended the Debye-Hückel equation into a one parameter equation for the activity coefficient. They have based their theory upon a statistical consideration of the volumes mutually excluded to the ions within the solution.

Bernal and Fowler (6) proposed a rather successful model for the structure of water from Raman spectra and X-ray data. With the aid of this model they estimated the degree of hydration of several ions and concluded that positive ions of large radii and most negative ions are not hydrated, whereas positive ions of smaller radii are probably hydrated to various degrees. Eley and Evans (27) and Verwey (103) have also proposed models for ionic environments and have calculated hydration energies on the basis of simple electrostatic interactions. Latimer, Pitzer, and Slansky (64) calculated the free energies of hydration for alkali halide ion-pairs and found their results could be made to agree with the simple expression derived by Born (11), provided the ionic radii were suitably modified so as to correspond to the radii of the cavities in the solvent. Born's equation, based upon simple electrostatic theory, gives the free energy of hydration as a function of only the radius of the ion and dielectric of the medium. A hydration-association model for strong electrolytes in dilute solutions has also been proposed by Frank (33). The final equation is very similar to the one given by Guggenheim (38).

Stokes and Robinson (102) have developed a remarkably successful equation for the activity coefficient of nonassociated electrolytes in binary solutions which takes into consideration both the Debye-Hückel electrostatic ion-ion interaction and hydration of ions in solution. These authors have stated that although their model is successful in accounting for the behavior of many electrolytes, and especially in concentrated solutions, it fails in two important respects. These are: (a) the hydration numbers required are in some cases unreasonably large, and (b) the hydration number of a given cation is often found to vary with the nature of the associated anion, even when it is believed that the anion is not hydrated. (88). These authors also point out, however, that the unreasonably large hydration numbers probably result because the hydration effect is made to include a number of other effects, one of the principal ones arising from the mixing of particles of different volumes. (89). Moore, Gootman, and Yates (76) have derived an expression for hydration in electrolyte mixtures containing any number of solutes from the Gibbs-Duhem relation and the Debye-Hückel equation that is essentially an extension of the Stokes-Robinson equation. Robinson and Stokes (91) have also extended their original equation to mixtures following a somewhat different approach. The hydration equation of Stokes and Robinson and its extension by Moore et al. are discussed in detail together with several examples in Chapter VI.

Betts and MacKenzie (7) determined the activity coefficient of alkali chlorides in low concentration in concentrated HCl solutions and applied the Stokes-Robinson equation to the results to calculate the distance of closest cation-anion approach, i.e., $\overset{\circ}{\underline{a}}$ values. The calculations showed that the $\overset{\circ}{\underline{a}}$ values for the alkali chlorides decreased while those for HCl increased with increased acid concentration. Burtch (16) evaluated hydration numbers for HCl and $MnCl_2$ in their aqueous mixtures from Glueckauf's (36) equation based on the Stokes-Robinson hydration model and mole-fraction statistics. He used these numbers in the extended form of the Stokes-Robinson equation (76) to calculate the activity coefficient of HCl and $MnCl_2$. Glueckauf (36) also used the Stokes and Robinson hydration model to develop a theory for single electrolytes in which the co-volume effect, or effect of mixing particles of different size, has been taken into consideration through the use of the volume statistics developed by Flory (29) and Huggins (47). The hydration numbers obtained do not show the abnormalities exhibited by corresponding values obtained with the Stokes-Robinson equation. For example, the cation hydration numbers are independent of the anion present. A more detailed discussion of Glueckauf's equation is given in Chapter VI. A hydration model very similar in many respects to Glueckauf's has recently been proposed by Miller (71).

Mayer (68) has formulated a statistical mechanical model for the activity coefficient of single strong electrolytes in dilute solutions that is unique in that it does not employ the Debye-Hückel theory as a starting point. Poirier in two very important papers (80, 81) derived several thermodynamic functions from Mayer's theory. The expression derived for the mean ionic molar activity coefficient gives good agreement with experimental data for NaCl up to 0.4 molar and for $CaCl_2$ up to 0.07 molar, but the agreements for 2-2 and 3-1 electrolytes are good only up to concentrations of 0.01 and 0.017 molar, respectively. Nevertheless, the theoretical implications of the method are of great importance. Eigen and Wicke (26) have developed a theory of the chemical potential that represents the approximate behavior of electrolyte solutions at higher concentrations with only a few parameters by taking into account the electrostatic interaction of the ions, the incomplete dissociation of the solute, and the co-volume effect of hydrated ions. A modification of the distribution law upon which the Debye-Hückel treatment rests is involved.

The number of water molecules tightly bound (primary hydration) to $CuCl_2$ has been studied by employing nonaqueous solutions. Absorption spectral data of anhydrous cupric chloride in ethanol-water mixtures have led to the conclusion that the hydration of this salt depends on the ethanol concentration and that the tendency for the $CuCl_2$ to solvate is in the order of $H_2O > CH_3OH > C_2H_5OH$. (82). Similar investigations showed the hydration number of $CuCl_2$ in ethanol-water mixtures to increase with salt concentration until a limiting hydration number of 4 is reached. (72). It seems significant that the hydration number of copper in $CuSO_4 \cdot 5H_2O$ is also 4.

CHAPTER II

EXPERIMENTAL

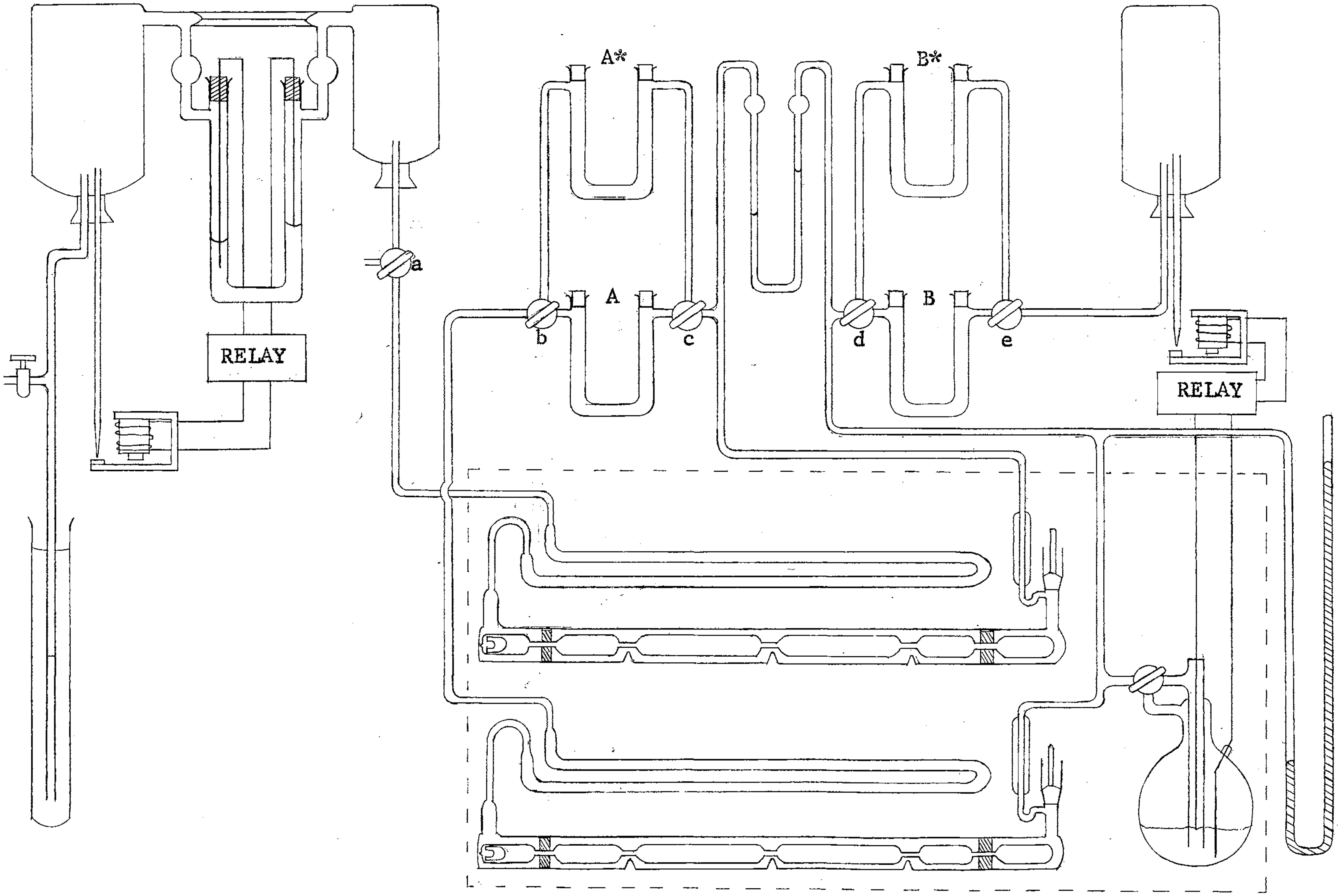
Description of Apparatus

The vapor pressure measuring apparatus employed in this research combined some of the most desirable features of several apparatus that have proved successful in measuring vapor pressures of liquids by the gas transpiration technique (see Fig. 1). In order to facilitate the discussion of the apparatus separate consideration is given to the gas-flow and pressure-control system, to the saturators or gas-saturation apparatus and to the absorption train.

The gas-flow and pressure-control system was essentially that described by Bechtold and Newton (4) with the exception that the flowmeter and its accessories were not used during the latter part of the investigation. Constant flow rate was maintained by use of a needle value inserted in the system between the nitrogen pressure regulator and the safety valve. (16).

The gas saturators were very similar to those developed by Smith, Combs and Googin (100). A few modifications were made, such as the omission of components for the drying cycle and an increase in the diameters of the rotating drums, from 25 mm. to 28 mm., and of the solution cells, from 38 mm. to 42 mm. As pointed out by Smith et al., this type of saturator has the outstanding features of negligible pressure drop and almost complete gas saturation at each of the four stages.

FIG. 1 APPARATUS FOR VAPOR PRESSURE MEASUREMENTS



The saturators are also advantageous in that they require only a small amount of liquid and in that stirring is continuous during the course of a measurement.

Preliminary determinations indicated incomplete saturation of carrier gas. This difficulty was readily overcome by passing the carrier gas through surface-flow type presaturators before passing it through the rotating-drum saturators. The presaturators were made of 70 cm. long, 1.5 cm. O.D. U-shaped glass tubes, and were placed parallel to the rotating-drum saturators on the saturator racks in the thermostated water bath.

The drum-rotating mechanism and saturator racks were mounted on a one-half inch brass framework; this in turn was fastened securely to the water bath. The drum-rotating mechanism consisted of two 4-ounce alnico magnets encased in glass and rotated through a belt-drive by a 1/15 h.p. universal motor. The speed of the motor was controlled manually with a Powerstat. Two-ounce magnets hermetically sealed in the ends of the saturator drums were magnetically coupled to the drum-rotating mechanism. The reference-saturator and the sample-saturator drums were rotated at the same speed, normally 200 to 300 r.p.m.

The absorbers consisted of 100 ml. U-type drying tubes of which the "solvent" set was filled with magnesium perchlorate and the "solution" set with sodium hydroxide-impregnated asbestos and 2 cm. of magnesium perchlorate on the exit side. Glass wool was packed above the absorbent material to prevent mechanical loss. The absorbers were stoppered with rubber stoppers and rubber caps were placed over the gas entrance and exit tubes when they were not in use.

The saturators, presaturators, manostat, drum-rotating mechanism and saturator racks were all kept in a constant-temperature bath that was maintained at 25.00 ± 0.01°C. by a mercury-toluene thermoregulator which activated a thyratron relay. The thermometer used was graduated in 0.05° divisions and standardized by the Continental Oil Company at Ponca City, Oklahoma, against a thermometer calibrated by the National Bureau of Standards. The bath water was circulated by a submersible pump which gently swirled the water in turbulent flow around the inside of the bath.

Both absorbers and differential oil manometer were enclosed in a constant-temperature air bath that was supported about eight inches above the water bath. The temperature of the air bath, which was not critical, was maintained somewhere in the range of from 30.0 ± 0.02°C. to 37.0 ± 0.02°C. throughout the course of the investigation. The desired temperature was controlled by a mercurial thermoregulator which activated a Fisher-Serfass electronic relay that in turn controlled the 100 watt light bulb used as a heater. The air was agitated by a small electric fan.

Preliminary density determinations of the di-n-butyl phthalate used in the differential manometer showed that 1 mm. of height of this fluid was equivalent to 0.0764 mm. Hg at 30° and 0.0761 mm. Hg at 37°. The conversion factor of 0.076 mm. Hg per mm. of manometric fluid was used for all measurements.

Auxiliary heaters consisting of nichrome wire heating elements were coiled around the exit tubes of the presaturators and saturators in order to prevent condensation of vapors in parts of the flow system that were not thermostated. The current passing through the heating system was regulated manually by a Powerstat in such a manner that the temperature in this part of the system was kept between 27° and 30°.

At places in the flow system were flexibility was required, connections were made by butting together the ends of glass tubing and connecting them with surgical rubber tubing. The absorbers were also connected into the system by surgical rubber tubing. These rubber connectors were frequently replaced so as to prevent leakage due to deterioration of the rubber. The ground-glass ball-and-socket joints used to connect the presaturators and saturators to the flow system were gasketed with gaskets cut from 0.5 mm. rubber tissue. All stopcocks and the ground-glass plugs in the saturators were lubricated with Apiezon "N" lubricating grease.

The manostat and flowmeter used to control the pressure and gas flow rate within the system were of the same general design as those used by Bechtold and Newton (4). The conducting liquids in both were di-n-butyl phthalate saturated with mercuric iodide.

The pressure-control valve (or gas-exit valve) and flow-rate valve were fashioned from 110 volt relay switches. The relays were actuated by the output from 2D21 thyratron tubes, which in turn were controlled by the make-and-break circuits in the manostat and flowmeter.

The pressure in the second saturator, i.e., the "solution" saturator, was measured by means of a mercury barometer. Pressures read from this barometer were corrected to 0°C. by multiplying the pressure reading by the ratio of the density of mercury at the given temperature and the density of mercury at 0° C. Altitude-gravity, latitude-gravity and capillary depression corrections were found to be unnecessary. The pressure in the first saturator, i.e., the "solvent" saturator, was calculated from the pressure in the second saturator and the pressure reading (mm. Hg) of the di-n-butyl phthalate differential manometer.

An Ainsworth DLB-type chainomatic balance was used for all weighings except those required in the preparations of solutions. Permas analytical balance weights adjusted to Class S tolerances of the National Bureau of Standards were used. The solution balance weights were calibrated by Burtch (16) using the method of substitution as described by Kolthoff and Sandell (59).

Vapor pressure procedure. The saturators and presaturators were first cleaned with hot chromic acid and rinsed thoroughly with distilled water and finally with ethyl alcohol. After drying, the saturators were rinsed with a small portion of the solution whose vapor pressure was to be measured and then filled to the proper levels. The saturators and presaturators were next mounted in the constant-temperature bath and connected to the flow system as described in the preceding section. The water-bath temperature was adjusted to 25.00 ± 0.01°C., and the auxilary heating system and air bath were put in operation. The apparatus was now allowed to remain in this condition over night.

The absorbers, after having been packed with absorbent material and wiped with a damp lintless cotton cloth, were allowed to stand in a covered container over night. The following morning the absorbers were placed in an open container by the balance for one hour before they were weighed. After weighing, the absorbers were placed in the air bath and connected to the flow system.

The apparatus was tested for leaks before each determination by putting a small pressure in the system and closing stopcocks a, b, and e, (Fig. 1). Pressure changes in either of the isolated parts of the system could be detected by the differential manometer. The absence of any changes in the manometer levels indicated that the system was free of leaks, and the test pressure was then released.

The drum-rotating mechanism was started and the saturator drums were rotated at a constant speed of approximately 250 r.p.m. The carrier-gas (nitrogen) flow rate and pressure within the system were adjusted to the proper values while the gas was passed through a dummy set of absorbers, A* and B* in Fig. 1. The apparatus was allowed to run for one hour before the gas flow was directed through the weighed absorbers, (A and B). The mercurial barometer and differential manometer were read at the beginning and just prior to the termination of each experiment. The absorbers were removed after the determination and reweighed following the procedure previously outlined. A second determination on the same solution was usually begun immediately.

Analytical Methods

Analysis for chloride in the absorbers. The contents of the NaOH absorber were placed in a 250 ml. beaker and the absorber tube rinsed first with distilled water, then with 25 percent (by volume) $HClO_4$ and finally with several small portions of distilled water. The excess NaOH was neutralized to a phenolphthalein endpoint with $HClO_4$ and the solution analyzed by titrating with standard $AgNO_3$ solution by the electromotive force method. (57).

The potentiometric titration employed a saturated-calomel reference electrode of large area. (58). This reference half cell was contained in a 400 ml. wide-mouthed bottle and electrical contact was made with the solution by a low-resistance salt bridge. A 1.5 cm. O.D. U-shaped tube having one third of its length filled with a gel of saturated KCl in agar and the remaining two thirds filled with a gel of two molar

NH_4NO_3 in agar served as the salt bridge. The saturated KCl end of the salt bridge was inserted into the wide-mouthed bottle containing the saturated-calomel half cell while the two molar NH_4NO_3 end dipped directly into the titrant. The indicating electrode was of the silver-silver chloride type.

The 250 ml. beaker containing the chloride solution was placed in an ice water bath during the titration to decrease the solubility of AgCl. The solution was continually stirred by means of a Magna-Stir magnetic stirrer. A Leeds and Northrup student-type potentiometer and a 1.34 volt mercury battery were used in the measurement of the voltages of the titration cell. The mercury battery voltage was constant over long periods of time and since the endpoint in this type of titration is determined by the voltage change and not its absolute value an extremely constant voltage standard cell was not required.

Analysis for copper. The copper content of the various solutions was determined by electrolysis. Two ml. of concentrated H_2SO_4 was added to ca. 5 g. of $CuCl_2$ solution in a 180 ml. electrolytic beaker. The chloride content was first decreased by heating this mixture gently over an electric heater until $CuSO_4$ began to precipitate. The remaining products were then diluted to 100 ml. with distilled water, and 1 ml. of concentrated HNO_3 was added. The copper was now determined by the electrodeposition method using a Sargent electro-analyzer. (61). Excellent results were obtained with an applied voltage of approximately 2.5 volts and a current of 0.2 amperes.

Analysis for sulfuric acid. The concentration of H_2SO_4 was determined by acid-base titration with standard NaOH. Potassium acid phthalate was used as the primary standard in the standardization of the base.

Analysis for chloride ion. The chloride ion content of the various solutions was determined gravimetrically as silver chloride. (60).

Analysis of solid phases. The composition of the solid phase in equilibrium with the ternary saturated solutions was determined by the wet-residue method of Schreinmaker. (28). The wet crystals were blotted with filter paper, weighed, dissolved in distilled water and analyzed for their copper and chloride content. A triangular graph representing the three-component system was constructed with lines drawn through the points corresponding to the concentration of each saturated solution and the composition of the wet crystals from the same solution. The intersection of the resulting tie-line with the $CuCl_2$-H_2O axis determined the composition of the solid phase in each case.

Preparation and Standardization of Solutions

Hydrochloric acid solutions. Binary solutions of HCl-H_2O were prepared by diluting concentrated C.p. HCl with distilled water. The molalities of these solutions were determined by an acid-base titration with standard NaOH.

Copper chloride solutions. Aqueous $CuCl_2$ solutions were prepared by addition of C.p. $CuCl_2 \cdot 2H_2O$ to distilled water. The solutions were adjusted to the desired molalities by the addition of small quantities of anhydrous $CuCl_2$ or water followed by a gravimetric chloride analysis.

Ternary solutions. The three-component systems, $CuCl_2$-HCl-H_2O, were prepared by adding $CuCl_2 \cdot 2H_2O$ to a HCl solution of approximately the desired molality until the concentration of copper chloride was near to that at saturation. The HCl concentration was then adjusted to the proper molality. Each addition of salt or acid was followed by an electrodeposition analysis for copper and a gravimetric analysis for chloride.

Stock solutions of HCl having the same concentrations as those in the ternary solutions were prepared by diluting C.p. HCl with distilled water. The HCl concentrations in these solutions were adjusted to the molality of the HCl in the corresponding ternary solutions by the addition of small quantities of acid or water. Each addition was followed by a gravimetric chloride analysis.

Series of solutions of constant HCl concentration and varying salt concentration were prepared by mixing weighed amounts of the ternary stock and corresponding acid stock solutions. The weighing was done on a solution balance and weighings were generally made with an accuracy of better than ±0.005 percent.

Saturated solutions. All saturated solutions were prepared by the addition of small quantities of anhydrous $CuCl_2$ to portions of the nearly saturated ternary stock solutions. The solutions were kept at 25° in a constant-temperature bath for not less than a week with frequent agitation. The composition of the liquid phase was determined by an electrodeposition analysis for the copper ion and a gravimetric analysis for the chloride ion.

Preparation of sodium hydroxide-asbestos mixture. A dry mixture of NaOH and asbestos was prepared by drying in an oven at 110° a slurry of Gooch-filter quality asbestos and approximately 4 molar NaOH. The dried mixture was ground to a fine consistency in a Waring Blendor.

Chemicals

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

Cupric Chloride (dihydrate): J. T. Baker Chemical Co., Baker's analyzed reagent grade, lot 4057; Eimer and Amend, E. & A. tested purity reagent grade. Both companies listed an assay of not more than 0.005% iron and 0.005% of other metals such as nickel.

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. Fredrick Smith Chemical Co. This material gave a negative test for chloride with silver ion.

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 material was distilled before it was used.

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

Asbestos: Powhatan Mining Co., Gooch acid-washed grade. The washings from this material gave a negative chloride test with silver ion.

