DETERMINATION OF ACTIVITIES IN HYDROCHLORIC ACID-WATER-NICKEL CHLORIDE OR COBALT CHLORIDE MIXTURES

By

ERNEST ALLEN GOOTMAN

Bachelor of Science
University of Miami
Miami, Florida
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Master of Science
University of Miami
Miami, Florida
1951

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Thesis Approved:

Tom E. Moore
Thesis Adviser

O.C. Dermer

H.M. Trimble

Paul Arthur

Robert MacVicar
Dean of the Graduate School

PREFACE

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INTRODUCTION

PURPOSE AND SCOPE OF INVESTIGATION

In 1949 Garwin and Hixon[1] published data on a method for the separation of cobalt chloride from nickel chloride involving the preferential extraction of the cobalt salt into a nonaqueous medium, 2-octanol. Although the solubility of anhydrous cobalt chloride in 2-octanol far exceeded that of anhydrous nickel chloride, extractions of their aqueous solutions did not give an appreciable extraction of the cobalt salt until its aqueous phase concentration approached saturation. However, in the presence of either calcium chloride or hydrochloric acid, a good separation of cobalt chloride from nickel chloride at low cobalt concentration could be effected by extraction of the cobalt chloride into the nonaqueous phase. Indeed commercial methods for the separation of these metals along the lines of solvent extraction seemed promising.[2]

Further study of this extraction system at Oklahoma A. and M. College has been directed toward attainment of a knowledge of the factors involved in the separation of these two transition metals with the aim that such information would later be useful in understanding the separation of other transition metals by solvent extraction.

Since preliminary investigations carried out in these laboratories showed that the promoting effect of added electrolytes was in the order hydrochloric acid $\simeq$ lithium chloride $>$ calcium chloride $>$ aluminum chloride $\simeq$ tetramethylammonium chloride, it was decided that a comprehensive study of the activities of all the components in the systems hydrochloric acid-water-cobalt chloride or nickel chloride, along with a correlative study of the extractibility of the salts from the hydrochloric acid-water mixtures, would be made. Furthermore, since the solubility of 2-octanol in water is approximately 0.1%,[3] its solubility in hydrochloric acid solutions would be expected to be a few percent at the most; therefore, the activity values determined for the ternary system hydrochloric acid-water-cobalt chloride or nickel chloride may reasonably be considered to be comparable to those in aqueous phases of the quaternary system octanol-hydrochloric acid-water-cobalt chloride or nickel chloride.

In addition to this proposed investigation of activities in the hydrochloric acid system, survey studies of the relation of the activity and solubility of cobalt chloride to extraction in ternary systems involving either lithium chloride, calcium chloride, or aluminum chloride as the promoting agent were undertaken.

Aside from the immediate application of the thermodynamic data obtained to the extraction problem, 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 become evident in later sections, quantitative information on ternary systems of electrolytes is limited, especially in concentrated solutions, since the acquisition of this information is a complex problem from both the theoretical and experimental viewpoints.

SOLVENT EXTRACTION AND ACTIVITY

The distribution of a solute such as a salt between two immiscible liquid phases is generally expressed by the ratio, M, of concentrations in the phases. This ratio, although of great practical importance, is seldom very constant (except for the case where the concentration in each phase is quite small) but varies with the concentration of the solute. As Hildebrand and Scott[4] point out, the partition coefficient, M, would not be expected to be constant where the mutual solubilities of the aqueous and nonaqueous phases are low.

The requirement that the partial molal free energy or chemical potential be constant for a solute in equilibrium distribution between phases can be expressed in terms of the activity function, a, first introduced by G. N. Lewis:[5]

$$\overline{F}(A) = \overline{F}^{\circ}(A) + RT \ln a(A) \qquad (1)$$

where $\overline{F}(A)$ = chemical potential in some selected state

$\overline{F}^{\circ}(A)$ = chemical potential in an arbitrarily chosen standard state.

In the case of the solute A in distribution equilibrium one has therefore

$$\overline{F}(A) = \overline{F}'(A) \qquad (2)$$

$$\overline{F}^{\circ}(A) - \overline{F}^{\circ\prime} = RT \ln K = RT \ln \frac{a'(A)}{a(A)} \qquad (3)$$

The primed terms refer to the second phase and the unprimed terms to the first.

