ACTIVITIES OF MANGANOUS CHLORIDE OR MANGANOUS SULFATE IN AQUEOUS HYDROCHLORIC ACID MIXTURES

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CHAPTER I

INTRODUCTION

Purpose and Scope of Investigation.

With the increased development within recent years of ion exchange and solvent extraction as separational methods for transition metal salts in mixtures, has come a need for more thermodynamic information about these mixtures. The separation of cobalt from nickel by the selective extraction of cobalt chloride from hydrochloric acid solutions of these salts by 2-octanol (107) initiated an investigation of the activity coefficients of cobalt and nickel chlorides in the ternary systems $CoCl_2$-HCl-H_2O and $NiCl_2$-HCl-H_2O (108). The extension of the study of solvent extraction to manganous chloride-hydrochloric acid mixtures in turn led to the present investigation of the activity relationships in the $MnCl_2$-HCl-H_2O system.

The present investigation was undertaken as part of a program designed to study activity relationships from the standpoint of solute-solvent and solute-solute interactions in ternary systems. The ternary systems of $MnCl_2$-HCl-H_2O and $MnSO_4$-HCl-H_2O at acid concentrations comparable to those studied by Moore, et. al. (108) for cobalt and nickel chlorides were investigated. An attempt has been made to interpret the data on the basis of the ionic hydration theory of Stokes and Robinson (158, 137) and the empirical relationships of Harned (67).

Aside from the possible application of the thermodynamic data obtained to various problems in chemistry, an investigation of this type is important in its own right in making a contribution to the field of thermodynamics of concentrated electrolyte solutions. As will be evidenced in later sections, quantitative information on ternary systems of electrolytes is limited, especially in concentrated solutions, since the acquisition and interpretation of this information is a complex problem from both theoretical and experimental viewpoints.

Literature Survey.

A survey of the literature has shown that there has been only one comparable investigation of the activities of transition metal salts in concentrated aqueous solutions of hydrochloric acid. In this study Moore, et. al. (108) determined the activities of all the components in the system.

Previous activity studies of ternary mixtures involving concentrated aqueous solutions of electrolytes have been made in only a few instances, and in no cases have the activities of all the components been determined in the system. In almost every case where the activity of the salt has been determined, measurements were made on cells involving an electrode reversible to the metal ion (113, 20, 130, 144, 59). A number of ternary systems involving dilute or moderately concentrated aqueous solutions of electrolytes have been investigated, however. Electromotive force measurements have been used in some instances to obtain the activity ratio of a salt and an acid (15, 18, 69, 17). In other instances solubility measurements (29) have been employed to obtain the activity of the salt in the presence of added electrolytes. Isopiestic measurements (117, 126, 132, 127, 146, 16) have been employed in some instances to obtain the isopiestic ratio of two salts in an aqueous mixture. Solvent extraction of transition metal salts (46, 112, 73) has also been reported as a means of obtaining the activity of one salt in the presence of another. Distillation methods (93) have been used to obtain the activity of water and alcohol in alcohol-water-salt mixtures. The activity coefficient of sulfuric acid has been determined by electromotive force methods in aqueous salt solutions (27) and in aqueous alcohol solutions (39). The determination of the activity coefficient of benzoic acid in aqueous salt solutions has also been reported in the literature (76, 143).

Studies directed toward understanding the nature of concentrated hydrochloric acid solutions of salts include the work of Yannakis (174) who studied the effect of salts on the total vapor pressure of the solution, and that of Morosov (109), who studied the effect of salts on the partial pressure of hydrochloric acid from the solution. Recently vapor pressure measurements of zinc or copper chloride in hydrochloric acid solutions have been reported by Lidlich and Timofeev (90).

Several investigators (58,54,122,66,65,68,160,96,55,32,33,53, 63,64,62,52) have measured the activity coefficient of hydrochloric acid in ternary mixtures with lithium, sodium, potassium, ammonium, magnesium, aluminum, calcium, barium, strontium, lanthanum, or cerium chloride by the electromotive force method. The same method was also employed to obtain the activity coefficient of hydrochloric acid in solutions of sodium or potassium perchlorates (8), and in solutions of sodium dithionate and perchloric acid (111).

Solubility measurements were used by Akerlof and Turck (4) to obtain the activity coefficient of hydrochloric acid in sodium and in potassium chloride solutions at high acid and salt concentration.

Photometric methods (147) have been employed to obtain the activity coefficient of hydrochloric acid in sulfuric acid solutions. Electromotive force methods (118) have been employed in the case of hydrochloric-hydrobromic acid mixtures to obtain the activity coefficient of hydrogen bromide. Ion exchange membranes (74) have also been employed to obtain the activity coefficient of hydrochloric acid in dilute aqueous acid mixtures.

The activity coefficient of hydrochloric acid has been determined by electromotive force methods in several aqueous ternary systems containing one organic component such as ethyl alcohol (110,115,173), methyl alcohol (2,116), glycerol (92), dioxane (60), 1-dodecanesulfonic acid (165), acetone (72), propyl alcohol (24), isopropyl alcohol (106), and butyl alcohol (71).

However, the results of most of these investigations are not particularly relevant to the hydrochloric acid-water-manganous chloride or manganous sulfate systems since the measurements were usually made on solutions which were relatively dilute in both hydrochloric acid and salt or organic component; and the activity of only one component, viz; hydrochloric acid, was measured.

It is evident, therefore, that the field of concentrated ternary salt systems is almost unexplored because of the difficulties encountered in the experimental determination of the activities of all the components. In the absence of suitable reversible electrodes, one is faced with the problem of using the Gibbs-Duhem equation to obtain the salt activities. With this point in mind let us turn to the theoretical aspects of solutions of electrolytes in general and then to concentrated ternary solutions in particular.

The general theory of solutions of electrolytes in relation to ionic interaction has been reconsidered recently from the viewpoint of the statistical mechanics of electrostatic interactions (77,145) with emphasis on the importance of taking into account the proper volume of ions in the ionic atmosphere. Wicke and Eigen (167) have taken into consideration the effect of ionic volumes in order to account theoretically for the increase in the activity as a function of electrolyte concentration in moderately concentrated solutions. Recently their theory has been extended to higher concentrations (34) of electrolytes. Schmutzer (148) and Falkhagen (35) have also extended the ionic volume theory to higher concentrations. The work of Huckel and Krafft (70), however, is not in agreement with the theory of Falkhagen or Wicke, et. al. at higher concentrations.

Revival of Bronsted's theory (19) of specific ionic interaction in mixed electrolyte solutions is shown in a recent discussion by Scatchard and Breckenridge (146). A revision of the best values of interionic interaction-coefficients in aqueous solutions of mixed electrolytes has been presented by Guggenheim and Turgeon (51). Their work was based on Bronsted's theory of specific interaction.

A recent discussion of mixed electrolytes in terms of heat content and molal volumes has been given by Young and Smith (175). Theoretical treatment of the experimental data on partial molal volumes for the aqueous ternary systems, potassium chloride-sodium chloride, potassium bromide-sodium chloride, potassium sulfate-sodium chloride (169), sodium chloride-hydrochloric acid (170), sodium acetate-acetic acid, and sodium chloride-acetic acid (171) have been reported by Wirth, and sodium perchlorate-perchloric acid by Wirth and Collier (172).

Harned's rule (67, 140) has been found to be a useful approximation for activity coefficients in mixed electrolyte solutions, and a recent thermodynamic corollary proposed by Glueckauf, et. al. (46) has been tested by Robinson (127, 129), Robinson and Lim (132), Jenkins and McKay (73), Harned (56), and Harned and Gary (62, 63, 64). Argersinger and Mohilner (6) have recently showed that for mixtures of hydrochloric acid with barium, strontium, and aluminum chlorides, the rule is followed approximately by both electrolytes. The applicability of Harned's rule to the data from electromotive force and solubility measurements of alkali chloride-hydrochloric acid-water systems has been thoroughly discussed by McKay (101). He has indicated that there exists larger and more widespread deviations than generally has been realized. Moore, et. al. (108) found in their study that Harned's rule was valid only as a first approximation for the nickel chloride-hydrochloric acid-water system, but not at all for the cobalt chloride-hydrochloric acid-water system.

An interesting discussion of ionic solvation theory has been presented by Bockris (14), stressing the structural aspects of the theory. Various methods of determining the hydration number of the solutes in electrolytic solutions are discussed. The values obtained are shown to be lower in general than the values reported by Stokes and Robinson (139). The structural theories of water by Bernal and

Fowler (11), Verwey (162), and Latimer, Pitzer, and Slansky (88) have been considered in relation to the hydration numbers of solutes in electrolytic solutions.

Efforts to relate the activity coefficients of binary solutions of electrolytes to ionic hydration have met with considerable success through a relation developed by Stokes and Robinson (158). The possibility of relating activities of mixed electrolytes to their hydration numbers in a similar fashion has been suggested by Robinson and Stokes (137). Moore, et. al. (108) have extended the theory to ternary mixtures and treated their experimental results according to this extended theory.

The influence of ionic hydration on activity coefficients in concentrated electrolyte solutions has been further considered by Glueckauf (44), who has suggested that the anomalies in the Stokes and Robinson hydration parameters are due to the disregard of co-volume effects (161). If volume fractional statistics are used instead of mole fractional statistics, an equation is obtained that is equally effective and easier to handle than that of Stokes and Robinson. Qualitatively Stokes and Robinson in their book (139) have drawn attention to the necessity for some consideration of the volumes of hydrated ions and have recognized that a reduction in the size of the hydration numbers would result. Still more recently another equally successful modification of the hydration theory has been proposed by Miller (105).

A hydration-association theory has been proposed by Frank (38) in which there is dealt with the effect of solvation in increasing the activity coefficient, and of ion-pairing formation (13) in counteracting this increase. Recently Reiss (125) has presented a refined theory of ion pairing which is free of many of the inconsistencies that are present in the older and simpler theory of ion-pairing based on mass action considerations (13, 42). The review by Redlich and Jones (124) has attempted to cover the recent literature on the subject of solutions of electrolytes through 1954.

The treatment of the experimental activity data obtained from studies of ternary solutions of electrolytes has been discussed by several investigators with respect to the integration of the Gibbs-Duhem equation. Nowotny and Orlicek (114) employed experimentally determined values of the slopes of the curves representing the total pressure as a function of two volatile components. The method appears laborious and is probably best suited to a system consisting of two highly volatile components. The integration of the ternary Gibbs-Duhem equation has also been discussed by Darken (28), McKay (100), and McKay and Perring (102), who have showed that integration is possible from a knowledge of but one of the partial molal quantities under isothermal conditions. The number of measurements required is very large, however, and this is a serious disadvantage to the employment of such a method. Robinson (128) and McCoy and Wallace (99) have applied the method of McKay and Perring to isopiestic data.

Argersinger (5) has similarly derived explicit relations for use with electromotive force measurements as has Friedman (40) for use with solubility measurements. Schuhmann (149) has derived relations between the tangent intercepts of isoactivity curves for various components and has made this the basis of a graphical procedure for constructing isoactivity curves. Moore, et. al. (108) have integrated the Gibbs-Duhem equation from a knowledge of the chemical potentials of two of the components and have calculated the activity of one component in varying concentrations in solutions having constant concentrations of the other two components.

Since during the course of this investigation vapor pressure measurements were made on the binary systems consisting of sulfuric acid-water, hydrochloric acid-water, manganous chloride-water, and manganous sulfate-water, a brief review of the literature values of the vapor pressures and activity coefficients of these systems follow.

The vapor pressure of water above its sulfuric acid solutions has been determined by several investigators. Of these Greenwalt (49) and Grollman and Fraser (50) are among the earliest with reliable data. Collins (25) has given a review of the work done on the sulfuric acid-water system up to 1933. More recently Shankman and Gordon (154) using a static method have measured the vapor pressure of water above sulfuric acid solutions at concentrations from 2 to 23 molal. The most recent studies are those of Stokes (157) and Glueckauf and Kitt (45) in which the osmotic coefficients obtained from isopiestic measurements have been converted to partial pressures of water.

The activities of both hydrochloric acid and water in aqueous solutions of hydrochloric acid have been determined by several investigators using various methods. Bates and Kirschman (7) directly determined the partial pressure of hydrochloric acid above its aqueous solutions at 25°C using the comparative gas-transpiration method. Zeisberg (176) has made a compilation of the literature values of the partial pressures of hydrochloric acid and water prior to 1925. A review of the work done up to 1928 has been given by Randall and Young (123) in their paper on the determination of the activity of hydrochloric acid by the electromotive force method.

Since 1928 several investigators (3,4,61) have determined the activity of hydrochloric acid in its aqueous solution by electromotive force and solubility methods. However, the usefulness of this data for comparative purposes depends partly upon the accuracy of the previous vapor pressure data and is further limited by the fact that in dilute solutions where the accuracy of these methods is high, the vapor pressure method is inapplicable because of the low partial pressure of the hydrochloric acid. The most recent measurements of hydrochloric acid activities in aqueous solutions are those of Robinson and Stokes (136) who have reported both the osmotic and activity coefficients of the acid. McCarty (98) and Fritz and Fuget (41) have also recently obtained the partial pressure of hydrochloric acid over its aqueous solutions by electromotive force methods.

The activity of both manganous chloride and manganous sulfate in their aqueous solutions has been determined from values of the water activities by integration of the Gibbs-Duhem equation. The water activities in the manganous chloride-water system were determined isopiestically at 25°C by Robinson and Stokes (135) up to 4.8 molal, and by Stokes (157) up to 8.0 molal. Robinson and Jones (131) have determined the water activities in the manganous sulfate-water system at 25°C up to 4.2 molal in manganous sulfate and Robinson and Stokes (134) have recalculated the data up to 4.0 molal.

Electromotive force methods, which in many cases have proved to be extremely valuable in determining salt activities in both binary and ternary systems, could not be used in this research. In the first place no reversible electrode with a reproducible potential for the manganese-manganous couple has ever been reported in the literature. Latimer (87) has relied heavily upon the work of Walkley (164) in his discussion of the manganese-manganous couple. Walkley, using thermal data, calculated a value of -1.18 ± 0.012 volts for the standard potential of the manganese-manganous couple. However, this value is more negative than the values usually quoted from electromotive force data and is more negative than the value reported by Agladze (1), who also used thermal measurements. Walkley has admitted that confirmation of his value by methods of modern precision calorimetry is clearly required. However, even if a reversible manganese metal-metal ion electrode were available, attack by hydrochloric acid would make it useless.

Since the saturated solutions and the solid phases in equilibrium with them were to be used as secondary reference states in obtaining the activities of the salt in the ternary systems, the literature was searched for data on the solubility and the composition of the solid phases in equilibrium with the saturated solutions, both for the binary and ternary systems.

Kapustinskii (75) found agreement with the data of Dawson and Williams (30) on the solubility of manganous chloride in water at 25°C, but the data of Benrath (10), however, does not agree with that of the above investigators. The solid phase in equilibrium with the saturated solution of manganous chloride was reported to be the tetrahydrate by Dawson and Williams (30). The solubility of manganous sulfate in a saturated aqueous solution at 25°C has been reported by Cottrell (26) and Krepelka and Rejka (85), who are in close agreement, but whose values differ somewhat from the value reported by Sidgwick (155). The composition of the solid phase in equilibrium with the saturated aqueous solution has been reported to be the pentahydrate by several investigators (26,85,155,163). A compilation of the literature values for the above aqueous binary systems can be found in Seidell (150,151) and Seidell and Linke (152,153).

No data for the solubility or the composition of the solid phases in equilibrium with the saturated solutions in ternary systems of hydrochloric acid and the manganous salts mentioned above were found. However, Ditte (31) has reported that the dihydrate of manganous chloride was the stable form obtained at very high hydrochloric acid concentrations.

CHAPTER II

EXPERIMENTAL

Apparatus.

The apparatus used was a modification by Gootman (48) of that described by Bechtold and Newton (9) for the measurement of water vapor pressure by the comparative gas-transpiration technique. The principle modification was in the absorbers, of which one set (the "solvent" or reference set) was filled with magnesium perchlorate and the other set (the "solution" set) with a mixture of anhydrous magnesium perchlorate and sodium hydroxide-impregnated asbestos. The latter material occupied about the first 2/3 of the absorption tube and pure magnesium perchlorate the remaining 1/3 of the exit end of the absorption tube. Preliminary experiments demonstrated the complete absorption of both HCl and H_2O vapors in the absorbers.

The actual apparatus and conditions of operation employed in this investigation were essentially identical with those used by Gootman except for the constant temperature water bath which was maintained at 25.00 ± 0.02°C instead of at 30°C. The thermometer used in controlling this bath was graduated in 0.05° divisions and standardized against a thermometer (No. 73035) calibrated by the U. S. National Bureau of Standards. The constant temperature air bath was maintained at 33.0 ± 0.5°C. The input flow-meter and its accessory components were removed during the course of the investigation and a needle valve was inserted in the system between the Linde valve of the nitrogen tank and the safety valve. The base section of a Tirrill gas burner was used as the needle valve assembly.

Preliminary density measurements at 33°C showed that a 1 mm height of n-dibutyl phthalate used in the differential manometer was equivalent to 0.0762 mm of Hg.

A mercurial barometer of the U. S. Signal Corp (Fortin Principle) type was used as a standard to calibrate the vapor pressure apparatus barometer. The standard barometer was a wall type and possessed a vernier graduated to read to 0.01 mm of Hg. The corrections necessary to give a reading at standard barometric conditions (0° C and gravity as at 45° latitude and sea level) were made according to the directions described by Lange (86).

The vapor pressure apparatus barometer was also corrected for temperature by multiplying the difference in the heights of the mercury columns (uncorrected pressure) by the ratio of the density of mercury at the given temperature and the density of mercury at 0° C. To the value thus obtained a correction factor of -0.7 mm for altitude-gravity and latitude-gravity was added to give a reading at standard barometric conditions. On comparison of the corrected values of the standard barometer and the vapor pressure apparatus barometer over a range of room temperatures, it was found that the two values agreed within the experimental error of reading the barometers.

The solution balance weights were calibrated by the method of substitution as described by Kolthoff and Sandell (80). A 1 gram weight from a set of Class S1 weights was used as a standard. A DLB type chainomatic balance was used for the calibration of the weights, except in the case of the 500 and 1,000 gram weights which were calibrated on the solution balance. The solution balance had a sensitivity of 10 mg per scale division with no load.

Since the initiation of this investigation, what appears to be an important modification of the apparatus which was used by us has been reported in the literature by Smith, Combs, and Googin (156). They have employed a rotating drum type of saturator rather than a flowing bubble type (9); thereby eliminating some pressure drop and possible entrainment of mist or spray in the gas stream. With this type of saturator they have reported increased precision in vapor pressure measurements by the gas transpiration method, using smaller volumes of solutions and shorter equilibration times.

Chemicals.

The manganous chloride ($MnCl_2 \cdot 4H_2O$) used in this study was Baker's Analyzed Reagent grade (Lot 3213) having a listed assay of not more than 0.0003% iron (Fe).

The manganous sulfate ($MnSO_4 \cdot H_2O$) used in this study was Baker's Analyzed Reagent grade (Lot 2679) having a listed assay of not more than 0.001% iron (Fe) and 0.002% nickel (Ni).

The hydrochloric acid used was Aloe, C. p. Analyzed and Baker's Reagent grade.

The nitric acid used was Aloe, C. p. Analyzed grade.

The ammonium hydroxide used was Aloe, C. p. Analyzed grade.

Mallinckrodt Analytical Reagent grade perchloric acid, 60%, with a listed assay of 0.001% Cl^- ion was used in neutralizing the sodium hydroxide in the absorber mixture.

Merck Reagent grade potassium acid phthalate, sodium chloride, and potassium chloride were used as primary standards.

The silver nitrate used in the chloride determinations was Mallinckrodt Analytical Reagent grade.

The ammonium nitrate used in the salt bridge was Merck Reagent grade with a listed assay of 0.0005% chloride.

Eimer and Amend Reagent grade sodium hydroxide with a listed assay of 0.005% chloride was used in the preparation of the sodium hydroxide-asbestos absorber mixture.

The n-dibutyl phthalate used in the differential manometer was a product of the Matheson Company.

The magnesium perchlorate (granular anhydrous) used in the absorbers was a G. Frederick Smith Chemical Company product. It failed to give a qualitative test for the chloride ion with silver nitrate.

The asbestos used in the absorber mixture was Eimer and Amend Asbestos (fine fibre) and E. H. Sargent and Company (medium fibre). Both were specified as being acid washed and chloride free.

The ammonium chloride used was Baker's C. p. Analyzed grade.

The ammonium phosphate (dibasic) used was Merck Reagent grade.

The tank nitrogen was a Linde product.

Distilled water was used throughout this study and will be designated simply by the term "water".

<u>Procedures.</u>

<u>Vapor Pressure Measurements.</u>

The procedure followed was essentially that used by Bechtold and Newton (9) and Gootman (48). In this study the constant temperature water bath was adjusted to 25°. The absorbers were kept in the constant temperature air bath at 33° for at least one hour and then weighed before beginning a measurement. At the end of a measurement the absorbers were removed from the air bath, wiped with a chamois cloth and weighed on a DLB type Ainsworth chainomatic balance having a sensitivity of ± 0.0001 gram. An empty absorption tube, serving as a counterpoise, was suspended above the right hand pan of the balance in all of the weighings of the absorption tubes. The weights used were Fisher "Perma" type adjusted to Class S tolerance of the U. S. National Bureau of Standards.

Analytical Methods.

I. Analysis for Chloride in the Absorbers. After completion of an experiment, the contents of the sodium hydroxide-asbestos absorber were placed in a 400 ml beaker and the absorber was rinsed first with distilled water, then with 25% perchloric acid by volume and finally three times with distilled water. After complete neutralization to the phenolphthalein endpoint with the perchloric acid, the solution was analyzed for chloride potentiometrically (79) employing an indicating silver electrode made from 3 inches of 21 gauge silver wire, and a saturated calomel half-cell as a reference electrode. The reference electrode was separated from the unknown solution by a 100 ml electrolytic beaker containing 1 molar ammonium nitrate and contacts were made by using an agar-ammonium nitrate salt bridge. The 400 ml beaker containing the unknown was placed in a black-painted 600 ml beaker which acted as a shield from the direct sunlight. This beaker also acted as a cooling bath as it contained an ice water mixture to lower the temperature of the unknown solution during the titration. During the titration the solution was continually stirred by means of a Magna-Stir magnetic stirrer.

A circuit described by Willard, Merritt, and Dean (168) was employed, using a 6 volt storage battery as a source of voltage. At the outset of this study a Rubicon High Precision, Type B potentiometer was used. Toward the end of the study a Leeds and Northrup Student type potentiometer was substituted for the Rubicon instrument, and a second Leeds and Northrup Student type potentiometer was used as a working resistance in order to obtain the fine adjustment necessary to null the galvanometer for a satisfactory reading during the course of the titration.

II. Analysis for the Chloride Ion. In addition to the method described above, solutions having a relatively high chloride content were analyzed for chloride gravimetrically as silver chloride (81).

III. Analysis for Manganese. Manganese was analyzed gravimetrically as the pyrophosphate according to the directions given by Kolthoff and Sandell (82). Recently a method for the analysis of manganese, employing 8-hydroxyquinoline as a precipitant, was showed by Miller (104) to have a higher degree of precision and accuracy than the pyrophosphate method.

Preparation and Standardization of the Solutions.

I. Sulfuric Acid Solutions. The sulfuric acid solutions used as vapor pressure standards were prepared by dilution of concentrated sulfuric acid with water. They were analyzed by an acid-base titration (84) with carbonate-free sodium hydroxide (83) to a phenolphthalein endpoint.

II. Hydrochloric Acid Solutions. The hydrochloric acid solutions were prepared by mixing concentrated hydrochloric acid and water in a ratio calculated to give an approximate molality which had been predetermined. Then by successive additions of small quantities of either water or acid, followed each time by an acid-base titration, the concentration of the solution was adjusted to the desired molality.

III. Ternary Mixtures. The ternary mixtures, hydrochloric acid-water-manganous chloride or manganous sulfate were prepared in the following manner. Water, hydrochloric acid, and the hydrated salt ($MnCl_2 \cdot 4H_2O$ or $MnSO_4 \cdot H_2O$), which had been pulverized with a mortar and pestle, were added in small increments until a stock solution of desired acid molality and near saturation with respect to the salt had been prepared. Stock hydrochloric acid solutions were prepared having the same molality as the hydrochloric acid contained in the stock ternary solutions. Portions of these two stock solutions were weighed into one liter ground glass-stoppered erlenmeyer flasks in varying ratios using a solution balance. In this manner three series of solutions of constant hydrochloric acid molality and varying salt molality were prepared.

A stock solution of predetermined molality was also prepared by mixing hydrated manganous chloride with water. The stock solution thus obtained was then added in varying amounts to three of the ternary solutions of the same salt molality, thereby obtaining a series of solutions of constant salt molality and varying acid molality. The analyses which were carried out to determine the composition of the stock solutions are described in the following section.

IV. Saturated Solutions. All saturated solutions, both binary and ternary, were prepared by periodically adding small amounts of the hydrated salt to appropriate (nearly saturated) solutions which were kept continuously at 25° in a water bath. The saturated solutions of manganous chloride, both binary and ternary, having small amounts of the solid phases in equilibrium were prepared with no particular difficulty. The saturated binary solution of manganous sulfate offered some difficulty because the phase diagram (26) for the system shows there is a triple point for mono, penta, and metastable tetra hydrate just above 25°. The dissolution of the hydrated manganous sulfate in the water was found to be exothermic; therefore a method similar to that described by Carnot (22) was employed to obtain the solid phase in equilibrium with the saturated solution. The solution was cooled down in an ice bath to approximately 10° C and then allowed to approach 25° C slowly. The saturated ternary solution of manganous sulfate and hydrochloric acid was prepared similarly. It might be noted here that Storonkin and Markuzin (159) have obtained equilibrium in saturated aqueous solutions of potassium chloride in hydrochloric acid at 25° C within 2.5 hours by intensive stirring. The concentrations of hydrochloric acid in their study varied from 0 to 18 molar.

Analyses were carried out to determine the composition of the solution phase. In the binary saturated solution of manganous chloride the composition was determined gravimetrically for both the cation and the anion. In the case of the binary solution saturated with manganous sulfate the solution was analyzed gravimetrically for the cation. In the ternary systems the manganese was determined gravimetrically as the pyrophosphate. Total chloride ion was then determined gravimetrically as silver chloride.

Analysis of the Solid Phases.

I. Binary Systems. For analysis of the solid phases in equilibrium with the binary solutions, samples of the wet solid were dried by blotting several times with filter paper before being weighed; they were then analyzed gravimetrically for the anion in the case of the manganous chloride and for the cation in the case of the manganous sulfate.