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

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

CHAPTER III

DETERMINATION OF ACTIVITIES

Methods applicable to the determination of activities of the three components in the ternary system, $CuCl_2$-HCl-H_2O, are limited from an experimental standpoint. Although, in principle the activities of both solutes can be determined from measurements of the solvent activity, in general it has not been found to be practicable to use such a method because of the large amount of accurate experimental data required. (20, 70). Freezing-point depression and boiling-point elevation measurements are, therefore, not very useful in systems of two solutes because these methods only give information about the solvent activity. Thus, although measurements of this type are often used to determine the solvent's activity, some additional method is required to obtain the activity of one of the solutes. The activity of $CuCl_2$, unfortunately, cannot be obtained from electromotive force measurements. All efforts to find an electrode reversible to the copper (II) ion with a reproducible potential in concentrated chloride solutions have been unsuccessful. (46). However, the electromotive force method is applicable to the determination of HCl activities in the presence of copper (II) ion. Technical difficulties and the inherent limitations of the methods themselves prevented the use of such phase equilibria as ion exchange, liquid-liquid extraction and solubility measurements for the determination of the $CuCl_2$ activity. Therefore, it was necessary to separately measure the activity of the

HCl and H_2O and to calculate that of the $CuCl_2$.

Gas Transpiration Method

The gas transpiration method provides a means by which the vapor pressures of the volatile components, HCl and H_2O, can be determined simultaneously.

The principle of this method, as applied to the measurement of the partial pressures of HCl and H_2O vapor, is extremely simple. An inert gas is saturated with H_2O vapor as it passes through a saturator containing pure water; the H_2O vapor is then collected in an absorbent material, and the carrier gas is finally passed through a second saturator containing aqueous HCl. Water and HCl vapors in the carrier gas are collected in a second absorber. Analysis of the saturated vapors gives the mole fractions in the gas phase, and the partial pressures are calculated from Dalton's Law,

$$P = NP^* \qquad (1)$$

where $\underline{P}$ and $\underline{N}$ are the partial pressure and mole fraction of the given component, respectively, and $\underline{P}^*$ is the experimentally determined total pressure within the system.

Activities, $\underline{a}$, of the volatile components are then calculated by assuming that the partial pressures, $\underline{P}$, may be substituted for the fugacities, $\underline{f}$,

$$a = f/f^o = P/P^o \qquad (2)$$

Here $\underline{f}^o$ and $\underline{P}^o$ represent the fugacity and pressure in the standard state. (55).

The Gibbs-Duhem Equation

Use of the Gibbs-Duhem equation extended to three-component systems permits one to calculate the activity of a third component from the activities of the other two provided the mole ratios of any two components are maintained constant throughout a particular set of measurements. The following derivation shows how the activity of component 3 can be calculated for a three-component system in which the mole ratios of components 1 and 2 are constant.

Under isothermal and isobaric conditions the Gibbs-Duhen equation for a three-component system may be written

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

where $\underline{n}_1$, $\underline{n}_2$, $\underline{n}_3$, represent the moles of each component and $\underline{\bar{\bar{F}}}_1$, $\underline{\bar{\bar{F}}}_2$, and $\underline{\bar{\bar{F}}}_3$ their respective partial molal free energies. By definition we have,

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

When equation (4) is differentiated with respect to $\underline{n}_3$ at constant $\underline{n}_1$ and $\underline{n}_2$ and the result is substituted into equation (3), one obtains

$$\left[n_1\left(\frac{\partial \ln a_1}{\partial n_3}\right)dn_3 + n_2\left(\frac{\partial \ln a_2}{\partial n_3}\right)dn_3 + n_3\left(\frac{\partial \ln a_3}{\partial n_3}\right)dn_3\right]_{n_1,n_2} = 0 \qquad (5)$$

Dividing equation (5) by $\underline{n}_3$ and converting to molal concentration units leaves

$$\left[\frac{m_1}{m_3}\left(\frac{\partial \ln a_1}{\partial m_3}\right)dm_3 + \frac{m_2}{m_3}\left(\frac{\partial \ln a_2}{\partial m_3}\right)dm_3 + \left(\frac{\partial \ln a_3}{\partial m_3}\right)dm_3\right]_{m_1,m_2} = 0 \qquad (6)$$

Integration and rearrangement of equation (6) gives

$$\ln\frac{a_3}{a_3^*} = m_1\int_{m_3}^{m_3^*}\frac{d\ln a_1}{m_3} + m_2\int_{m_3}^{m_3^*}\frac{d\ln a_2}{m_3} \qquad (7)$$

where the asterisk superscripts refer to the upper limits of the intergration. Thus, if $CuCl_2$ is designated as component 3 and relations expressing $\underline{a}_1$ and $\underline{a}_2$ as functions of the $CuCl_2$ molality $\underline{m}_3$ are found and substituted into equation (7), the activity of $CuCl_2$ can be calculated as a function of its molality in solutions of constant acid concentration.

The activity of $CuCl_2$ similarly can be determined as a function of the HCl molality if the Gibbs-Duhem equation is integrated under the condition that the mole ratio of salt-to-water is constant. Differentiation of equation (4) with respect to $\underline{n}_2$ at constant $\underline{n}_1$ and $\underline{n}_3$ and substitution into equation (3) gives

$$\left[n_1\left(\frac{\partial \ln a_1}{\partial n_2}\right) dn_2 + n_2\left(\frac{\partial \ln a_2}{\partial n_2}\right) dn_2 + n_3\left(\frac{\partial \ln a_3}{\partial n_2}\right) dn_2\right]_{n_1,n_3} = 0 \qquad (8)$$

After dividing through by $\underline{n}_3$ and converting to molal concentration units one obtains

$$\left[\frac{m_1}{m_3}\left(\frac{\partial \ln a_1}{\partial m_2}\right) dm_2 + \frac{m_2}{m_3}\left(\frac{\partial \ln a_2}{\partial m_2}\right) dm_2 + \left(\frac{\partial \ln a_3}{\partial m_2}\right) dm_2\right]_{m_1,m_3} = 0 \qquad (9)$$

Rearrangement and integration of equation (9) gives

$$\ln \frac{a_3}{a_3^*} = \frac{m_1}{m_3} \ln \frac{a_1^*}{a_1} + \frac{1}{m_3}\int_{m_2}^{m_2^*} m_2 \, (d\ln a_2) \qquad (10)$$

Again if empirical relations for $\underline{a}_1$ and $\underline{a}_2$ as functions of the HCl molality are substituted into the above equation, the activity of the salt can be calculated as a function of acid molality in solutions of constant salt concentration.

CHAPTER IV

DATA AND CALCULATIONS

In order to determine the accuracy with which the activities of H_2O and HCl could be measured by the technique employed in this research, preliminary measurements were made with solutions of known activity. The results of such measurements made on aqueous H_2SO_4 solutions at 25° are compared in Table I with literature values accepted as isopiestic standards. (101). Since the partial pressure of SO_3 in the vapor phase was negligible, it was not included in the calculations. (1, 67).

Measurements also were made of the partial pressures of HCl and H_2O in aqueous HCl solutions at 25°. The results are listed in Table II. A graphical comparison of the experimental partial pressures of HCl with those determined by Bates and Kirschman (3) is given in Fig. 3. Similar comparisons of the experimental partial pressures of H_2O in the solutions with those determined indirectly by Randall and Young (85), and with those compiled by Zeisberg (108) are shown in Fig. 2.

In all tables the last digit in columns marked with an asterisk was retained only for computational purposes unless otherwise noted.

Vapor Pressure Measurements

Ternary systems. Vapor pressure measurements were made on three series of ternary solutions; in each series the mole ratios of HCl to H_2O were constant, and the $CuCl_2$ concentration was varied from 0.2

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. Hg)	$\bar{P}_{H_2O}$ (mm. Hg)	Activity H_2O	P_{H_2O} (mm. Hg)	Activity H_2O
0.000	11	23.75	23.75	0.9996	23.76	1.0000
2.609	14	20.85	20.84	0.8771	20.84	0.8771
2.609	16	20.83				
3.771	24	18.93	18.94	0.7971	18.93	0.7967
3.771	25	18.94				
4.530	22	17.55	17.56	0.7391	17.58	0.7399
4.530	23	17.56				

TABLE II

VAPOR PRESSURE DATA FOR THE SYSTEM $HCl-H_2O$

Molality HCl	Run Number	P_{HCl*} (mm. Hg)	$\bar{P}_{HCl*}$ (mm. Hg)	Activity HCl*	P_{H_2O} (mm. Hg)	$\bar{P}_{H_2O}$ (mm. Hg)	Activity H_2O
4.70	78-2	0.0444	0.0435	113.1	18.04	18.03	0.7588
4.70	78-3	0.0424			18.03		
4.70	78-4	0.0436			18.02		
5.86	37-1	0.1254	0.1254	325.0	16.11	16.09	0.6772
5.86	39-1	0.1254			16.08		
7.00	45-1	0.3599	0.3559	925.6	14.17	14.18	0.5968
7.00	56-1	0.3554			14.16		
7.00	56-2	------			14.20		
7.00	56-4	0.3515			-----		
7.94	32-1	0.8342	0.832	2.163	12.67	12.63	0.5316
7.94	33-1	0.8286			-----		
7.94	34-1	------			12.61		
7.94	35-1	0.8252			12.59		
7.94	36-1	0.8386			12.63		
8.54	29-1	1.349	1.354	3.520	11.68	11.66	0.4907
8.54	30-1	1.359			11.63		
8.54	31-1	-----			11.66		
9.00	76-1	1.963	1.966	5.112	11.13	11.14	0.4688
9.00	76-2	1.969			11.15		

molal to saturation in intervals of approximately 0.25 molal units. Partial pressures of H_2O and HCl were measured above a series of solutions in which the $CuCl_2$ molality was constant and the HCl concentration varied from 4.7 to 9.0 molal in 0.5 molal intervals.

A system consisting of mixtures of $CuCl_2$ and HCl at constant total chloride concentration was also studied. Most of the data for this study were obtained from the afore-mentioned constant-acid and constant-salt series; however, additional measurements were made on two solutions containing 4.0 and 4.5 molal $CuCl_2$ in 2.0 and 1.0 molal HCl solutions, respectively. The vapor pressure of H_2O was also found for saturated aqueous $CuCl_2$. The results of these measurements are listed in Table VII.

Calculation of partial pressures. Vapor pressures of all solutions were determined by the comparative gas-transpiration method as outlined in the preceding chapter, and partial pressures of H_2O and HCl were computed from the following relations based upon Dalton's Law. (83).

The number of moles of inert gas (nitrogen) was calculated by

$$n_x = n_w \frac{P_1}{P^o} - n_w \qquad (1)$$

where: P_1 = total pressure in the reference saturator,

P^o = vapor pressure of pure H_2O at 25°,

n_w = moles of water collected in the reference absorber,

n_x = moles of nitrogen gas passed through the system.

The amount of HCl absorbed in the second absorber was determined by a potentiometric chloride analysis and the corresponding amount of H_2O vapor was calculated by difference from the weight increase of the absorber. The vapor pressure of HCl was then obtained from the relation

$$P_{HCl} = \frac{n_2}{n_x + n_w' + n_2} P_2 \qquad (2)$$

where: P_{HCl} = vapor pressure of the hydrochloric acid,

P_2 = total pressure in the solution saturator,

n_2 = moles of hydrogen chloride collected in second absorber,

n_w' = moles of water vapor collected in the second abosrber,

n_x = moles of carrier gas passed through the system.

The partial pressures of H_2O in the solutions were calculated similarly.

Calculation of Activities

It follows from the definitions of fugacity and activity that for a given component

$$\bar{F} - \bar{F}^o = RT \ln f/f^o = RT \ln a \qquad (3)$$

where: $\bar{F}$ = the partial molal free energy in the given state,

$\bar{F}^o$ = the partial molal free energy in the standard state,

f = the fugacity in the given state,

f^o = the fugacity in the standard state,

a = the activity in the given state.

It is evident from the above equation that the activity is a measure of the differences in partial molal free energies between any particular state and the standard state; therefore, precise definitions of the standard states must be given if the activities are to have significance.

Standard state of the solvent. In keeping with convention, pure liquid water at 25° and 1 atm. of pressure was chosen as the standard state of the solvent. The value 23.756 mm. Hg was taken as the vapor pressure of the solvent in the standard state, and this was assumed to be equal to the fugacity of pure water under these conditions. (104). The activity of the water in all solutions at 25° and 1 atm. of pressure were calculated by the following equation

$$a_1 = \frac{P_1}{23.756} \tag{4}$$

where a_1 and P_1 are the activity and vapor pressure of the water in any given solution, respectively.

Standard state of hydrochloric acid. The vapor pressure of HCl in a hypothetical mean one-molal solution of the acid was determined by comparing the HCl activities obtained from electromotive force measurements by Randall and Young (85) with the vapor pressures of HCl solutions measured in this research. (56). An average value of $(2.60 \pm 0.02) \times 10^3$ was obtained for the ratio of the activity to the vapor pressure. This value compares with the value of $(2.67 \pm 0.02) \times 10^3$ calculated from the data of Bates and Kirschman (3), which were considered the most reliable values available by Randall and Young. The activities of HCl in both the binary and ternary solutions were calculated using the mean value of 2.60×10^3 for the ratio.

Since

$$\frac{a_{HCl}}{P_{HCl}} = \frac{1}{P_2^o} = k \tag{5}$$

and

$$a_2 = \frac{P_2}{P_2^o} \tag{6}$$

then

$$a_2 = k \cdot P_2 = 2600\ P_2 \tag{7}$$

The results of the experimental vapor pressure measurements and corresponding calculated activities are given in Tables III through VII.

Standard state of the cupric chloride. The saturated solution of cupric chloride in each constant acid series was chosen as a reference state and the $CuCl_2$ activity in the reference state was related through the solid phase to that in the conventional standard state; i.e., a hypothetical mean one-molal solution of $CuCl_2$ in H_2O. This choice of a standard state permitted comparisons to be made between the $CuCl_2$ activities in different acid solutions and avoided the necessity for an extrapolation of the vapor pressure data to the state of an infinitely dilute solution of $CuCl_2$ in aqueous HCl.

For the solid hydrate in equilibrium with a binary solution of $CuCl_2$ one may write

$$CuCl_2 \cdot nH_2O \rightleftharpoons CuCl_2 + nH_2O \qquad (8)$$

Since at equilibrium the free energy change of the system is zero one has

$$\bar{\bar{F}}_h^o + RT \ln a_h = \bar{\bar{F}}_s^o + RT \ln a_s + n\bar{\bar{F}}_w^o + nRT \ln a_w \qquad (9)$$

where the subscripts h, s, and w refer to the hydrate, salt and water, respectively. Equation (9) upon rearrangement becomes

$$(\bar{\bar{F}}_h^o - \bar{\bar{F}}_s^o)_b = n(\bar{\bar{F}}_w^o)_b + RT(\ln a_s + n \ln a_w - \ln a_h)_b \qquad (10)$$

where the subscript b indicates the binary system.

Since the hydrochloric acid does not enter into the hydrate-solution equilibrium, an equation similar to equation (10) may be written for the ternary system also

$$(\bar{\bar{F}}_h^o - \bar{\bar{F}}_s^o)_t = n'(\bar{\bar{F}}_w^o)_t + RT(\ln a_s + n' \ln a_w - \ln a_h)_t \qquad (11)$$

After equating equations (10) and (11) and rearranging one obtains

$$(n - n')\bar{\bar{F}}_w^o = RT \left[(\ln a_s + n' \ln a_w)_t - (\ln a_s + n \ln a_w)_b \right] \qquad (12)$$

When the solid phases in the ternary and binary solution are identical, as was the case in this investigation, then n and n' are equal and equation (12) may be written as

TABLE III

VAPOR PRESSURE DATA FOR THE $CuCl_2$-HCl-H_2O SYSTEM

4.7 MOLAL HYDROCHLORIC ACID SERIES

Molality $CuCl_2$	Run Number	P_{HCl} (mm. Hg)	$\bar{P}_{HCl}$ (mm. Hg)	Activity HCl*	P_{H_2O} (mm. Hg)	$\bar{P}_{H_2O}$ (mm. Hg)	Activity H_2O
0.2342	84-1	0.0520	0.0517	134.4	17.66	17.65	0.7428
0.2342	84-3	0.0514			17.64		
0.4684	80-1	0.0612	0.0610	158.6	17.32	17.32	0.7290
0.4684	80-2	0.0608			17.31		
0.7026	81-1	0.0717	0.0713	185.4	16.97	16.99	0.7151
0.7026	81-2	0.0708			17.01		
0.9368	82-3	0.0817	0.0821	213.5	16.67	16.67	0.7016
0.9368	82-4	0.0824			16.67		
1.171	83-1	0.0944	0.0947	246.2	16.33	16.32	0.6869
1.171	83-2	0.0949			16.31		
1.405	85-1	0.107	0.107	278.2	16.03	16.03	0.6747
1.405	85-2	0.107			16.03		
1.641	86-1	0.120	0.121	313.6	15.74	15.75	0.6629
1.641	86-2	0.121			15.76		
1.874	87-1	0.138	0.136	352.8	15.47	15.47	0.6511
1.874	87-2	0.133			15.46		
2.108	88-2	0.154	0.153	397.5	15.18	15.19	0.6393
2.108	88-3	0.152			15.19		
2.342	89-1	0.176	0.175	455.5	14.87	14.87	0.6258
2.342	89-2	0.174			14.86		
2.576	90-1	0.196	0.196	509.6	14.58	14.58	0.6136
2.576	90-2	0.196			14.58		
2.810	91-1	0.217	0.216	561.6	14.34	14.34	0.6035
2.810	91-2	0.215			14.34		
3.046	92-1	0.241	0.242	629.7	14.10	14.09	0.5930
3.046	92-2	0.243			14.08		
3.134	93-1	0.251	0.249	648.4	14.00	13.99	0.5888
3.134	93-3	0.249			14.00		
3.134	93-4	0.248			13.98		

TABLE IV

VAPOR PRESSURE DATA FOR THE $CuCl_2$-HCl-H_2O SYSTEM

7.0 MOLAL HYDROCHLORIC ACID SERIES

Molality $CuCl_2$	Run Number	$\bar{P}_{HCl}$ (mm. Hg)	$\bar{\bar{P}}_{HCl}$ (mm. Hg)	Activity HCl*	P_{H_2O} (mm. Hg)	$\bar{P}_{H_2O}$ (mm. Hg)	Activity H_2O
0.2510	46-1	0.401	0.399	1,037	-----	14.00	0.5892
0.2510	46-2	0.396			14.00		
0.2510	46-3	0.400			-----		
0.2510	46-4	-----			13.99		
0.5021	48-1	0.440	0.359	1,136	13.77	13.78	0.5800
0.5021	48-2	0.443			13.78		
0.7531	60-1	0.492	0.490	1,274	13.52	13.53	0.5694
0.7531	60-2	0.488			13.54		
1.004	64-1	0.549	0.547	1,409	13.28	13.28	0.5589
1.004	64-2	0.546			13.27		
1.004	50-2	0.546			13.30		
1.256	51-1	0.600	0.601	1,563	13.08	13.09	0.5509
1.256	51-2	-----			13.10		
1.256	51-3	0.601			13.10		
1.506	61-3	0.662	0.659	1,716	12.81	12.81	0.5391
1.506	61-4	0.656			12.81		
1.757	53-3	0.712	0.714	1,856	12.60	12.61	0.5307
1.757	54-1	0.713			12.60		
1.757	54-2	0.717			12.62		
2.009	57-1	0.798	0.795	2,067	12.32	12.32	0.5185
2.009	57-2	0.792			12.31		
2.260	58-1	0.862	0.865	2,249	12.08	12.08	0.5084
2.260	58-2	0.867			12.07		
2.313	59-1	0.885	0.883	2,296	12.03	12.03	0.5063
2.313	59-2	0.880			12.03		

TABLE V

VAPOR PRESSURE DATA FOR THE $CuCl_2$-HCl-H_2O SYSTEM

9.0 MOLAL HYDROCHLORIC ACID SERIES

Molality $CuCl_2$	Run Number	P_{HCl} (mm. Hg)	$\bar{P}_{HCl}$ (mm. Hg)	Activity HCl*	P_{H_2O} (mm. Hg)	$\bar{P}_{H_2O}$ (mm. Hg)	Activity H_2O
0.2657	66-1	2.105	2.111	5,489	11.00	10.99	0.4625
0.2657	66-2	2.117			10.98		
0.5312	75-1	2.274	2.273	5,910	10.78	10.80	0.4545
0.5312	75-2	2.271			10.81		
0.7969	68-3	2.438	2.435	6,331	10.64	10.63	0.4474
0.7969	68-4	2.432			10.62		
1.062	69-1	2.578	2.583	6,716	10.48	10.47	0.4407
1.062	69-2	2.587			10.46		
1.328	70-1	2.779	2.775	7,215	10.25	10.27	0.4322
1.328	70-2	2.770			10.28		
1.594	71-3	2.973	2.968	7,717	10.07	10.07	0.4238
1.594	77-1	2.968			10.09		
1.594	77-2	2.962			10.04		
1.859	72-1	3.165	3.164	8,226	9.89	9.90	0.4167
1.859	72-2	3.162			9.91		
1.992	73-1	3.279	3.286	8,544	9.81	9.79	0.4121
1.992	73-2	3.292			9.77		
2.102	74-1	3.339	3.349	8,707	9.73	9.72	0.4091
2.102	74-2	3.359			9.71		

TABLE VI

VAPOR PRESSURE DATA FOR THE $CuCl_2$-HCl-H_2O SYSTEM

1.0 MOLAL CUPRIC CHLORIDE SERIES

Molality HCl	Run Number	P_{HCl} (mm. Hg)	$\bar{P}_{HCl}$ (mm. Hg)	Activity HCl*	P_{H_2O} (mm. Hg)	$\bar{P}_{H_2O}$ (mm. Hg)	Activity H_2O
4.697	----	-----	0.085	221.3	-----	16.58	0.6978
5.198	94-1	0.133	0.133	344.8	15.83	15.84	0.6667
5.198	94-4	0.132			15.84		
5.704	95-1	0.195	0.195	505.7	15.12	15.12	0.6364
5.704	95-2	0.194			15.11		
6.200	96-1	0.290	0.290	753.2	14.45	14.46	0.6086
6.200	96-2	0.289			14.47		
6.691	97-1	0.435	0.434	1,128	13.71	13.70	0.5766
6.691	97-2	0.433			13.69		
7.001	----	-----	0.541	1,407	-----	13.31	0.5602
7.501	98-1	0.812	0.812	2,111	12.60	12.59	0.5299
7.501	98-2	0.812			12.57		
7.999	99-2	1.207	1.207	3,138	11.89	11.88	0.5000
7.999	99-3	1.206			11.88		
7.999	99-4	1.207			11.87		
8.465	100-1	1.750	1.751	4,553	11.16	11.18	0.4705
8.465	100-2	1.752			11.19		
8.997	----	-----	2.556	6,646	-----	10.50	0.4419

TABLE VII

MISCELLANEOUS VAPOR PRESSURE DATA

m_3 ($CuCl_2$)	m_2 (HCl)	Run Number	P_{HCl} (mm. Hg)	$\bar{P}_{HCl}$ (mm. Hg)	Activity HCl*	P_{H_2O} (mm. Hg)	$\bar{P}_{H_2O}$ (mm. Hg)	Activity H_2O
5.668	0.000	63-1	-----	-----	-----	16.18	16.18	0.6810
5.668	0.000	63-2	-----			16.18		
4.500	1.001	102-1	0.032	0.030	78.0	16.62	16.62	0.6995
4.500	1.001	102-2	0.027			16.62		
4.000	2.001	101-1	0.055	0.054	140.	16.15	16.17	0.6806
4.000	2.001	101-2	0.053			16.18		

$$(a_s \cdot a_w^n)_t = (a_s \cdot a_w^n)_b \tag{13}$$

Substitution of equation (4) into equation (13) now gives after rearrangement

$$(a_s)_t = \frac{(a_s \cdot P_1^n)_b}{(P_1^n)_t} \tag{14}$$

The activity of the saturated binary solution referred to the hypothetical mean one-molal solution was obtained from the isopiestic data of Stokes. (100). The water vapor pressure of the saturated binary solution was determined and found to be 0.3% lower than the value calculated from the osmotic coefficient given by Stokes. The water vapor pressures in the saturated ternary solutions were also determined, a search of the literature having failed to reveal any previous measurements on these solutions. The activities of the various reference states calculated from equation (14) are given in Table VIII.