In order to relate the experimentally determined values of the chemical potential (and hence activity) to the concentration of solute, one uses the concept of an activity coefficient, γ, such that

$$a(A) = \gamma \cdot f(m) \tag{4}$$

Here f(m) is some function of the solute concentration such as the concentration itself. The forms of equation (4) in general use are discussed adequately in any standard text on thermodynamics such as that of Rossini.[6] The equilibrium constant is seen to be related to the partition coefficient and the activity coefficient by

$$K = \frac{a'(A)}{a(A)} = \frac{\gamma'(A)m'(A)}{\gamma(A)m(A)} = \frac{\gamma'(A)}{\gamma(A)} \cdot M \tag{5}$$

$$\text{where } M = \frac{m'(A)}{m(A)}$$

DETERMINATION OF ACTIVITY

Binary Systems.

In the case of binary systems there have been employed a variety of methods for obtaining the activity of either the solute or the solvent. These methods include measurement of the partial vapor pressures, solvent boiling or freezing temperatures, distribution ratios, and electromotive force of suitable cells. These and other methods are discussed in such general references as Harned and Owen[7] and Lewis and Randall.[5] Once one has obtained the activity of either of the components, the activity of the other can be calculated through the use of the Gibbs-Duhem equation to be discussed in the next section.

Ternary Systems.

The problem involved in the measurement of activities of the components in a ternary system involving either nickel chloride or cobalt chloride is a difficult one from an experimental standpoint. This is because measurement of the solvent activity alone is insufficient to enable one to simply calculate the activity of either of the other components.

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

$$n_1 d\overline{F}_1 + n_2 d\overline{F}_2 + n_3 d\overline{F}_3 = 0 \qquad (6)$$

where n_1, n_2, n_3, are the moles of components and $\overline{F}_1$, $\overline{F}_2$, $\overline{F}_3$ are the chemical potentials.

It can be seen from this equation, however, that given the concentration terms n_1, n_2, n_3, and the variation in two of the chemical potential terms F_1 and F_2, it is possible in principle to calculate the third chemical potential $\overline{F}_3$.

Measurements by freezing point depression in which there is actually measured the effect of the solute on the solvent activity are not readily applicable to the calculation of the activity of either solute in a ternary system since in effect one is dealing with a system of two solutes and the results of measurements of this type are dependent on both solute activities. Nevertheless such measurements could be used to obtain the solvent activity in dilute solutions of the two solutes.

Electromotive force measurements which have proved to be very useful in determining activities both in binary systems and in ternary systems, were not applicable to the systems under consideration. Although by the use of an electrode reversible to chloride ion and one reversible to hydrogen ion it is possible to obtain data on the hydrochloric acid activity; electromotive force measuremnts could not be used to obtain the transition metal salt activity since no reversible electrodes for either cobalt or nickel have ever been found. For example, the potential of the cobalt-cobaltous couple has been reported at various times in the literature[8-13] at values ranging from 0.246 to 0.298 volts whereas the nickel-nickelous couple has been reported at +0.227[14], +0.231[15], and +0.248[16] volts. It is apparent, therefore, that although the electromotive force method could be used to obtain the hydrochloric acid activity, some other method would have to be used to obtain one of the other two activities needed before the third one could be calculated from the Gibbs-Duhem equation.

Consideration was then given to vapor pressure measurements to obtain both the activity of the solvent and of hydrochloric acid. There are several experimental techniques that can be employed in vapor pressure measurements, namely static, dynamic, dewpoint, isopiestic, and gas transpiration.

In the static method[17] the pressure of a solution is obtained by placing the mixture in an evacuated container connected to a manometer and reading the pressure. Aside from the usual sources of error, arising from inaccurate pressure readings, dissolved air and other impurities, the method would not be applicable to our system since the observed pressure would be the sum of the partial pressures of the hydrochloric acid and the water and not the individual pressures.

The dynamic method[18] consists of heating a liquid under variable external pressure until boiling begins at a predetermined temperature. The vapors are then condensed and analyzed. Superheating and boiling point changes while the sample is being collected make the determination of the boiling point temperature difficult. A further difficulty is encountered in the quantitative condensation and analysis of vapors.

The dew point method[19] consists of cooling the equilibrium vapors until visible condensation begins. However, this method could not be applied to the hydrochloric acid-water-salt system because of the difficulty in finding surfaces that would separately indicate the dew points of each of the volatile components.