II. Ternary Systems. In three-component solutions the composition of the solid phase in equilibrium with the saturated solution was determined by the wet-residue method of Schreinmaker (36). A weighed sample of the wet crystals was dissolved in water, diluted to 500 ml, and a 50 ml aliquot analyzed for both the cation and anion. On the usual tringular graph for three component systems a line was drawn through points corresponding to the composition of the wet crystals and the concentration of the saturated solution. The intersection of this line with the manganous chloride or sulfate axis determined the percentage of manganese and water in the solid phase.

Density Determinations.

A Reimann thermometer-plummet and a DLB-type chainomatic balance were used initially in determining the density of the solutions. The solutions were kept in a 25° water bath prior to use; and about 60 ml of the solution was used for the determination. Later it was observed that in order to calculate the apparent molal volumes with an accuracy of at least 1.0 percent, the densities needed to be measured with a precision of 0.05 percent. Since the hydrostatic weighing method (166) did not meet this requirement, a Leach type specific gravity bottle of 50 ml capacity was employed. This bottle was first calibrated with water at 25°C. The solution was chilled to about 15° before being added to the bottle, and then the bottle and the solution were placed in a carefully regulated thermostat at 25°. Excess solution was drained away through a capillary side arm as the solution warmed up slowly. When 25° was reached the bottle was capped, dried, and weighed.

Preparation of Fine Asbestos.

Fine-fibre asbestos was found to be more convenient for packing in the absorption tubes, and solutions were easier to titrate than when medium-fibre asbestos was used because of the continual stirring required. Because fine-fibre asbestos was not always obtainable the following method of preparation is described. Medium-fibre asbestos was made into a slurry with distilled water and then introduced into a Waring blendor and ground until the correct consistency had been obtained. Most of the water was removed by suction using a Buchner funnel. The asbestos was then placed in an oven to dry at 130°C. Occassional stirring of the asbestos facilitated the drying process.

Sodium Hydroxide-Asbestos Mixture.

The mixture of sodium hydroxide and asbestos was prepared by adding a solution of approximately 0.8 molar carbonate-free sodium hydroxide to Gooch filter quality asbestos in a 100 ml beaker and evaporating to dryness at 130°C. At least a fourfold excess of sodium hydroxide solution over that calculated to be necessary for the average length of an experiment was added to insure complete absorption of the hydrochloric acid vapors.

CHAPTER III

DETERMINATION OF ACTIVITY

Binary Systems.

In the case of binary systems there have been employed a variety of methods to obtain the activity of either the solute or the solvent. Those methods applicable to the direct determination of the solute activity include vapor pressure measurements, solubility determinations, liquid-liquid equilibria, ion exchange equilibria, and electromotive force measurements. Methods applicable to the direct determination of the solvent include vapor pressure measurements, freezing point and boiling point determinations. These methods and others are discussed in such standard references as Harned and Owen (67), Lewis and Randall (89), and Robinson and Stokes (139). Once one has obtained the activity of either of the components, the activity of the other component can be calculated by means of the Gibbs-Duhem equation as described, for example, by Klotz (78).

Ternary Systems.

The problems involved in the measurement of the activities of the components in a ternary system containing either manganous chloride or sulfate is a difficult one from an experimental standpoint. Measurement of the solvent activity alone does not enable one to calculate the activity of either of the other components from a single series of measurements (100, 102).

Applying the Gibbs-Duhem relation to a ternary system one obtains an equation of the form

$$n_1\ d\bar{F}_1 + n_2\ d\bar{F}_2 + n_3\ d\bar{F}_3 = 0 \qquad (1)$$

where n_1, n_2, and n_3 are the moles of each component and $\bar{F}_1$, $\bar{F}_2$, and $\bar{F}_3$ are the respective partial molal free energies. It can be seen from this equation, therefore, that given the composition terms n_1, n_2, n_3, and the variation in two of the partial molal free energies, $\bar{F}_1$ and $\bar{F}_2$, it is possible to calculate directly the third partial molal free energy.

Measurement by freezing point depression was not applicable as there were two solutes (HCl and salt) in the system under consideration and their individual activities could not be differentiated from the total effect observed. Furthermore, as mentioned in an earlier section, electromotive force measurements could not be used since no reversible electrode with a reproducible potential for manganese has ever been obtained.

Because there were two measurably volatile components (HCl and H_2O) consideration was given to the possible use of vapor pressure measurements to obtain both the activity of the solvent and the hydrochloric acid. There are several experimental techniques that have been employed in vapor pressure measurements, namely static (21), dynamic (142), dew point (97), isopiestic (133), and gas transpiration (121). Of the above methods only the last is suited for the simultaneous measurement of both vapor pressures.

Most of the data on the activities of the binary systems used as references in this study were taken from the literature; however, since the values were determined isopiestically, a short discussion of the method seemed appropriate at this point. In the isopiestic method two vessels at the same temperature but containing different solutes in the same solvent are placed in an enclosed container. Since the vapor pressure of the two solutions are ordinarily different, solvent distills from one vessel into the other until the vapor pressures are equalized. From the knowledge of the vapor pressure of one solution (the reference) over a range of compositions, the vapor pressure and concentration of the unknown solution in vapor-phase equilibrium with the reference solution can be calculated from an analysis of both solutions.

In the gas transpiration method, which was the method adopted for this work, one saturates a known amount of gas by passage through the solution whose vapor pressure is to be determined and analyzes the saturated vapors. Making use of the relation (Dalton's law).

$$p_1 = N_1 \, p \tag{2}$$

where p_1 = partial pressure of component 1

N_1 = mole fraction of component 1

p = total pressure

one calculates the partial pressure of each component of the gaseous mixture from experimental knowledge of p, N_1, and N_2.

Having obtained the partial pressures of two of the components of a ternary mixture and one can then use suitable formulas derived from Eq. 1 to obtain the activity of the third component. Using the usual definition of the activity

$$\overline{F}_j = \overline{F}_j^o + RT \ln a_j \tag{3}$$

then differentiating (1) with respect to n_3, and dividing through by n_1 gives

$$\left(\frac{\partial \ln a_1}{\partial n_3}\right)_{n_1,n_2} dn_3 + \frac{n_2}{n_1}\left(\frac{\partial \ln a_2}{\partial n_3}\right)_{n_1,n_2} dn_3 + \frac{n_3}{n_1}\left(\frac{\partial \ln a_3}{\partial n_3}\right)_{n_1,n_2} dn_3 = 0 \quad (4)$$

Since for the volatile components (assuming ideal behavior in the gas phase)

$$a_j = p_j/p_j^o \quad (5)$$

where a_j = activity of component j

p_j = vapor pressure of component j

p_j^o = vapor pressure of pure component j

Eq. 4 becomes

$$d\phi = \frac{-n_3}{n_1} \times \left(\frac{\partial \ln a_3}{\partial n_3}\right)_{n_1,n_2} dn_3 \quad (6)$$

where $\phi = \ln p_1 p_2^k - \ln p_1^o p_2^{o^k}$ and (7)

$$k = n_2/n_1 = m_2/55.51 \quad (8)$$

Integration of Eq. 6 along lines of constant n_2/n_1 then permits evaluation of a_3 as a function of the mole ratio n_3/n_1. If component 1 is chosen as H_2O, component 2 as HCl, and component 3 as the salt, integration gives the salt activity as a function of its molality in solutions of fixed HCl molality.

As an alternative to graphical integration, one might wish to carry out the integration with empirically determined analytical functions. If one starts with Eq. 7, rearranges it to give

$$\phi = \ln p_1/p_1^o + k \ln p_2/p_2^o \quad (9)$$

and substitutes Eq. 5 into Eq. 9, one obtains

$$\phi = \ln a_1 + k \ln a_2 \quad (10)$$

The derivative of Eq. 10 gives

$$d\phi = d\ln a_1 + k\, d\ln a_2 \quad (11)$$

Substituting Eq. 11 into Eq. 6, one obtains

$$d\ln a_1 + k\, d\ln a_2 = -\frac{n_3}{n_1}\left(\frac{\partial \ln a_3}{\partial n_3}\right)_{n_1, n_2} dn_3 \tag{12}$$

Integrating and rearranging Eq. 12 gives

$$\ln a_3''/a_3' = -55.51/m_3 \left[\int_{a_1'}^{a_1''} d\ln a_1 + k \int_{a_2'}^{a_2''} d\ln a_2 \right] \tag{13}$$

$$\text{where } n_3/n_1 = m_3/55.51$$

If analytical functions can be obtained for a_1 and a_2 as functions of composition from experimental data, they can be substituted into Eq. 13 to allow calculation of the activity of the salt to be made as a function of its molality in solutions of fixed HCl molality.

The ternary Gibbs-Duhem equation can also be used to obtain the activity of component 3 in a system where the salt concentration is held constant and the acid concentration varied. If Eq. 4 is integrated under these restrictions, one obtains the following

$$\int_{a_1'}^{a_1''} d\ln a_1 + \frac{1}{n_1}\int_{a_2'}^{a_2''} n_2\, d\ln a_2 = -\beta \int_{a_3'}^{a_3''} d\ln a_3 \tag{15}$$

$$\text{where } \beta = n_3/n_1 = m_3/55.51 \tag{16}$$

or by rearranging

$$\ln a_3'/a_3'' = 55.51 \ln a_1''/a_1' + \int_{m_2'}^{m_2''} m_2\, d\ln a_2 \tag{17}$$

Again if analytical functions of composition can be obtained for a_1 and a_2 from experimental data, they can be substituted into Eq. 17. One then obtains by integration the activity of the salt as a function of the acid molality in solutions of fixed salt molality.

CHAPTER IV

DATA AND CALCULATIONS

Preliminary Check of Apparatus.

Sulfuric Acid-Water and Hydrochloric Acid-Water Systems.

Measurements were first made on solutions whose vapor pressures were available from the literature (7,136,154,157,176) in order to test the accuracy of the experimental procedures. The results of such measurements on aqueous sulfuric acid solutions are presented in Table 1. The literature values cited are those of Stokes (157). Both these and all subsequent vapor pressure measurements were made at 25°C unless otherwise noted. As the partial pressure of sulfur trioxide in equilibrium with these solutions was very small, it was neglected in the calculations. Measurements of the partial pressures of hydrochloric acid and water in aqueous hydrochloric acid solutions at several molalities are listed in Table 2. Fig. 6 presents for comparison the experimental values of the partial pressure of hydrochloric acid along with those of Bates and Kirschman (7) and Fig. 5 compares the partial pressure of water in hydrochloric acid solutions with those of Zeisberg (176) and also those of Robinson and Stokes (136). In all tables the last digit in columns marked with an asterisk was retained for computational purposes. In all the tables of vapor pressure data, P_1 is the pressure at the first set of saturators (reference) and P_2 is the pressure at the second set of saturators (binary or ternary).

TABLE I

VAPOR PRESSURE DATA FOR THE SYSTEM H_2SO_4-H_2O

$m_2(H_2SO_4)$	Trial No.	P_1^a (mm. Hg)	P_2^b (mm. Hg)	Length of Exp. (hr.)	H_2O in First Absorber (g.)	Moles of Inert Gas	Rate of Gas Flow (moles/hr.)	Wt. in Second Absorber (g.)	p_{H_2O} (mm. Hg)	Avg. p_{H_2O} (mm. Hg)	p_{H_2O} Literature Value (mm. Hg)
1.852	1	761.5	756.5	7.50	0.7869	1.3560	0.18	0.7263	21.85	21.85	21.85
1.852	2	743.8	739.0	7.00	0.5022	0.8447	0.12	0.4638	21.85		
3.818	1	742.5	737.2	7.66	0.7758	1.3020	0.17	0.6152	18.84	18.85	18.85
3.818	3	748.0	742.7	7.00	0.6271	1.0610	0.15	0.4985	18.86		
6.100	1	747.5	741.7	8.00	0.8483	1.4340	0.18	0.5215	14.67	14.67	14.67
6.100	2	756.8	750.7	8.00	0.7816	1.3380	0.17	0.4804	14.66		

a. P_1 = pressure at first set of saturators.

b. P_2 = pressure at second set of saturators.

TABLE 2

VAPOR PRESSURE DATA FOR THE SYSTEM $HCl-H_2O$

m_2(HCl)	Run No.	Trial No.	P_1 (mm. Hg)	P_2 (mm. Hg)	Length of Exp. (hrs.)	H_2O Absorbed in First Absorber (g.)	Moles of Inert Gas	Rate of Gas Flow (moles/ hr.)	Wt. in Second Absorber (g.)	Meq. $AgNO_3$ Used	p_{H_2O} (mm. Hg)	p_{HCl} (mm. Hg)
4.67	116	1	759.8	754.7	7.00	1.0206	1.754	0.25	0.7762	0.0902	18.01	0.038
4.67	118	3	748.5	743.7	7.00	0.9050	1.532	0.22	0.6880	0.0773	18.01	0.037
6.03	204	1	745.0	740.7	9.00	0.7835	1.320	0.15	0.5331	0.2753	15.93	0.151
6.03	205	2	745.8	741.5	8.50	0.8751	1.476	0.17	0.5949	0.3174	15.91	0.156
7.05	165	1	745.3	741.0	7.00	1.0237	1.725	0.25	0.6412	0.9181	14.21	0.387
7.05	166	2	748.2	743.6	7.00	0.9593	1.623	0.23	0.6007	0.8600	14.19	0.386
7.27	214	1	750.4	745.3	7.50	0.7872	1.336	0.18	0.4863	0.8635	13.81	0.472
7.27	215	2	747.8	742.8	7.60	0.6703	1.134	0.17	0.4144	0.7419	13.81	0.472
7.93	201	2	746.2	741.2	7.00	0.7568	1.277	0.18	0.4601	1.4660	12.85	0.835
7.93	202	3	746.1	741.0	6.00	0.5556	0.938	0.16	0.3376	1.0750	12.85	0.834
8.49	206	1	745.3	741.0	6.50	0.7496	1.263	0.19	0.4573	2.3530	11.88	1.356
8.49	207	2	745.1	740.8	6.50	0.9337	1.573	0.24	0.5692	2.9060	11.90	1.344
9.01	195	1	742.8	738.7	7.00	0.8551	1.436	0.21	0.5484	4.0690	11.22	2.056
9.01	200	6	741.1	736.7	6.25	0.7780	1.303	0.21	0.4996	3.7110	11.22	2.060

Calculations and Activities.

Method of Approach.

In view of the difficulty and uncertainty involved in measurements and extrapolations of vapor pressures in dilute solutions, it was decided to use the saturated solution in each series as a reference state. The activity of the saturated solution could then be readily related through the equilibrium solid phase to the conventional standard reference states of solutes in binary aqueous solutions (119,138); i.e., to hypothetical mean one molal ideal solutions. This choice of standard states, rather than the alternative choice of states in which each $HCl-H_2O$ mixture was considered a mixed solvent containing salt as a solute, permitted comparison between series of different HCl/H_2O mole ratios.

In order to make use of the above relationship, the equilibrium vapor pressures of the hydrates and the saturated solutions needed to be known together with the activities in the saturated aqueous binary solution also referred to an ideal (hypothetical) mean one molal solution.

Manganous Chloride.

The desired data at 25°C for manganous chloride from 0.1 molal to saturation were available (157), and also that for manganous sulfate from 0.1 molal to very near saturation (134). The missing data were easily obtained at saturation by a short extrapolation of the activity coefficient versus salt molality curve on a large scale plot.

From the activity of manganous chloride in its saturated solution, the activity of the tetrahydrate of manganous chloride was calculated according to the relation

$$RT \log a\,(\mathrm{salt}.4H_2O) = RT \log a\,(\mathrm{salt}) + 4RT \log p_1/p_1^o \tag{18}$$

where $a(\mathrm{salt}.4H_2O)$ and $a(\mathrm{salt})$ refer to the activity of the solid hydrate and the salt in the saturated solution respectively, and p_1/p_1^o is the activity of water referred to pure water.

Manganous Sulfate.

From the activity of the manganous sulfate in its saturated binary solution the activity of the pentahydrate was calculated from a relation similar to that described above. The corresponding activity of the monohydrate was then calculated from the data of Carpenter and Jette (23) for the equilibrium vapor pressure of the system

$$MnSO_4 \cdot 5H_2O \rightleftharpoons MnSO_4 \cdot H_2O + 4H_2O \tag{19}$$

and the activity of the pentahydrate.

The activity of manganous chloride or manganous sulfate in each of the salt-saturated ternary solutions was calculated from values of the activity of the solid hydrate and the experimentally measured water activity. The activities in each of the reference states described are listed in Table 3 for manganous chloride and in Table 4 for manganous sulfate.

To obtain the salt activity in a ternary solution Eq. 6 was integrated at constant HCl/H_2O ratio with the saturated solution as the upper limit. The integrations initially were made graphically by Simpson's rule (94) from the ϕ curves constructed from large scale plots of the experimental data. For purposes of the graphical integration Eq. 6 was integrated by parts to give the following relation

$$\log a_3''/a_3' = \frac{(\phi/r)' - (\phi/r)''}{2.303} - \int_{m_3'}^{m_3''} (\phi/r)\, d\log m_3 \tag{20}$$

where $r = n_3/n_1 = m_3/55.51$.

TABLE 3

ACTIVITIES OF MANGANOUS CHLORIDE IN

ITS REFERENCE STATES

State	$a_3(MnCl_2)$
Saturated aqueous solution (25°)	6,548.0
$MnCl_2 \cdot 4H_2O$	642.9[c]
Saturated solution in 4.67 molal HCl	11,930
Saturated solution in 7.05 molal HCl	22,030
Saturated solution in 9.01 molal HCl	45,010

TABLE 4

ACTIVITIES OF MANGANOUS SULFATE IN

ITS REFERENCE STATES

State	$a_3(MnSO_4)$
Saturated aqueous solution (25°)	0.05640
$MnSO_4 \cdot 5H_2O$	0.02261[c]
$MnSO_4 \cdot H_2O$	0.05099[c]
Saturated solution in 7.27 molal HCl	0.1020

c = activity of hydrated salt.

This function was found to be relatively insensitive to errors in plotting and in the graphical integration. The curves obtained by plotting $-(\phi/r)$ versus $\log m_3$ are shown in Fig. 1 and Fig. 2.

Hydrochloric Acid and Water.

The water activities in the ternary mixtures (Tables 5 to 9) were calculated directly from the water partial pressures using the relation

$$a_{H_2O} = p_1/p_1^o \tag{21}$$

where p_1 = observed vapor pressure of water

p_1^o = vapor pressure of water at 25°C

By comparison of the literature values of the activity of hydrochloric acid (136) over the range of 4 to 11 molal acid with the experimental partial pressure of hydrochloric acid (7) over the same range of acid molality, an average value of 2670 per mm was obtained for the ratio, $(a_{HCl}/p_{HCl})^*$. Using this constant the activity of the hydrochloric acid in the ternary mixtures (Tables 5 to 9) was calculated in the following manner. Since

$$a_{HCl} = p_2/p_2^o \tag{22}$$

then

$$1/p_2^o = (a_{HCl}/p_2)^* \tag{23}$$

and by substituting into an equation similar to Eq. 21, one obtains the following relation

$$a_{HCl} = (a_{HCl}/p_2)^* \; p_2 = 2670 \; p_2 \tag{24}$$

In order to eliminate some of the irregularities introduced in the results from the graphical integration, it was decided to use analytical integration (Eq. 13) as an alternate method of calculation. The average activities of H_2O and HCl were first computed from the arithmetic-mean values of the experimental vapor pressures. Empirical expressions for

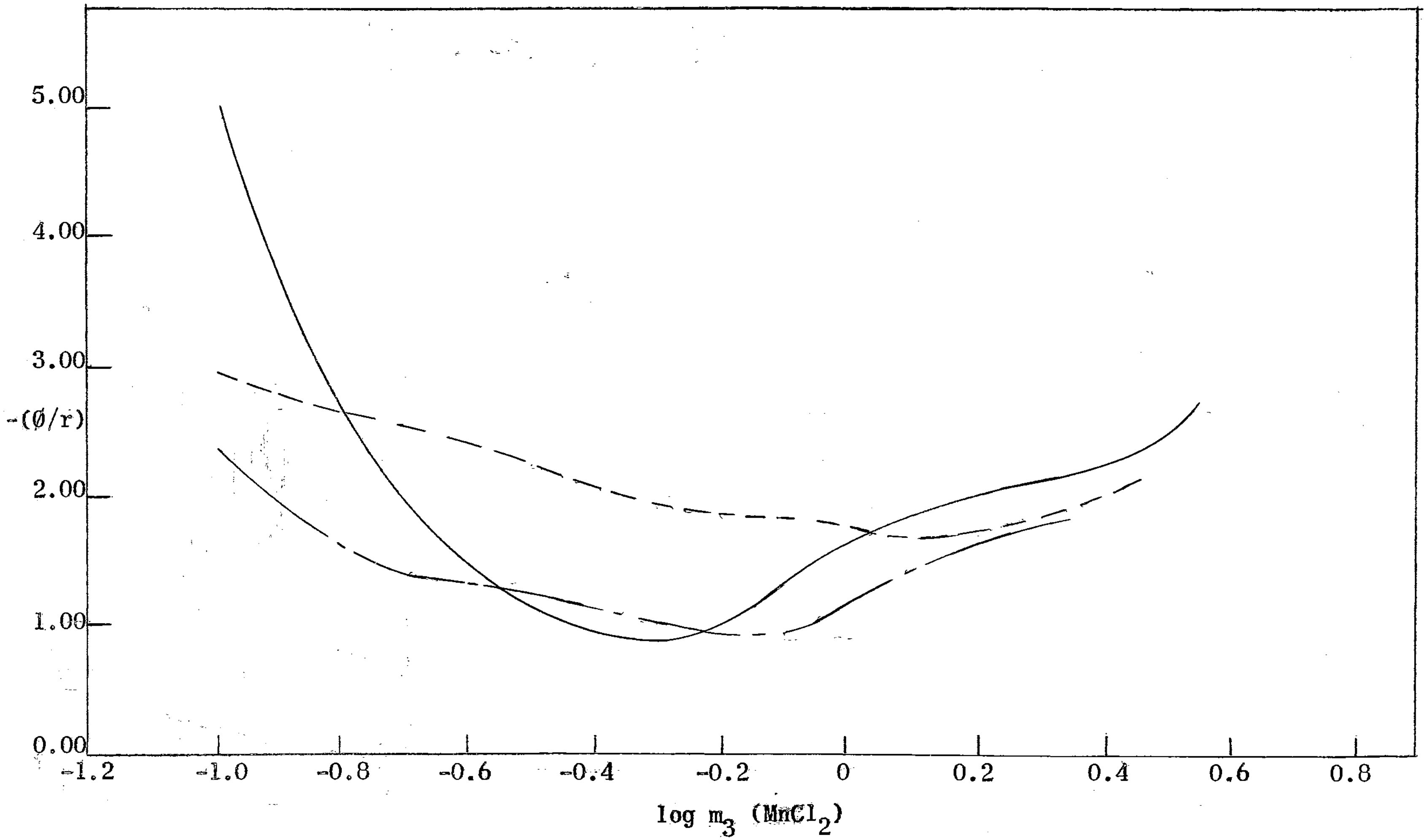

Fig. I -(Ø/r) plots for the $HCl-H_2O-MnCl_2$ systems. ——— HCl = 4.67 molal; - - - - HCl = 7.05 molal; ——— — ——— HCl = 9.01 molal.

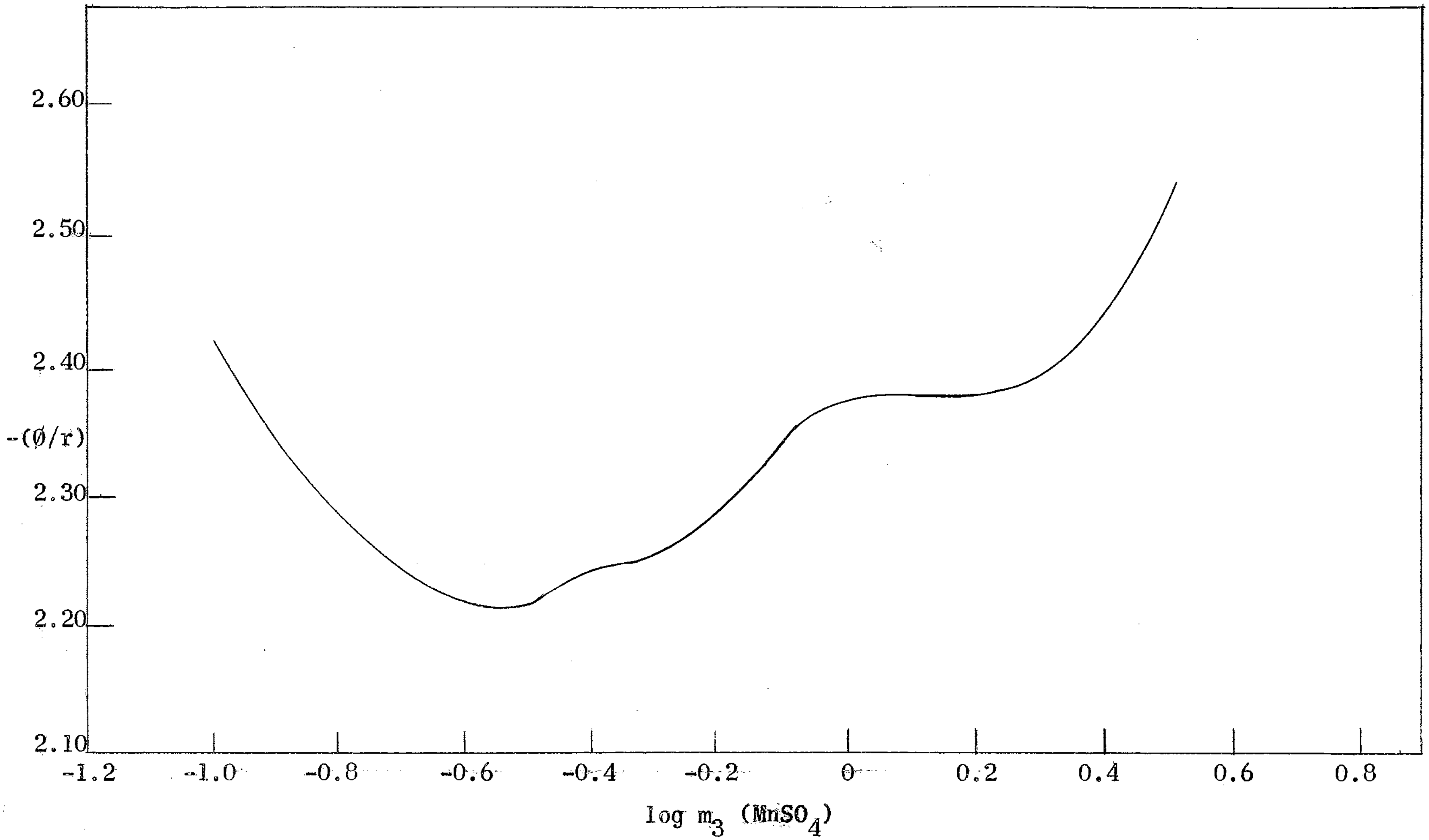

Fig. 2 -(Ø/r) plots for the HCl-H_2O-$MnSO_4$ system. HCl = 7.27 molal.