TABLE VIII

ACTIVITIES OF CUPRIC CHLORIDE IN THE REFERENCE STATES

State	a_3 ($CuCl_2$)
Saturated Aqueous Solution at 25° C.	205.3
4.7 m HCl Solution Saturated with $CuCl_2$	274.6
7.0 m HCl Solution Saturated with $CuCl_2$	371.4
9.0 m HCl Solution Saturated with $CuCl_2$	568.9

Treatment of data. Activities of $CuCl_2$ in the constant-acid series were calculated by an analytical integration of the Gibbs-Duhem equation.

Empirical expressions for both the H_2O and the HCl activities as functions of the $CuCl_2$ molality were determined from the arithmetical mean values of the experimental vapor pressures by the method of least squares. (18). The assumed empirical equations expressed the logarithms of the H_2O and HCl activities as polynomials in the $CuCl_2$ molality

$$\log a_i = A + Bm + Cm^2 + \cdots \tag{15}$$

Four such polynomials; linear, quadratic, cubic, and quartic were found, and of these equations, the ones giving the best fit to the experimental data; i.e., the ones of minimum probable error, were chosen to represent the data. (19).

Substitution of these expressions into equation (7) of Chapter III and integration between the limits of m_3 and m_3^*, the molality of the reference state, gives an empirical expression for the activity of $CuCl_2$ as a function of its molality m_3 in solutions of fixed hydrochloric acid concentration. The general form of the final equation for the activity is

$$\log a_3/a_3^* = 55.51 \left[\alpha \log m_3^*/m_3 + \beta(m_3^* - m_3) + \gamma(m_3^* - m_3)^2 + \delta(m_3^* - m_3)^3\right] \tag{16}$$

where the constants α, β, γ, and δ are functions of the ratio m_2/m_1 and of the coefficients of the empirical equations for the activity of the volatile components.

Empirical equations for the activities of H_2O and HCl in the constant-salt series were also determined as a function of the hydrochloric acid molality in a manner similar to that described for the constant-acid series.

Substitution of the resulting polynomials into equation (10) of Chapter III and integration between the limits m_2 and m_2^* leads to an equation for the calculation of the activity of the salt as a function of the acid molality. The equation has the following general form

$$\log a_3/a_3^* = 55.51/m_3 \left[\alpha'(m_2^* - m_2) + \beta'(m_2^* - m_2)^2 + \ldots. \eta'(m_2^* - m_2)^5\right] \quad (17)$$

where α', β', ... η', are functions of $1/m_1$ and the constants of the empirical expressions for the activity of H_2O and HCl.

The upper limits of the integration was chosen to be the activity and corresponding molality of the 1 molal $CuCl_2$ solution obtained from the 4.7 molal hydrochloric acid series. Thus, salt activities calculated from the above relation are related to the same reference state as those calculated for the 4.7 molal constant-acid series.

The least-squares procedure used in finding the empirical expressions for the H_2O and HCl activities and also the integration of the Gibbs-Duhem equation for the fixed-acid series were carried out with the aid of an IBM 650 digital computer. The analytical expressions resulting from these computations are given in Appendix A.

Activities and activity coefficients of the various components in the constant-acid series are tabulated in Tables IX through XI, and in Table XII there are listed the corresponding values for the components in the constant-salt series.

Analyses of Saturated Solutions and Solid Phases

Binary system. The saturated aqueous $CuCl_2$ solution was found to contain 43.27 percent $CuCl_2$ at 25°. This compares with values of 43.60 percent reported by Chretien and Weil (17), 43.32 percent given by Foote (30), and 43.3 percent found by Boye (12). The solid phase in equilibrium with the saturated binary solution has been reported to be the dihydrate of cupric chloride by several investigators. (5, 12, 22, 30, 48).

Ternary systems. Results of the analyses of the liquid phases and

TABLE IX

ACTIVITY DATA FOR THE $CuCl_2$-HCl-H_2O SYSTEM

4.7 MOLAL HYDROCHLORIC ACID SERIES

Molality $CuCl_2$	Activity H_2O	Activity HCl*	$\gamma_\pm$ HCl	Activity $CuCl_2^*$	$\gamma_\pm$ $CuCl_2^*$
0.1	0.7520	122.0	2.30	1.02	0.752
0.2	0.7454	131.7	2.34	2.54	0.788
0.3	0.7390	141.7	2.39	4.42	0.807
0.4	0.7327	152.0	2.43	6.65	0.819
0.5	0.7266	163.0	2.46	9.24	0.828
0.6	0.7206	173.6	2.50	12.2	0.836
0.7	0.7148	185.0	2.54	15.5	0.842
0.8	0.7090	196.7	2.58	19.3	0.846
0.9	0.7033	208.8	2.61	23.5	0.851
1.0	0.6977	221.3	2.65	28.1	0.855
1.1	0.6921	234.3	2.69	33.2	0.859
1.2	0.6866	247.9	2.73	38.9	0.863
1.3	0.6811	262.0	2.77	45.1	0.866
1.4	0.6757	276.7	2.80	51.8	0.870
1.5	0.6703	292.0	2.84	59.1	0.873
1.6	0.6649	307.9	2.88	67.1	0.876
1.7	0.6602	324.6	2.92	75.7	0.879
1.8	0.6534	342.1	2.96	84.9	0.882
1.9	0.6490	360.4	3.00	94.9	0.884
2.0	0.6438	379.5	3.05	106.	0.887
2.1	0.6386	399.4	3.09	117.	0.889
2.2	0.6334	420.2	3.14	129.	0.891
2.3	0.6283	442.0	3.18	142.	0.893
2.4	0.6233	464.3	3.23	155.	0.895
2.5	0.6183	487.9	3.27	169.	0.896
2.6	0.6135	511.4	3.32	184.	0.898
2.7	0.6086	536.7	3.36	200.	0.899
2.8	0.6039	562.3	3.41	216.	0.899
2.9	0.5992	588.5	3.45	233.	0.900
3.0	0.5947	614.8	3.50	250.	0.900
3.1	0.5906	641.4	3.54	268.	0.900
3.2	0.5861	667.8	3.58	287.	0.899

TABLE X

ACTIVITY DATA FOR THE $CuCl_2$-HCl-H_2O SYSTEM

7.0 MOLAL HYDROCHLORIC ACID SERIES

Molality $CuCl_2$	Activity H_2O	Activity HCl*	$\gamma_{\pm}$ HCl	Activity $CuCl_2^*$	$\gamma_{\pm}$ $CuCl_2^*$
0.1	0.5938	966	4.38	29.6	1.79
0.2	0.5903	1,009	4.41	36.1	1.49
0.3	0.5867	1,054	4.45	42.2	1.35
0.4	0.5831	1,099	4.49	48.4	1.26
0.5	0.5794	1,146	4.52	54.9	1.20
0.6	0.5756	1,195	4.56	62.0	1.15
0.7	0.5719	1,246	4.60	69.6	1.12
0.8	0.5681	1,298	4.64	77.9	1.10
0.9	0.5642	1,351	4.68	87.1	1.08
1.0	0.5603	1,407	4.73	97.0	1.06
1.1	0.5564	1,464	4.77	108.	1.05
1.2	0.5525	1,522	4.81	120.	1.04
1.3	0.5484	1,583	4.85	133.	1.04
1.4	0.5444	1,645	4.90	148.	1.03
1.5	0.5403	1,709	4.94	164	1.03
1.6	0.5362	1,774	4.99	182.	1.03
1.7	0.5321	1,842	5.03	201.	1.03
1.8	0.5280	1,911	5.08	223.	1.03
1.9	0.5238	1,982	5.12	246.	1.03
2.0	0.5196	2,055	5.17	272.	1.04
2.1	0.5153	2,130	5.21	301.	1.05
2.2	0.5111	2,206	5.26	332.	1.05
2.3	0.5068	2,284	5.30	367.	1.06
2.4	0.5025	2,365	5.35	405.	1.07

TABLE XI

ACTIVITY DATA FOR THE $CuCl_2$-HCl-H_2O SYSTEM

9.0 MOLAL HYDROCHLORIC ACID SERIES

Molality $CuCl_2$	Activity H_2O	Activity HCl*	$\gamma_{\pm}$ HCl	Activity $CuCl_2^*$	$\gamma_{\pm}$ $CuCl_2^*$
0.1	0.4664	5,257	7.97	21.9	1.37
0.2	0.4638	5,399	7.99	36.2	1.27
0.3	0.4611	5,543	8.01	50.0	1.22
0.4	0.4585	5,691	8.03	64.1	1.19
0.5	0.4558	5,842	8.06	78.9	1.16
0.6	0.4530	5,997	8.08	94.6	1.15
0.7	0.4502	6,154	8.11	111.	1.14
0.8	0.4474	6,315	8.14	130.	1.13
0.9	0.4446	6,479	8.16	149.	1.13
1.0	0.4418	6,647	8.19	170.	1.12
1.1	0.4389	6,818	8.22	194.	1.12
1.2	0.4360	6,993	8.25	219.	1.12
1.3	0.4331	7,171	8.29	246.	1.12
1.4	0.4302	7,352	8.32	275.	1.12
1.5	0.4272	7,538	8.35	308.	1.13
1.6	0.4242	7,727	8.39	342.	1.13
1.7	0.4212	7,919	8.42	380.	1.13
1.8	0.4182	8,115	8.46	422.	1.14
1.9	0.4151	8,316	8.50	466.	1.14
2.0	0.4121	8,519	8.53	515.	1.15
2.1	0.4090	8,727	8.57	568.	1.16
2.2	0.4059	8,939	8.61	625	1.17

TABLE XII

ACTIVITY DATA FOR THE $CuCl_2$-HCl-H_2O SYSTEM

1.0 MOLAL CUPRIC CHLORIDE SERIES

Molality HCl	Activity H_2O	Activity HCl^*	$\gamma_{\pm}$ HCl	Activity $CuCl_2^*$	$\gamma_{\pm}$ $CuCl_2^*$
4.7	0.6967	224.3	2.64	28.2	0.856
4.8	0.6909	243.5	2.75	30.4	0.869
5.0	0.6792	286.8	2.86	35.1	0.895
5.2	0.6674	337.7	3.00	40.4	0.920
5.4	0.6556	397.3	3.15	46.2	0.945
5.6	0.6437	467.2	3.31	52.5	0.969
5.8	0.6317	549.0	3.48	59.3	0.992
6.0	0.6169	645.1	3.67	66.8	1.01
6.2	0.6076	757.0	3.86	74.7	1.04
6.4	0.5955	888.1	4.06	83.2	1.06
6.6	0.5834	1,042	4.28	92.2	1.08
6.8	0.5714	1,220	4.52	100.	1.10
7.0	0.5593	1,429	4.76	112.	1.11
7.2	0.5472	1,673	5.03	123.	1.13
7.4	0.5352	1,958	5.31	134.	1.15
7.6	0.5232	2,289	5.60	145.	1.16
7.8	0.5113	2,675	5.92	158.	1.18
8.0	0.4994	3,124	6.25	170.	1.19
8.2	0.4876	3,647	6.60	184.	1.21
8.4	0.4759	4,255	6.98	197.	1.22
8.6	0.4642	4,962	7.38	212.	1.24
8.8	0.4527	5,782	7.80	227.	1.25
9.0	0.4412	6,735	8.25	242.	1.26

the wet-solids obtained from the saturated ternary solutions are given in Tables XIII and XIV. Literature values cited for the solubility of $CuCl_2$ in the ternary solutions were obtained by graphical interpolation of data presented by Foote (30).

TABLE XIII

COMPOSITION OF SATURATED LIQUID PHASES IN THE TERNARY SYSTEMS

m_2 (HCl)	% $CuCl_2$	% H_2O	% HCl	% $CuCl_2$ Lit. Value
4.70	26.47	62.78	10.75	26.62
7.00	19.85	63.86	16.29	19.95
9.00	17.55	62.08	20.37	17.25

TABLE XIV

ANALYSES OF THE WET SOLID PHASES FROM THE SATURATED TERNARY SYSTEMS

m_2 (HCl)	% $CuCl_2$	% H_2O	% HCl
4.70	71.80	26.74	1.46
7.00	71.39	26.61	2.00
9.00	71.19	26.62	2.19

Graphical analysis of the data listed in these tables, according to the method of Schreinemaker (28), showed that $CuCl_2 \cdot 2H_2O$ was the solid phase in equilibrium with each of the three saturated ternary solutions. Foote (30) also states that the dihydrate of cupric chloride is the only solid present in saturated cupric chloride solutions containing from 0 to 17 molal hydrochloric acid at 25°.

Densities and Molal Volumes

Density measurements. The densities of all ternary solutions were measured at 25° with an estimated accuracy of ± 0.02 percent. The result of these measurements are tabulated in Tables XV and XVI. As a first approximation, the density may be taken as a linear function of the variable component in the four series studied.

Apparent and partial molal volumes. Apparent and partial molal volumes of cupric chloride in 4.7, 7.0, and 9.0 molal HCl solutions and those of HCl in 1.0 molal $CuCl_2$ solutions were calculated from the measured densities according to the procedure described by Klotz (54).

Total volumes of solutions containing 1000 g. of water were first determined from the densities and the apparent molal volumes obtained. Apparent molal volumes of $CuCl_2$ in solutions of constant acid molalities were then plotted as a function of the salt molality and a curve drawn to give the best fit with the data. A plot of $\Delta\phi_3/\Delta m_3$ versus m_3 was constructed and again a smooth curve was drawn. From these two plots, i.e., ϕ_3 versus m_3 and $\Delta\phi_3/\Delta m_3$ versus m_3, and the following relation the partial molal volumes of $CuCl_2$ were calculated

$$\bar{\bar{V}}_3 = \phi_3 + m_3\left(\frac{\partial\phi_3}{\partial m_3}\right)_{1,2} \tag{18}$$

Partial molal volumes of HCl in 1.0 molal $CuCl_2$ solutions were calculated in a similar manner. The results of these calculations are tabulated in Tables XVII and XVIII. The accuracy of the partial molal volumes, based upon the estimated accuracy of the density measurements, is approximately ±0.1 cc.

TABLE XV

DENSITY DATA FOR THE $CuCl_2$-HCl-H_2O SYSTEM AT 25° C.

CONSTANT-ACID SERIES

4.7 Molal HCl		7.0 Molal HCl		9.0 Molal HCl	
$m_3(CuCl_2)$	Density (g./cc.)	$m_3(CuCl_2)$	Density (g./cc.)	$m_3(CuCl_2)$	Density (g./cc.)
0.0000	1.0683	0.0000	1.0965	0.0000	1.1190
0.2342	1.0909	0.2510	1.1190	0.2657	1.1408
0.4684	1.1135	0.3122	1.1242	0.5312	1.1622
0.7026	1.1350	0.5021	1.1409	0.7969	1.1833
0.9368	1.1565	0.7531	1.1623	1.062	1.2040
1.171	1.1775	1.004	1.1834	1.328	1.2245
1.405	1.1981	1.256	1.2041	1.594	1.2446
1.641	1.2184	1.506	1.2247	1.859	1.2643
1.874	1.2384	1.757	1.2447	1.992	1.2742
2.108	1.2580	2.009	1.2646	2.102	1.2824
2.342	1.2772	2.260	1.2839		
2.576	1.2961	2.313	1.2875		
2.810	1.3148				
3.046	1.3331				
3.134	1.3402				

TABLE XVI

DENSITY DATA FOR THE $CuCl_2$-HCl-H_2O SYSTEM AT 25° C.

CONSTANT-SALT SERIES AND MISCELLANEOUS

1.0 Molal $CuCl_2$		Miscellaneous		
m_2(HCl)	Density (g./cc.)	m_3($CuCl_2$)	m_2(HCl)	Density (g./cc.)
0.000	1.1112	5.668	0.000	1.5228
4.697	1.1630*	4.000	2.001	1.3984
5.198	1.1670	4.500	1.001	1.4549
5.704	1.1718			
6.200	1.1760			
6.691	1.1804			
7.001	1.1827*			
7.501	1.1872			
7.999	1.1914			
8.465	1.1955			
8.997	1.2005*			

*Obtained by graphical interpolation of the constant-acid series' density plots.

TABLE XVII

TOTAL AND APPARENT MOLAL VOLUMES FOR THE

$CuCl_2$-HCl-H_2O SYSTEM AT 25° C.

4.7 molal HCl series			7.0 molal HCl series		
$m_3(CuCl_2)$	Volume(cc.)	$Ø_3$(cc.)	$m_3(CuCl_2)$	Volume(cc.)	$Ø_3$(cc.)
0.0000	1096.4	----	0.0000	1144.7	----
0.2342	1102.6	26.5	0.2510	1151.9	28.7
0.4684	1108.5	25.9	0.3122	1153.9	29.5
0.7026	1115.2	26.7	0.5021	1159.3	29.1
0.9368	1121.7	27.0	0.7531	1167.1	29.7
1.171	1128.5	27.4	1.004	1174.8	30.1
1.405	1135.4	27.7	1.256	1182.7	30.2
1.641	1142.5	28.1	1.506	1190.4	30.3
1.874	1149.4	28.3	1.757	1198.3	30.5
2.108	1156.4	28.5	2.009	1206.2	30.6
2.342	1163.7	28.8	2.260	1214.4	30.8
2.576	1171.1	29.0	2.313	1216.5	31.0
2.810	1178.3	29.1			
3.046	1186.0	29.4			
3.134	1188.5	29.4			

9.0 molal HCl series			1.0 molal $CuCl_2$ series		
$m_3(CuCl_2)$	Volume(cc.)	$Ø_3$(cc.)	m_2(HCl)	Volume(cc.)	$Ø_2$(cc.)
0.0000	1186.8	----	0.000	1021.0	----
0.2657	1195.4	32.3	4.697	1122.8	21.7
0.5313	1204.1	32.6	5.198	1134.5	21.8
0.7969	1212.9	32.7	5.704	1145.7	21.9
1.062	1221.6	32.8	6.200	1157.0	21.9
1.328	1230.4	32.8	6.691	1167.8	21.9
1.594	1239.3	33.0	7.001	1175.1	22.0
1.859	1248.1	33.0	7.501	1186.0	22.0
1.992	1252.5	33.0	7.999	1197.0	22.0
2.102	1256.0	33.0	8.465	1207.1	22.0
			8.997	1218.2	21.9

TABLE XVIII

PARTIAL MOLAL VOLUMES FOR THE $CuCl_2$-HCl-H_2O SYSTEM AT 25° C

	Constant-Acid Series Partial molal volume, $\bar{V}_3$(cc.)			Constant-Salt Series 1.0 m $CuCl_2$	
m_3($CuCl_2$)	4.7 m HCl	7.0 m HCl	9.0 m HCl	m_2(HCl)	$\bar{V}_2$(cc.)
0.20	26.6	29.2	32.4	4.60	22.7
0.40	27.3	30.0	32.8		
0.60	27.8	30.5	33.0	5.00	22.7
0.80	28.3	30.8	33.1	5.50	22.8
1.00	28.8	31.0	33.2	6.00	22.7
1.20	29.2	31.2	33.2	6.50	22.6
1.40	29.7	31.4	33.2		
1.60	30.0	31.5	33.2	7.00	22.4
1.80	30.4	31.6	32.1	7.50	22.2
2.00	30.6	31.7	32.1	8.00	22.1
2.20	30.9	31.7	32.1	8.50	21.9
2.40	31.0	31.8			
2.60	31.1			9.00	21.8
2.80	31.2				
3.00	31.1				
3.20	31.0				

CHAPTER V

ACCURACY AND PRECISION

Binary Systems

An estimate of the accuracy with which activities of the volatile components in the ternary systems were determined can be obtained by a comparison of the activities of these components in binary solutions, as determined in this research, with comparable measurements made by other investigators.

Activity of water. It can be seen from Table I that the observed vapor pressure of pure water agrees within 0.05 percent with that accepted as the vapor pressure of the pure solvent. (104). Activities of H_2O in H_2SO_4 solutions show an average accuracy of ± 0.1 percent when compared with those adopted as isopiestic standards by Stokes (101). The measurements, however, were made with an average percision of better than 0.1 percent.

The values obtained for the partial pressures of H_2O in aqueous HCl solutions, Table II, agree quite well with those calculated from electromotive force measurements by Randall and Young (85). Fig. 2 illustrates the fact that the observed vapor pressures of H_2O were uniformly slightly lower than those calculated by Randall and Young, the greatest deviation, approximately 0.2 mm. Hg, occurring at about 7.8 molal HCl. Comparable values compiled by Ziesberg (108) average about 0.4 mm. Hg lower than those of Randall and Young.