TABLE 5

ACTIVITY DATA FOR THE $MnCl_2$-HCl-H_2O SYSTEM

HCl = 4.67 Molal

H_2O and HCl Activities				$MnCl_2$ Activities	
$m_3(MnCl_2)$	$a_1(H_2O)$*	$a_2(HCl)$*	$\gamma_{\pm}(HCl)$	$a_3(MnCl_2)$*	$\gamma_{\pm}(MnCl_2)$
0.100	0.7483	116.3	2.26	5.88	1.35
0.200	0.7381	132.3	2.36	15.67	1.45
0.300	0.7285	149.4	2.46	29.06	1.52
0.400	0.7191	168.8	2.57	46.46	1.57
0.500	0.7096	190.3	2.68	68.39	1.62
0.600	0.7001	214.0	2.79	95.55	1.67
0.700	0.6909	240.1	2.91	128.7	1.71
0.800	0.6819	268.9	3.03	168.7	1.75
0.900	0.6728	300.6	3.15	216.5	1.79
1.000	0.6645	335.1	3.28	273.3	1.83
1.100	0.6559	372.1	3.41	340.2	1.87
1.200	0.6473	414.2	3.54	418.6	1.91
1.300	0.6388	459.1	3.68	509.8	1.95
1.400	0.6306	507.8	3.82	615.8	1.99
1.500	0.6225	560.6	3.96	737.7	2.03
1.600	0.6145	617.6	4.10	878.1	2.07
1.700	0.6066	679.1	4.24	1,039.	2.11
1.800	0.5988	745.1	4.39	1,221.	2.15
1.900	0.5913	816.6	4.54	1,429.	2.19
2.000	0.5838	892.6	4.69	1,665.	2.23
2.100	0.5764	975.5	4.85	1.932.	2.27
2.200	0.5691	1,061.	5.00	2,228.	2.31
2.300	0.5621	1,153.	5.16	2,566.	2.35
2.400	0.5551	1,252.	5.32	2,944.	2.39
2.500	0.5482	1,356.	5.48	3,358.	2.43
2.600	0.5416	1,456.	5.64	3,824.	2.47
2.700	0.5350	1,581.	5.80	4,340.	2.51
2.800	0.5287	1,704.	5.96	4,908.	2.55
2.900	0.5222	1,832.	6.12	5,544.	2.59
3.000	0.5160	1,966.	6.28	6,233.	2.63
3.100	0.5099	2,157.	6.52	6,999.	2.67
3.200	0.5040	2,255.	6.60	7,836.	2.71
3.300	0.4982	2,409.	6.77	8,743.	2.75
3.400	0.4925	2,569.	6.93	9,740.	2.79
3.500	0.4869	2,733.	7.08	10,830	2.83
3.594	0.4818	2,895.	7.23	11,930	2.87

*The last digit in these columns has been retained for computations.

TABLE 6

ACTIVITY DATA FOR THE $MnCl_2$-HCl-H_2O SYSTEM

HCl = 7.05 Molal

H_2O and HCl Activities				$MnCl_2$ Activities	
$m_3(MnCl_2)$	$a_1(H_2O)$*	$a_2(HCl)$*	$\gamma_{\pm}(HCl)$	$a_3(MnCl_2)$*	$\gamma_{\pm}(MnCl_2)$
0.100	0.5857	1,135.	4.71	71.12	2.38
0.200	0.5751	1,267.	4.91	353.7	3.17
0.300	0.5660	1,409.	5.11	657.0	3.34
0.400	0.5578	1,561.	5.31	811.4	3.21
0.500	0.5513	1,723.	5.51	917.0	3.05
0.600	0.5440	1,893.	5.71	1,015.	2.92
0.700	0.5369	2,073.	5.90	1,174.	2.86
0.800	0.5297	2,264.	6.09	1,375.	2.84
0.900	0.5227	2,464.	6.28	1,619.	2.84
1.000	0.5160	2,674.	6.47	1,916.	2.86
1.100	0.5091	2,894.	6.66	2,270.	2.89
1.200	0.5024	3,124.	6.85	2,693.	2.93
1.300	0.4958	3,367.	7.03	3,191.	2.98
1.400	0.4892	3,619.	7.22	3,744.	3.03
1.500	0.4828	3,884.	7.40	4,450.	3.08
1.600	0.4764	4,160.	7.59	5,234.	3.15
1.700	0.4701	4,450.	7.77	6,130.	3.21
1.800	0.4639	4,756.	7.96	7,148.	3.27
1.900	0.4578	5,077.	8.15	8,298.	3.34
2.000	0.4517	5,415.	8.34	9,595.	3.40
2.100	0.4458	5,771.	8.53	11,290.	3.47
2.200	0.4399	6,151.	8.73	12,620	3.52
2.300	0.4341	6,554.	8.93	14,360	3.58
2.400	0.4285	6,980.	9.14	16,250	3.64
2.500	0.4228	7,441.	9.36	18,280	3.68
2.600	0.4172	7,931.	9.58	19,970	3.71
2.670	0.4133	8,295.	9.74	22,030	3.77

TABLE 7

ACTIVITY DATA FOR THE $MnCl_2$-HCl-H_2O SYSTEM

HCl = 9.01 Molal

	H_2O and HCl Activities			MnCl$_2$ Activities	
$m_3(MnCl_2)$	$a_1(H_2O)$*	$a_2(HCl)$*	$\gamma_{\pm}(HCl)$	$a_3(MnCl_2)$*	$\gamma_{\pm}(MnCl_2)$
0.100	0.4643	5,891.	8.43	673.0	4.30
0.200	0.4580	6,368.	8.67	1,052.	3.90
0.300	0.4516	6,873.	8.91	1,438.	3.73
0.400	0.4454	7,410.	9.16	1,870.	3.65
0.500	0.4393	7,974.	9.40	2,346.	3.60
0.600	0.4333	8,568.	9.65	2,900.	3.59
0.700	0.4274	9,199.	9.90	3,544.	3.60
0.800	0.4215	9,857.	10.15	4,294.	3.63
0.900	0.4159	10,540	10.40	5,172.	3.66
1.000	0.4101	11,260	10.63	6,199.	3.71
1.100	0.4045	12,010	10.90	7,409.	3.77
1.200	0.3989	12,780	11.15	8,826.	3.84
1.300	0.3954	13,590	11.40	10,490	3.91
1.400	0.3875	14,420	11.64	12,470	4.00
1.500	0.3823	15,280	11.88	14,720	4.08
1.600	0.3772	16,150	12.12	17,260	4.17
1.700	0.3721	17,050	12.35	20,130	4.25
1.800	0.3672	17,960	12.58	23,350	4.34
1.900	0.3625	18,880	12.79	26,930	4.42
2.000	0.3579	19,820	13.00	30,970	4.50
2.100	0.3534	20,770	13.21	34,880	4.58
2.200	0.3492	21,710	13.41	40,570	4.68
2.280	0.3458	22,480	13.56	45,010	4.75

TABLE 8

ACTIVITY DATA FOR THE $MnSO_4$-HCl-H_2O SYSTEM

HCl = 7.27 Molal

	H_2O and HCl Activities			$MnSO_4$ Activities	
$m_3(MnSO_4)$	$a_1(H_2O)$*	$a_2(HCl)$*	$\gamma_{\pm}(HCl)$*	$a_3(MnSO_4)$*	$\gamma_{\pm}(MnSO_4)$*
0.100	0.5790	1,265.	4.900	0.0000[2]	0.0412
0.200	0.5763	1,271.	4.904	0.0001	0.0524
0.300	0.5733	1,274.	4.908	0.0003	0.0587
0.400	0.5706	1,276.	4.911	0.0006	0.0632
0.500	0.5676	1,282.	4.917	0.0011	0.0669
0.600	0.5652	1,284.	4.925	0.0018	0.0701
0.700	0.5626	1,287.	4.931	0.0026	0.0727
0.800	0.5599	1,292.	4.937	0.0036	0.0748
0.900	0.5561	1,295.	4.943	0.0047	0.0767
1.000	0.5546	1,298.	4.950	0.0062	0.0784
1.100	0.5520	1,303.	4.958	0.0077	0.0799
1.200	0.5492	1,306.	4.964	0.0095	0.0812
1.300	0.5468	1,308.	4.972	0.0115	0.0825
1.400	0.5442	1,311.	4.981	0.0137	0.0836
1.500	0.5418	1,314.	4.988	0.0161	0.0846
1.600	0.5392	1,319.	4.996	0.0188	0.0855
1.700	0.5368	1,322.	5.002	0.0216	0.0864
1.800	0.5342	1,327.	5.014	0.0248	0.0875
1.900	0.5319	1,330.	5.020	0.0281	0.0882
2.000	0.5292	1,335.	5.026	0.0318	0.0893
2.100	0.5269	1,338.	5.035	0.0358	0.0901
2.200	0.5244	1,340.	5.041	0.0399	0.0908
2.300	0.5220	1,343.	5.049	0.0447	0.0919
2.400	0.5194	1,348.	5.055	0.0494	0.0926
2.500	0.5168	1,351.	5.061	0.0546	0.0934
2.600	0.5144	1,356.	5.068	0.0602	0.0943
2.700	0.5119	1,359.	5.075	0.0663	0.0953
2.800	0.5095	1,362.	5.078	0.0727	0.0963
2.900	0.5068	1,364.	5.082	0.0795	0.0972
3.000	0.5046	1,369.	5.087	0.0868	0.0982
3.100	0.5020	1,372.	5.090	0.0950	0.0994
3.185	0.4999	1,375.	5.095	0.1020	0.1003

TABLE 9

ACTIVITY DATA FOR THE $MnCl_2$-HCl-H_2O SYSTEM

$MnCl_2$ = 1.00 Molal

H_2O and HCl Activities				$MnCl_2$ Activities	
m_2(HCl)	$a_1(H_2O)$*	a_2(HCl)*	$\gamma_{\pm}$(HCl)	$a_3(MnCl_2)$*	$\gamma_{\pm}(MnCl_2)$
4.67	0.6645	335.1	3.28	273.3	1.83
4.80	0.6555	376.7	3.40	340.0	1.95
5.00	0.6416	450.7	3.59	455.0	2.10
5.20	0.6282	540.9	3.80	581.7	2.24
5.40	0.6146	649.8	4.03	724.2	2.36
5.60	0.6020	779.9	4.28	857.0	2.46
5.80	0.5894	935.5	4.55	987.0	2.53
6.00	0.5769	1,119.	4.83	1,123.	2.60
6.20	0.5648	1,336.	5.13	1,240.	2.64
6.40	0.5530	1,587.	5.43	1,358.	2.68
6.60	0.5413	1,875.	5.75	1,506.	2.73
6.80	0.5297	2,202.	6.07	1,662.	2.78
7.00	0.5187	2,568.	6.38	1,888.	2.86
7.20	0.5076	2,987.	6.72	2,192.	2.96
7.40	0.4966	3,462.	7.06	2,420.	3.01
7.60	0.4860	4,015.	7.42	2,758.	3.10
7.80	0.4751	4,652.	7.80	3,093.	3.18
8.00	0.4645	5,394.	8.21	3,370.	3.23
8.20	0.4538	6,253.	8.65	3,703.	3.29
8.40	0.4431	7,249.	9.11	4,105.	3.36
8.60	0.4323	8,401.	9.60	4,591.	3.44
8.80	0.4217	9,739.	10.13	5,049.	3.51
9.01	0.4101	11,370	10.70	5,957.	3.66

these activities were then found by the method of least squares (95) in those cases where the data appeared nonlinear. The equations assumed were of the form

$$\log a = a + bm + cm^2 + dm^3 \tag{25}$$

where m is the salt molality. In the cases where the data were approximately linear, a straight line function was assumed. The functions obtained for log a_1 and log a_2 were substituted into Eq. 13 and this equation was integrated from an arbitrary lower limit in concentration to saturation at constant HCl/H_2O ratio. The activities and mean activity coefficients of manganous chloride are tabulated in Tables 5 to 7 and those of manganous sulfate in Table 8. Appendix A gives the empirical functions used in the calculations. The averages of the percentage difference between the experimental values and those calculated by the empirical equations was 0.4% for water and 0.2% for hydrochloric acid in the constant HCl/H_2O mole-ratio series. In the case of the manganous sulfate series the average of the percentage difference between experimental and calculated values was 0.2% for water and 0.1% for hydrochloric acid. It is believed that both the accuracy of the measurements and the fit of the data to the empirical equations is as good as the accuracy in the determination of the composition of the solutions.

In the series where the salt molality was held constant and the acid molality was varied, the activity of the H_2O and HCl were calculated in the manner described above. The appropriate analytical functions were substituted, however, into Eq. 17 and integrated between arbitrarily chosen HCl concentrations at constant $MnCl_2/H_2O$ mole ratio to obtain the activity of the salt. The activities and mean activity coefficients of manganous chloride are tabulated in Table 9. The average of the percentage difference between the experimental values and those calculated from the empirical equations was 0.4% for water and 0.4% for hydrochloric acid. These results are summarized in Table 20.

Experimental Data Used in the Calculations.

The vapor pressure measurements consisted of (a) measurements of the partial pressure of water in saturated binary solutions of manganous chloride and sulfate, and (b) measurements of the partial pressure of both hydrochloric acid and water in ternary mixtures of manganous chloride or sulfate over a range of salt concentration from 0.2 molal up to saturation at three constant hydrochloric acid molalities; viz., 4.67, 7.05, and 9.01 molal. Similar measurements were also made for a single series of mixtures of manganous sulfate with hydrochloric acid at an acid concentration of 7.27 molal. One series of solutions having a constant manganous chloride molality of 1.00 and an acid molality of from 4.67 to 9.01 was also measured for manganous chloride.

Vapor Pressure.

In Tables 10 to 15 are tabulated the vapor pressure data. The partial pressures of water and hydrochloric acid were obtained as follows:

First the number moles of nitrogen gas passed through the apparatus was calculated.

$$n_x = n_y \, (p_1/p^o) - n_y \tag{26}$$

where p^o = vapor pressure of pure water at 25°C

p_1 = total pressure at first set of saturators

TABLE 10

VAPOR PRESSURE DATA FOR THE SATURATED BINARY SOLUTIONS OF $MnCl_2$ AND $MnSO_4$ AT 25°

m_3	Run No.	Trial No.	P_1 (mm. Hg)	P_2 (mm. Hg)	Length of Exp. (hrs.)	H_2O Absorbed in First Absorber (g.)	Moles of Inert Gas	Rate of Gas Flow (moles/hr.)	Wt. in Second Absorber (g.)	p_{H_2O} (mm. Hg)
$MnCl_2$										
6.122	42	2	750.7	745.4	8.00	0.8389	1.424	0.18	0.4662	13.30
6.122	43	3	748.5	743.2	8.00	0.7728	1.308	0.16	0.4294	13.30
6.122	44	4	749.8	744.0	8.00	0.8100	1.374	0.17	0.4505	13.30
$MnSO_4$										
4.399	210	3	743.7	741.2	6.00	1.3545	2.278	0.38	1.1254	19.78
4.399	211	4	744.8	742.5	6.16	1.3590	2.290	0.37	1.1300	19.79

TABLE 11

VAPOR PRESSURE DATA FOR THE SYSTEM $HCl-H_2O-MnCl_2$

m_2 (HCl) = 4.67 Molal

$m_3(MnCl_2)$	Run No.	Trial No.	P_1 (mm. Hg)	P_2 (mm. Hg)	Length of Exp. (hrs.)	H_2O Absorbed in First Absorber (g.)	Moles of Inert Gas	Rate of Gas Flow (moles/ hr.)	Wt. in Second Absorber (g.)	Meq. $AgNO_3$ Used	p_{H_2O} (mm. Hg)	p_{HCl} (mm. Hg)
0.0000	116	1	759.8	754.7	7.00	1.0206	1.754	0.25	0.7762	0.0902	18.01	0.038
0.0000	118	3	748.5	743.7	7.00	0.9050	1.532	0.22	0.6880	0.0773	18.01	0.037
0.2002	114	1	751.9	746.7	7.00	0.9919	1.687	0.24	0.7349	0.1102	17.53	0.048
0.2002	115	2	758.5	753.7	7.50	1.0460	1.795	0.24	0.7730	0.1126	17.51	0.046
0.3999	112	1	748.5	743.7	7.00	1.0135	1.716	0.25	0.7338	0.1542	17.10	0.065
0.3999	113	2	746.0	742.2	7.00	0.9097	1.534	0.22	0.6563	0.1385	17.08	0.066
0.5986	110	1	749.9	744.7	7.00	0.8601	1.459	0.21	0.6068	0.1681	16.64	0.084
0.5986	111	2	751.1	745.9	7.00	0.8513	1.446	0.21	0.6021	0.1657	16.68	0.084
0.7999	108	1	749.7	744.9	7.00	0.8237	1.397	0.20	0.5658	0.1899	16.18	0.099
0.7999	109	2	751.6	746.8	7.00	0.7232	1.229	0.18	0.4968	0.1688	16.19	0.100
0.9978	106	1	752.7	746.8	7.00	0.8565	1.458	0.21	0.5777	0.2557	15.80	0.128
0.9978	107	2	746.9	741.2	7.00	0.8933	1.509	0.22	0.6014	0.2612	15.79	0.126
1.194	104	1	752.8	746.7	7.00	0.6351	1.081	0.15	0.4186	0.2256	15.40	0.153
1.194	105	2	756.2	750.1	7.00	0.8226	1.407	0.20	0.5422	0.2894	15.40	0.151
1.402	102	1	755.7	749.7	7.00	0.7426	1.269	0.18	0.4779	0.3166	14.98	0.183
1.402	103	2	754.8	748.8	7.00	0.7815	1.334	0.19	0.5028	0.3308	14.97	0.182
1.609	99	6	749.1	743.6	7.50	1.1278	1.910	0.26	0.7120	0.6249	14.59	0.238
1.609	100	7	744.4	738.9	7.00	0.5983	1.007	0.14	0.3787	0.3322	14.62	0.239
1.807	76	1	760.3	754.2	8.00	1.0292	1.771	0.22	0.6377	0.6891	14.19	0.288
1.807	78	3	754.6	748.3	8.75	1.0026	1.711	0.20	0.6193	0.6698	14.16	0.287
1.997	74	2	752.2	745.9	8.00	0.7317	1.245	0.16	0.4463	0.5585	13.89	0.328
1.997	75	3	750.5	744.2	7.75	0.8472	1.438	0.19	0.5168	0.6452	13.90	0.328

TABLE 11 - CONTINUED

$m_3(MnCl_2)$	Run No.	Trial No.	P_1 (mm. Hg)	P_2 (mm. Hg)	Length of Exp. (hrs.)	H_2O Absorbed in First Absorber (g.)	Moles of Inert Gas	Rate of Gas Flow (moles/ hr.)	Wt. in Second Absorber (g.)	Meq. $AgNO_3$ Used	p_{H_2O} (mm. Hg)	p_{HCl} (mm. Hg)
2.254	71	5	755.1	748.8	8.00	0.6066	1.038	0.13	0.3618	0.5837	13.37	0.413
2.254	72	6	755.3	749.0	8.00	0.7035	1.204	0.15	0.4198	0.6720	13.39	0.410
2.387	65	1	751.3	744.3	8.00	0.6963	1.183	0.15	0.4121	0.7382	13.20	0.456
2.387	66	2	751.5	744.5	7.25	0.6755	1.148	0.16	0.3996	0.7121	13.20	0.454
2.557	123	1	756.0	749.7	7.00	0.9593	1.641	0.23	0.5608	1.1790	12.90	0.529
2.557	124	2	751.7	745.7	7.00	0.9542	1.622	0.23	0.5583	1.1750	12.92	0.530
2.736	63	1	753.6	746.6	8.00	0.6733	1.147	0.14	0.3936	0.9629	12.71	0.616
2.736	64	2	754.3	747.3	7.25	0.5884	1.004	0.14	0.3439	0.8465	12.70	0.619
2.857	121	1	750.2	745.2	6.50	0.9082	1.541	0.24	0.5235	1.3910	12.48	0.662
2.857	122	2	753.9	748.7	7.25	0.9870	1.683	0.23	0.5692	1.5150	12.47	0.662
3.008	119	1	752.4	746.7	7.00	0.8872	1.510	0.22	0.5106	1.5190	12.29	0.739
3.008	120	2	752.4	746.7	7.00	0.9851	1.676	0.24	0.5657	1.6890	12.26	0.740
3.173	60	3	755.6	748.3	8.00	0.4922	0.841	0.11	0.2817	0.9549	11.99	0.836
3.173	62	5	750.6	744.2	7.75	0.8700	1.477	0.19	0.4980	1.6870	12.00	0.836
3.404	125	1	757.0	751.7	5.00	0.7245	1.240	0.25	0.4108	1.6070	11.67	0.959
3.404	126	2	753.4	748.0	6.75	0.8839	1.506	0.22	0.5034	1.9710	11.71	0.963
3.594	54	1	750.9	745.5	8.00	0.5336	0.906	0.11	0.3038	1.3438	11.44	1.087
3.594	55	2	750.1	744.7	7.75	0.4332	0.735	0.10	0.2464	1.0866	11.44	1.083

TABLE 12

VAPOR PRESSURE DATA FOR THE SYSTEM $HCl-H_2O-MnCl_2$

m_2 (HCl) = 7.05 Molal

$m_3(MnCl_2)$	Run No.	Trial No.	P_1 (mm. Hg)	P_2 (mm. Hg)	Length of Exp. (hrs.)	H_2O Absorbed in First Absorber (g.)	Moles of Inert Gas	Rate of Gas Flow (moles/ hr.)	Wt. in Second Absorber (g.)	Meq. $AgNO_3$ Used	p_{H_2O} (mm. Hg)	p_{HCl} (mm. Hg)
0.0000	165	1	745.3	741.0	7.00	1.0237	1.725	0.25	0.6412	0.9181	14.21	0.387
0.0000	166	2	748.2	743.6	7.00	0.9593	1.623	0.23	0.6007	0.8600	14.19	0.386
0.2016	159	3	744.5	739.6	7.00	0.9662	1.627	0.23	0.5947	1.0730	13.74	0.478
0.2016	160	4	746.5	741.6	7.00	0.8338	1.408	0.20	0.5116	0.9295	13.70	0.480
0.4020	155	1	748.2	743.6	7.00	0.8221	1.391	0.20	0.4996	1.1150	13.27	0.581
0.4020	156	2	748.2	743.6	6.83	0.9005	1.523	0.22	0.5423	1.2190	13.23	0.584
0.6076	153	1	744.2	739.1	7.00	0.9433	1.587	0.23	0.5670	1.5530	12.94	0.710
0.6076	154	2	744.6	739.5	7.00	0.6846	1.152	0.17	0.4092	1.1240	12.88	0.709
0.8103	151	1	748.1	743.0	7.00	0.9389	1.588	0.23	0.5625	1.8640	12.61	0.856
0.8103	152	2	746.3	741.2	7.00	0.9053	1.527	0.22	0.5423	1.5270	12.61	0.855
1.002	149	1	744.1	739.2	6.66	0.8890	1.495	0.22	0.5279	2.0400	12.22	0.990
1.002	150	2	747.9	743.0	7.00	0.9103	1.539	0.22	0.5404	2.0860	12.21	0.989
1.207	147	1	748.8	743.7	7.00	0.8540	1.446	0.21	0.5086	2.2820	11.93	1.153
1.207	148	2	746.3	741.2	7.00	0.8434	1.423	0.20	0.5030	2.2700	11.92	1.161
1.392	145	1	747.1	741.6	7.00	0.8019	1.355	0.19	0.4804	2.4930	11.62	1.341
1.392	146	2	751.7	746.2	7.00	0.8894	1.512	0.22	0.5311	2.7610	11.59	1.339
1.604	143	1	742.7	737.5	7.00	0.8244	1.384	0.20	0.4990	2.9570	11.37	1.549
1.604	144	2	737.2	732.0	7.00	0.9041	1.506	0.22	0.5472	3.2410	11.37	1.547
1.801	141	1	729.3	724.4	7.00	0.9599	1.582	0.23	0.5862	3.9690	11.03	1.786
1.801	142	2	740.3	735.5	7.00	1.0395	1.739	0.25	0.6361	4.3350	11.02	1.801
2.021	139	1	742.1	737.5	7.00	0.9197	1.543	0.22	0.5740	4.4680	10.71	2.099
2.021	140	2	744.1	739.5	7.00	0.9257	1.557	0.22	0.5745	4.4870	10.65	2.095

TABLE 12 - CONTINUED

$m_3(MnCl_2)$	Run No.	Trial No.	P_1 (mm. Hg)	P_2 (mm. Hg)	Length of Exp. (hrs.)	H_2O Absorbed in First Absorber (g.)	Moles of Inert Gas	Rate of Gas Flow (moles/hr.)	Wt. in Second Absorber (g.)	Meq. $AgNO_3$ Used	p_{H_2O} (mm. Hg)	p_{HCl} (mm. Hg)
2.300	137	1	737.2	732.0	7.00	0.9032	1.505	0.22	0.5831	5.2920	10.34	2.529
2.300	138	2	744.7	739.5	7.00	0.8258	1.390	0.20	0.5300	4.8320	10.27	2.527
2.500	163	3	743.1	737.7	7.00	1.0825	1.819	0.26	0.7037	6.8370	10.04	2.728
2.500	164	4	741.1	735.7	7.00	1.0600	1.776	0.25	0.6913	6.7170	10.08	2.735
2.670	127	1	748.9	743.7	7.00	0.8884	1.505	0.22	0.5947	6.3280	9.80	3.072
2.670	128	2	750.7	744.7	7.00	0.8853	1.503	0.21	0.5941	6.3280	9.82	3.078

TABLE 13

VAPOR PRESSURE DATA FOR THE SYSTEM $HCl-H_2O-MnCl_2$

m_2 (HCl) = 9.01 Molal

$m_3(MnCl_2)$	Run No.	Trial No.	P_1 (mm. Hg)	P_2 (mm. Hg)	Length of Exp. (hrs.	H_2O Absorbed in First Absorber (g.)	Moles of Inert Gas	Rate of Gas Flow (moles/ hr.)	Wt. in Second Absorber (g.)	Meq. $AgNO_3$ Used	p_{H_2O} (mm. Hg)	p_{HCl} (mm. Hg)
0.0000	195	1	742.8	738.7	7.00	0.8551	1.436	0.21	0.5484	4.0690	11.22	2.056
0.0000	197	3	746.6	742.3	7.00	0.8455	1.428	0.20	0.5411	4.0310	11.16	2.058
0.2000	188	1	747.3	742.7	7.00	0.9783	1.653	0.24	0.6421	5.4370	10.87	2.399
0.2000	189	2	745.8	741.4	7.00	0.9373	1.580	0.23	0.6147	5.1750	10.89	2.385
0.4009	186	1	742.6	738.0	6.33	0.8975	1.507	0.24	0.6068	5.8120	10.54	2.796
0.4009	187	2	742.8	738.4	7.00	0.8633	1.449	0.21	0.5822	5.5920	10.51	2.799
0.5986	184	1	749.6	745.0	7.00	0.8459	1.434	0.21	0.5944	6.2570	10.36	3.190
0.5986	185	2	744.2	739.6	7.00	0.9524	1.602	0.23	0.6665	7.0340	10.31	3.187
0.8018	182	1	745.1	740.0	7.00	0.9874	1.663	0.24	0.7204	8.4130	10.03	3.675
0.8018	183	2	744.1	739.0	7.00	1.0146	1.707	0.24	0.7397	8.6250	10.03	3.665
1.003	180	1	745.1	740.2	6.50	0.8742	1.473	0.23	0.6665	8.5550	9.71	4.219
1.003	181	2	746.6	741.7	7.00	1.1669	1.970	0.28	0.8872	11.380	9.68	4.203
1.195	178	1	746.7	742.0	7.00	0.9562	1.614	0.23	0.7645	10.530	9.52	4.747
1.195	179	2	750.6	745.9	7.00	0.8944	1.518	0.22	0.7133	9.827	9.50	4.738
1.398	176	1	745.6	740.4	6.66	0.8964	1.511	0.23	0.7555	11.240	9.22	5.400
1.398	177	2	746.7	741.3	7.00	0.9560	1.614	0.23	0.8050	11.950	9.23	5.382
1.599	174	1	743.2	738.4	7.00	0.8713	1.464	0.21	0.7739	12.200	9.02	6.025
1.599	175	2	748.1	743.3	6.25	0.7835	1.326	0.21	0.6927	10.960	8.94	6.018
1.803	172	1	742.1	736.9	7.00	0.9103	1.527	0.22	0.8591	14.350	8.81	6.776
1.803	173	2	742.1	736.9	7.00	0.8557	1.436	0.21	0.8084	13.500	8.81	6.781
2.051	170	2	745.0	739.0	7.00	0.8831	1.488	0.21	0.8939	16.050	8.32	7.797
2.051	171	3	746.7	741.6	7.00	0.8183	1.382	0.20	0.8256	14.850	8.29	7.797
2.280	193	6	745.5	740.3	6.50	0.7673	1.293	0.20	0.8082	14.780	8.37	8.275
2.280	194	7	744.2	738.7	6.00	0.8930	1.503	0.25	0.9402	17.220	8.33	8.276

TABLE 14

VAPOR PRESSURE DATA FOR THE SYSTEM $HCl-H_2O-MnSO_4$

m_2 (HCl) = 7.27 Molal

$m_3(MnSO_4)$	Run No.	Trial No.	P_1 (mm. Hg)	P_2 (mm. Hg)	Length of Exp. (hrs.)	H_2O Absorbed in First Absorber (g.)	Moles of Inert Gas	Rate of Gas Flow (moles/hr.)	Wt. in Second Absorber (g.)	Meq. $AgNO_3$ Used	p_{H_2O} (mm. Hg)	p_{HCl} (mm. Hg)
0.0000	214	1	750.4	745.3	7.50	0.7872	1.336	0.18	0.4863	0.8635	13.81	0.472
0.0000	215	2	747.8	742.7	6.50	0.6703	1.134	0.17	0.4144	0.7419	13.81	0.476
0.2003	245	1	740.0	734.9	7.00	0.9286	1.553	0.22	0.5688	1.0230	13.69	0.475
0.2003	246	2	744.8	739.7	7.00	0.8073	1.360	0.19	0.4948	0.8594	13.69	0.478
0.3980	243	1	745.9	740.5	7.00	0.6766	1.141	0.16	0.4100	0.7483	13.52	0.476
0.3980	244	2	737.0	731.9	6.66	0.9343	1.556	0.23	0.5660	1.0360	13.53	0.478
0.6005	241	1	746.8	741.9	6.83	0.7522	1.270	0.18	0.4529	0.8293	13.45	0.476
0.6005	242	2	751.9	746.8	6.66	0.6719	1.143	0.17	0.4043	0.7462	13.43	0.479
0.7993	239	4	748.1	742.5	6.50	0.7921	1.340	0.21	0.4739	0.8848	13.34	0.482
0.7993	240	5	755.1	750.0	7.00	0.9731	1.662	0.24	0.5806	1.0980	13.29	0.486
1.003	234	1	740.9	736.6	7.16	0.9113	1.526	0.21	0.5385	1.0360	13.16	0.491
1.003	235	2	738.5	734.2	7.00	0.9116	1.522	0.22	0.5396	1.0360	13.19	0.490
1.206	232	1	751.6	747.0	7.00	0.7308	1.242	0.18	0.4290	0.8251	13.07	0.487
1.206	233	2	749.3	744.7	7.00	0.9088	1.540	0.22	0.5316	1.0190	13.03	0.484
1.394	230	1	745.8	740.3	6.50	0.7505	1.266	0.20	0.4379	0.8485	12.97	0.487
1.394	231	2	743.4	737.9	7.66	1.0544	1.772	0.23	0.6145	1.2070	12.94	0.493
1.597	247	3	735.9	730.7	7.33	0.9141	1.520	0.21	0.5283	1.0590	12.82	0.500
1.597	248	4	762.2	757.1	7.75	0.8930	1.541	0.20	0.5147	1.0230	12.79	0.494
1.797	226	1	746.7	741.0	7.00	0.9597	1.621	0.23	0.5492	1.1110	12.67	0.499
1.797	227	2	746.7	741.0	7.00	1.0078	1.702	0.24	0.5766	1.1640	12.68	0.498
1.997	224	1	746.8	741.0	6.50	0.8284	1.399	0.22	0.4713	0.9658	12.59	0.502
1.997	225	2	744.5	738.7	7.00	0.9599	1.616	0.23	0.5465	1.1020	12.61	0.495

TABLE 14 - CONTINUED

$m_3(MnSO_4)$	Run No.	Trial No.	P_1 (mm. Hg)	P_2 (mm. Hg)	Length of Exp. (hrs.)	H_2O Absorbed in First Absorber (g.)	Moles of Inert Gas	Rate of Gas Flow (moles/ hr.)	Wt. in Second Absorber (g.)	Meq. $AgNO_3$ Used	p_{H_2O} (mm. Hg)	p_{HCl} (mm. Hg)
2.247	249	3	753.6	748.1	6.66	0.7901	1.347	0.20	0.4433	0.9082	12.43	0.496
2.247	250	4	746.5	741.0	7.00	0.8584	1.449	0.21	0.4818	0.9914	12.43	0.498
2.496	220	1	747.0	741.0	6.00	0.7150	1.208	0.20	0.3989	0.8453	12.32	0.510
2.496	221	2	747.3	741.3	7.00	1.0783	1.823	0.26	0.6027	1.2640	12.35	0.505
2.754	218	1	748.3	742.2	6.83	0.6290	1.065	0.16	0.3454	0.7313	12.11	0.501
2.754	219	2	750.1	744.0	7.00	0.9475	1.607	0.23	0.5209	1.0960	12.14	0.499
2.937	216	1	746.1	740.4	7.75	0.7657	1.292	0.17	0.4182	0.9104	12.03	0.513
2.937	217	2	745.0	739.2	6.00	0.7556	1.273	0.21	0.4118	0.9018	12.00	0.514
3.185	212	1	747.3	741.2	6.50	0.7321	1.237	0.19	0.3933	0.8744	11.81	0.515
3.185	213	2	742.9	736.8	7.00	0.6687	1.123	0.16	0.3589	0.7988	11.80	0.515

TABLE 15

VAPOR PRESSURE DATA FOR THE SYSTEM $HCl-H_2O-MnCl_2$

$m_3(MnCl_2) = 1.00$ Molal

$m_2(HCl)$	Run No.	Trial No.	P_1 (mm. Hg)	P_2 (mm. Hg)	Length of Exp. (hrs.)	H_2O Absorbed in First Absorber (g.)	Moles of Inert Gas	Rate of Gas Flow (moles/hr.)	Wt. in Second Absorber (g.)	Meq. $AgNO_3$ Used	p_{H_2O} (mm. Hg)	p_{HCl} (mm. Hg)
4.67[a]	---	---	---	---	---	---	---	---	---	---	15.79	0.128
5.30	267	1	749.7	744.2	6.50	0.7379	1.251	0.19	0.4684	0.3288	14.77	0.192
5.30	268	2	750.7	745.2	6.00	0.6873	1.167	0.20	0.4388	0.3507	14.79	0.220
5.80	263	1	757.2	752.0	7.00	0.9279	1.589	0.23	0.5735	0.8220	14.01	0.381
5.80	264	2	743.4	738.2	7.00	0.8995	1.501	0.21	0.5547	0.7781	14.08	0.375
6.32	259	1	756.0	750.8	6.50	0.9459	1.617	0.25	0.5652	1.2060	13.18	0.550
6.32	260	2	755.9	750.7	6.00	0.9247	1.582	0.26	0.5524	1.1830	13.17	0.551
7.05[a]	---	---	---	---	---	---	---	---	---	---	12.26	1.001
7.44	261	1	756.9	751.8	8.00	1.0200	1.746	0.22	0.6123	3.1130	11.71	1.317
7.44	262	2	756.9	751.8	7.00	0.9447	1.618	0.23	0.5670	2.8820	11.72	1.316
7.92	269	1	749.8	744.4	7.25	0.7126	1.208	0.17	0.4394	2.9810	11.11	1.806
7.92	270	2	746.1	740.7	6.25	0.6226	1.050	0.17	0.3854	2.6740	11.09	1.855
8.28	257	1	748.6	743.2	7.00	0.9042	1.531	0.22	0.5845	5.0200	10.63	2.395
8.28	258	2	758.2	752.8	6.00	0.7703	1.321	0.22	0.4978	4.2960	10.60	2.406
8.71	265	1	745.9	740.7	6.50	0.8493	1.433	0.22	0.5992	6.5430	10.15	3.319
8.71	266	2	748.2	743.0	6.50	0.8801	1.489	0.23	0.6177	6.7070	10.15	3.287
9.01[a]	---	---	---	---	---	---	---	---	---	---	9.74	4.258

a = values calculated from plots of log a_1 and log a_2 versus m_3 for 1.00 molal $MnCl_2$ in their respective HCl series.

n_y = moles of water absorbed in first absorber

n_x = moles of nitrogen gas

Then from Dalton's law (43) and knowledge of the number of moles of hydrochloric acid absorbed (determined by the chloride analysis), the partial pressure of the hydrochloric acid was calculated from the following relation

$$p_{HCl} = \frac{n_{HCl}}{n_{HCl} + n_{H_2O} + n_x} \cdot p_2 \qquad (27$$

where p_{HCl} = vapor pressure of hydrochloric acid

p_2 = total pressure at second set of absorbers

n_{HCl} = moles of hydrochloric acid

n_{H_2O} = moles of water

n_x = moles of nitrogen gas

The partial pressure of water was calculated similarly.

Solid Phase Analysis.

Table 16 lists the composition of the saturated solutions in the ternary systems and also gives the composition of the corresponding equilibrium solid phases. In the binary systems the solid phase in equilibrium with the saturated solution of manganous chloride contained 62.96% manganous chloride compared with the theoretical value of 63.62% for $MnCl_2 \cdot 4H_2O$, and the solid phase in equilibrium with the saturated solution of manganous sulfate contained 62.80% manganous sulfate compared with the theoretical value of 62.67% for $MnSO_4 \cdot H_2O$.

Density Determination.

The densities of the ternary manganous chloride and manganous sulfate solutions are tabulated in Table 18. Figures 3 and 4 represent graphically the density as a function of concentration.

TABLE 16

COMPOSITION OF THE SATURATED SOLUTIONS

AND EQUILIBRIUM SOLID PHASES

LIQUID PHASES

$MnCl_2$-HCl-H_2O System

m_2(HCl)	% $MnCl_2$	% H_2O	% HCl
4.67	27.87	61.64	10.49
7.05	21.08	62.77	16.14
9.01	17.75	61.90	20.34

$MnSO_4$-HCl-H_2O System

m_2(HCl)	% $MnSO_4$	% H_2O	% HCl
7.27	27.58	57.24	15.18

WET SOLID PHASES

$MnCl_2$-HCl-H_2O System

m_2(HCl)	% $MnCl_2$	% H_2O	% HCl
4.67	62.86	37.11	0.03
7.05	62.85	37.45	0.01
9.01	63.42	36.57	0.01

$MnSO_4$-HCl-H_2O System

m_2(HCl)	% $MnSO_4$	% H_2O	% HCl
7.27	80.16	17.36	2.49

TABLE 17

CHARACTERIZATION OF THE WET SOLID PHASES

$MnCl_2$-HCl-H_2O System

m_2(HCl)	% $MnCl_2$	% $MnCl_2$ in $MnCl_2 \cdot nH_2O$	n
4.67	63.60	63.62	4
7.05	63.52	63.62	4
9.01	63.60	63.62	4

$MnSO_4$-HCl-H_2O System

m_2(HCl)	% $MnSO_4$	% $MnSO_4$ in $MnSO_4 \cdot nH_2O$	n
7.27	89.40	89.35	1

TABLE 18

DENSITY DATA FOR THE SYSTEMS $HCl-H_2O-MnCl_2$ OR $MnSO_4$ AT 25°C

m_2 = 4.67 HCl		m_2 = 7.05 HCl		m_2 = 9.01 HCl		m_2 = 7.27 HCl		m_3 = 1.00 $MnCl_2$	
$m_3(MnCl_2)$	d	$m_3(MnCl_2)$	d	$m_3(MnCl_2)$	d	$m_3(MnSO_4)$	d	$m_2(HCl)$	d
0.0000	1.0713	0.0000	1.0976	0.0000	1.1204	0.0000	1.1001	0.00	1.1001
0.3999	1.1022	0.2016	1.1149	0.2000	1.1351	0.2003	1.1203	4.67	1.1510
0.5986	1.1188	0.4020	1.1301	0.4009	1.1507	0.3980	1.1399	5.30	1.1580
0.9978	1.1516	0.6076	1.1466	0.5986	1.1660	0.6005	1.1597	5.80	1.1640
1.402	1.1835	0.8103	1.1622	0.8018	1.1814	0.7993	1.1795	6.32	1.1708
1.807	1.2153	1.207	1.1926	1.398	1.2253	1.003	1.1986	7.05	1.1790
2.254	1.2494	1.604	1.2221	1.803	1.2540	1.206	1.2175	7.44	1.1837
2.736	1.2846	1.801	1.2365	2.051	1.2710	1.394	1.2345	7.92	1.1872
3.173	1.3144	2.021	1.2520			1.597	1.2536	8.28	1.1900
		2.300	1.2718			1.797	1.2709	8.71	1.1927
		2.500	1.2958			1.997	1.2888	9.01	1.1950
						2.247	1.3105		
						2.496	1.3314		
						2.754	1.3525		
						3.185	1.3913		

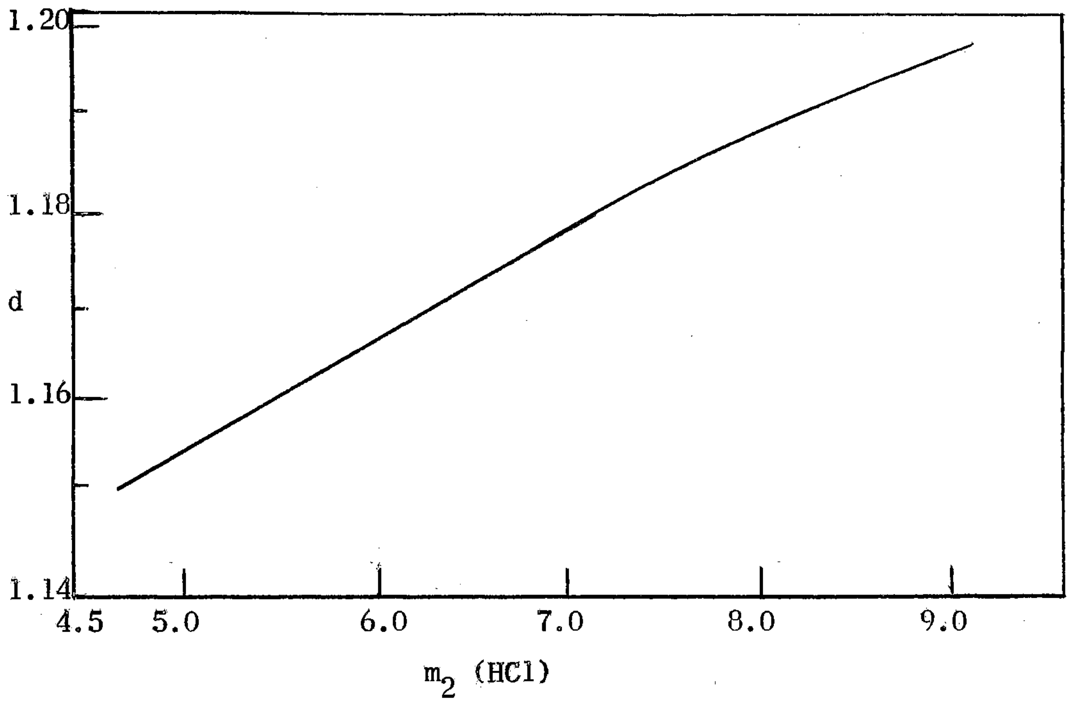

Fig. 3 Densities of the solutions of the HCl-H_2O-$MnCl_2$ system; $MnCl_2$ - 1.00 molal.

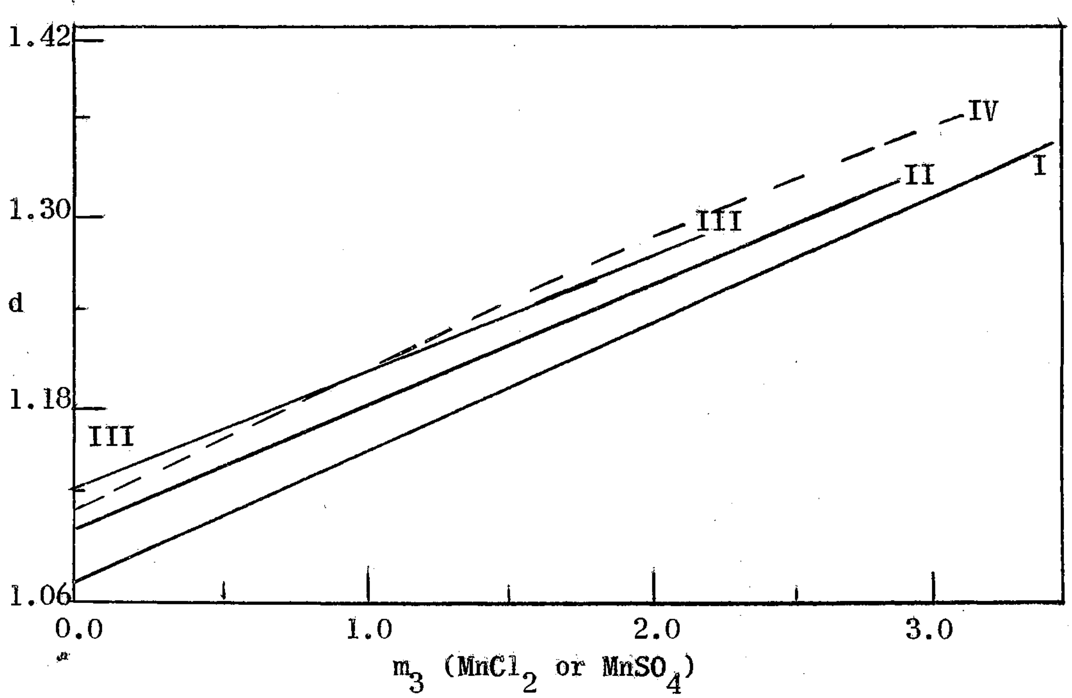

Fig. 4 Densities of the solutions of the HCl-H_2O-$MnCl_2$ or $MnSO_4$ systems; I - $MnCl_2$-4.67 m HCl; II-$MnCl_2$-7.05 m HCl; III - $MnCl_2$-9.01 m HCl; IV - $MnSO_4$-7.27 m HCl.

CHAPTER V

ACCURACY AND PRECISION OF MEASUREMENTS

Since there are no data in the literature on the activities of the components in the ternary systems investigated, one can estimate the accuracy of the data only by comparing the results with those reported by other investigators for the binary systems.

Binary Systems.

Sulfuric Acid-Water.

It can be seen from Table 1 that the experimental values of the average partial pressure of water agree within 0.1% with the values calculated from the osmotic coefficients of Stokes (157). The measurements were also reproducible with less than 0.1% error.

Hydrochloric Acid-Water.

The experimental points for the partial pressure of water fell on a smooth curve (Fig. 5) lying slightly above that determined from the values listed in the compilation by Zeisberg (176) and slightly below that representing the results of the isopiestic measurements of Robinson and Stokes (136). Similarly the hydrochloric acid partial pressures fell on a smooth curve (Fig. 6) drawn slightly above the points reported by Bates and Kirschman (7) for higher concentrations (HCl>5.0 molal).

Manganous Chloride-Water.

The experimental vapor pressure of water in the saturated aqueous solution of manganous chloride was found to agree within 0.2% with that reported by Stokes (157) who used the isopiestic method. Considering that independent methods were used, this was considered to be rather good agreement and within the probable experimental error.

Manganous Sulfate-Water.

The experimental vapor pressure of water for the saturated solution of manganous sulfate was found to agree within 0.1% with that calculated by extrapolation of the data of Robinson and Stokes (134) to saturation.

Ternary Systems.

Hydrochloric Acid-Water-Salt.

The hydrochloric acid vapor pressure measurements in the ternary systems were made with an average deviation of ± 0.003 mm. from the average of two experiments at each concentration. The corresponding deviation in the water vapor pressure measurements was ± 0.012 mm. Table 19 tabulates the deviation in vapor pressure measurements for the various series investigated.

Solid Phase Analysis.

The solid phase in equilibrium with the saturated aqueous solution of manganous chloride at 25°C was found to be the tetrahydrate, which is in agreement with that reported in the literature (30). The solid phase in equilibrium with the saturated aqueous solution of manganous sulfate at 25°C was found to be the pentahydrate, which is also in agreement with that reported in the literature (26,85).

In the ternary systems involving hydrochloric acid, the composition of the solid phases in equilibrium with the saturated solutions

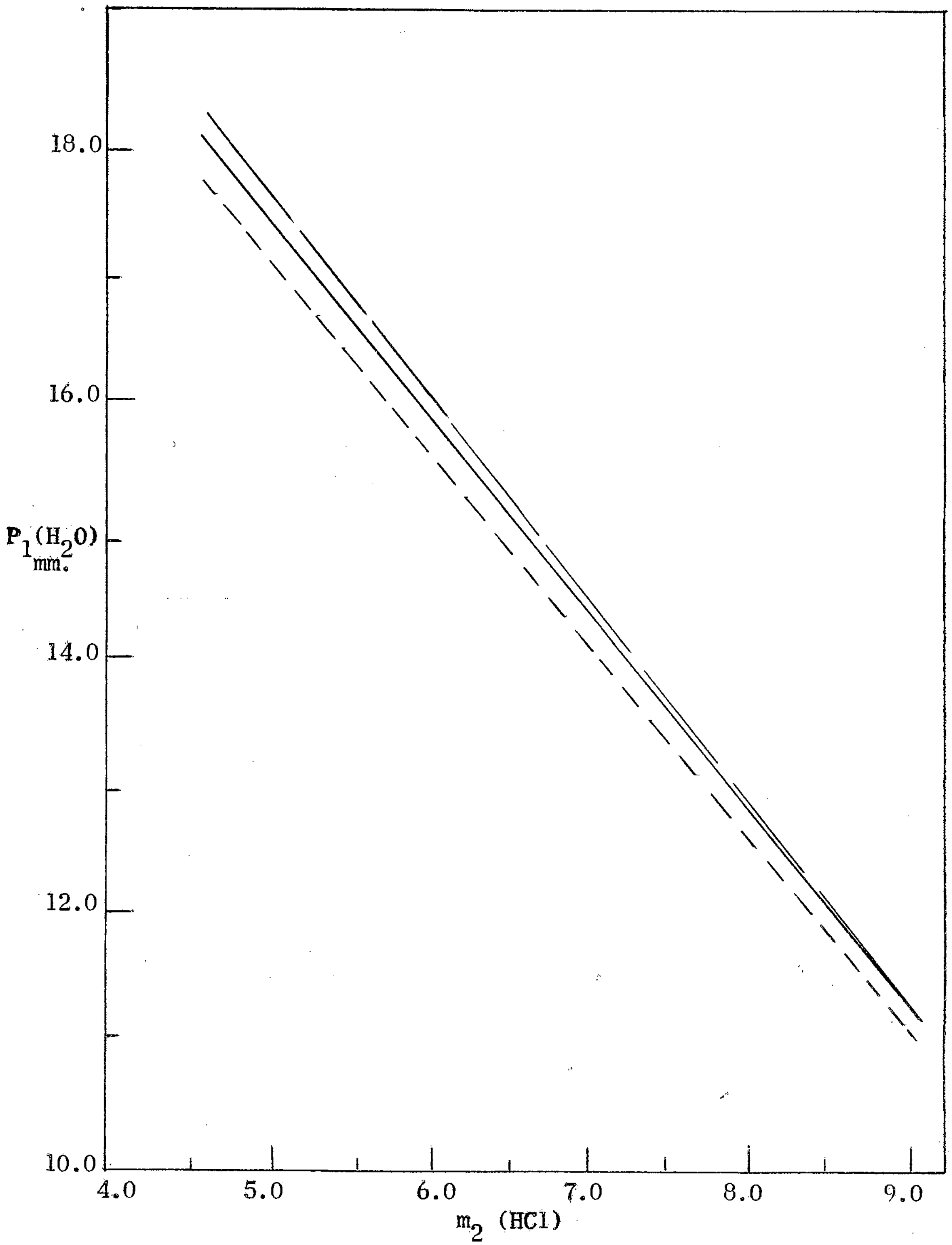

Fig. 5. Vapor pressure of H_2O in the HCl-H_2O solutions. ——Experimental values; —— ——Values of Robinson and Stokes; -----Values of Zeisberg.