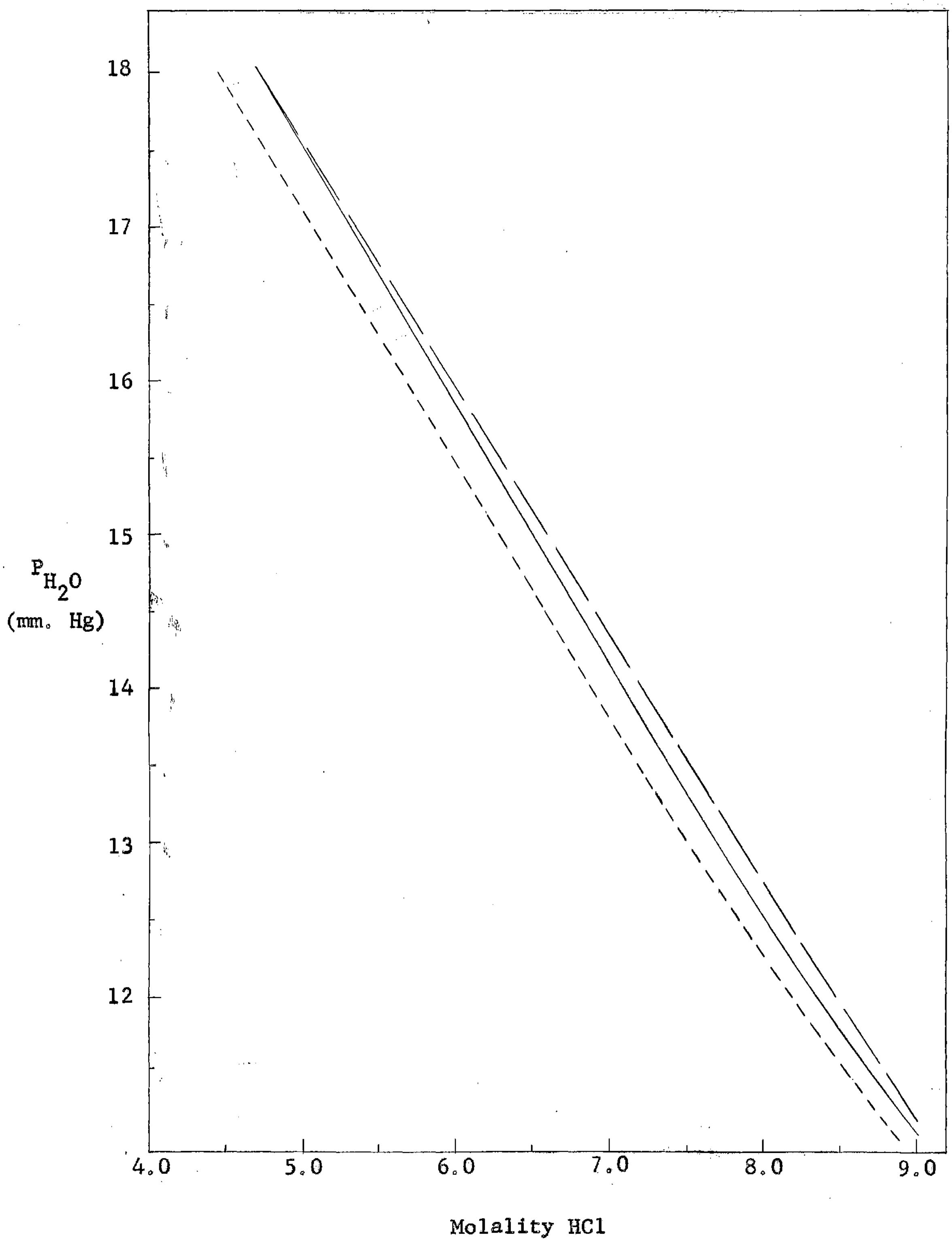


Fig. 2 Vapor pressure of H_2O in aqueous HCl solutions: ————, experimental values; — — —, values of Randall and Young; - - - - - -, values of Zeisberg.

Activity of hydrochloric acid. Partial pressures of HCl as determined in this research averaged about 2 percent higher than those measured by Bates and Kirschman (3), Fig. 3, and approximately 1.5 percent higher than those listed by Randall and Young (85). In view of the facts that most of the deviations were less than 0.01 mm. Hg and that other investigators have reported consistant results which differ by more than 2 percent from those selected for comparison here, we consider our data to be as reliable as any. (2, 16, 108).

Ternary Systems

Activity of water and hydrochloric acid. The average precision with which the vapor pressures of H_2O and HCl were measured varied slightly for each series. In Table XIX there is listed the average precision of the measurements in the four ternary systems. The average precision, $\bar{p}$, is defined as

$$\bar{p} = 1/n\sum d_i \qquad (1)$$

where d_i is the average deviation (mm. Hg) from the mean of two or more vapor pressure measurements made at the same $CuCl_2$ molality and n is the number of different $CuCl_2$ concentrations within the given series.

Average differences between the logarithms of the observed activities and those calculated from the empirical equations are listed in Table XX. The percentages of the average differences in activities show that the empirical equations describe the experimental data with an accuracy comparable to the experimental precision.

Activity of cupric chloride. The total uncertainty in the values of the activities of water and hydrochloric acid calculated from the empirical equations were taken as the sum of the uncertainties due to

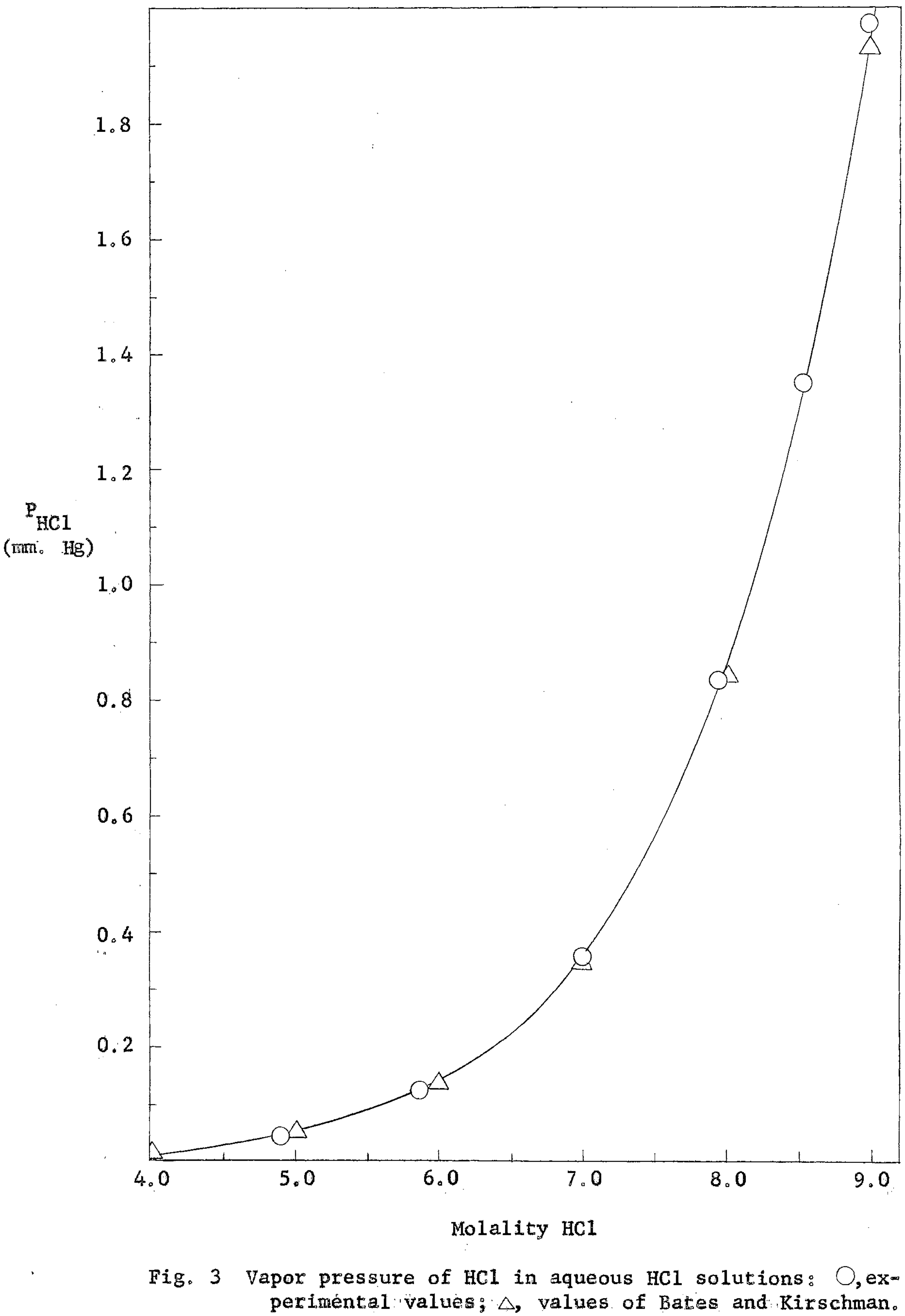


Fig. 3 Vapor pressure of HCl in aqueous HCl solutions: ○, experimental values; △, values of Bates and Kirschman.

TABLE XIX

PRECISION OF VAPOR PRESSURE MEASUREMENTS

System	Average Deviation (mm. Hg) H_2O	HCl	Average Deviation (percentage) H_2O	HCl
4.7 m $HCl-H_2O-CuCl_2$	±0.007	±0.0006	±0.042	±0.50
7.0 m $HCl-H_2O-CuCl_2$	±0.006	±0.003	±0.086	±0.47
9.0 m $HCl-H_2O-CuCl_2$	±0.01	±0.005	±0.115	±0.18
1.0 m $CuCl_2-H_2O-HCl$	±0.01	±0.0006	±0.074	±0.16

TABLE XX

DIFFERENCES IN EXPERIMENTAL AND CALCULATED VALUES

System	Log a_1 (H_2O)	Log a_2 (HCl)	Percentage a_1	a_2
4.7 m $HCl-H_2O-CuCl_2$	±0.00034	±0.0022	±0.08	±0.51
7.0 m $HCl-H_2O-CuCl_2$	±0.00051	±0.0013	±0.12	±0.30
9.0 m $HCl-H_2O-CuCl_2$	±0.00032	±0.0010	±0.07	±0.24
1.0 m $CuCl_2-H_2O-HCl$	±0.00074	±0.0046	±0.17	±1.03

the experimental measurements and curve fitting. The uncertainties, Δa_3, in the value for the activity of the cupric chloride were calculated from the Gibbs-Duhem relation

$$-\,d\ln a_3 = (m_1/m_3)(d\ln a_1) + (m_2/m_3)(d\ln a_2) \tag{2}$$

or

$$\pm\Delta a_3/a_3 = \pm\,(m_1/m_3)(\Delta a_1/a_1) \pm (m_2/m_3)(\Delta a_2/a_2) \tag{3}$$

It was assumed that the deviations of a_1 and a_2 were additive; therefore, it is considered that these estimates are of the order of maximum uncertainties in a_3. The calculated uncertainties in $CuCl_2$ activities in 1 molal solutions are given in Table XXI.

TABLE XXI

UNCERTAINTY IN CALCULATED ACTIVITIES

System	% a_2 (H_2O)	% a_2 (HCl)	% a_3 ($CuCl_2$)*
4.7 m $HCl-H_2O-CuCl_2$	±0.12	±1.01	±10.8
7.0 m $HCl-H_2O-CuCl_2$	±0.21	±0.77	±17.4
9.0 m $HCl-H_2O-CuCl_2$	±0.19	±0.42	±14.9
1.0 m $CuCl_2-H_2O$-4.7 m HCl	±0.24	±1.19	±20.3
1.0 m $CuCl_2-H_2O$-7.0 m HCl	±0.24	±1.19	±23.5
1.0 m $CuCl_2-H_2O$-9.0 m HCl	±0.24	±1.19	±26.4

*Uncertainty at 1 molal $CuCl_2$.

An estimate of the consistency of the data for the three series of solutions of constant acid molality was obtained through the cross differentiation of the partial differentials of the total free energy with respect to concentration.

Since the differential of the free energy with respect to the concentrations of the components is an exact function, the following relation from the principles of calculus must apply

$$\frac{\partial}{m_3}\left(\frac{\partial F}{\partial m_2}\right)_{m_3} = \frac{\partial}{m_2}\left(\frac{\partial F}{\partial m_3}\right)_{m_2} \qquad (4)$$

Substitution of the definition for the chemical potential into equation (4) and differentiating gives

$$\left(\frac{\partial \ln a_2}{\partial m_3}\right)_{m_2} = \left(\frac{\partial \ln a_3}{\partial m_2}\right)_{m_3} \qquad (5)$$

Equation (5) imposes the condition that slopes of the two curves, ln a_2 vs. m_3 and ln a_3 vs. m_2, are equal at common values of m_2 and m_3. Slopes of the ln a_2 vs. m_3 curves were obtained by differentiating the empirical equations for the activity of HCl as a function of salt molality with respect to m_3. An expression of the form

$$\ln a_3 = A + Bm_2 + Cm_2^2 + Dm_2^3 \qquad (6)$$

was assumed for the relation of ln a_3 as a function of HCl molality. Differentiation of this equation with respect to acid molality gives

$$\left(\frac{\partial \ln a_3}{\partial m_2}\right)_{m_3} = B + 2Cm_2 + 3Dm_2^2 \qquad (7)$$

Three equations were obtained by setting the right-hand side of the above equation equal to the slopes of the ln a_2 vs. m_3 curves (see equation 5). These equations were solved simultaneously, and the resulting values of B, C, and D were then substituted into equation (6). The remaining unknown constant, A, was evaluated by substituting the ln a_3 value calculated from the Gibbs-Duhem equation for a solution of given $CuCl_2$

molality in 4.7 molal HCl into equation (6). Corresponding $CuCl_2$ activities in the 7.0 and 9.0 molal HCl solutions were then calculated from this equation. Activities calculated in this manner were relative to those of the 4.7 molal constant-acid series. A graphical comparison between these values and those calculated from the Gibbs-Duhem equations for the 7.0 and 9.0 molal HCl series is given in Fig. 4.

It is apparent from Fig. 4 that the relative error increases rapidly as the salt molality decreases below 1 molal. This is to be expected, for examination of equation (3) reveals that as m_3 approaches zero the error in a_3 approaches infinity.

From the information obtained from this evaluation, it is estimated that the $CuCl_2$ activities calculated from the Gibbs-Duhem equation are reliable within ± 5 to 10 percent for the constant-acid solutions of $CuCl_2$ at concentrations of the latter greater than 1 molal. In solutions of lower salt molality the accuracy is more difficult to estimate. As a first approximation one could probably say that the salt activities reported for the 0.5 molal $CuCl_2$ solutions may be as much as 100 percent in error, and below this concentration only the order of magnitude is probably reliable.

Calculated $CuCl_2$ activities for the constant-salt series are not considered to be as reliable as those for the constant-acid series. The maximum uncertainty in a_3, due mostly to curve fitting of the a_2 data, is shown in Table XXI for solutions of 1 molal $CuCl_2$ in 4.7, 7.0, and 9.0 molal HCl solutions. It is evident from this table and equation (3) that for systems of constant salt-to-water molal ratios, the average error in the calculated a_3 values increases with increasing acid molality.

When comparison is made between the 1 molal $CuCl_2$ activities in the

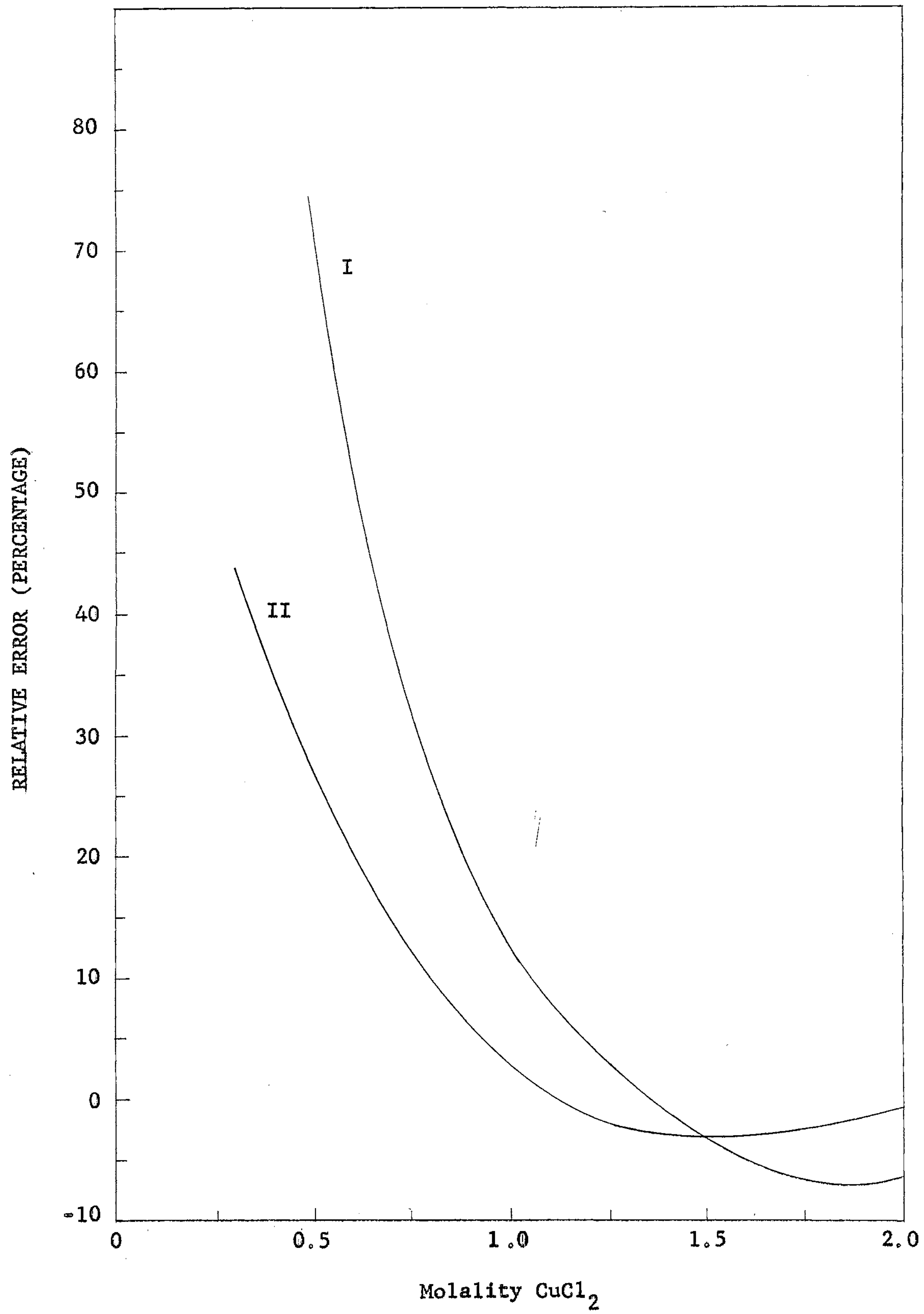


Fig. 4 Percentage of differences in $CuCl_2$ activity relative to $CuCl_2$ activity in 4.7 m HCl series: I, 7.0 m HCl series; II, 9.0 m HCl series.

constant-salt and constant-acid series, it is found that values calculated for the constant-salt series at 7.0 and 9.0 molal HCl are approximately 15 percent and 42 percent larger, respectively, than corresponding activities calculated for the constant-acid series. The error in the salt activity of the 7.0 molal HCl is within the uncertainty estimated in Table XXI, but the error in the salt activity in the 9.0 molal HCl solution is somewhat larger than the estimated value. It seems probable, therefore, that the shapes of the water and HCl activity curves above 7.0 molal are such that the method of estimating the possible error in $\underline{a}_3$ is not valid in this region.

Similar comparisons between the H_2O and HCl activities of these same solutions show that the H_2O and HCl activities average 0.15 percent higher and 1.3 percent lower, respectively, in the constant-salt series than do the corresponding values in the constant-acid series.

CHAPTER VI

DISCUSSION OF RESULTS

The problem of giving a theoretical interpretation to activity data in concentrated electrolyte solutions is usually approached by one or the other of two ways. The first attempts to modify the Debye-Hückel theory so as to make it applicable to moderately concentrated solutions. This is usually done by introducing corrections for such things as the structure of the solvent, solute solvation, heat and entropy of mixing solvated ions, etc., through the introduction of one or more arbitrary parameters into the Debye-Hückel equation. A historical résumé of some of the more successful extensions of the Debye-Hückel equation to moderately concentrated solutions is given by Robinson and Stokes (89). The alternative approach to the problem is to first correlate the data through empirical relations which apply to a given system. In this way it is hoped that results generally useful in attacking the larger problems of electrolyte solutions will become evident.

Thermodynamic Properties of Cupric Chloride

Cupric chloride activity. A comparison of the $CuCl_2$ activities in aqueous solutions containing HCl with those of aqueous $CuCl_2$ is given in Fig. 5. Curve I for the binary system, $CuCl_2$-H_2O, makes use of the data of Stokes (101). This plot and Fig. 7 clearly show that the $CuCl_2$ activity increases with both increasing $CuCl_2$ and HCl concentrations;

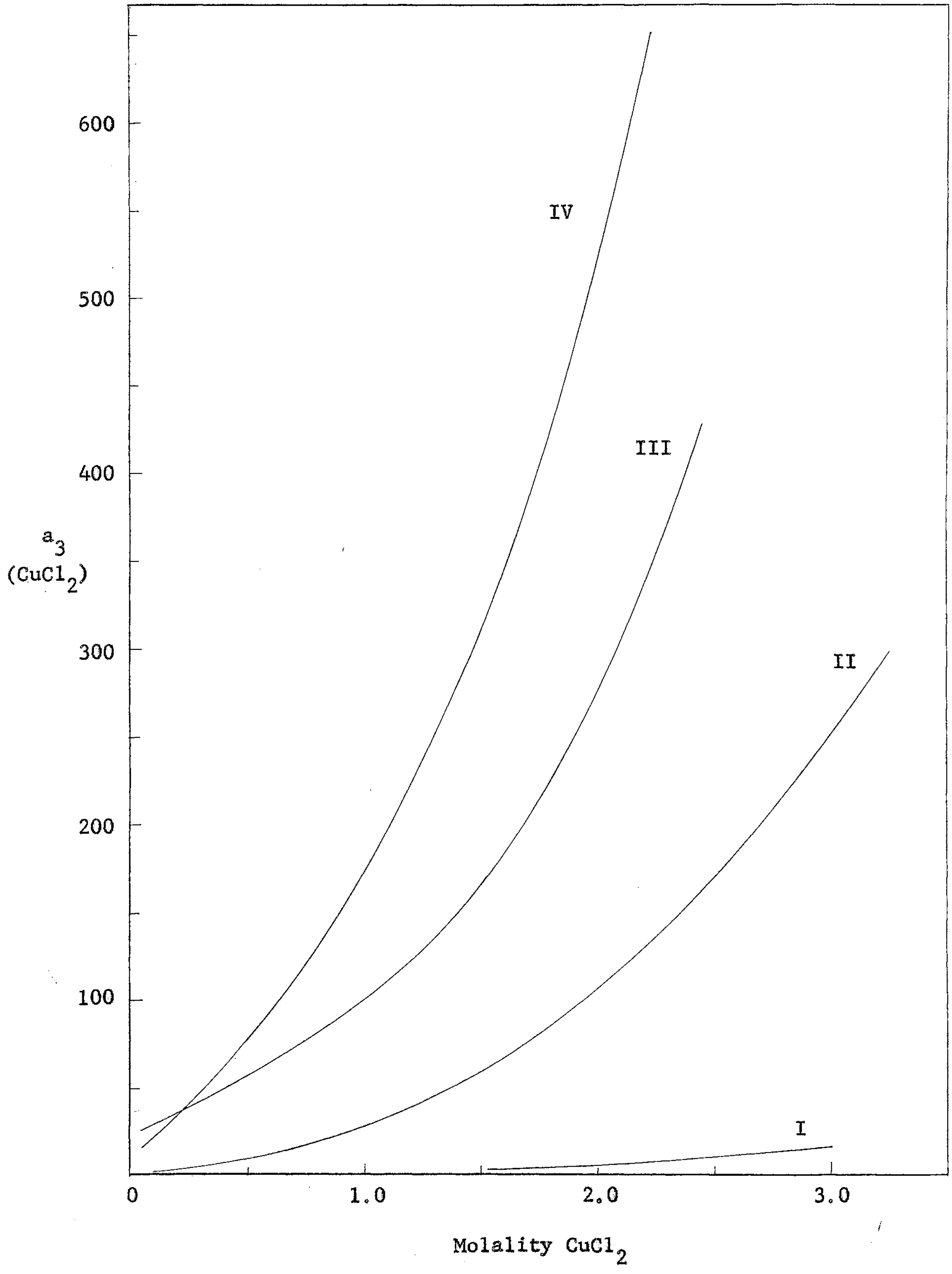


Fig. 5 Activity of $CuCl_2$ in the $CuCl_2$-HCl-H_2O system: I, binary system; II, 4.7 m HCl; III, 7.0 m HCl; IV, 9.0 m HCl.

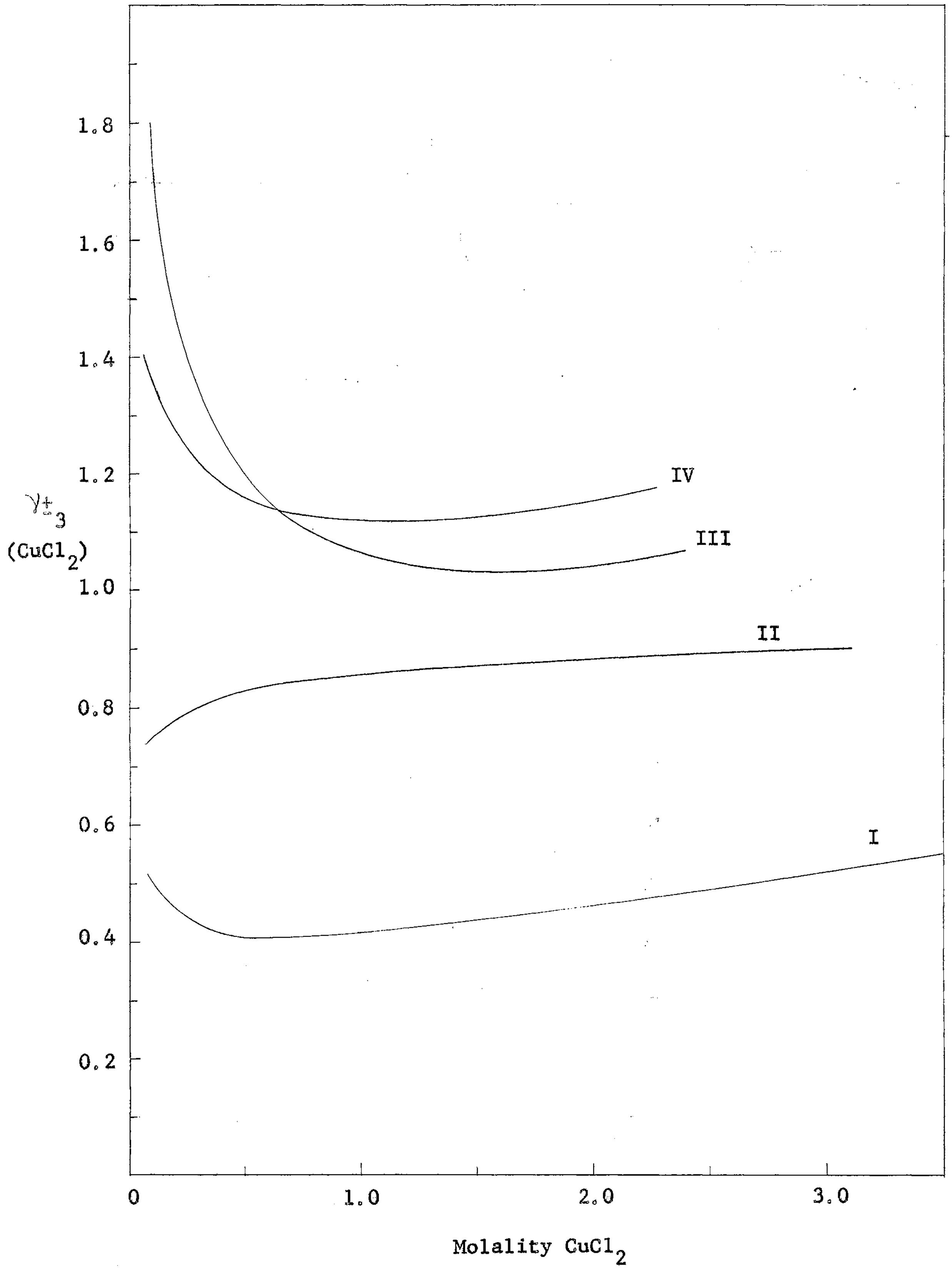


Fig. 6 Activity coefficient of $CuCl_2$ in $CuCl_2$-HCl-H_2O systems of constant acid molality: I, binary system; II, 4.7 m HCl; III, 7.0 m HCl; IV, 9.0 m HCl.

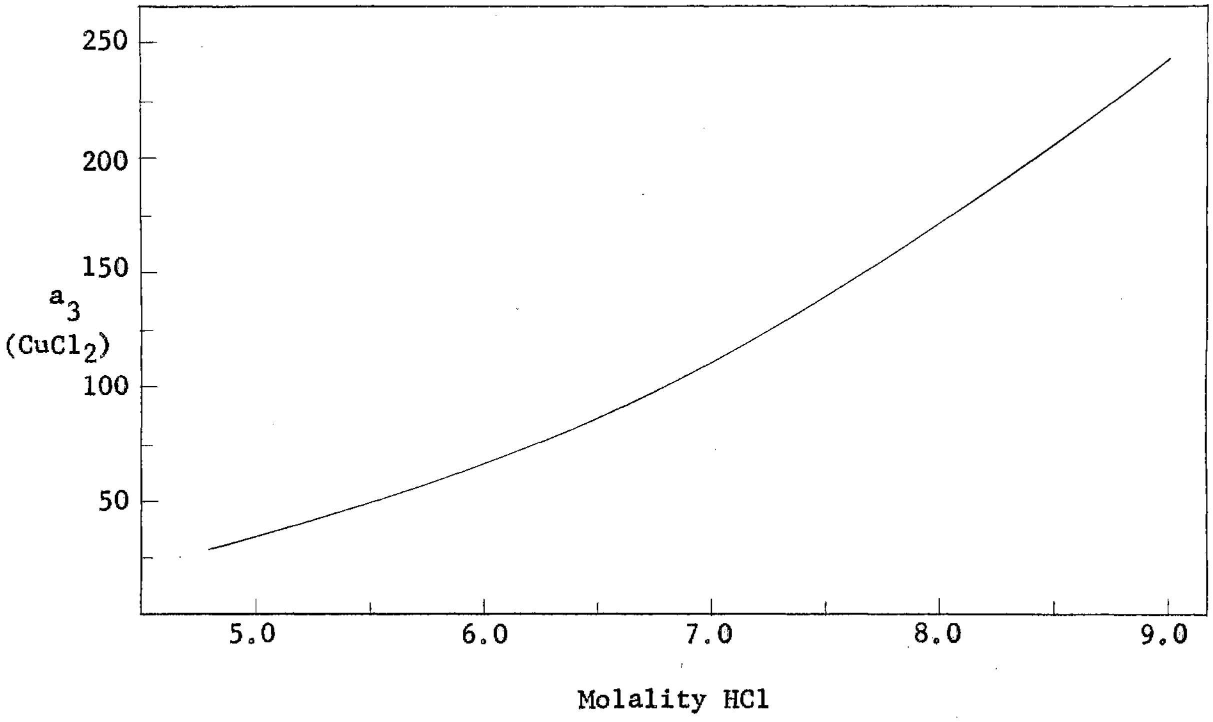


Fig. 7 Activity of $CuCl_2$ in the 1 molal $CuCl_2$-HCl-H_2O system.

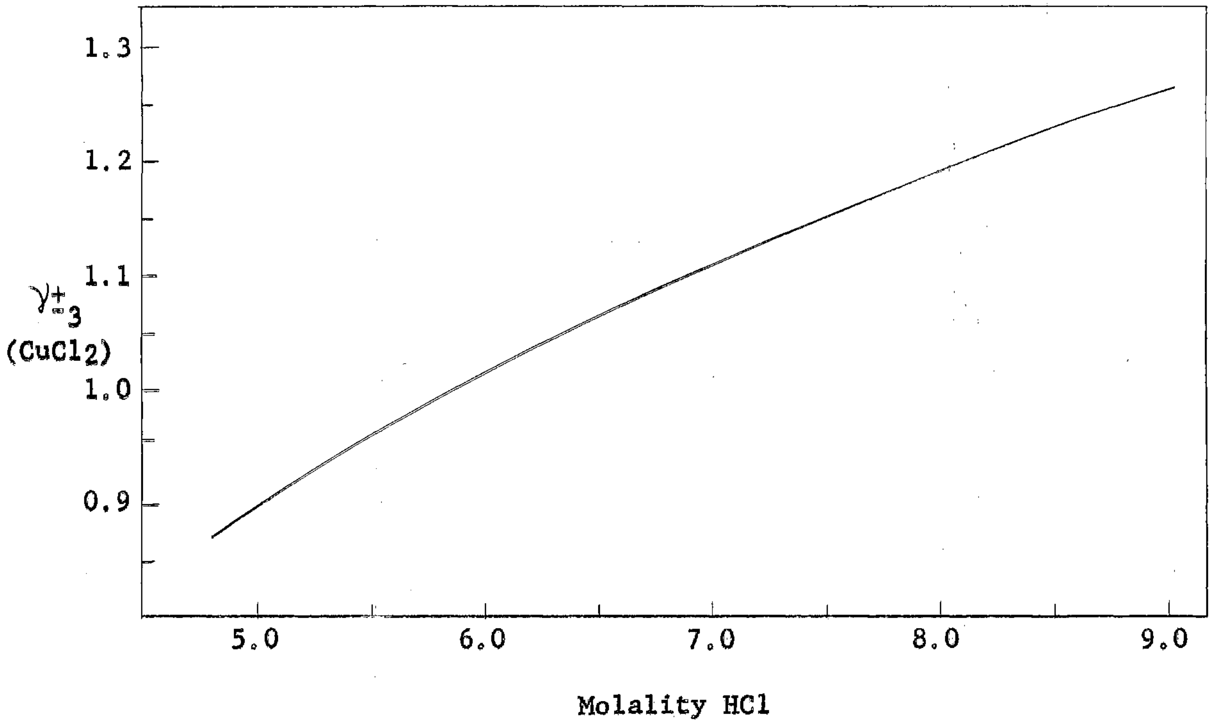


Fig. 8 Activity coefficient of $CuCl_2$ in the 1 molal $CuCl_2$-HCl-H_2O system.

however, the $CuCl_2$ activity is much smaller than that found for the chlorides of manganese (II), cobalt (II), and nickel (II) in comparable solutions. (16, 37). The effect of HCl on the activities of these metal chlorides may be seen from Table XXII.

It is readily observed that the presence of hydrochloric acid increases the salt activity in the order $NiCl_2 > CoCl_2 > MnCl_2 > CuCl_2$, and it appears significant that this is almost the reverse of the order of the cations in forming chlorocomplexes. That $CoCl_2$ and $MnCl_2$ are incompletely dissociated is shown by a variety of evidence. The results of activity studies made on concentrated solutions of $NiCl_2$ and $CoCl_2$ in HCl by Moore et al. (76) for example, have indicated that whereas the association of nickel (II) and chloride ions are probably not extensive, the undissociated $CoCl_2$ molecule is present in mixtures of $CoCl_2$ and HCl. Herber and Irving (43) have estimated from optical and anion exchange studies that solutions of 0.0422 molal $CoCl_2$ in 9 molal HCl contain 98 percent of the $CoCl_2$ as undissociated molecules. Robinson and Brown (86) from spectrophotometric data have estimated the concentration of undissociated $CoCl_2$ to be 4 and 15 percent in aqueous solutions of 1 and 5 molal $CoCl_2$, respectively. The color changes observed in $MnCl_2$-HCl solutions with increasing $MnCl_2$ or HCl concentrations have also been attributed to association of manganous and chloride ions. (16). From the data presented in Table XXII it appears likely that ion association is even more extensive in $CuCl_2$-HCl solutions than in the other three metal chloride-acid systems. Further evidences for ion association in the $CuCl_2$-HCl-H_2O system are that the H_2O activity is greater and the HCl activity smaller than in comparable solutions of $MnCl_2$, $CoCl_2$, or $NiCl_2$ and also that the color of the solutions varies from blue to green to

TABLE XXII

RATIO OF ACTIVITIES OF TRANSITION-METAL CHLORIDES IN HYDROCHLORIC ACID SOLUTIONS TO THEIR ACTIVITY IN BINARY SOLUTIONS AT A SALT CONCENTRATION OF 1.5 MOLAL

m_2(HCl)	$CuCl_2$	$MnCl_2$	$CoCl_2$	$NiCl_2$
4.7	52	312	1,000	1,800
7.0	144	1,880	6,500	18,600
9.0	270	6,220	21,000	------

yellowish-green with increased $CuCl_2$ or HCl molality. (99).

There is a great deal of evidence in the literature for the association of copper (II) and chloride ions both in aqueous solutions of $CuCl_2$ and in mixtures of $CuCl_2$ with HCl (see Chapter I). Optical studies have proven generally useful in studying the chlorocomplexes of copper only in dilute solutions of $CuCl_2$, but which may be concentrated with respect to HCl (up to ca. 6 molar HCl) (45); however, all attempts to study the concentrated $CuCl_2$-HCl-H_2O solutions of this research using a Beckman model DK-1 Spectrophotometer and employing cells with optical thicknesses as small as 0.5 mm proved unsuccessful because of the high absorbencies of the solutions.

The influence of chlorocomplexing upon the H_2O activity in $CuCl_2$-HCl-H_2O systems of constant chloride molality is shown in Fig. 9. There, the vapor pressure lowering is plotted against the Cu/Cl mole ratio for solutions of equal chloride concentration. As shown in the following section, if the electrolytes were completely dissociated a plot such as this would be expected to be a straight line with a slope proportional to the difference between the water vapor pressure lowering of two hydrogen ions and one copper (II) ion. Instead, a change in slope is observed at a mole ratio of about 0.25 corresponding to a 4 to 1 Cl/Cu ratio. By contrast, straight line relations were found to hold within experimental error when similar plots were made using data on $NiCl_2$-HCl in 10 molal chloride solutions, $CoCl_2$-HCl in 8 molal chloride solutions, and $MnCl_2$-HCl in 10 and 11 molal chloride solutions throughout the entire range of mole ratios. This may be taken as a further indication that the degree of chlorocomplexing in the $CuCl_2$-HCl-H_2O system is much greater than in either the $CoCl_2$-HCl or $MnCl_2$-HCl systems.

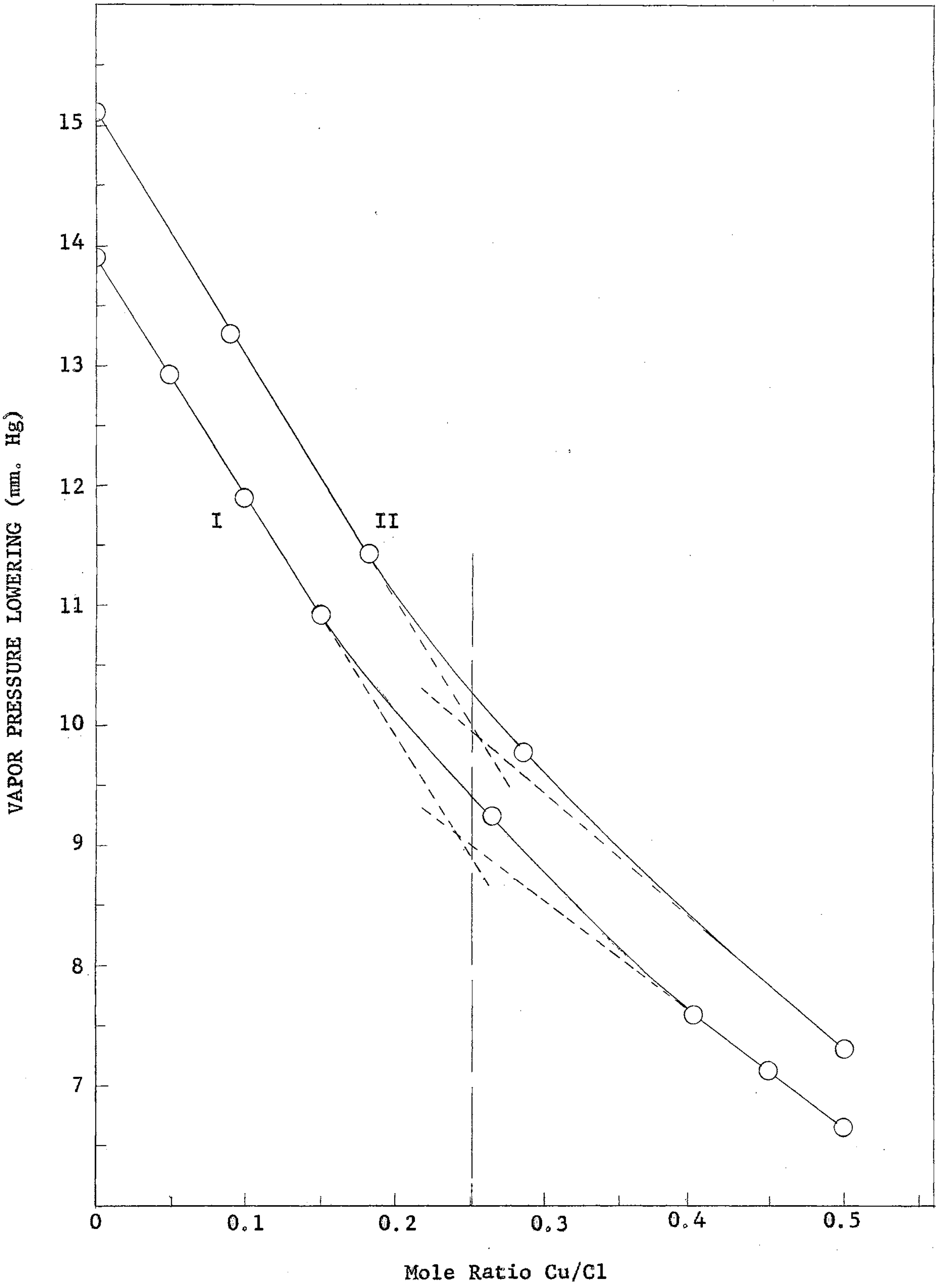


Fig. 9 Vapor pressure lowering in $CuCl_2$-HCl-H_2O systems of constant Cl^- molality: I, 10 molal Cl^-; II, 11 molal Cl^-.