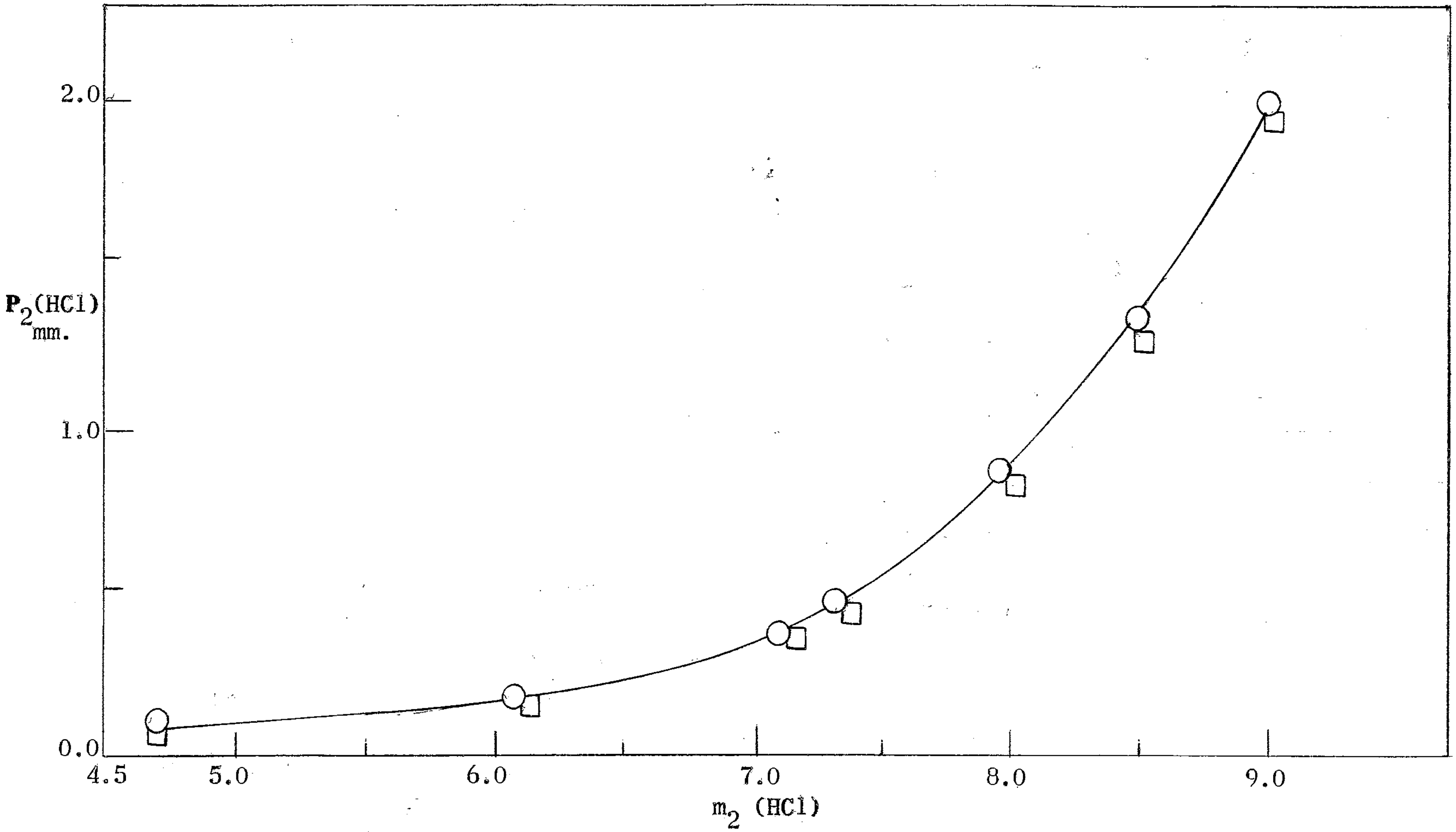

Fig. 6 Vapor pressure of HCl in the HCl-H_2O solutions. O, Experimental values; □, Values of Bates and Kirschman.

TABLE 19

DEVIATIONS IN VAPOR PRESSURE MEASUREMENTS

System	Average Deviation from Average Value in p_{HCl} (mm.)	Average Deviation from Average Value in p_{H_2O} (mm.)
4.67 HCl - $MnCl_2$	± 0.001	± 0.008
7.05 HCl - $MnCl_2$	± 0.002	± 0.014
9.01 HCl - $MnCl_2$	± 0.004	± 0.016
7.27 HCl - $MnSO_4$	± 0.002	± 0.010
1.00 $MnCl_2$ - HCl	± 0.008	± 0.010

TABLE 20

DIFFERENCES BETWEEN EXPERIMENTAL AND CALCULATED VALUES OF THE LOGARITHM OF ACTIVITY

System	Average Percentage Difference in log a_{HCl}	Average Percentage Difference in log a_{H_2O}
4.67 HCl - $MnCl_2$	0.29	0.25
7.05 HCl - $MnCl_2$	0.18	0.25
9.01 HCl - $MnCl_2$	0.08	0.55
7.27 HCl - $MnSO_4$	0.06	0.22
1.00 $MnCl_2$ - HCl	0.34	0.35

were not to be found in the literature.

Saturated Solution Analysis.

The solubility of manganous chloride at 25°C was found to be 770.3 g. $MnCl_2$/1000 g. H_2O compared with the values of 771.8 g. reported by Dawson and Williams (30), 772.7 g. by Kapustinskii (75), and 763.0 g. by Benrath (10). The saturated aqueous solution of manganous sulfate was found to have a concentration of 664.2 g. $MnSO_4$/1000 g. H_2O compared with the values of 651.0 g. reported by Krepelka (85), 647.8 g. by Cottrell (26), and 684.0 g. reported by Sidgwick (155). In view of the variance in the values reported, it was felt that our experimental values were probably as reliable as those cited in the literature.

The solubilities of manganous chloride or sulfate in hydrochloric acid solutions have not been previously reported, and consequently, it was not possible to determine the reliability of the experimental data.

Density Measurements and Apparent Molal Volumes.

The densities were measured with a precision of 0.05% or better. The apparent molal volumes, therefore, are regarded as accurate to about 1%.

CHAPTER VI

DISCUSSION OF THE RESULTS

Any adequate theory of concentrated solutions of electrolytes must recognize or take into account the following factors which have been summarized by Glueckauf (44) and by Robinson and Stokes (139):

(1) the electrostatic forces of the Debye-Huckel type which predominate at low concentration;

(2) changes in the dielectric constant of the solvent;

(3) ionic association;

(4) the effect of ionic sizes, not only on the Debye-Huckel term, but also on the co-volume entropy effect;

(5) the effect of ionic hydration.

As pointed out by Glueckauf, since the Debye-Huckel theory is not applicable to concentrated solutions, and since (2)-(5) all result in near linear terms, it is not expected that a general solution can be found where the various terms can be separated. For electrolytes which show a strong hydration effect and little ionic polarization, one can assume that (3) can be neglected, and that the deviations of the Debye-Huckel term (1), including the effect (2), are at higher concentrations relatively unimportant. The most important effects to be theoretically accounted for are the hydration effect and the ionic volume effect which is itself largely determined by the degree of hydration of the ions. These two factors are discussed more fully in the following section along with the results of an attempt to apply a model of ionic hydration to the interpretation of the data from this study of the $HCl-MnCl_2$ system.

Constant Acid Series - Manganous Chloride.

Water Activities and Hydration Theory.

The water activities as a function of the salt concentration in the three constant $HCl-MnCl_2$ series are presented in Fig. 7. Aside from the obvious decrease in the water activity of the ternary system compared to that of the binary system (salt-water) arising from the presence of the hydrochloric acid, and the additional lowering in a given constant acid series because of the increasing concentration of the salt, one notes that the lowerings of the water activity is relatively smaller in concentrated hydrochloric acid solutions than in the more dilute solutions. At the higher concentrations of salt a leveling off of the water activity can be observed in Curves III and IV. Moore, et. al. (108) have found a similar effect for nickel chloride in 9.12 molal hydrochloric acid and for cobalt chloride in 10.65 molal hydrochloric acid. The lowering in each constant acid series can be attributed in part to the ionic hydration of the salt in solution which results in the removal of the effective solvent or free water (158). By way of comparison, the water activity as a function of the acid concentration in the constant salt series is presented in Fig. 8, where it is readily observed that an increase of acid concentration lowers the water activity for a constant salt concentration, and this again may be attributed in part to the ionic hydration of the acid.

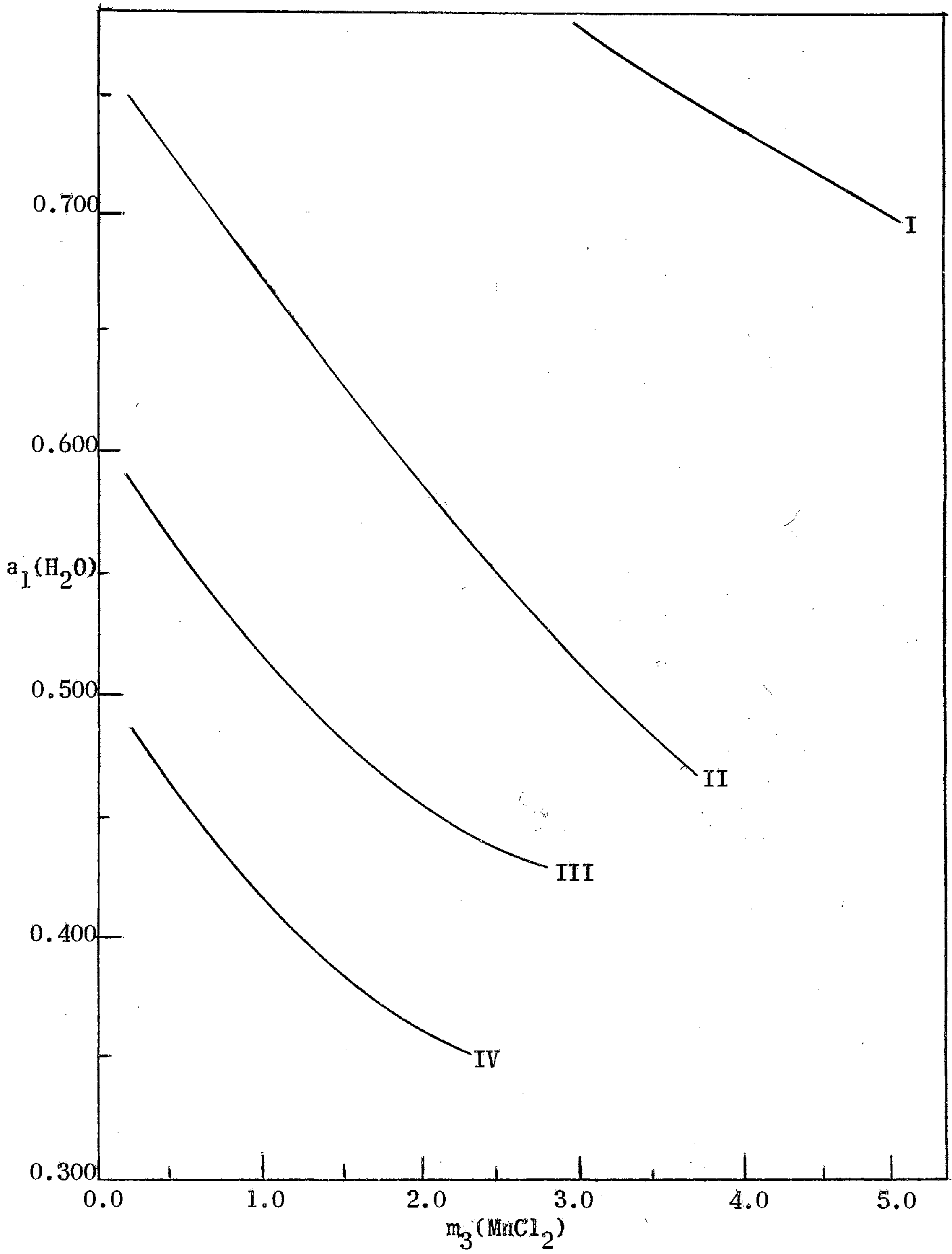

Fig. 7 Activity of H_2O in the HCl-H_2O-$MnCl_2$ system: I 0 m. HCl; II 4.67 m HCl; III 7.05 m HCl; IV 9.01 m HCl.

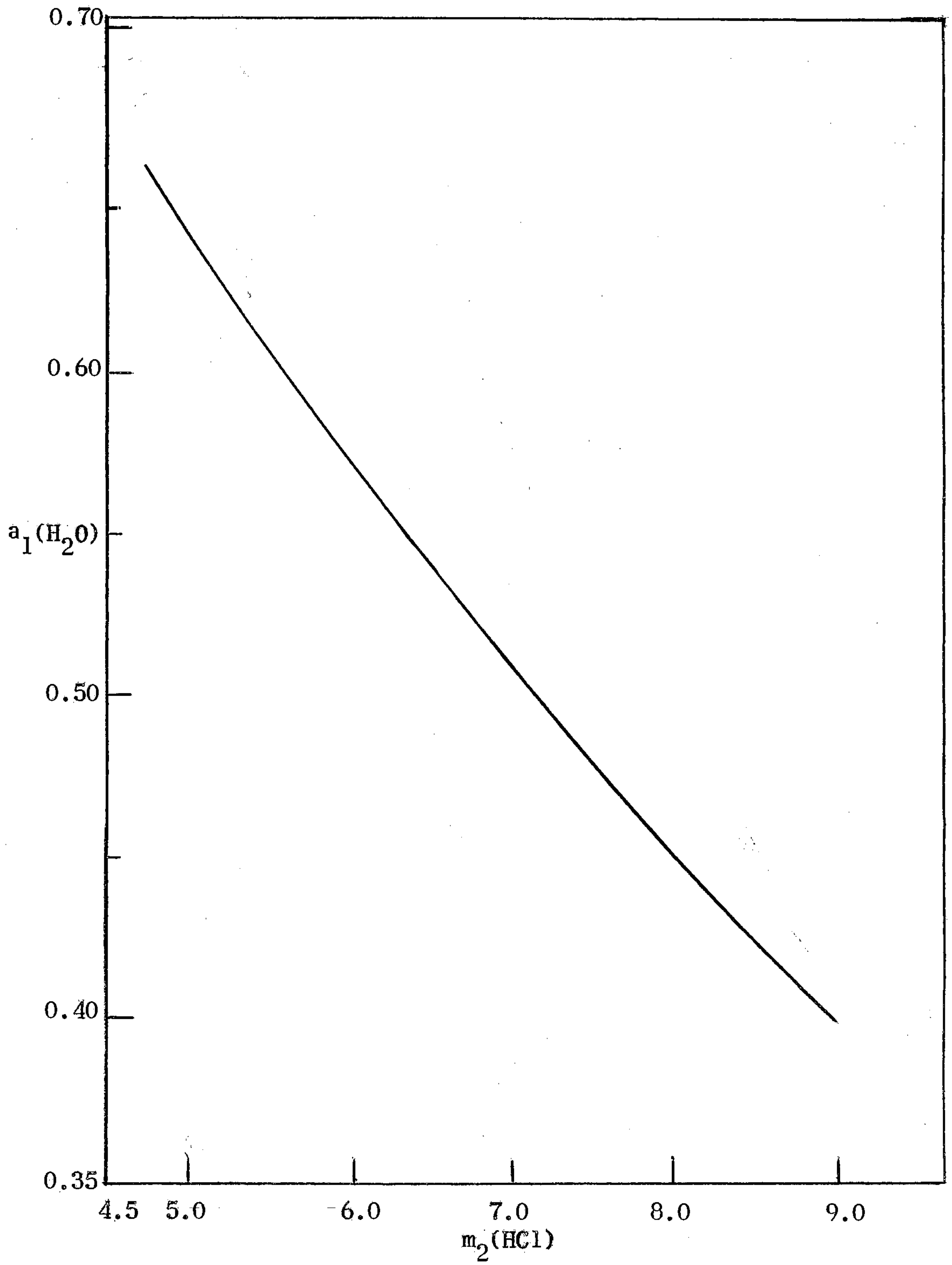

Fig. 8 Activity of H_2O in the $HCl-H_2O-MnCl_2$ system at 1 m. $MnCl_2$.

As early as 1920 Bjerrum (12) had proposed a theory of ionic hydration based on a simple lattice model which received little recognition at the time. A little later a similar treatment based on the mass action law was presented by Harned (57). A somewhat similar hydration-association theory, based on an association-penetration model, was also proposed by Frank (38) in 1941 in which it was emphasized that while ionic solvation increases the activity coefficient ion-pair formation correspondingly opposes this increase in the activity coefficient. In 1948 Stokes and Robinson (158) modernized Bjerrum's hydration theory by the introduction of the Debye-Huckel equation for the mean rational ionic activity coefficient of the ions. The equation which they developed for the effect of solvation on the activity coefficient contains two adjustable parameters, $\overset{o}{a}$ and n, where $\overset{o}{a}$ is the distance of closest approach of the hydrated ions and n, though not to be interpreted necessarily as the number of molecules in the layer around the ion, is a "number introduced to allow for the average effect of all ion-solvent interactions where these are large compared to kT". Their equation has been extensively tested and found to be very successful with non-associated electrolytes. For certain salts, such as the alkali and alkaline earth halides, a simple relation between the parameters $\overset{o}{a}$ and n has been obtained by using the concept of limited penetration of the anion into the hydration sheath of the cation. This reduces their hydration expression to a one parameter equation involving only n. Unfortunately the empirical hydration numbers often become so large that at high concentrations all of the water theoretically becomes combined with the ions and none exists as solvent. Obviously such a result calls for a decrease in n with increasing concentration of electrolyte, a situation which would require the penetration of the ions into the hydration sheath of the other ions in a manner similar to that described by Frank (38).

Glueckauf (44) using a model similar to that of Stokes and Robinson, but employing volume fraction statistics has derived an equation for the activity coefficient in which the hydration numbers obtained for the individual ions do not show the anomalies which characterize the Stokes-Robinson hydration parameters. A critique of the Stokes-Robinson equation is also given by Glueckauf in which the use of the Debye-Huckel expression for the electrostatic contribution to the Gibbs function rather than the chemical potential of the hydrated electrolyte is recommended.

Miller (105) as well as Robinson and Stokes (139) have recognized the possibility that an ideal mixture of "uncharged ions" and solvent molecules probably should be treated on the basis of volume fraction statistics rather than by mole fraction statistics. Unfortunately, however, lack of knowledge of the proper volumes to use with the model makes the use of volume fractions probably no more nearly correct than the use of mole fractions.

Moore, et. al (108) have applied the theory of Stokes and Robinson to mixtures of two electrolytes. They obtained rather good agreement between the experimental and theoretically calculated activity coefficients for the presumably non-associated electrolyte, nickel chloride, in hydrochloric acid solutions. A trial and error method of obtaining the hydration parameters of hydrochloric acid and nickel chloride was employed, however.

In order to test the application of the hydration model to the $HCl-MnCl_2$ system, a more fundamental method of determining the hydration numbers seemed desirable. Following Glueckauf (44) the total free energy of the solution is written as

$$G = n_1 u_1^o + n_2 u_2^o + n_3 u_3^o + G^{el} + G^s \tag{28}$$

where u_1^o = standard-state chemical potential of "free water"

u_2^o = standard state chemical potential of hydrated hydrochloric acid

u_3^o = standard-state chemical potential of hydrated manganous chloride

n_2 = moles of hydrochloric acid

n_3 = moles of manganous chloride

n_w = moles of total water

$n_1 = n_w - h_2 n_2 - h_3 n_3$ (free water)

h_2 = hydration parameter for hydrochloric acid

h_3 = hydration parameter for manganous chloride

G^{el} = electrostatic contribution to the Gibbs function (see Ref. 37, Eq. 918.1)

G^s = entropy contribution (see eg. Ref. 91)

By differentiating with respect to the free water, n_1, at constant acid and salt concentration, n_2 and n_3, respectively, one obtains

$$\left(\frac{\partial G}{\partial n_1}\right)_{n_2,n_3} = u_1^o + \left(\frac{\partial G^{el}}{\partial n_1}\right)_{n_2,n_3} + \left(\frac{\partial G^s}{\partial n_1}\right)_{n_2,n_3} \tag{29}$$

where by the Debye-Hückel theory

$$\left(\frac{\partial G^{el}}{\partial n_1}\right)_{n_2,n_3} = \sum_i \frac{n_i N z_i^2 |e|^2 k\sigma(ka)}{6D} \cdot \frac{\bar{v}_1}{V} \tag{30}$$

and

$$\left(\frac{\partial G^s}{\partial n_1}\right)_{n_2, n_3} = RT \frac{\partial}{\partial n_1} \Big[n_1 \ln n_1\bar{v}_1/V + n_2 \ln n_2\bar{v}_{H^+}/V + (n_2 + 2n_3) \ln (n_2 + 2n_3)\, \bar{v}_{Cl^-}/V + n_3 \ln n_3\bar{v}_{Mn^{++}}/V \Big] \quad (31)$$

or

$$\left(\frac{\partial G^s}{\partial n_1}\right)_{n_2, n_3} = RT(1 + \ln n_1\bar{v}_1/V) - (n_1 + 2n_2 + 3n_3)\, \bar{v}_1/V \quad (32)$$

on the basis of volume fraction statistics.

Using the usual definition of the activity

$$\left(\frac{\partial G}{\partial n_j}\right) = u_j = u_j^o + RT \ln a_j \quad (33)$$

and substituting into Eq. (32) one finally obtains

$$\ln a_1 = \frac{N\, |e|^2\, k\sigma(ka)}{3\, RTD} \cdot \bar{v}_1 \cdot I + (1 + \ln n_1\bar{v}_1/V) - (n_1 + 2n_2 + 3n_3)\, \bar{v}_1/V \quad (34)$$

where $I = 1/2 \sum_i n_i\, z_i^2/V = 1/2 \sum_i c_i z_i^2$

This is the volume fraction statistics equation for the activity of the free water. Here

$$V = n_1\bar{v}_1 + n_2\bar{v}_2 + n_3\bar{v}_3 \quad (35)$$

where V = the total molar volume

$\bar{v}_1$ = partial molar volume of water

$\bar{v}_2$ = partial molar volume of hydrated hydrochloric acid

$\bar{v}_3$ = partial molar volume of hydrated manganous chloride

If one differentiates Eq. (28) with respect to the free water, $\underline{n}_1$, at constant acid and salt concentration, $\underline{n}_2$ and $\underline{n}_3$, respectively, but uses mole fractions rather than volume fractions, there is obtained in the place of Eq. (34)

$$\ln a_1 = \frac{N\ |e|^2\ k\,\sigma(ka)}{3\ RTD} \cdot \bar{v}_1 \cdot I + \ln n_1/n_1 + 2n_2 + 3n_3 \qquad (36)$$

It was necessary to estimate the partial molar volume of the free water, $\bar{v}_1$, in order to compute the value of the electrostatic term of Eq. (34) or (36). To do this it was assumed that the partial molar volume of the total water could be used in place of the partial molar volume of the free water. Then since

$$V = 55.51\ \bar{v}_w + n_2\left(\frac{\partial V}{\partial n_2}\right)_{n_w, n_3} + n_3\left(\frac{\partial V}{\partial n_3}\right)_{n_w, n_2} \qquad (37)$$

where $\bar{v}_w$ = partial molar volume of the total water

n_w = total number of moles of water or 55.51

V = total molar volume of the solution

the second term on the right of Eq. (37) can be obtained from a plot of V versus n_2 at constant salt concentration, and the third term can be obtained from a plot of V versus n_3 at constant acid concentration. In this investigation the only point where there was sufficient data to fulfill these requirements was at a salt concentration of 1.00 molal. It was assumed, therefore, that $\bar{v}_w = \bar{v}_1$ and that the value was constant for each constant hydrochloric acid series. The values obtained for the various constant acid series are as follows: $m_2 = 4.67$, $\bar{v}_1 = 18.6$ cc.; $m_2 = 7.05$, $\bar{v}_1 = 18.0$ cc.; $m_2 = 9.01$, $\bar{v}_1 = 17.6$ cc. The partial molar volumes of water decrease with acid concentration as might be expected (170). It is easily shown, moreover, that the value chosen is not critical as the magnitude of the electrostatic term is small. Thus if one now arbitrarily assumes that $\mathring{a} = 4.80$ for all ion-ion interactions and places it into the electrical term of Eq. (36), one finds that the value of this term varies only from 0.01 to 0.02 over the entire range of concentrations.

Expressing the free water in terms of hydration numbers one has from Eq. (36) for the water activity

$$[55.51 + a_1 (2n_2 + 3n_3)/(a_1 - e^B)] = h_2n_2 + h_3n_3 \tag{38}$$

where B = the electrical term = $\left(\frac{k^3}{24\pi} \sigma(ka) \bar{v}_1 \right)$

$k = 0.3286 \sqrt{I}$ at 25°C (see Ref. 139, p. 491) if $\mathring{a} = 4.8$

If one now writes Eq. (38) in the form of

$$y = a + h_3m_3 \tag{39}$$

and plots $\underline{y}$ versus $\underline{m}_3$, the slope will be equal to $\underline{h}_3$ for constant $\underline{h}_3$. The intercept at zero salt concentration will give $\underline{h_2n_2}$ which is assumed constant for a given acid series. It was found that the data from the 4.67 m HCl series fell on a curved line up to 1.5 m salt but became linear at higher concentrations. The 7.05 m HCl series data gave a straight line above 0.5 m salt, and the 9.01 m HCl series fell on an essentially straight line over the entire range of concentrations. The values calculated for the various hydration parameters are listed in Table 21. The values for $\underline{h}_2$ are comparable to those obtained by Moore, et. al. (108) and Glueckauf (44) and decrease with increase in acid concentration from one series to the next as would be expected (158). Although the values for $\underline{h}_3$ seem suspiciously low when compared, for example, to $NiCl_2$ in comparable mixtures with HCl or to $MnCl_2$ in a binary solution (158), they also decrease with increasing acid concentration as one would expect.