Simple complex ion theory. The effect of ion association upon the H_2O activity in concentrated $CuCl_2$-HCl solutions may be interpreted semi-quantatitively (90) if one assumes that all the copper (II) ions in solutions of low Cu/Cl mole ratios are in the form of a complex, i.e., $CuCl_n^{2-n}$. A solution of m_3 molal $CuCl_2$ and m_2 molal HCl will then have the following total concentration of ions

$$(m_2)H^+ + (k - m_3n)Cl^- + (m_3)CuCl_n^{2-n} \qquad (1)$$

where k is the total chloride concentration $(m_2 + 2m_3)$ and n is the number of chloride ions associated with a copper (II) ion in the complex. The summation of the ion concentrations in these solutions is, therefore,

$$\sum_i = 2k - m_3(n + 1) \qquad (2)$$

Under the further assumption that all chloride ions in solutions of high Cu/Cl mole ratio are associated with copper (II) ions to form the same complex, one may write

$$\sum_i^* = (m_2)H^+ + (m_3 - k/n)Cu^{++} + (k/n)CuCl_n^{2-n} = k - m_3 \qquad (3)$$

for the ion concentrations in solutions of m_3 and m_2 molal $CuCl_2$ and HCl, respectively. Consideration of the relations (2) and (3) at intermediate Cu/Cl mole ratios shows that there will be a point of transition, i.e., where

$$\sum_i = \sum_i^* \qquad (4)$$

Upon equating equations (2) and (3) and solving for the Cu/Cl ratio one obtains

$$m_3k = 1/n \qquad (5)$$

From Fig. 9 it is readily seen that in agreement with this the water vapor pressure lowering in solutions of low and also high Cu/Cl ratios can be expressed as linear functions to the Cu/Cl mole ratio, i.e.,

$$\triangle P = B(m_3/k) + A \tag{6}$$

and

$$\triangle P' = B'(m_3/k) + A' \tag{7}$$

respectively, where $\underline{B}$ and $\underline{B'}$ are the slopes and $\underline{A}$ and $\underline{A'}$ are the intercepts of the respective curves. If one can assume as a first approximation that the vapor pressure lowering is a function of the number of ions in solution only, it follows that when $\underline{\Delta P} = \underline{\Delta P'}$ then $\Sigma_{\underline{i}} = \Sigma_{\underline{i}}^{*}$ and $\underline{m}_3/\underline{k} = 1/\underline{n}$. When equations (6) and (7) are equated and $1/\underline{n}$ is substituted for $\underline{m}_3/\underline{k}$ one has upon solving for $\underline{n}$

$$n = (B' - B)/(A - A') \tag{8}$$

Even more simply, $\underline{n}$ may be evaluated graphically since it is the reciprocal of the abscissa of the intersection point of the two line segments. The data represented in Fig. 9 gives $\underline{n}$ values of 4.1 and 3.8 for the 10 and 11 molal chloride solutions, respectively.

On the basis of the theory presented above, therefore almost all of the copper (II) ions in solutions for which $m_2 \geqq 2m_3$ can be considered to be associated with chloride ions as the tetrachlorocuprate (II) ion, and similarly solutions of $m_2 \leqq 2m_3$ have almost all the chloride in the form of the same complex. This treatment is admittedly very crude indeed, for it is quite evident that in solutions such as these there are also ionic equilibria involving several intermediate ionic species, i.e., Cu^{++}, $CuCl^{+}$, $CuCl_2$, $CuCl_3^{-}$, and $CuCl_4^{--}$. Nevertheless, the vapor pressure evidence presented here clearly shows that the tetrachlorocuprate

(II) ion is the complex species present to the greatest extent.

Thermodynamic Properties of the Solvent

Water activity. The water activities in the ternary systems at constant acid molalities of 4.7, 7.0, and 9.0 are compared with that of aqueous cupric chloride in Fig. 10. This figure shows that the water activity is lowered with increasing hydrochloric acid molality, and that the lowering of the water activity per mole of $CuCl_2$ is smaller in solutions containing HCl than in simple aqueous solutions of the salt. This may be seen more readily from Fig. 11, where the water activity in systems of constant cupric chloride molality are plotted as a function of HCl molality.

The large decrease in water activity upon the addition of electrolytes is generally attributed to hydration of solute ions, i.e., the removal of "free" water by ion-solvent interaction, the hydration theory of Stokes and Robinson (102) has met with considerable success in quantitatively accounting for the solute activity in binary nonassociated solutions of alkali, alkali earth, and some transition metal halides. This theory is really an extension of the Debye-Hückel theory and takes into consideration the relation between the rational activity coefficient of the solvated solute and the conventional activity coefficient computed with disregard to solvation. The resulting equation for the electrolyte activity coefficient contains two adjustable parameters; $\mathring{a}$, the distance of closest anion-cation approach and n, the effective hydration number. When dealing with the halides of hydrogen, the alkali metals and the alkali earth metals, these authors have further obtained a relation between $\mathring{a}$ and n by using the concept of limited penetration of the anion into the hydration sheath of the cation. They have thus been able to reduce their

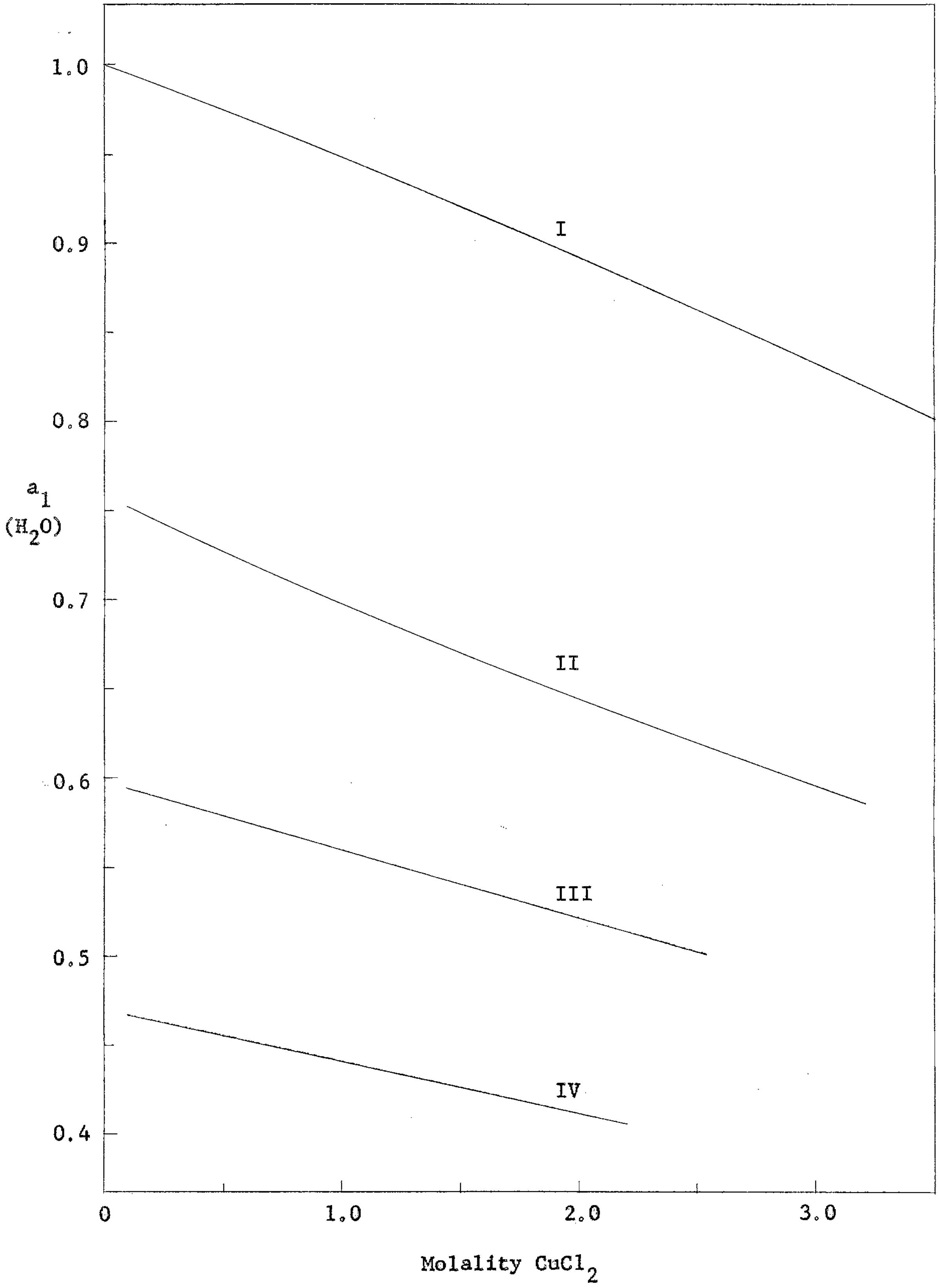


Fig. 10 Activity of H_2O in $CuCl_2$-HCl-H_2O systems of constant acid molality: I, binary system; II, 4.7 m HCl; III, 7.0 m HCl; IV, 9.0 m HCl.

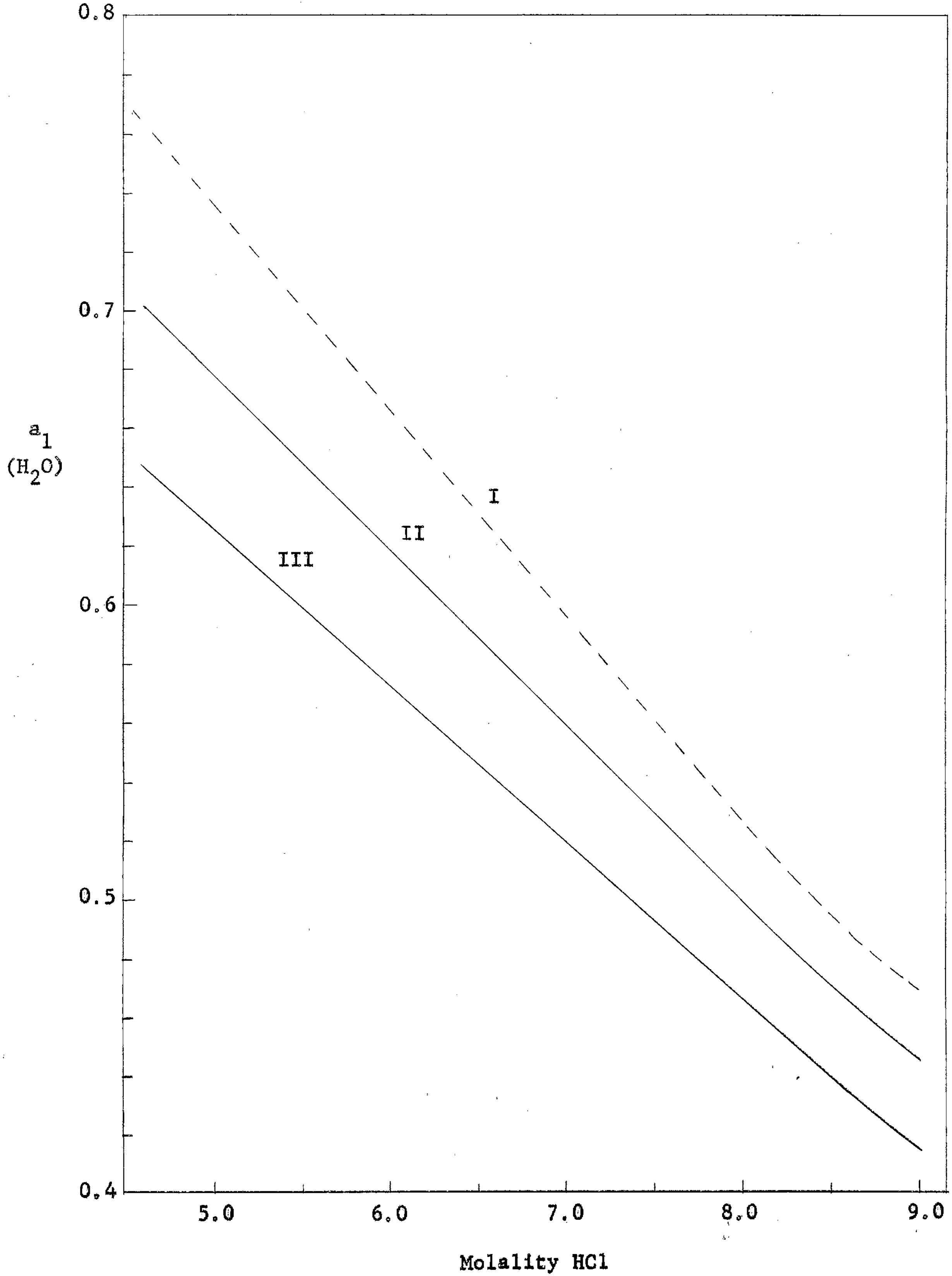


Fig. 11 Activity of H_2O in $CuCl_2$-HCl-H_2O systems of constant salt molality: I, 0 m $CuCl_2$; II, 1 m $CuCl_2$; III, 2 m $CuCl_2$.

original equation to a one parameter equation, capable of representing experimental activity coefficients of the above-mentioned halides with an accuracy of better than 1 percent in solutions of an ionic strength up to about 4. More recently, Glueckauf (36) has improved the theory through the use of volume fractions rather than mole fractions.

Moore et al. (76) have shown that Stokes' and Robinson's two parameter equation is, in principle, applicable to nonassociated systems containing any number of solutes. While this extended theory was successful in representing the activity coefficient of $NiCl_2$ in concentrated HCl solutions, it failed when applied to the partially associated electrolyte $CoCl_2$ in HCl.

In both the theory of Stokes and Robinson and its extension by Moore et al., the hydration numbers are empirically determined constants which are needed to give agreement between calculated and experimental activity coefficients over a reasonable concentration range. A more rigorous approach is to evaluate the hydration parameters from the properties of the solvent and to use the values to calculate the activity coefficient of the solute by the theory of Stokes and Robinson. (16).

Owing to the lack of complete dissociation in the systems under study, the data do not affort a fair test of the hydration theory. Nevertheless, hydration numbers of HCl and $CuCl_2$ in the $CuCl_2$-HCl-H_2O system have been calculated by three slightly different methods, based on the use, respectively, of (a) mole-fraction statistics, (b) volume-fraction statistics, and (c) the assumption that the activity of the solvent is proportional to the "free" water. The principles upon which each of these methods are based are discussed fully in the succeeding sections.

Mole-fraction statistics. The number of moles of "free" water per

1000 g. of water in an aqueous mixture of $CuCl_2$ and HCl is given by

$$n_1 = 55.51 - h_2m_2 - h_3m_3 \tag{9}$$

where $\underline{h}_2$ and $\underline{h}_3$ are the average number of moles of water bound to a mole of HCl and $CuCl_2$, respectively. For the free energy of this system one may write (see reference 36)

$$F = n_1\bar{\bar{F}}_1^o + m_2\bar{\bar{F}}_2^o + m_3\bar{\bar{F}}_3^o + F^{el} + F^s \tag{10}$$

where

n_1, m_2, m_3 have the same significance as in equation (9),
$\bar{\bar{F}}_1^o$ = standard-state chemical potential of "free" water,
$\bar{\bar{F}}_2^o$ = standard-state chemical potential of hydrated HCl,
$\bar{\bar{F}}_3^o$ = standard-state chemical potential of hydrated $CuCl_2$,
F^{el} = electrostatic contribution to the free energy,
F^s = entropy contribution to the free energy.

Differentiation of equation (10) with respect to "free" water at constant $\underline{m}_2$ and $\underline{m}_3$ gives for the chemical potential of "free" water

$$\bar{\bar{F}}_1 = \bar{\bar{F}}_1^o + \left(\frac{\partial F^{el}}{\partial n_1}\right)_{2,3} + \left(\frac{\partial F^s}{\partial n_1}\right)_{2,3} \tag{11}$$

Fowler and Guggenheim (32) show the electrostatic contribution to be

$$\left(\frac{\partial F^{el}}{\partial n_1}\right)_{2,3} = RT\left[\frac{K^3\sigma(Ka)\bar{\bar{V}}_1}{24\pi}\right] \tag{12}$$

where $\underline{K}$ is given by the Debye-Hückel treatment

$$K = \left[\frac{4\pi|e|^2\sum N_iz_i^2}{DKTV}\right]^{\frac{1}{2}} = b(\tfrac{1}{2}\sum C_iz_i^2)^{\frac{1}{2}} = b(I)^{\frac{1}{2}} \tag{13}$$

in which $\underline{I}$ is the ionic strength of the solution, $\sigma(Ka)$ is given by

$$\sigma(Ka) = f(b,\overset{o}{a},I^{\frac{1}{2}}) \tag{14}$$

and $\bar{\bar{V}}_1$ is the partial molal volume of "free" water.

The statistical contribution to the free energy of "free" water is based upon the statistical mechanical treatment of the mixing of ideal particles. (31). The last term on the right in equation (11) becomes, therefore,

$$\left(\frac{\partial F^s}{\partial n_1}\right)_{2,3} = \frac{\partial}{n_1}\left[RT\left[n_i \ln(n_i/D)\right]\right]_{2,3} \tag{15}$$

where n_i is the number of moles of the given ionic or molecular species and $D = \sum n_i$. For ternary systems of two nonassociated electrolytes the above equation reduces to

$$\left(\frac{\partial F^s}{\partial n_1}\right)_{2,3} = RT\left[\ln(n_1/D)\right] \tag{16}$$

and

$$D = \sum n_i = n_1 + \nu_2 m_2 + \nu_3 m_3 \tag{17}$$

where ν_2 and ν_3 are the number of moles of ions formed when 1 mole of component 2 or component 3 is added to the system, respectively. Substitution of equations (12) and (16) into equation (11) leaves

$$\left(\frac{\partial F}{\partial n_1}\right)_{2,3} = \bar{\bar{F}}_1^o + RT\left[\frac{K^3\sigma(Ka)\bar{\bar{V}}_1}{24\pi}\right] + RT\left[\ln(n_1/D)\right] \tag{18}$$

Using the definition for the chemical potential of the "free" water and rearranging equation (18), one obtains

$$\ln a_1 = B + \ln(n_1/D) \tag{19}$$

where

$$B \equiv K^3\sigma(Ka)\bar{\bar{V}}_1/24\pi \tag{20}$$

Substitution of equations (9) and (17) into equation (19) finally gives for the "bound" water

$$\frac{a_1(\nu_2 m_2 + \nu_3 m_3)}{a_1 - e^B} + 55.51 = h_2 m_2 + h_3 m_3 \qquad (21)$$

If the assumption that h_2 and h_3 remain constant for a given acid series were valid, a plot of the left member of equation (21) versus m_3 at constant m_2 would be a straight line intersecting the ordinate at $h_2 m_2$ and having a slope of h_3.

To evaluate the electrostatic term B in equation (21) it was necessary to assume the partial molal volume of "free" water was constant and equal to the partial molal volume of total water in each series of solutions of the same acid molality. The partial molal volume of total water was evaluated at a salt concentration of 1 molal using the data listed in Tables XVII and XVIII together with the following equation

$$\bar{\bar{V}}_w = \frac{V - m_2\bar{\bar{V}}_2 - m_3\bar{\bar{V}}_3}{55.51} \qquad (22)$$

where

$\bar{V}_w$ = partial molal volume of total water,

V = total volume per 1000 g. of total water,

$\bar{V}_2$ = partial molal volume of hydrochloric acid,

$\bar{V}_3$ = partial molal volume of cupric chloride.

The partial molal volume of "free" water was found to be 17.8 cc. in each of the three constant-acid series at a salt molality of unity. This value and the value chosen for the distance of closest anion-cation approach (assumed to be 4.80 Ångströms for all solutions) were used in equation (20) for the evaluation of B. The values chosen for $\bar{V}_1$ and $\mathring{a}$ are not critical however, for calculations show that, if the electrostatic term is neglected entirely, the error introduced in the final value of the "free" water is only about 3 percent over the entire concentration range.

In view of the evidence obtained for complex ion formation in the $CuCl_2$-HCl-H_2O systems under study and since the exact composition of the solutions could not be determined for lack of appropriate stability constants, the hydration parameters were calculated for the limiting cases of (a) complete dissociation of the solutes and (b) complete formation of the tetrachlorocuprate (II) ion. However, the resulting hydration parameters are very dependent upon the assumptions underlying their calculation. For if one considers the hydration of the individual ion, then in the case of completely dissociated solutes the "bound" water is given by

$$m_2h_2 + m_3h_3 = m_2h_{H^+} + m_3h_{Cu^{++}} + (m_2 + 2m_3)h_{Cl^-} \qquad (23)$$

where

$$h_2 = h_{H^+} + h_{Cl^-} \qquad (24)$$

and

$$h_3 = h_{Cu^{++}} + 2h_{Cl^-} \qquad (25)$$

whereas under the assumption of complete complex formation one obtains

$$m_2h_2 + m_3h_3 = m_2h_{H^+} + m_3h_{CuCl_4^{--}} + (m_2 - 2m_3)h_{Cl^-} \qquad (26)$$

where

$$h_2 = h_{H^+} + h_{Cl^-} \qquad (27)$$

and

$$h_3 = h_{CuCl_4^{--}} - 2h_{Cl^-} \qquad (28)$$

It is seen from equations (24) and (27) that the hydration parameter for HCl, $\underline{h}_2$, represents the same effect in both cases and is therefore independent of the original assumptions regarding $\underline{h}_3$. The significance of the $\underline{h}_3$ values is dependent upon the assumptions for although $\underline{h}_3$ represents the hydration of the salt in the limiting cases, it is a different function of the ionic hydration numbers in each case.

The plotted values of the "bound" water, based on the assumption of complete solute dissociation for the 4.7 molal HCl series, fell on a straight line over the entire concentration range as required by equation (21), while those for the 7.0 molal and 9.0 molal HCl series fell on smooth curves that showed an apparent increase in the amount of "free" water upon the addition of $CuCl_2$. This could possibly be attributed to the removal of HCl through complex formation.

Calculations made on the assumption of complete $CuCl_4^{--}$ complex formation gave values of the "bound" water for the 4.7 molal constant-acid series that fell on a smooth nonlinear curve over the concentration range studied while the values obtained for the 7.0 molal and 9.0 molal constant-acid series were found to vary linearly within the limits of estimated accuracy. These hydration numbers are listed in Table XXIII.

The average values obtained by mole-fraction statistics for the HCl hydration number in the 4.7, 7.0., and 9.0 molal acid series are 5.9, 5.1, and 4.5, respectively. These values compare favorably with the values of 5.7, 5.1, and 4.5 calculated by Burtch (16) for the HCl in the comparable series of solutions of $MnCl_2$-HCl-H_2O. Burtch has also pointed out that his HCl hydration parameters are in accord with those obtained by Moore et al. (76) for HCl solutions containing $NiCl_2$ and $CoCl_2$ and show an expected decrease with increase in HCl concentration from series to series.

<u>Volume-fraction</u> <u>statistics</u>. For mixtures of particles of different

TABLE XXIII

HYDRATION PARAMETERS FOR THE $CuCl_2$-HCl-H_2O SYSTEM

Method of Evaluation	4.7 m HCl		7.0 m HCl		9.0 m HCl	
	h_2	h_3	h_2	h_3	h_2	h_3
Mole-Fraction Statistics*	6.1	7.0	5.1	3.6	4.5	2.3
Mole-Fraction Statistics**	5.7	0.8	5.0	-0.4	4.5	-0.5
Volume-Fraction Statistics*	4.7	4.3	4.2	2.6	3.9	1.7
Volume-Fraction Statistics**	4.4	1.9	4.2	0.7	3.9	0.3
$a_1 = n_1/55.51$	2.9	3.0	3.2	2.2	3.3	1.6

* Based on complete formation of $CuCl_4^{--}$

** Based on complete dissociation of both HCl and $CuCl_2$

sizes the statistical contribution to the free energy is probably better expressed by volume-fraction statistics than mole-fraction statistics. For polymer solutions $\underline{F}^s$ has been shown by Flory (29) and Huggins (47) to be given by

$$F^s = RT \sum n_i \left[\ln(n_i \bar{\bar{V}}_i / V) \right] \tag{29}$$

where

n_i = moles of the given species,
$\bar{\bar{V}}_i$ = partial molal volume of the given species
V = total volume of solution per 1000 g. of water.

When the form of equation (29) appropriate to the $CuCl_2$-HCl-H_2O system is differentiated with respect to the moles of "free" water (n_1) at constant HCl and $CuCl_2$ molalities, one obtains

$$\left(\frac{\partial F^s}{\partial n_1}\right)_{2,3} = RT \left[1 + \ln(\bar{\bar{V}}_1/V) - (\bar{\bar{V}}_1/V)(n_1 + \nu_2 m_2 + \nu_3 m_3) \right] \tag{30}$$

The expression for the chemical potential of "free" water in terms of volume statistics is then obtained when equations (12) and (30) are substitued into equation (11). The resulting equation is

$$2.303(\log X) - X = 2.303(\log a_1) - (B + 1) + (\bar{\bar{V}}_1/V)(\nu_2 m_2 + \nu_3 m_3) \tag{31}$$

where

$X \equiv n_1 \bar{\bar{V}}_1 / V$ and $\underline{B}$ is the electrostatic term (see equation 20).

This is the equation given by Burtch (16).

The electrical term was evaluated using the same assumptions as those used with mole-fraction statistics, i.e., $\bar{V}_1 = \bar{V}_w$ and $\mathring{a} = 4.80$. This term contributes very little to the final results, for calculations show that neglecting $\underline{B}$ in equation (31) alters the values obtained for the "free" water only about 2.0 to 2.5 percent for all solutions studied.

Calculations based upon the assumption of the complete dissociation of the solutes gave results that fell on a smooth nonlinear curve for each constant-acid series. Values calculated for the 4.7 m HCl series indicated a decrease in $CuCl_2$ hydration with increased salt molality, while those for the 7.0 m and 9.0 m HCl series showed an apparent increase in salt hydration with increased molality. In view of the evidence for extensive complexing, the hydration numbers so calculated, however, are probably of doubtful significance. The values for the 4.7 m HCl series calculated on the basis of complex ion formation also fell on a smooth curve exhibiting less curvature than that shown by corresponding values from calculations using mole-fraction statistics. Similarly, values calculated for the 7.0 m and 9.0 m HCl series could be more closely fitted by straight lines than could the data obtained by mole-fraction statistics calculations. The hydration parameters are also included in Table XXIII.

Hydration parameters from water activities. A simple way to correlate water activities with hydration has been proposed by Moore et al. (76). Although it is entirely empirical, the method has been shown to give hydration parameters for HCl and $NiCl_2$ in mixtures of constant HCl concentration which agree acceptably with those calculated from the solute activity data. If one assumes the vapor pressure of water to be proportional to the number of moles of "free" water per 1000 g. of total water in the solution then

$$P = K(n_1) \qquad (32)$$

For 1000 g. of pure water in the standard state, $n_1 = 55.51$ and $P = P^o$; these values then give a proportionally constant of $P^o/55.51$ in equation

(32), hence

$$a_1 = n_1/55.51 \tag{33}$$

where a_1 is the activity of the water.

Hydration parameters obtained from the experimental water activities, using equation (33), are also listed in Table XXIII for comparison. The values of the hydrate water for solutions from 0.5 to 2.0 molal $CuCl_2$ in 4.7 molal HCl acid could be satisfactorily represented by a straight line when plotted against m_3. Values of "bound" water from 7.0 molal HCl solutions containing more than 0.5 molal $CuCl_2$ and also those for the entire 9.0 molal HCl series were also a linear function of the salt concentration.

Additivity rule. The vapor pressure lowering of mixed electrolyte solutions can sometimes be approximated, with fair degree of accuracy, by a simple additivity rule. (91, 93). This empirical rule states that the vapor pressure lowering of solutions containing mixed electrolytes at a constant total ionic strength is the sum of the contributions to the vapor pressure lowering from each electrolyte considered separately. The vapor pressure lowering of each electrolyte is taken as the product of the molal vapor pressure lowering for the electrolyte in a binary solution and its molality in the mixed electrolyte solution of the same total ionic strength. For the case of the $CuCl_2$-HCl-H_2O system this rule becomes

$$\left(\frac{\Delta P_1}{P_1^o}\right)_x = \frac{m_2}{m_2'}\left(\frac{\Delta P_1}{P_1^o}\right)_2 + \frac{m_3}{m_3'}\left(\frac{\Delta P_1}{P_1^o}\right)_3 \tag{34}$$

where the subscripts x, 2, and 3, refer to the mixed electrolyte solution, HCl and $CuCl_2$ solutions of equal total ionic strength, respectively.

As usual $\underline{m}_2$ and $\underline{m}_3$ represent the respective molalities of HCl and $CuCl_2$ in the mixture, and the primed quantities represent the molalities in the corresponding binary solutions.

Stokes and Robinson (91) have found that the agreement between observed and calculated values for the KCl-$MgCl_2$ system was within 1.3 percent for mixtures up to an ionic strength of unity. Agreements usually better than 1 percent have been obtained for aqueous mixtures of LiCl + $CoCl_2$, LiCl + $Co(NO_3)_2$, $CaCl_2$ + $CoCl_2$, and $CaCl_2$ + $MgCl_2$ having total molalities between 2 and 4. For more concentrated mixtures, i.e., 4 M $CaCl_2$ + 8 M LiCl and 4.7 M $LiNO_3$ + 5.3 M LiCl, agreements within 4 and 1.5 percent respectively were obtained. Brown (15) has found that the more associated systems of LiCl + $CuCl_2$ and $CaCl_2$ + $CuCl_2$ have vapor pressure lowerings that are from about 7 to 12 percent lower than those predicted by the additivity rule.

This rule was applied to the $CuCl_2$-HCl-H_2O system using the data of Randall and Young (85) to obtain the molal vapor pressure lowerings in binary solutions of HCl. The data of Stokes (101) was used for obtaining the molal vapor pressure lowerings of binary $CuCl_2$ solutions. Calculations were made on the basis of complete dissociation and also on the assumption of complete formation of the tetrachlorocuprate (II) ion in the electrolyte mixture. The $CuCl_2$ in binary solution was assumed to be completely dissociated in both cases, since the effect of ionic strength on the molal vapor pressure lowering in these solutions proved to be negligible.

Values calculated on the basis of complete dissociation averaged 7.0, 5.1, and 1.5 percent above the observed values, while those based on the assumption of complex ion formation averaged 2.3, 6.4, and 6.3

percent above the observed values for the 4.7, 7.0, and 9.0 molal hydrochloric acid series, respectively. A graphical comparison between the observed and calculated vapor pressure lowerings is given in Fig. 12. The percentage agreement in either case is impressive in view of the high concentrations and complexities of these solutions. However, the agreement between the shapes of the experimental and calculated curves is less satisfactory.

Thermodynamic Properties of Hydrochloric Acid

Hydrochloric acid activity. It has been mentioned previously that the activity, and consequently the activity coefficient, of hydrochloric acid is comparatively smaller in HCl solutions containing $CuCl_2$ than in comparable solutions of either $NiCl_2$, $CoCl_2$, or $MnCl_2$. This has been attributed to more extensive ion association in the $CuCl_2$ solutions.

The effect upon the activity of HCl produced by the addition of $CuCl_2$ may be seen in Figs. 13 and 14. Aside from the obvious increase in the acid activity, it should also be noted that the increase in activity per mole of added $CuCl_2$ is greater at the higher acid concentrations. These effects are reasonably attributed to increased chloride concentration from the added salt and to an increase in the effective concentration arising from the removal of "free" water through hydration of the salt. The effect on the hydrochloric acid activity of increasing acid and chloride concentrations is shown more readily in Fig. 15 where the activity of hydrochloric acid in 1 molal $CuCl_2$ solutions and that in the binary system are compared.

Activity coefficients and hydration theory. Theoretical values of the activity coefficients of hydrochloric acid in $CuCl_2$ solutions were

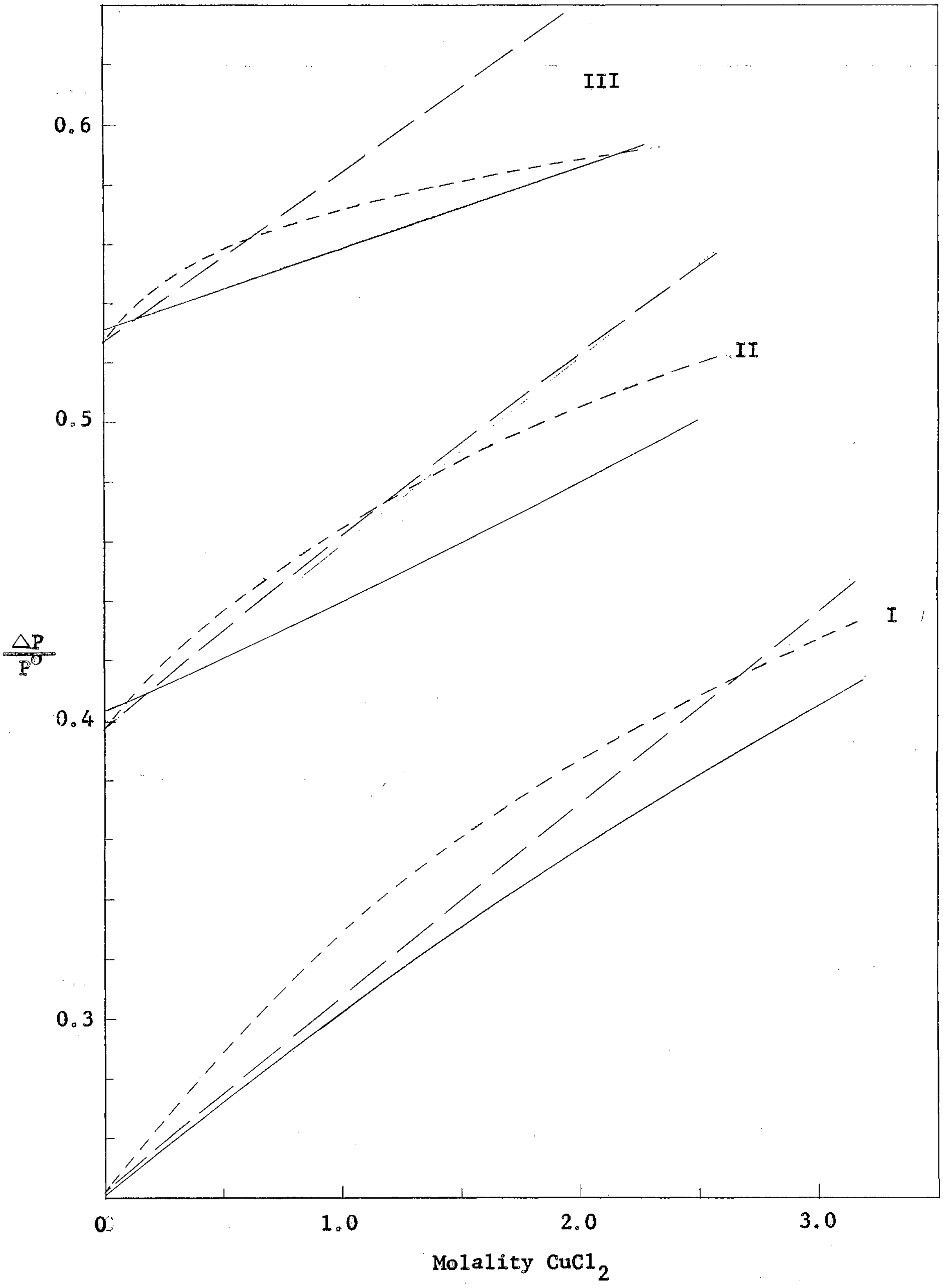


Fig. 12. Vapor pressure lowering of H_2O in $CuCl_2$-HCl-H_2O systems of constant acid molality: experimental values, ________; calculated values for completely dissociated solutes, - - - - - - - -; calculated values for complex formation, ____ ____ ____; I, 4.7 m HCl; II, 7.0 m HCl; III, 9.0 m HCl.

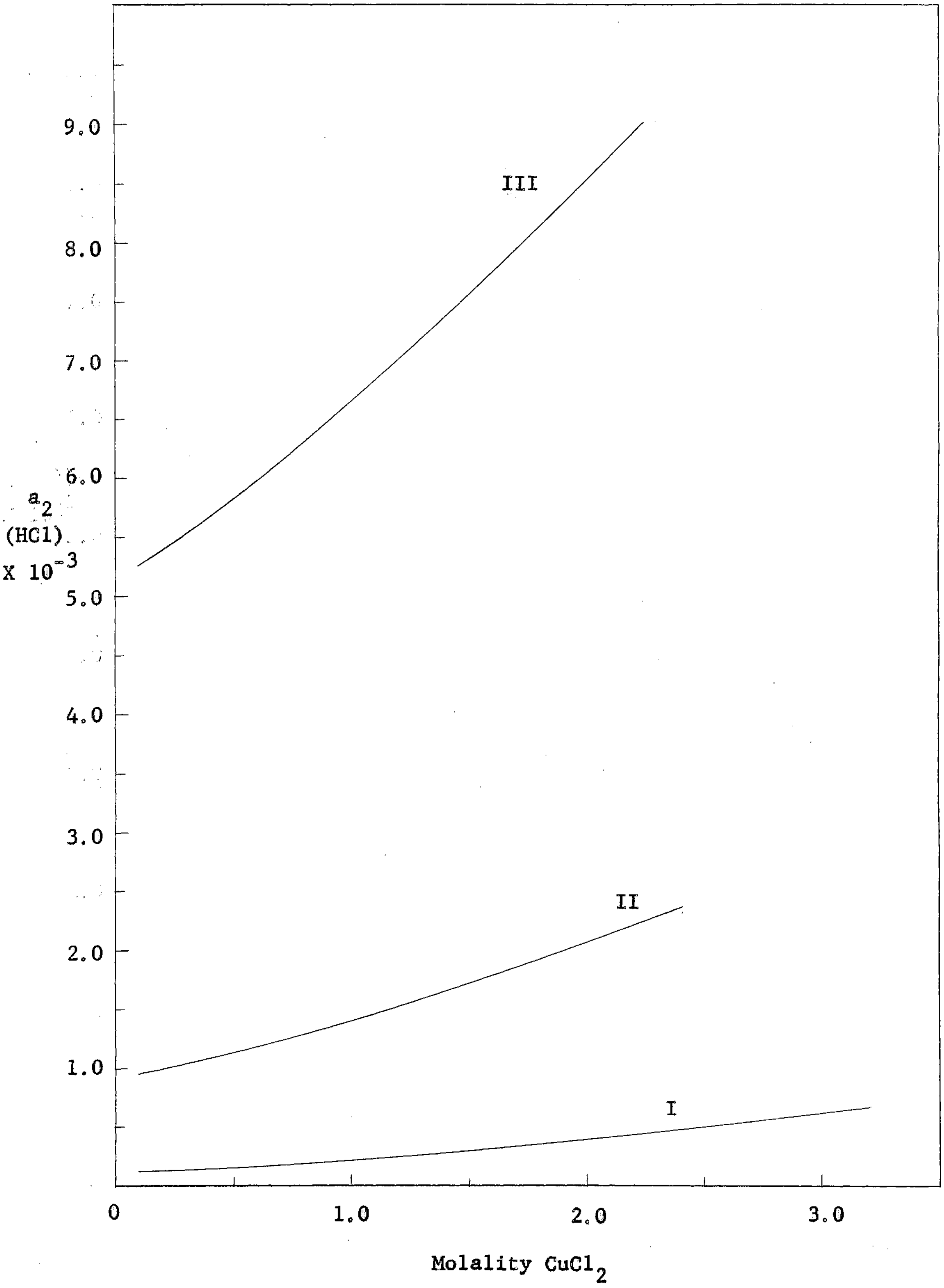


Fig. 13 Activity of HCl in $CuCl_2$-HCl-H_2O systems of constant acid molality: I, 4.7 m HCl; II, 7.0 m HCl; III, 9.0 m HCl.

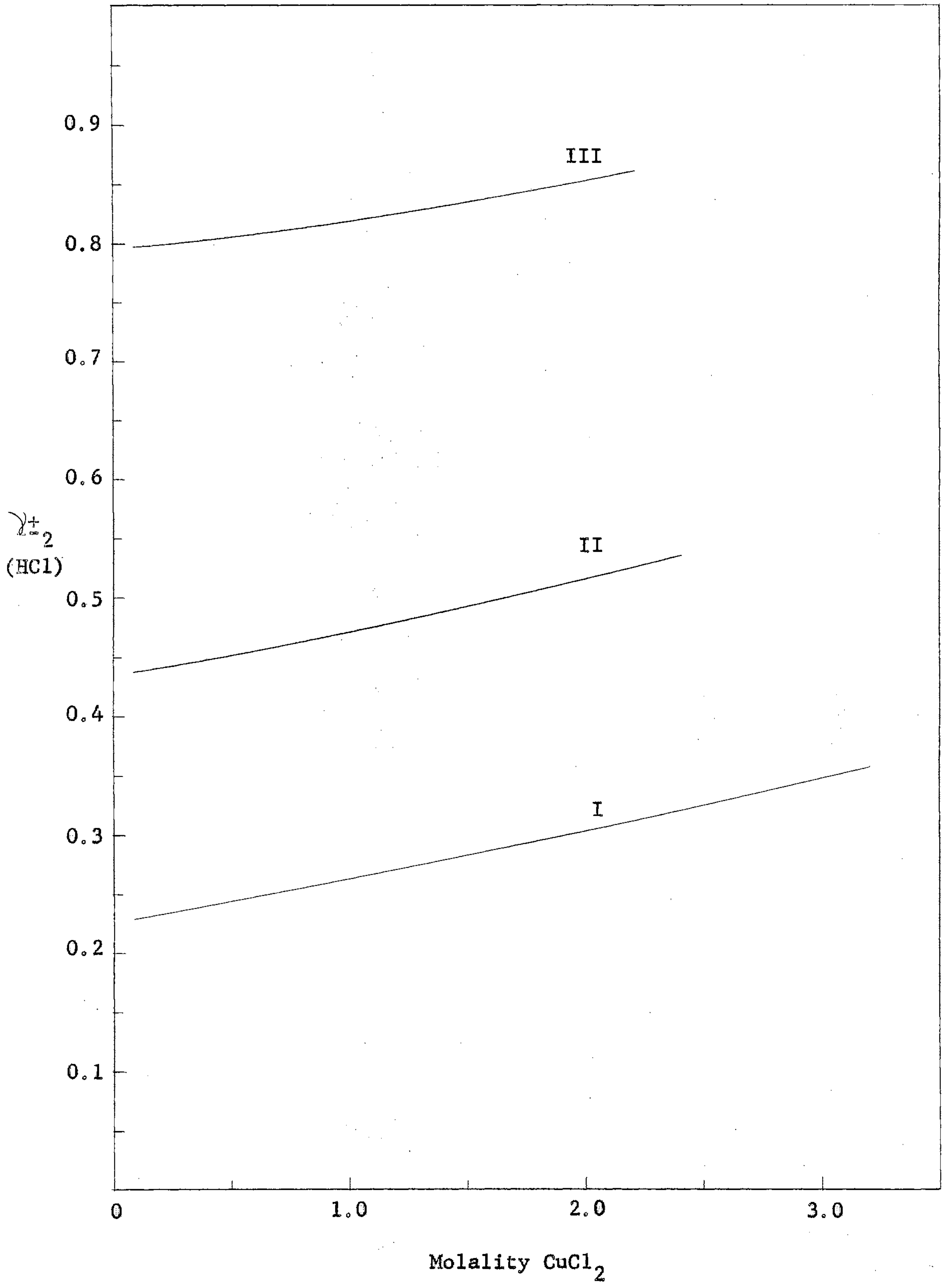


Fig. 14 Activity coefficient of HCl in $CuCl_2$-HCl-H_2O systems of constant acid molality: I, 4.7 m HCl; II, 7.0 m HCl; III, 9.0 m HCl.

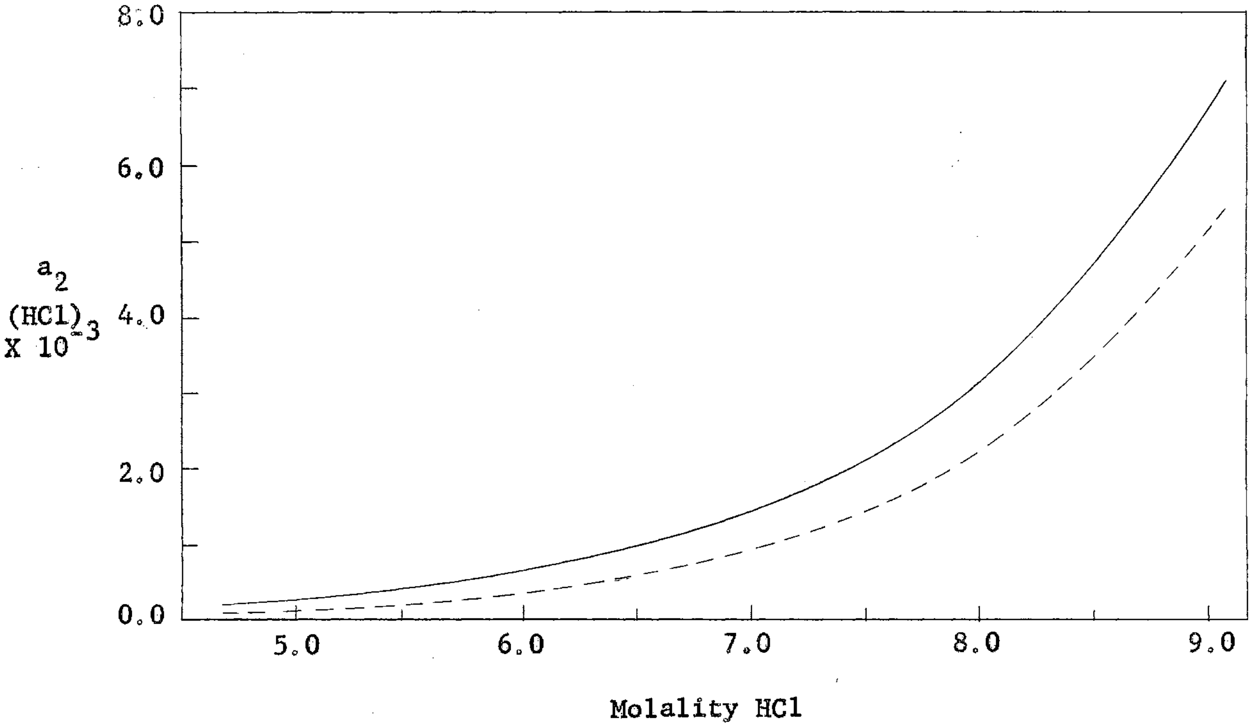


Fig. 15 Activity of HCl in the HCl-H_2O system, - - - - - -, and 1 molal $CuCl_2$-HCl-H_2O system, ———.