An attempt was also made to calculate the hydration numbers

TABLE 21

HYDRATION PARAMETER VALUES FOR MOLE FRACTION STATISTICS

Constant Acid Series	h_2	h_3
4.67	5.7	6.5 - 3.4
7.05	5.1	1.7
9.01	4.5	1.2

from volume-fraction statistics and the following equation

$$\log a_1 - 0.4343(B + 1) + 0.4343(2n_2 + 3n_3)\,\bar{v}_1/V = \log X - 0.4343\,X \qquad (40)$$

where B = electrical term (see Eq. 34)

$X = n_1\bar{v}_1/V$

which is merely a rearrangement of Eq. (34). By using an approximation method (95) the equation was solved for X. From the calculated value of X the value of $\underline{n}_1$, the number of moles of free water, was computed. The values of n_1 obtained, however, were impossibly high, exceeding even the 55.51 moles of total water in the solution.

Hydrochloric Acid and Mananous Chloride.

The addition of manganous chloride to hydrochloric acid greatly increases the activity of the acid, and correspondingly the activity of manganous chloride is increased at constant concentration by hydrochloric acid. These conclusions are obvious from a consideration of Fig. 9, 10, 13, 15. A large part of the observed increase in the activities can reasonably be attributed to the much higher concentration of chloride ions in the mixtures compared to the binary solutions; however, as Fig. 11,12,14,16 show, the mean molal activity coefficients of both the salt and the acid similarly increase with increasing concentration of the other.

Qualitatively, "the salting-out" observed in this system can be attributed to ionic hydration as discussed in connection with the water activity data in the preceding section. It can be seen, however, upon comparison of the shapes of the curves that while hydration might be the most important factor affecting the activity coefficient of hydrochloric acid, the activity coefficient of manganous chloride is apparently the result of the operation of two or more factors. This is shown by the minima found below 1 molal in the two higher acid series and by the tendency of the curves to flatten out at the highest salt concentrations. It should be pointed out in this connection that the activity coefficient curves for manganous chloride may not be very reliable below about 0.5 molal since experimental uncertainties in the shapes of the water and hydrochloric acid activity curves become very critical at the lowest salt concentrations in the determination of the manganous chloride activity through the Gibbs-Duhem equation. Among the probable factors which would oppose the increase in the activity coefficient arising from hydration is ionic association. Unfortunately, there is no way to determine the extent of this factor from the data obtained. Changes in the color of the solution with increase in hydrochloric acid concentration were observed, however. The smaller values of the activity coefficient of manganous chloride in binary solutions compared to other transition metal salts lead Stokes and Robinson (135) to conclude that ion-paring may be appreciable in such solutions.

The most nearly comparable systems for which activity data has been obtained are the $NiCl_2$-HCl and $CoCl_2$-HCl systems which were studied at 30°C. Although the binary aqueous solutions of nickel

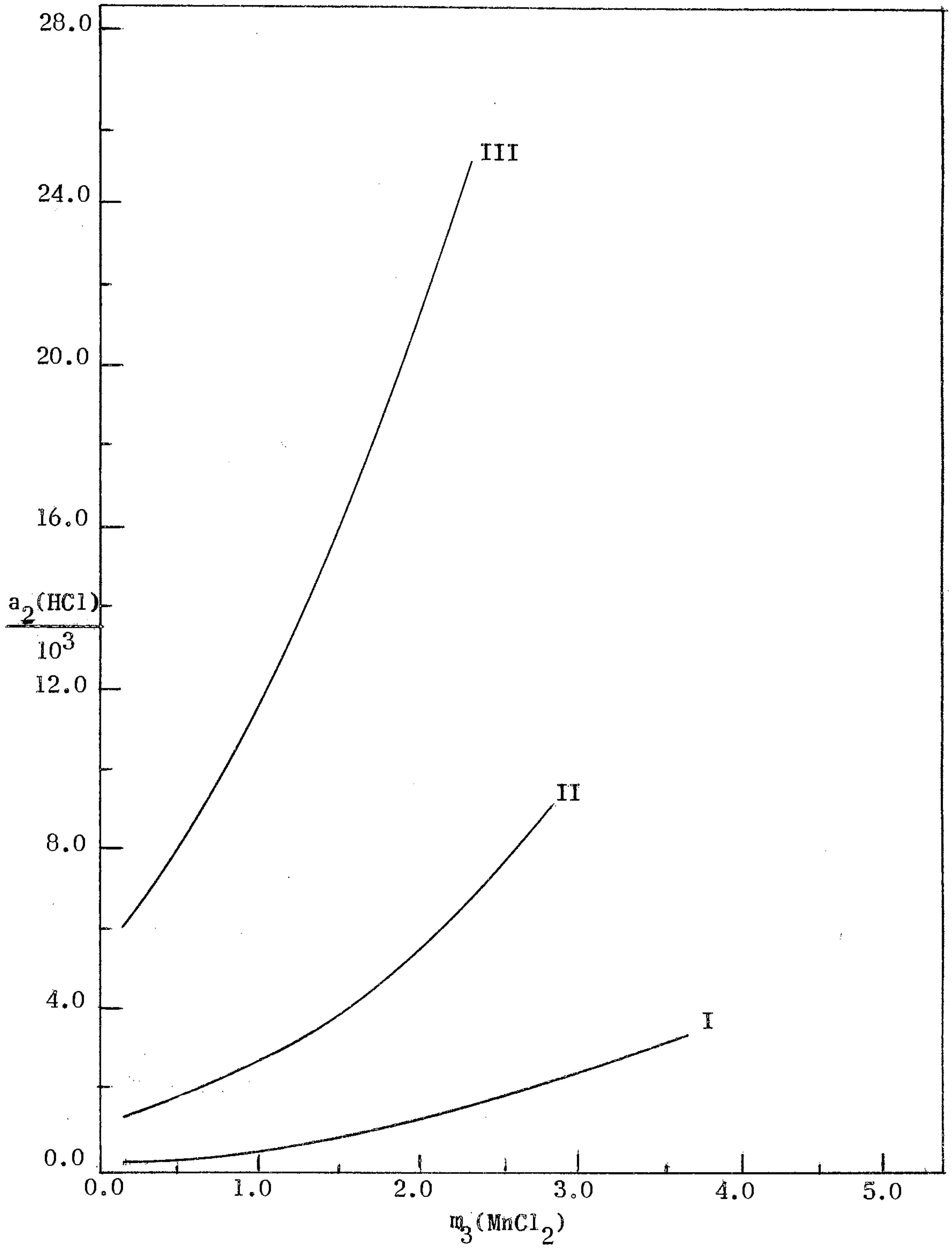

Fig. 9 Activity of HCl in the $HCl-H_2O-MnCl_2$ system: I, 4.67 m HCl; II, 7.05 m HCl; III, 9.01 m HCl.

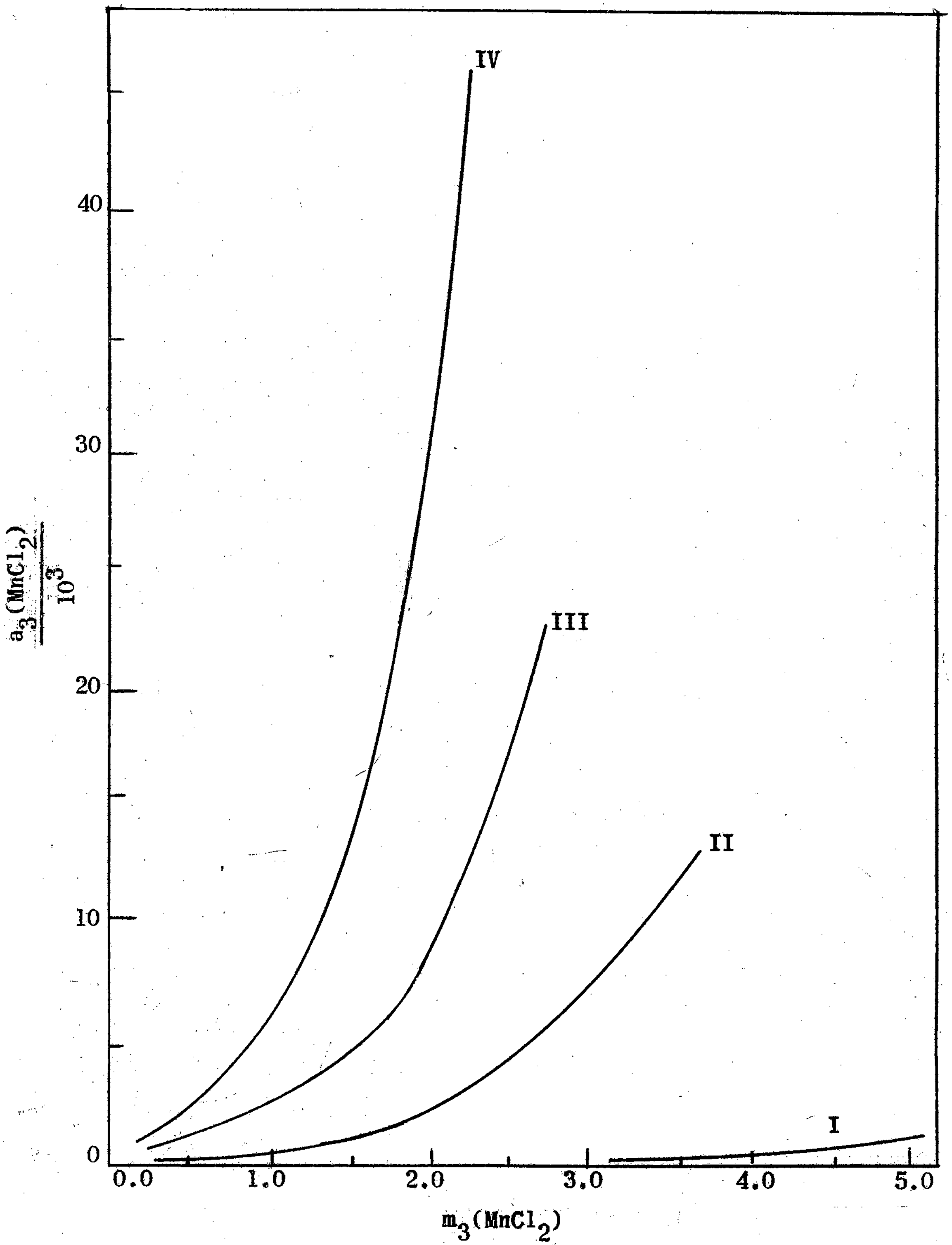

Fig. 10 Activity of $MnCl_2$ in the HCl-H_2O-$MnCl_2$ system: I, 0 m HCl; II, 4.67 m HCl; III, 7.05 m HCl; IV, 9.01 m HCl.

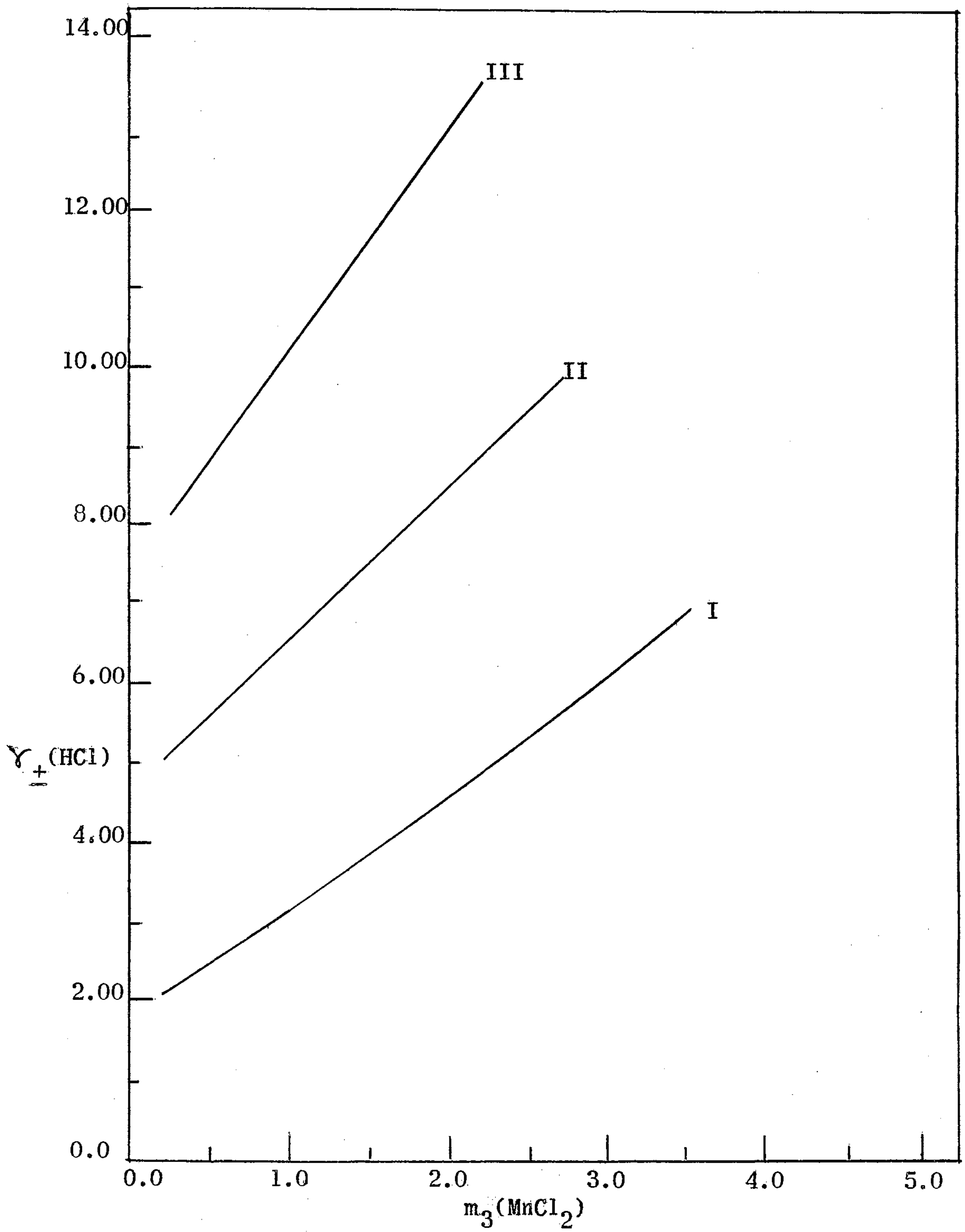

Fig. 11 Activity coefficient of HCl in the $HCl-H_2O-MnCl_2$ system: I, 4.67 m HCl; II, 7.05 m HCl; III, 9.01 m HCl.

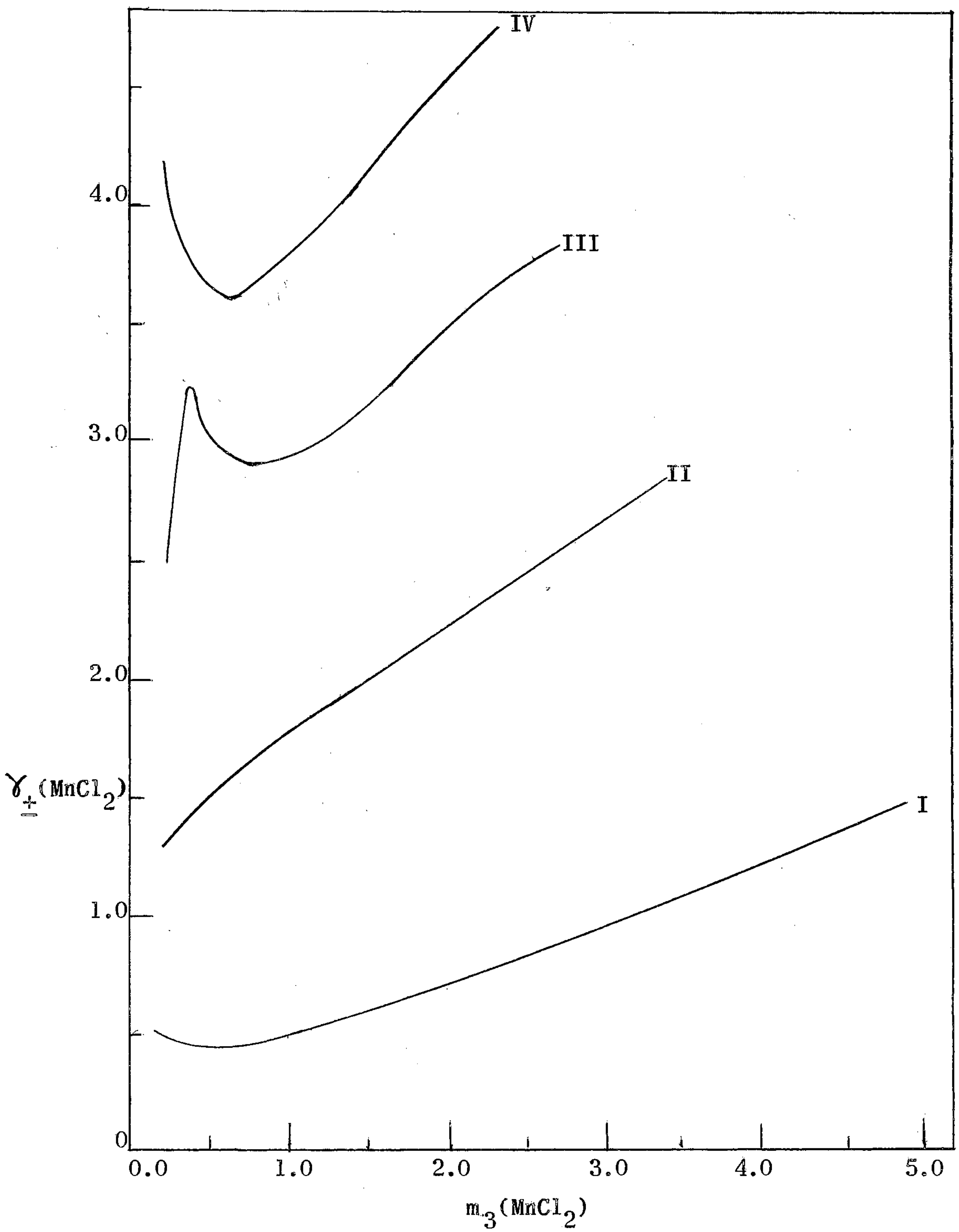

Fig. 12 Activity coefficient of $MnCl_2$ in the HCl-H_2O-$MnCl_2$ system: I, 0 m HCl; II, 4.67 m HCl; III, 7.05 m HCl; IV, 9.01 m HCl.

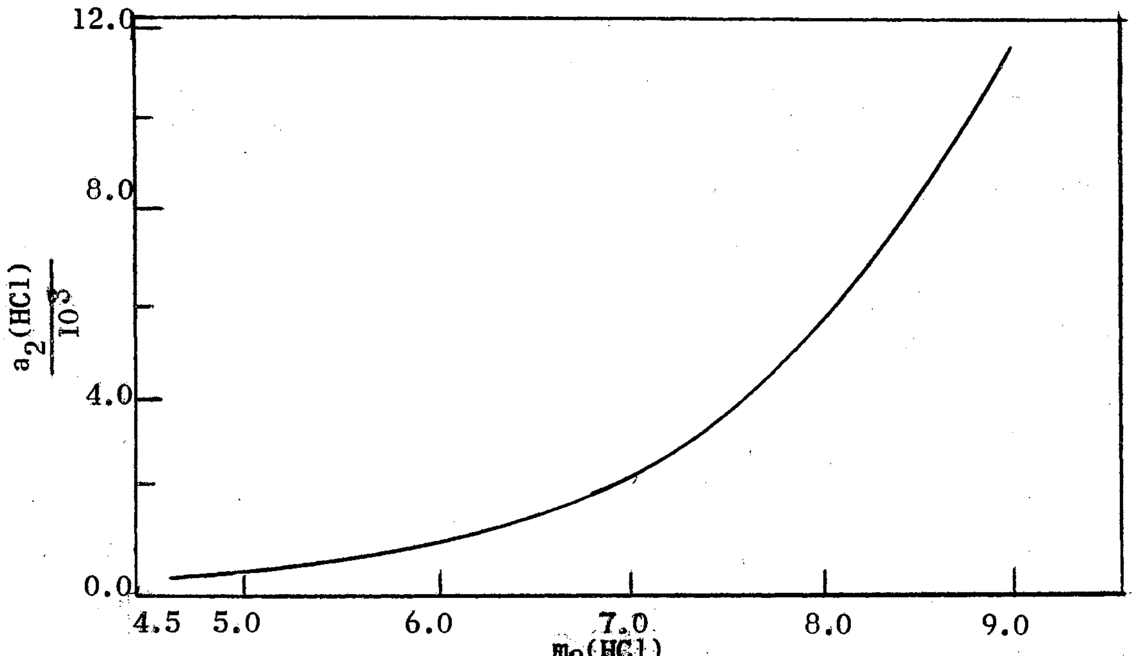

Fig. 13 Activity of HCl in the HCl-H_2O-$MnCl_2$ system at constant $MnCl_2$ concentration: $MnCl_2$ = 1.00 m.

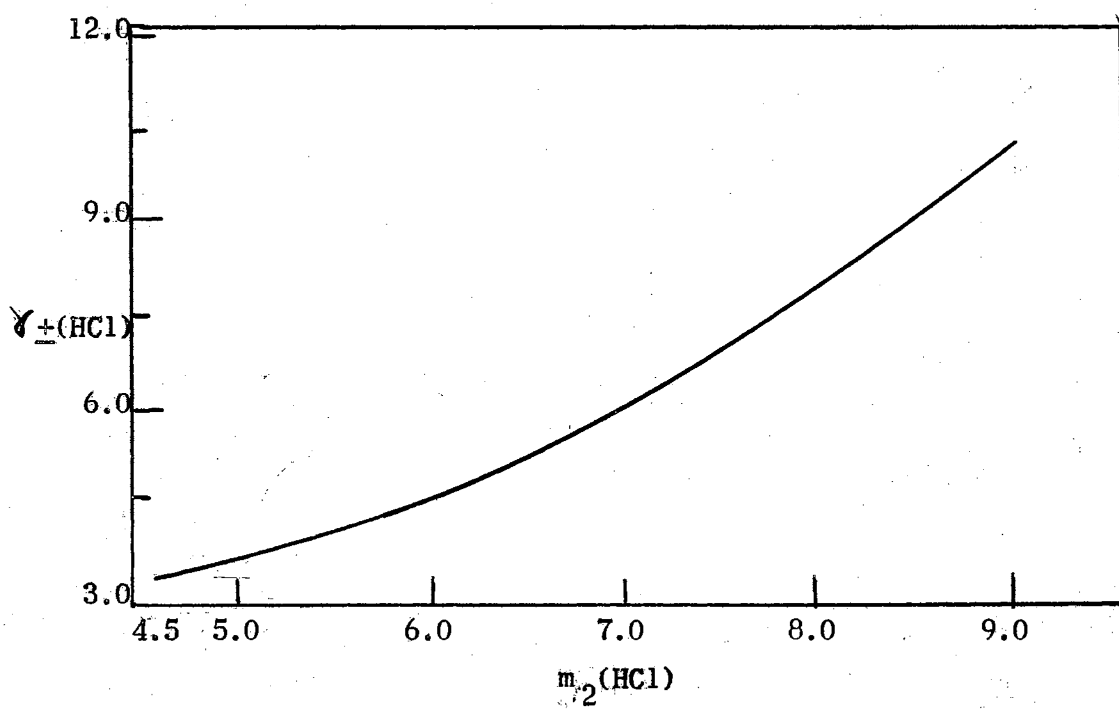

Fig. 14 Activity coefficient of HCl in the HCl-H_2O-$MnCl_2$ system at constant $MnCl_2$ concentration: $MnCl_2$ = 1.00 m.

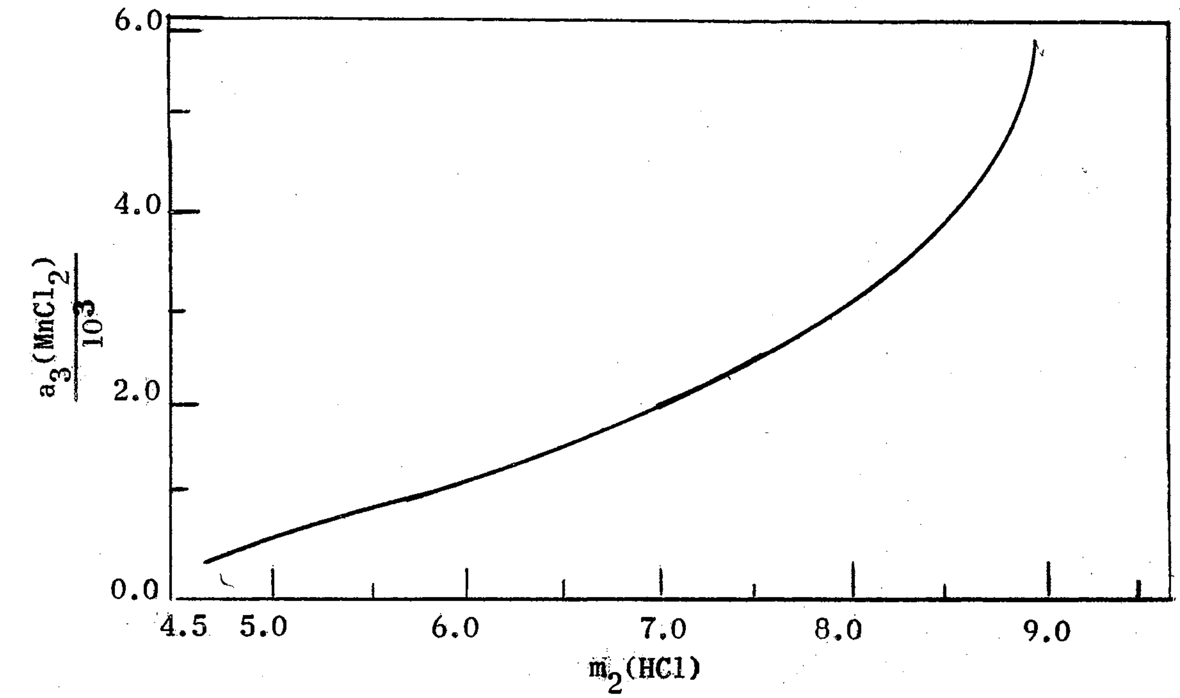

Fig. 15 Activity of $MnCl_2$ in the $HCl-H_2O-MnCl_2$ system at constant $MnCl_2$ concentration: $MnCl_2$ = 1.00 m.

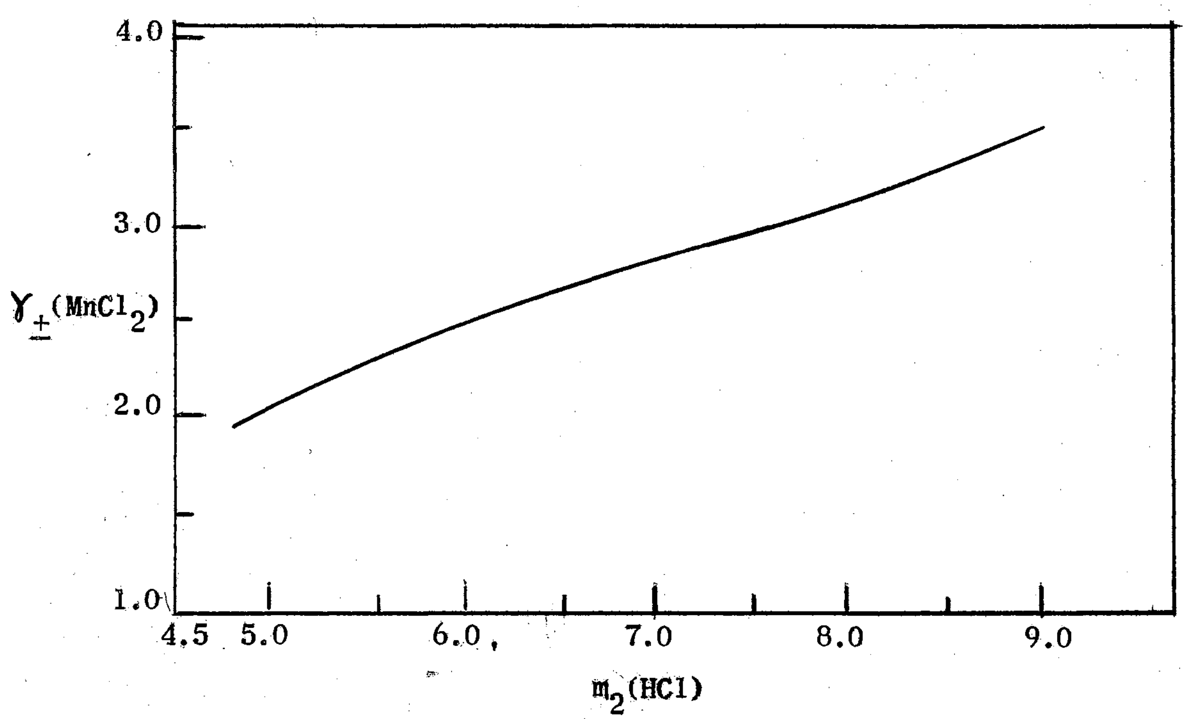

Fig. 16 Activity coefficient of $MnCl_2$ in the $HCl-H_2O-MnCl_2$ system at constant $MnCl_2$ concentration: $MnCl_2$ = 1.00 m.

and cobalt chloride are closely similar in their activity coefficients up to moderately high concentrations, the activity coefficient of manganous chloride is lower at all concentrations than either of the above salts, especially in the more concentrated region.

Comparison of manganous chloride with both nickel and cobalt chloride in hydrochloric acid of about the same concentration (ca. 4.7 molal) shows that manganous chloride similarly has an activity which is markedly less than that of either of the other two salts. For example, at a 1.00 molal concentration the activity of nickel chloride is approximately 2200, cobalt chloride approximately 1600, and manganous chloride approximately 273. Differences of this order of magnitude cannot be simply accounted for by consideration of electrostatic or long range forces only since the salts are of the same valence type. Examination of the relative effects of these salts upon the water activity and the hydrochloric acid activity coefficient, as well as the magnitude of the individual activities under similar conditions of concentration, leads one to conclude that maganous chloride is probably the most highly ionically associated and the least hydrated salt of the group in hydrochloric acid, this is in spite of having the largest crystallographic (ionic) radius (47,120).

A test of the adequacy of the hydration model for the $MnCl_2$-HCl system would be to be able to use the values for the hydration numbers obtained from the water activity data to calculate the solute activity coefficients. The mathematical formulas needed for this computation have been presented by Moore, et. al. (108) and by Stokes and Robinson (137). Both of these references include only the case of constant hydration numbers for each component and apply only to completely dissociated solutes. For hydrochloric acid the formula is

$$\log \gamma_2 = -h_2/2 \log a_1 - \log(n_1 + 2n_2 + 3n_3) - \frac{0.509\ I^{1/2}}{1 + 1.577\ I^{1/2}} + C_2 \qquad (41)$$

where $\underline{I}$ is the ionic strength and $\underline{C}_2$ is a constant whose value is determined from the data at some reference concentration. A similar equation applies to the manganous chloride data. Again the value of 4.8 is given to $\mathring{\underline{a}}$. Figure 17 shows the comparison of the experimental and calculated values of the activity coefficients in the 7.05 and 9.01 molal hydrochloric acid series using the values for the hydration parameters, $\underline{h}_2$ and $\underline{h}_3$, tabulated in Table 21. The agreement is rather good for the acid but similar calculations give very poor results with manganous chloride. In view of the considerable amount of evidence supporting ion-pair formation by the manganous and chloride ions, the applicability of the simple hydration theory to the salt without correction for ion-pair formation would hardly have been expected; however, for the same reasons the agreement found for the acid is surprising because of the interdependence of the assumptions regarding the dissociation of both the acid and the salt.

Harned's Rule.

For mixtures of hydrochloric acid with the alkali metal halides and with certain other electrolytes where extremely strong ionic interaction would not be expected, the logarithm of the activity coefficient of hydrochloric acid has been found to be a linear function of the molality of the other electrolyte in mixtures of constant ionic

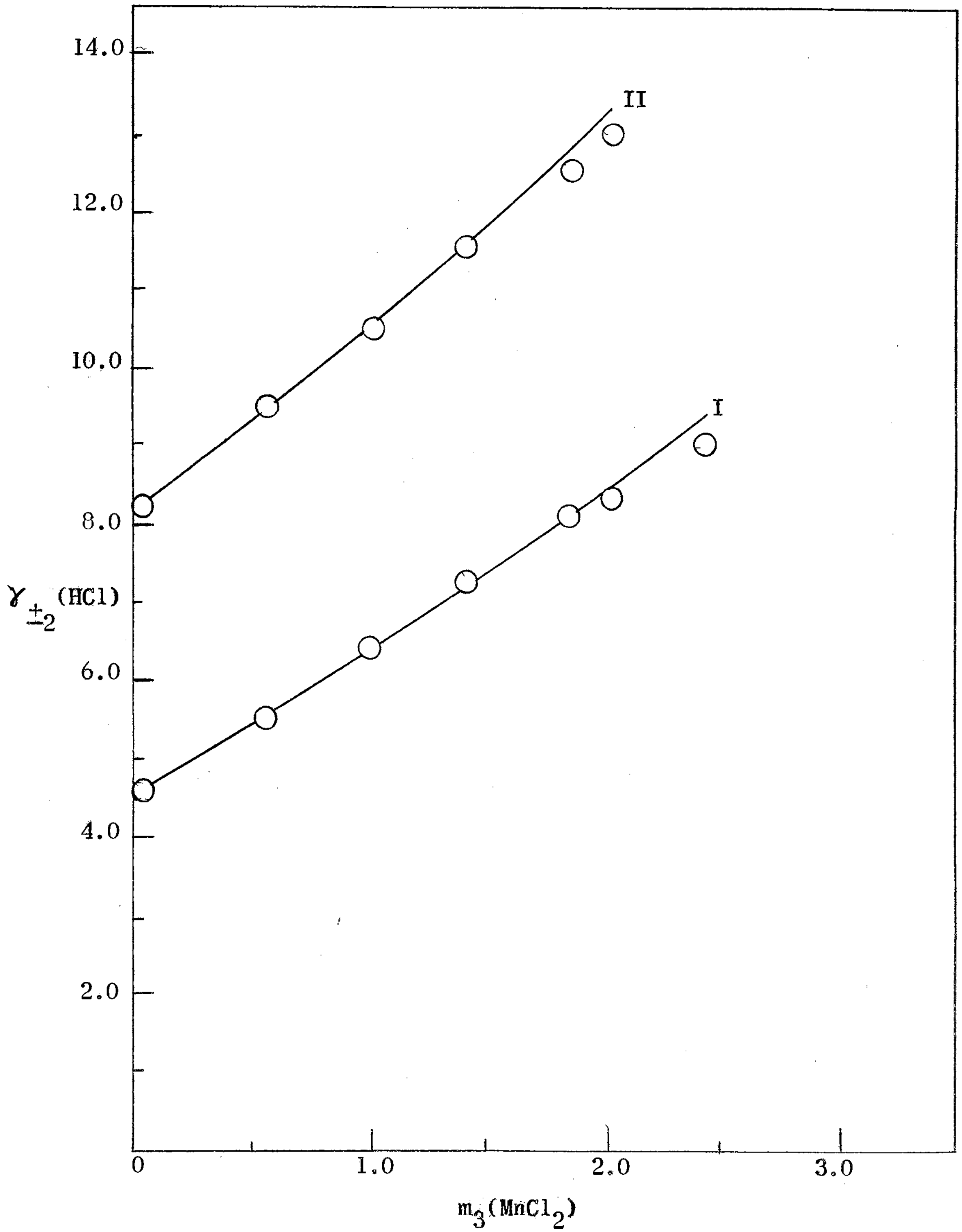

Fig. 17 Comparison of theoretical (lines) and experimental (circles) values of the activity coefficient of HCl in mixtures with $MnCl_2$: I, 7.05 m HCl, h_2 = 4.97; II, 9.01 m HCl, h_2 = 4.5.

strength (67,140). Such a relationship often holds when other simple relationships fail as has been pointed out by Scatchard and Breckenridge (146). The following empirical equation expresses the data in the $MnCl_2$-HCl system at constant ionic strengths of from 10 to 15:

$$\log \gamma_{\pm 2} = A - \alpha m_3 + \beta m_3^2 \qquad (42)$$

where α and β are functions of the ionic strength and have the values as shown in Table 22. The constant $\underline{A}$ equals $\log \gamma_{\pm 2}$ for pure hydrochloric acid at the same ionic strength as in the mixtures and $\underline{m_3}$ is the salt molality. The values for $\underline{\alpha}$ and $\underline{\beta}$ were determined from experimental data by the method of least squares (95).

As shown in Fig. 18, at ionic strengths below 10 the value of $\underline{\beta}$ in Eq. (42) is zero and $\underline{\alpha}$ is independent of the ionic strength. However, departures from a linear relationship become more serious at higher ionic strengths, and no such relationship holds for manganous chloride at all. It seems likely, as suggested in an earlier section, that at the highest ionic strengths stronger interactions between the ions of the acid and the salt are occurring.

Apparent and Partial Molal Volumes.

It has been previously stated that the ionic hydration and ionic volume are probably two of the most important effects in determining the behaviour of the activity coefficient of nonassociated electrolytes at high concentrations. In an attempt to derive a theoretical expression for the activity coefficient based upon a hydration model which would fit the experimental data, consideration was given to a correction for the difference in size of the solvent and solute particles by employing volume statistics (44). In order

TABLE 22

DATA ON HARNED'S RULE

Ionic Strength	m_2(HCl)	m_3($MnCl_2$)	log $\gamma_{\pm 2}$(HCl)	α	β
10.00	4.67	1.78	0.639	-0.212	0.0000
10.00	7.05	0.98	0.808		
10.00	9.01	0.33	0.954		
10.00	10.00	0.00	1.019		
11.00	4.67	2.11	0.687	-0.213	0.0017
11.00	7.05	1.32	0.849		
11.00	9.01	0.66	0.991		
11.00	11.00	0.00	1.130		
12.00	4.67	2.44	0.731	-0.215	0.0026
12.00	7.05	1.65	0.886		
12.00	9.01	1.00	1.028		
12.00	12.00	0.00	1.237		
13.00	4.67	2.77	0.772	-0.218	0.0048
13.00	7.05	1.98	0.919		
13.00	9.01	1.33	1.060		
13.00	13.00	0.00	1.338		
14.00	4.67	3.11	0.815	-0.221	0.0065
14.00	7.05	2.32	0.952		
14.00	9.01	1.66	1.089		
14.00	14.00	0.00	1.436		
15.00	4.67	3.44	0.845	-0.225	0.0071
15.00	7.05	2.65	0.985		
15.00	9.01	2.00	1.114		
15.00	15.00	0.00	1.533		

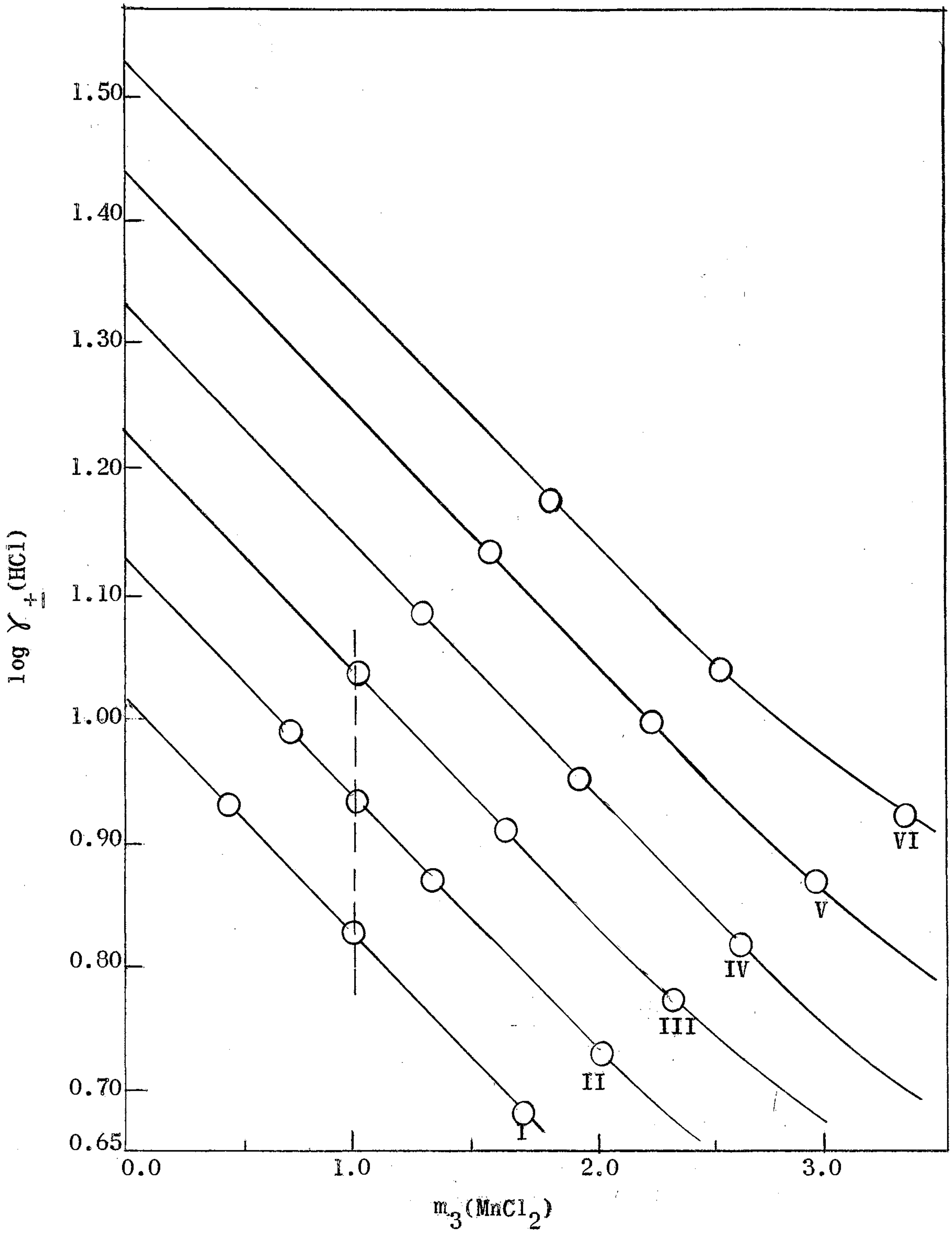

Fig. 18 Variation of log $\gamma_{\pm}$(HCl) with $MnCl_2$ molality at constant ionic strengths: I, μ = 10; II, μ = 11; III, μ = 12; IV, μ = 13; V, μ = 14; VI, μ = 15.

to make this correction, it was necessary to be able to estimate the partial molal volumes in the system under study.

Since the density (Table 18) of the ternary solutions had been determined, a procedure similar to that described by Klotz (78) was followed. The total volume of the solution per 1,000 gm. of water was obtained from the following equation:

$$V = \frac{1000 + m_2(36.5) + m_3(W_3)}{p} \tag{43}$$

where V = total volume of the solution in cc.

m_2 = molality of the hydrochloric acid

m_3 = molality of the salt

W_3 = gram-molecular weight of the salt

p = density of the solution at 25°C

From the values of the total volume of the solution (Table 23) the apparent molal volume, $\underline{\phi_3}$, was calculated by using the following equation:

$$\phi_3 = \frac{V - V^o}{m_3} \tag{44}$$

where ϕ_3 = apparent molal volume in cc.

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

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

m_3 = molality of the salt

The values of the apparent molal volume obtained are also shown in Table 23 for both manganous chloride and for manganous sulphate. The effect of salt concentration on the apparent molal volume of manganous chloride in the constant acid series is presented graphically in Fig. 19. It can be observed that at the higher concentrations the curves seem to be approaching a constant value and that all of

TABLE 23

TOTAL VOLUME AND APPARENT MOLAL VOLUME FOR THE SYSTEMS

$HCl-H_2O-MnCl_2$ AND $HCl-H_2O-MnSO_4$ AT 25°C

m_2 = 4.67 HCl			m_2 = 7.05 HCl			m_2 = 9.01 HCl			m_2 = 7.27 HCl		
$m_3(MnCl_2)$	V (cc)	ϕ_3 (cc)	$m_3(MnCl_2)$	V (cc)	ϕ_3 (cc)	$m_3(MnCl_2)$	V (cc)	ϕ_3 (cc)	$m_3(MnSO_4)$	V (cc)	ϕ_3 (cc)
0.0000	1092.4	---	0.0000	1145.3	---	0.0000	1185.8	---	0.0000	1143.4	---
0.3999	1107.6	38.0	0.2016	1150.3	31.8	0.2000	1192.1	31.5	0.2003	1145.3	9.5
0.5986	1114.2	36.4	0.4020	1157.2	33.0	0.4009	1198.5	31.7	0.3980	1147.5	10.3
0.9978	1125.3	33.0	0.6076	1163.1	31.6	0.5986	1204.1	30.5	0.6005	1149.9	10.8
1.402	1137.9	32.5	0.8103	1168.5	30.4	0.8018	1210.0	30.2	0.7993	1151.7	10.4
1.807	1150.1	31.9	1.207	1181.5	31.2	1.398	1227.9	30.1	1.003	1154.8	10.4
2.254	1163.7	31.6	1.604	1193.8	31.1	1.803	1240.4	30.2	1.206	1157.9	12.0
2.736	1179.4	31.8	1.801	1199.9	31.0	2.501	1248.4	30.5	1.394	1161.0	12.6
3.173	1194.2	32.1	2.021	1207.2	31.4				1.597	1163.8	12.8
			2.300	1216.0	31.4				1.797	1167.7	13.5
			2.500	1212.9	27.6				1.997	1171.0	13.8
									2.247	1175.7	14.1
									2.496	1180.7	14.9
									2.754	1186.3	15.6
									3.185	1192.2	15.3

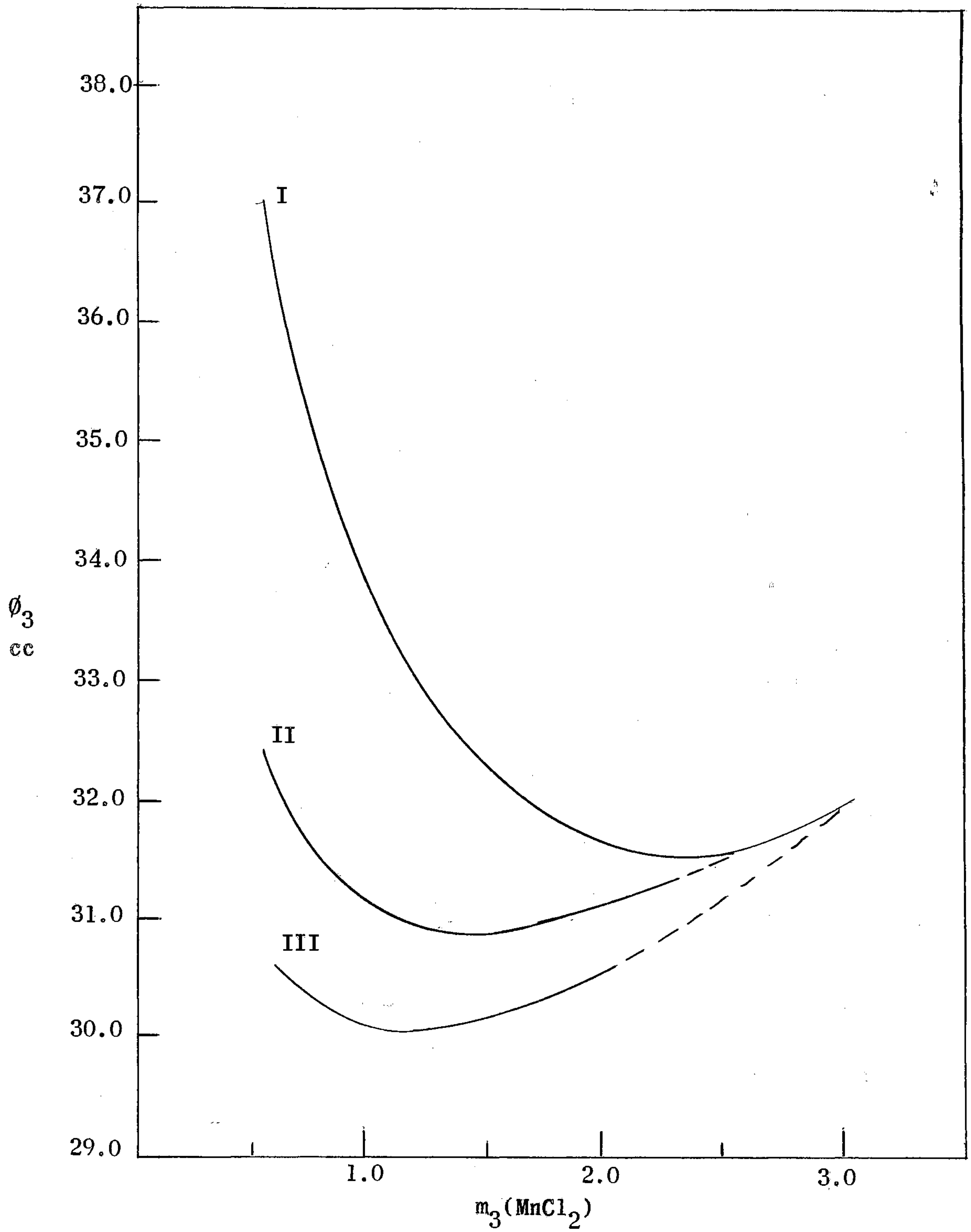

Fig. 19 Apparent molal volumes of $MnCl_2$ for the system $HCl-H_2O-MnCl_2$: I, 4.67 m HCl; II, 7.05 m HCl; III, 9.01 m HCl.

the curves apparently have a broad minimum which is shifted slightly toward the more dilute end with increasing acid concentration. The apparent molal volumes in the 7.05 and 9.01 series may be considered constant within the experimental uncertainty at salt concentrations above about 0.6 molal. The curves are drawn to give the best fit with the data, and smoothed values of the apparent molal volume were used to calculate the partial molal volume of the salt from the relationship between the apparent and true molal volumes:

$$\bar{V}_3 = \frac{\partial V}{\partial m_3} = \phi_3 + \left(\frac{\partial \phi_3}{\partial m_3}\right) m_3 \qquad (45)$$

where $\bar{V}_3$ = partial molal volume in cc.

V = total volume of the solution

ϕ_3 = apparent molal volume of the salt

m_3 = molality of the salt

The smoothed values of the apparent molal volume and the calculated values of the partial molal volume of the salt are presented in Table 24.

Constant Acid Series-Manganous Sulfate.

The activities in one series of mixtures of manganous sulfate and hydrochloric acid (7.27 molal) were determined for comparison with those in the corresponding 7 molal hydrochloric acid series of mixtures of manganous chloride. The very much smaller values of the activity coefficient of the sulfate compared to the chloride in binary solutions is a characteristic of 2:2 type electrolytes which is normally attributed to ion pair formation resulting from the much higher electrostatic forces between the multiple charged ions. In mixtures with hydrochloric acid, therefore, one would expect

TABLE 24

APPARENT MOLAL VOLUME AND PARTIAL MOLAL VOLUME FOR THE SYSTEM

$HCl-H_2O-MnCl_2$ AT 25°C

m_2 = 4.67 HCl			m_2 = 7.05 HCl			m_2 = 9.01 HCl		
$m_3(MnCl_2)$	ϕ_3 (cc)	$\bar{V}_3$ (cc)	$m_3(MnCl_2)$	ϕ_3 (cc)	$\bar{V}_3$ (cc)	$m_3(MnCl_2)$	ϕ_3 (cc)	$\bar{V}_3$ (cc)
0.50	37.0	31.8	0.50	32.3	30.1	0.60	30.6	28.5
0.75	34.9	29.7	0.75	31.4	29.6	0.75	30.3	28.9
1.00	33.4	29.1	1.00	31.0	30.0	1.00	30.0	29.4
1.25	32.6	29.5	1.25	30.9	30.6	1.25	30.0	30.0
1.50	32.1	29.7	1.50	30.9	31.5	1.50	30.1	30.7
1.75	31.9	30.3	1.75	31.0	32.2	1.75	30.2	31.6
2.00	31.7	30.9	2.00	31.2	33.2	2.00	30.4	32.4
2.25	31.7	31.7	2.25	31.4	34.1			
2.50	31.6	32.4						
2.75	31.7	33.4						
3.00	32.0	34.7						

that at constant acid concentration the activity and the activity coefficient of hydrochloric acid would be almost constant or perhaps increase very slightly with manganous sulfate concentration. This is what is found experimentally (Figs. 20,21). The apparent effect of hydration upon the activity and the activity coefficient of manganous sulfate in mixtures with hydrochloric acid is also shown quite clearly in Figs. 22,23, respectively, where there is plotted for comparison the activity of aqueous manganous sulfate.