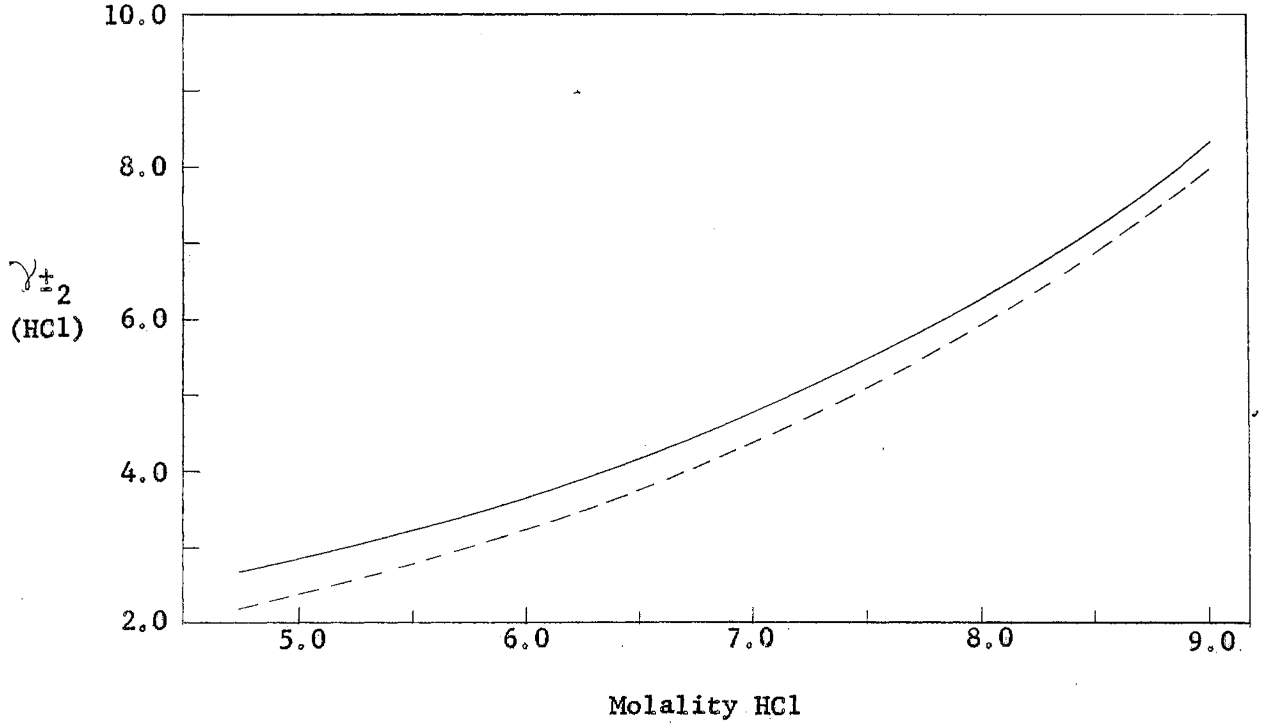


Fig. 16 Activity coefficient of HCl in the HCl-H_2O system, - - - - - -, and 1 molal $CuCl_2$-HCl-H_2O system, ———.

calculated according to the extension of the hydration theory of Stokes and Robinson (102, 91) by Moore et al. (76). According to this theory the activity coefficient of HCl is given by

$$\log \gamma_{\pm 2} = -(h_2/\nu_2)(\log a_1) - E - \log(n_1 + \nu_2 m_2 + \nu_3 m_3) + C \quad (35)$$

where $\underline{h}_2$ is the hydration number for HCl, $\underline{E}$ represents the usual Debye-Hückel expression for the rational activity coefficient

$$\log f_{\pm} = -\frac{A\, Z^{+} Z^{-} \sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} \quad (36)$$

and $\underline{C}$ is a constant of integration to be determined from experimental data. This equation, which is applicable to nonassociated electrolytes only, takes into account both ionic hydration and inter-ionic attraction. Activity coefficients of HCl in the three constant-acid series were calculated by using the hydration parameters found by each of the three methods outlined in the previous section. Agreement between calculated and experimental values was not good. The only values that a agreed within 1 percent were those calculated using the hydration numbers determined by volume statistics, assuming complete dissociation in the 4.7 molal HCl series of solutions. This is probably fortuitous, for the assumption of complete dissociation is almost certainly incorrect. The other calculated values deviated from 1 to 10 percent from the experimental values of the activity coefficient.

The results of the calculations made with equation (35) for the $CuCl_2$-HCl-H_2O system cannot be taken as a test of the hydration model of Stokes and Robinson, however, for their model can hardly be expected to be applicable to this system without appropriate corrections for ion association. A critique of Stokes' and Robinson's hydration equation has also been given by Glueckauf (36), in which it is pointed out that the correct form of the Stokes-Robinson equation is obtained by using the Debye-Hückel expression for the electrostatic contribution to the Gibbs free energy function, rather than to the chemical potential. Although Glueckauf's relation can be related directly to equation (21), and is correct for the Stokes-Robinson model, Glueckauf also points out that both equations will represent experimental activity coefficient data for nonassociated electrolytes about equally well.

Harned's rule. Harned (41) has shown from the results of many measurements made on solutions of constant total molality that the logarithm of the activity coefficient of one electrolyte in mixtures of constant total ionic strength is often linearly related to the molality of the other solute. This empirical rule can be written as

$$\log \gamma_{\pm 2} = \log \gamma^{o}_{\pm 2} - \alpha_2 m_3 \qquad (36)$$

where the superscript $\underline{o}$ refers to the activity coefficient of component 2 in solutions of zero molality in component 3 and $\underline{\alpha}_2$ is a function only of the total ionic strength and independent of the individual molalities of the solutes. A similar expression frequently holds for component 3. The form of equation (36) can be deduced from the theoretical considerations of Brönsted (14) and Guggenheim (38) in their treatment of the specific interaction of ions in dilute solutions of mixed electrolytes. (91).

Some systems of completely dissociated metal chlorides and perchlorates have been shown to obey Harned's rule up to a total molality of about 6. These have been summarized by Robinson and Stokes (91). Gootman (37) found this rule represented the activity coefficient of HCl in mixtures with $NiCl_2$ of total ionic strengths of 10 to 13, but failed when applied to similar solutions in the system $CoCl_2$-HCl-H_2O. Even in cases where equation (36) is known to fail, the logarithm of the activity coefficient of one solute can usually be expressed as a quadratic function of the other solute's molality. (40). Burtch (16) was able to represent the activity of HCl in solutions containing $MnCl_2$ of ionic strengths of from 10 to 15 by a quadratic equation.

The variation of the logarithm of the HCl activity coefficient with $CuCl_2$ molality is given in Fig. 17. In this plot the logarithm of the acid's activity coefficient is seen to vary linearly with salt molality over the range of HCl concentrations from 7 to 14 molal. Solutions containing less than 7 molal HCl have greater acid activity coefficients than predicted by Harned's rule. The deviations from linearity are also much greater and apparently occur more abruptly than those found in the $MnCl_2$-HCl-H_2O system by Burtch. Robinson and Farrelly (87) have similarly found that the activity coefficients in the $ZnCl_2$-$CaCl_2$ system do not follow Harned's rule in solutions having a total molality of 2.5 and 5.0 where extensive complex ion formation occurs. Failure of the rule to represent log $\gamma\pm_2$ in the $CuCl_2$-HCl-H_2O system at all ionic strengths is not unexpected, but that it is applicable to solutions of higher acid concentrations (above 7 molal) and not lower concentrations is a little surprising.

The $CuCl_2$ activity coefficient data could not be represented by Harned's rule.

An empirical relation for the $CuCl_2$-HCl-H_2O system. Attempts to investigate the applicability of Harned's rule to the $CuCl_2$-HCl-H_2O system led to the discovery of the following interesting relation. It was found that the logarithm of the HCl activity coefficient can be expressed as a linear function of $CuCl_2$ or HCl molality in systems of

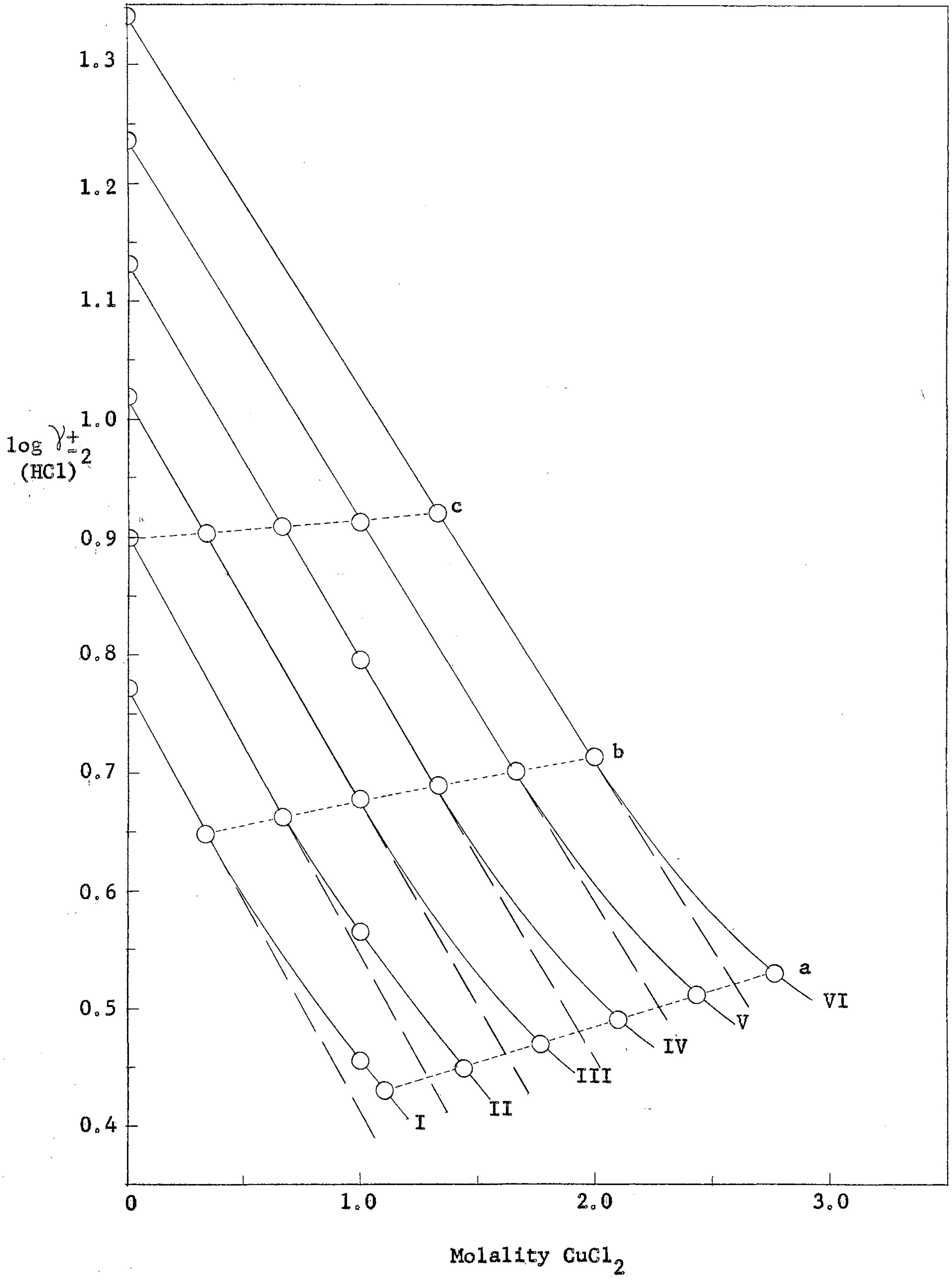


Fig. 17 Log $\gamma_{\pm}^{2}$ (HCl) verses molality of $CuCl_2$ at constant ionic strengths: I, μ= 8; II, μ= 9; III, μ= 10; IV, μ =11; V, μ= 12; VI, μ= 13; a, 4.7 m HCl; b, 7.0 m HCl; c, 9.0 m HCl.

constant HCl/$CuCl_2$ mole ratio. Empirical equations illustrating the above relation were found for five values of this ratio from 4 to 8 by the method of least squares. These equations are given in Appendix B. The validity of this empirical relation is shown in Table XXIV where calculated and experimental values for the HCl activity coefficient are compared.

In view of the complexity of the $CuCl_2$-HCl-H_2O system and the limited concentration range over which the empirical relation has been tested, one cannot say just how generally useful the relation may prove to be. There is, of course, the possibility that it is merely a unique property of the $CuCl_2$-HCl-H_2O system.

Attempts to find a similar relation for the activity coefficient of $CuCl_2$ in the solutions were unsuccessful.

TABLE XXIV

CALCULATED HYDROCHLORIC ACID ACTIVITY COEFFICIENTS

m(HCl)/m($CuCl_2$)	m_3	Calc. $\gamma\pm_2$	Exp'l. $\gamma\pm_2$
4	1.18	2.69	2.71
4	1.75	5.04	5.05
4	2.25	8.71	8.63
5	0.94	2.63	2.62
5	1.00	2.85	2.86
5	1.40	4.91	4.90
5	1.80	8.43	8.46
6	0.78	2.56	2.57
6	1.00	3.67	3.67
6	1.16	4.78	4.79
6	1.50	8.35	8.35
7	0.67	2.52	2.53
7	1.00	4.74	4.73
7	1.29	8.28	8.28
8	0.59	2.49	2.50
8	0.88	4.72	4.67
8	1.00	6.22	6.25
8	1.13	8.20	8.23

CHAPTER VII

SUMMARY AND CONCLUSIONS

The gas-transpiration method has been employed to simultaneously measure the vapor pressures of H_2O and HCl above four series of $CuCl_2$-HCl-H_2O solutions at 25°. Three of the series were composed of solutions having constant HCl concentrations of 4.7, 7.0, and 9.0 molal, respectively, and having $CuCl_2$ molalities varying from 0 to saturation in 0.25 molal increments. The fourth series was made up of solutions containing 1 molal $CuCl_2$ with HCl concentrations varying from 4.7 to 9.0 molal in 0.5 molal increments.

The activity of the volatile components were calculated directly from the measured vapor pressures after choice of appropriate standard states. Empirical expressions for the H_2O and HCl activities as functions of the $CuCl_2$ molality were obtained by the method of least squares. The resulting empirical equations were substituted into the Gibbs-Duhem equation and an empirical equation for the $CuCl_2$ activity was obtained by integration. The mean molal activity coefficients of both HCl and $CuCl_2$ were also calculated and are tabulated at even molal intervals.

Studies were made of the three-phase equilibria in the $CuCl_2$-HCl-H_2O system. The solubilities of $CuCl_2$ in each constant-acid series, the composition of the equilibrium solid phases, and the corresponding vapor pressures of the saturated solutions were determined.

The total volumes of the solutions per 1000 g. of H_2O, the apparent molal volumes and the partial molal volumes of $CuCl_2$ were obtained from the measured densities of the three constant-acid series. The apparent and partial molal volumes of HCl in the constant-salt series were similarly calculated.

The probable accuracy of the activity data has been evaluated. Preliminary vapor pressure measurements showed an agreement with literature values of the vapor pressure of H_2O above aqueous H_2SO_4 solutions of better than 0.1 percent, but the experimental HCl vapor pressures averaged between 1.5 and 2.0 percent higher than the literature values. However, on the basis of the precision of the measurements and the lack of concordance between independent investigations reported in the literature, it is concluded that the reliability of the HCl vapor pressures is as good as any reported to date. The precision of the H_2O and HCl vapor pressure measurements was generally better than ± 0.1 and ± 0.5 percent, respectively.

The probable uncertainties in the activities calculated from the empirical equations were estimated by considering the probable errors involved in (a) the experimental measurements, (b) curve fitting, and (c) integration of the Gibbs-Duhem equation. An approximate evaluation of the consistence of the $CuCl_2$ activities in the three constant-acid series was made from the second partial derivative of the free energy. It was concluded that the accuracy of the $CuCl_2$ activities is about ± 5 to ± 10 percent for solutions having $CuCl_2$ concentrations greater than 1 molal, but that this accuracy decreases rapidly as the salt molality decreases below 1 molal.

The activity of H_2O was found to decrease almost linearly with increasing concentrations of HCl in aqueous $CuCl_2$ solutions. However, the molal lowering of the H_2O vapor pressure is much greater for the acid than for the salt.

The increase in HCl activity and the decrease in H_2O activity upon the addition of $CuCl_2$ was found to be much less than that produced by $MnCl_2$, $CoCl_2$, or $NiCl_2$ at comparable concentrations. This, and the changes in the color of the solutions with changes in $CuCl_2$ or HCl molality lead to the conclusion that ionic association is more extensive in $CuCl_2$-HCl solutions than in similar systems of the other three transition metal chlorides. The H_2O vapor pressure lowerings found for solutions of constant chloride concentration were shown to be consistent with the formation of the tetrachlorocuprate (II) ion on the basis of simple complex formation theory. Hydration numbers for HCl and $CuCl_2$ in the ternary systems were calculated by the use of three slightly different hydration equations. Individual sets of calculations were made with models based on mole-fraction statistics and volume-fraction statistics. The calculations were made both under the assumption of complete dissociation of the solutes and also complete formation of the $CuCl_4^{--}$ ion. Attempts to evaluate the activity coefficients of the solutes by using the hydration numbers so obtained together with the hydration equation of Stokes and Robinson were unsuccessful. This is ascribed in part to the inability to properly account for the strong ionic association in the systems. The applicability of the vapor pressure lowering additivity rule of Robinson and Stokes was also tested. The calculated H_2O vapor pressure lowerings were larger than the corresponding observed values, and this is again attributed to the failure to correct for ionic association.

It was found that although Harned's rule holds pretty well for the HCl activity coefficient in $CuCl_2$-HCl-H_2O solutions having an acid molality greater than 7, departure from the rule increases with increasing $CuCl_2$ molality in solutions of lower HCl molality. The logarithm of the HCl mean activity coefficient was found to be a linear function of $CuCl_2$ or HCl molality in series of constant HCl/$CuCl_2$ mole ratio. Empirical equations for representing the HCl activity coefficient by this relation were obtained by the method of least squares. No simple numerical relation could be found to connect the $CuCl_2$ activity coefficient with the concentrations.

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APPENDIX A

EQUATIONS FOR COMPUTING ACTIVITIES OF SOLUTION COMPONENTS IN $CuCl_2$-HCl-H_2O SYSTEMS AT 25°

4.7 molal HCl-$CuCl_2$-H_2O system

$$\log a_1 = -0.1198 - 0.03981m_3 + 0.005258m_3^2 - 0.002309m_3^3 + 0.0003534m_3^4$$

$$\log a_2 = 2.052 + 0.3559m_3 - 0.08620m_3^2 + 0.02720m_3^3 - 0.003572m_3^4$$

$$\log a_3 = 1.2259 + 1.239 \log m_3 + 0.2260m_3 + 0.00062m_3^2 - 0.003782m_3^3$$

7.00 molal HCl-$CuCl_2$-H_2O system

$$\log a_1 = -0.2238 - 0.02526m_3 - 0.002515m_3^2$$

$$\log a_2 = 2.966 + 0.1907m_3 - 0.008682m_3^2$$

$$\log a_3 = 1.5862 + 0.1558 \log m_3 + 0.4007m_3$$

9.00 molal HCl-$CuCl_2$-H_2O system

$$\log a_1 = -0.3288 - 0.02379m_3 - 0.002156m_3^2$$

$$\log a_2 = 3.709 + 0.1164m_3 - 0.002854m_3^2$$

$$\log a_3 = 1.9408 + 0.6294 \log m_3 + 0.2908m_3$$

1.00 molal $CuCl_2$-HCl-H_2O system

$$\log a_1 = -0.03836 - 0.01431m_2 - 0.002324m_2^2$$

$$\log a_2 = 0.6071 + 0.3854m_2 - 0.003049m_2^2$$

$$\log a_3 = -1.0873 + 0.7942m_2 - 0.06369m_2^2 + 0.002033m_2^3$$

APPENDIX B

EQUATIONS FOR COMPUTING HYDROCHLORIC ACID ACTIVITY COEFFICIENTS IN $CuCl_2$-HCl-H_2O SYSTEMS OF CONSTANT HCl-to-$CuCl_2$ MOLE RATIOS AT 25°

$m(HCl)/m(CuCl_2) = 4.0$: $\log \gamma_{\pm 2} = 0.475m_3 - 0.129$

$m(HCl)/m(CuCl_2) = 5.0$: $\log \gamma_{\pm 2} = 0.589m_3 - 0.134$

$m(HCl)/m(CuCl_2) = 6.0$: $\log \gamma_{\pm 2} = 0.715m_3 - 0.150$

$m(HCl)/m(CuCl_2) = 7.0$: $\log \gamma_{\pm 2} = 0.834m_3 - 0.158$

$m(HCl)/m(CuCl_2) = 8.0$: $\log \gamma_{\pm 2} = 0.961m_3 - 0.167$

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