A very crude calculation was made of the number of oppositely charged bivalent ions expected within the volume defined by the spherical shells of radii, r = 14.3 Å and r = 3 Å, which are respectively the Bjerrum critical distance for ion-pair formation and the Debye-Hückel distance of "closest approach" estimated by considering the sulfate ion equivalent to a sphere of radius 2.2 Å to which was added the crystallographic radius of the Mn^{++} ion. This calculation shows that even at a concentration of 1 molal manganous sulfate the number of such ions within the volume of the shells is greater than one. Although the validity of a treatment of ion-pairing by the Bjerrum method (13) is as doubtful as the estimation of the electrostatic contribution to the chemical potential by the Debye-Hückel treatment, it seems reasonable that ion-pairing would be very extensive, if not complete. If one then assumes complete ion-pair formation, he is tempted to proceed as before and to calculate the hydration parameters in the mixtures with hydrochloric acid. This was done, and a linear relationship was found with respect to the manganous sulfate molality from which the slope (h_3) was calculated to be 0.83 and the intercept (h_2) to be 4.8. These parameters were in turn

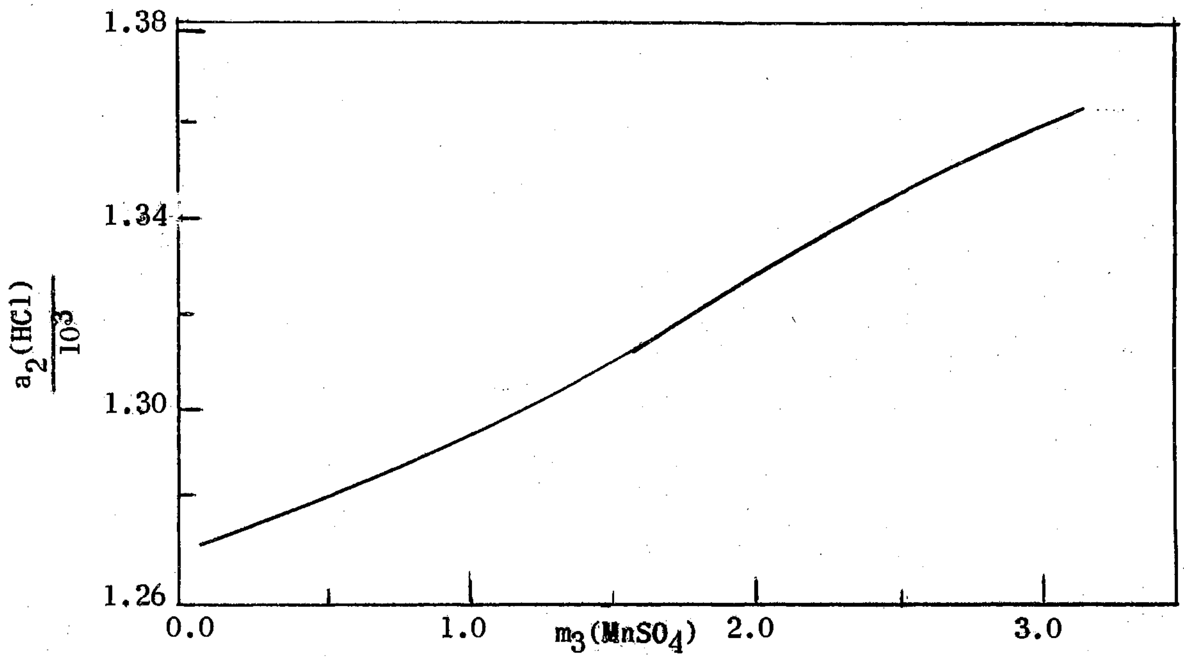

Fig. 20 Activity of HCl in the $HCl-H_2O-MnSO_4$ system.
$HCl = 7.27$ m.

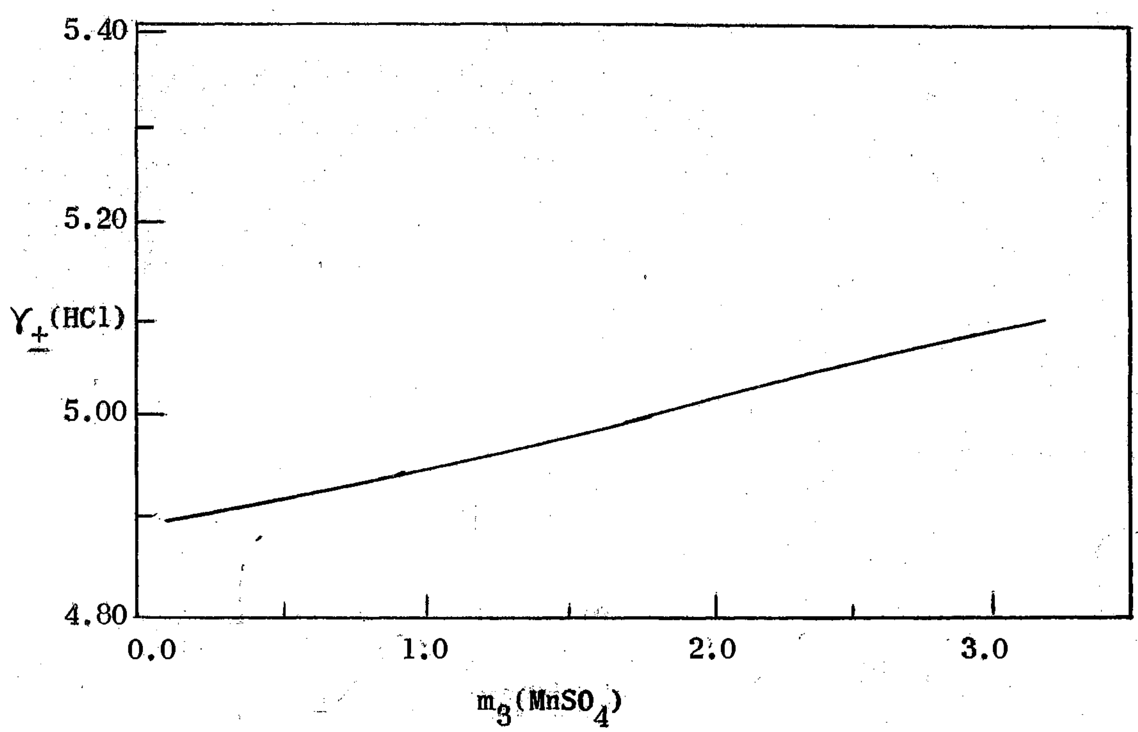

Fig. 21 Activity coefficients of HCl in the $HCl-H_2O-MnSO_4$ system. $HCl = 7.27$ m.

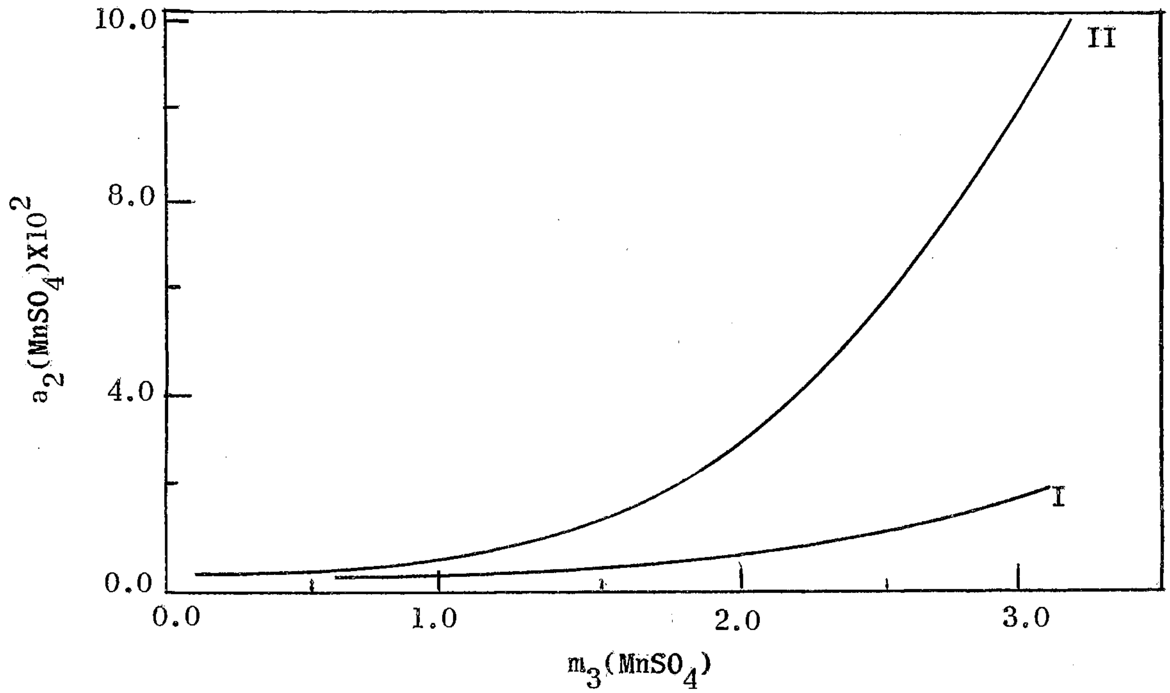

Fig. 22 Activity of $MnSO_4$ in the $HCl-H_2O-MnSO_4$ system: I, aqueous binary; II, 7.27 m HCl.

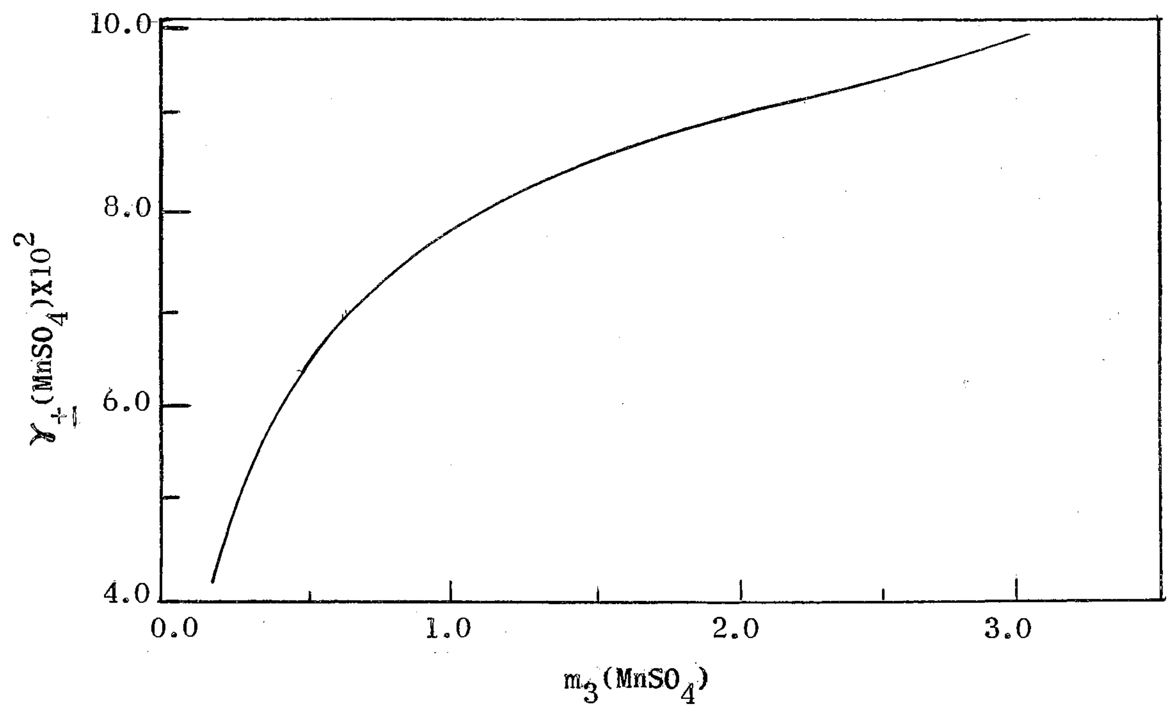

Fig. 23 Activity coefficients of $MnSO_4$ in the $HCl-H_2O-MnSO_4$ system. HCl = 7.27 m.

used in an effort to correct the activity coefficients of hydrochloric acid for hydration as outlined in an earlier section. It was necessary to assume that the manganous sulfate ion-pairs contributed nothing to the ionic strength of the solution. The activity coefficients calculated in this manner were found to be too high, increasing more rapidly with concentration than the experimental values. Although it is almost certain that total disregard of the electrical field associated with the ion-pairs is much too drastic a simplification, the inclusion of a dipolar field superimposed upon the ionic field in the Debye-Hückel theory still leaves the fundamental question of the applicability of that theory to solutions at the high concentrations studied. In spite of the uncertainties involved in correctly accounting for the electrical forces in electrolyte mixtures at high concentrations, the hydration numbers calculated from experimental values of the water activity (Fig. 24) may still be significant. This is because the electrical forces between ions probably have less influence upon the water activity than does ionic hydration. Thus the comparatively small value of 0.8 for $\underline{h}_3$ seems reasonable since one would expect that only favorably oriented solvent molecules would be bound strongly enough to a manganous sulfate dipole to be effectively a part of it as a kinetic entity.

The concentration dependence of the apparent molal volumes of manganous sulfate is shown in Fig. 25. Since the relationship is linear, the partial molal volumes would also be linearly related to the manganous sulfate concentration. An increase in the molal volume of the solute (such as is here observed) is normally attributed to a structure-breaking effect upon the solvent which results from

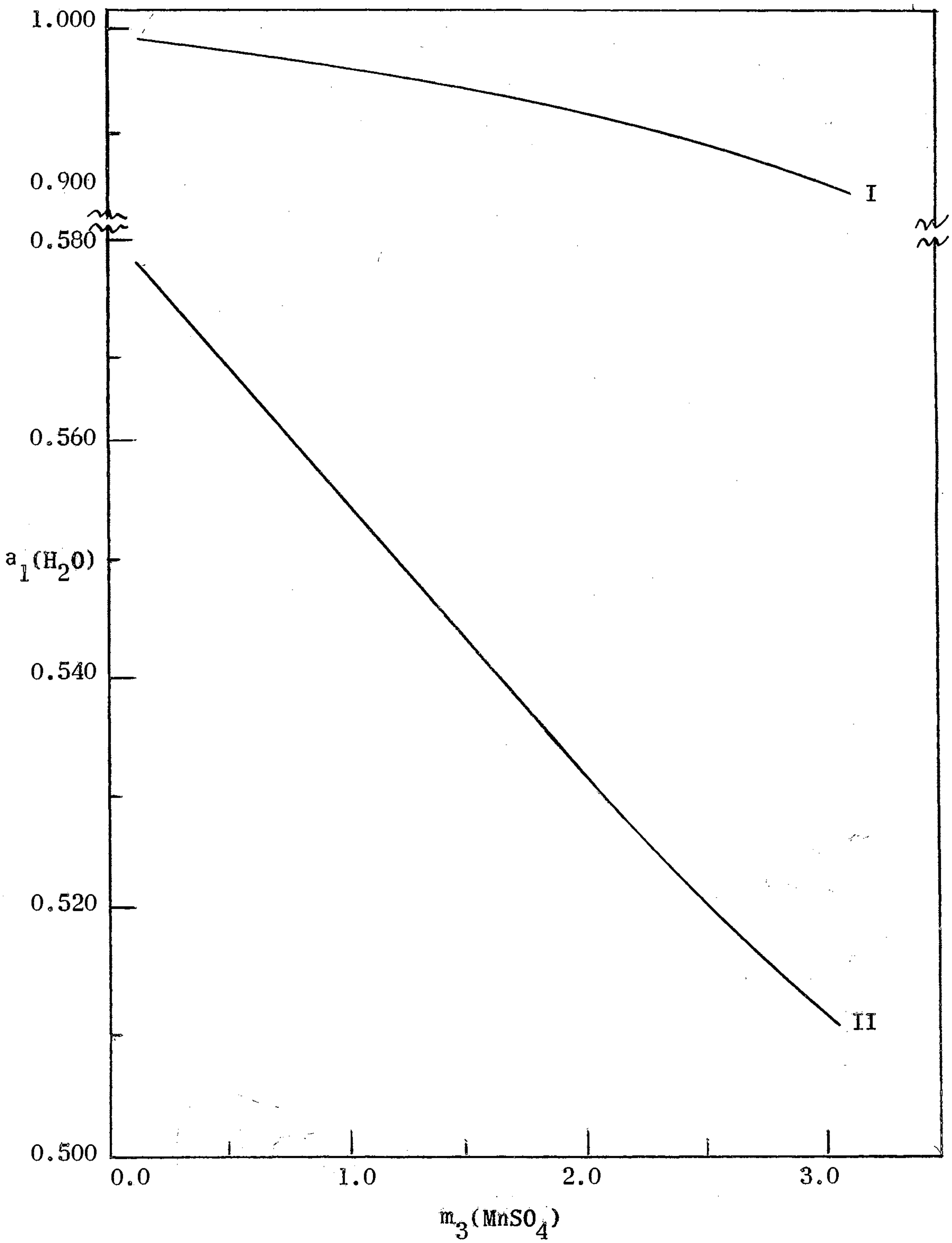

Fig. 24 Activity of H_2O in the HCl-H_2O-$MnSO_4$ system:
I, 0 m HCl; II, 7.27 m HCl.

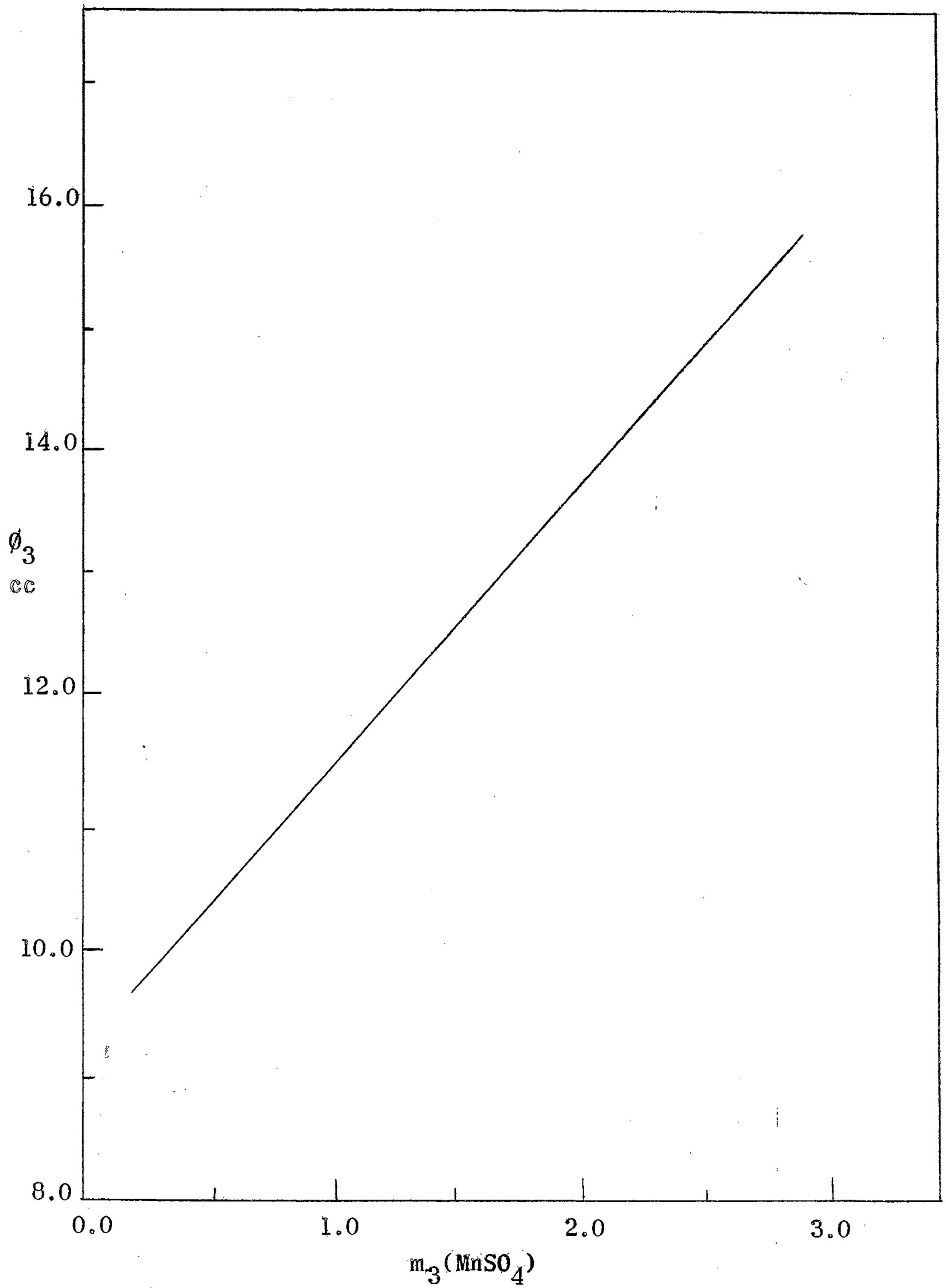

Fig. 25 Apparent molal volumes of $MnSO_4$ for the system $HCl-H_2O-MnSO_4$: HCl = 7.27 molal.

the hydration of the solute; however, although extensive hydration is not indicated by the $\underline{h}_3$ value, the water structure may well be destroyed by the high concentration of manganous sulfate ion-pairs.

It should be pointed out also that throughout this discussion the possibility of the reaction $H^+ + SO_4^= = HSO_4^-$ has not been considered although the magnitudes of the dissociation constants are probably of the same order. The large number of possible interactions thus makes the quantitative interpretation of the data extremely complex.

CHAPTER VII

SUMMARY

The activities of water, hydrochloric acid and manganous chloride in mixtures having constant hydrochloric acid concentrations of 4.67, 7.05, and 9.01 molal were determined at 25°. In each series of constant-acid mixtures the manganous chloride concentration was varied from saturation to about 0.2 molal. Vapor pressures of water and hydrochloric acid were measured by the comparative gas-transpiration method, and the activity of manganous chloride was calculated from the data by the Gibbs-Duhem equation.

Empirical equations were found by the method of least squares for expressing the activities of water, hydrochloric acid, manganous chloride, and manganous sulfate as a function of salt concentration. The data on activity coefficients have also been expressed by empirical equations at several constant (molal) ionic strengths.

During the course of the investigation the solubilities of manganous chloride and manganous sulfate were measured in hydrochloric acid solutions of the molalities represented by the different series studied. The composition of the equilibrium solid phases and the corresponding vapor pressures were determined also.

From the measured values of the ternary solution densities the apparent molal volumes and the partial molal volumes were calculated for manganous chloride and manganous sulfate.

It was found that both hydrochloric acid and manganous chloride in ternary mixtures mutually increase the mean activity coefficient of the other above the values in corresponding binary solutions at the same concentration. This was assumed to be the result of solute hydration, and the simple hydration model of Stokes and Robinson was used as a theoretical basis for correcting the activity coefficients for the effects of hydration employing mole fraction statistics. Hydration numbers, assuming complete dissociation of both electrolytes, were calculated from equations derived for the solvent activity, and were used in the correction of the hydrochloric acid and manganous chloride activity coefficients. The theory was found to be successful when applied to hydrochloric acid, but it failed to give satisfactory results with manganous chloride. Ion-association is believed to be extensive in solutions of manganous chloride in mixtures with hydrochloric acid and may be the principal cause for the failure of the theory to give satisfactory agreement with experiment.

Another series of similar measurements was made involving 7.27 molal hydrochloric acid and manganous sulfate. The effect of ionic association was very evident in this series of solutions as shown by the small values of the activity coefficient of manganous sulfate and its comparatively slight effect upon the activity coefficient of hydrochloric acid. The hydration model was found inadequate to account for the variations observed in the activity coefficients because of the lack of any information regarding the degree of dissociation of manganous sulfate, sulfuric acid, or manganous chloride which presumably coexist in such solutions.

It was concluded from this investigation that most of the very great increase found in the acitivties of hydrochloric acid and manganous chloride in their mixtures relative to their binary solutions can be ascribed to the "salting-out" effect of the high chloride ion concentrations and to the removal of "free" solvent water by ionic hydration. There also seems to be good evidence that manganous chloride is more fully associated and less extensively hydrated than either nickel or cobalt chlorides in similar mixtures with hydrochloric acid even though the crystallographic radius of the manganous ion is larger than that of either of the others.

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APPENDIX

EMPIRICAL ANALYTICAL FUNCTIONS OF THE EXPERIMENTAL DATA

4.67 m HCl Series

$$\log a_1 = -0.1204 - 0.05712\ m_3 - 0.0003309\ m_3^2 + 0.0002758\ m_3^3$$

$$\log a_2 = 2.0100 + 0.5624\ m_3 - 0.04845\ m_3^2 + 0.001208\ m_3^3$$

7.05 m HCl Series

$0 < m_3 < 0.4$

$$\log a_1 = -0.2236 - 0.0914\ m_3 + 0.0421\ m_3^2$$

$0.4 < m_3 < 2.67$

$$\log a_1 = -0.2298 - 0.05764\ m_3$$

$0 < m_3 < 2.67$

$$\log a_2 = 3.0048 + 0.5102\ m_3 - 0.1029\ m_3^2 + 0.0150\ m_3^3$$

9.01 m HCl Series

$0 < m_3 < 1.4$

$$\log a_1 = -0.3272 - 0.05994\ m_3^2$$

$1.4 < m_3 < 2.28$

$$\log a_1 = -0.3200 - 0.07115\ m_3 + 0.004023\ m_3^2$$

$0 < m_3 < 2.28$

$$\log a_2 = 3.7358 + 0.3467\ m_3 - 0.02880\ m_3^2 - 0.002099\ m_3^3$$

7.27 m HCl-$MnSO_4$ Series

$$\log a_1 = -0.2351 - 0.02171\ m_3 + 0.000966\ m_3^2 - 0.000209\ m_3^3$$

$$\log a_2 = 3.1029 + 0.005366\ m_3 + 0.005236\ m_3^2 - 0.00111\ m_3^3$$

1.00 m $MnCl_2$ Series

$4.67 < m_2 < 7.05$

$\log a_1 = 0.0382 - 0.04618\ m_2$

$\log a_2 = 2.0604 - 0.3831\ m_2 + 0.1456\ m_2^2 - 0.009048\ m_2^3$

$7.05 < m_2 < 9.01$

$\log a_1 = 0.1978 - 0.1222\ m_2 + 0.01192\ m_2^2 - 0.0006174\ m_2^3$

$\log a_2 = 1.1655 + 0.3208\ m_2$

VITA

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Candidate for the degree of

Doctor of Philosophy

Thesis: ACTIVITIES OF MANGANOUS CHLORIDE OR MANGANOUS SULFATE IN AQUEOUS HYDROCHLORIC ACID MIXTURES

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