In the isopiestic method[20] two vessels at the same temperature but containing different solutes in the same solvent are placed in an enclosed container and since the vapor pressures of the two solutions are ordinarily different, solvent distills from one vessel into the other until the vapor pressures are equalized. From a knowledge of the vapor pressure of one solution as a reference over a range of compositions the vapor pressure of the unknown solution at a determined concentration can be calculated from an analysis of both solutions. Although the method is extremely precise, it could not be applied to the hydrochloric acid-water-salt system because of the volatility of both the water and the hydrochloric acid.

In the gas transpiration method,[21] which was the method adopted in this work, one saturates a known amount of gas by passage through the solution whose vapor pressure is to be determined and analyzes the exit vapors. Making use of the relation

$$P_a = N_a P \tag{7}$$

where P_a = partial pressure of component 1
N_a = 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 and N_a, N_b, N_c.

If the experimental difficulties in such a measurement are overcome, one can obtain the partial pressures of two of the components of a ternary mixture and use a derived form of equation (6) to obtain the activity of the third component.

If one divides each term in equation (6) by n_1 and sets the ratio n_2/n_1 equal to a constant K, one obtains

$$d\overline{F}_1 + K\, d\overline{F}_2 + \frac{n_3}{n_1}\, d\overline{F}_3 = 0 \tag{8}$$

Writing equation (8) to show the change in chemical potential with respect to n_3, the number of moles of nonvolatile component, the equation takes the form:

$$\frac{\partial\overline{F}_1}{\partial n_3}\, dn_3 + K\,\frac{\partial\overline{F}_2}{\partial n_3}\, dn_3 + \frac{n_3}{n_1}\,\frac{\partial\overline{F}_3}{\partial n_3}\, dn_3 = 0 \tag{9}$$

Substitution of equation (1) and the following relation between the partial molal free energy and the partial pressure of a volatile component into the above equation gives the relation shown in equation (11)

$$\bar{F} = \bar{F}^{o} + RT \ln \frac{p}{p^{o}} \tag{10}$$

where p^{o} = vapor pressure of the component in its standard state

$$\frac{\partial \ln p_1}{\partial n_3} dn_3 + K \frac{\partial \ln p_2}{\partial n_3} dn_3 + \frac{n_3}{n_1} \frac{\partial \ln a_3}{\partial n_3} dn_3 = 0 \tag{11}$$

Consider a function ϕ defined by

$$\phi = \ln p_1 p_2^{K} = \ln p_1 + K \ln p_2 \tag{12}$$

Differentiation of ϕ with respect to n_3 yields

$$d\phi = \frac{\partial \ln p_1}{\partial n_3} dn_3 + K \frac{\partial \ln p_2}{\partial n_3} dn_3 \tag{13}$$

Solving equations (11) and (13) simultaneously yields

$$d\phi = -\frac{n_3}{n_1} \frac{\partial \ln a_3}{\partial n_3} dn_3 \tag{14}$$

Integration of (14) leaves

$$\int_{\phi'}^{\phi''} \frac{n_1}{n_3} d\phi = -\int_{a'}^{a_3''} d \ln a_3 = \ln \frac{a_3'}{a_3''} \tag{15}$$

From (15) it follows that a plot of n_1/n_3 versus ϕ can be integrated to yield the desired activity of component 3. The experimental determination of p_1 and p_2 will be discussed in a later section.

LITERATURE SURVEY

A survey of the literature has shown that there have been no really comparable investigations of the activities of transition metal salts in concentrated aqueous solutions of hydrochloric acid. One can go further and say that activity studies in ternary mixtures involving concentrated aqueous solutions of electrolytes have been made only in a few instances, and in no case have the activities of all of the components been determined in the same 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.[22-24] Two important investigations have been made, however, in connection with the problem of solvent extraction of transition metal salts.

Glueckauf, McKay, and Mathieson[25] measured the activity of uranyl nitrate in solutions of sodium nitrate by partition experiments into ether and related their results to the sodium nitrate-promoted extraction of uranyl nitrate by that solvent.

Nachtrieb and Fryxell[26] by means of the ferrous-ferric ion couple measured against the calomel electrode were able to study the activity in ferric chloride in hydrochloric acid solutions. Theirs, however, was a four-component system at constant ferrous chloride activity. Again the results were discussed in relation to the extraction of ferric chloride in aqueous hydrochloric acid by ether. Additional reference to this and the uranyl nitrate system will be made later.

Studies relating to the nature of concentrated hydrochloric acid solutions of salts include the work of Morosov[27] who published data on the partial pressure of hydrochloric acid at 25° in both ternary and quaternary hydrochloric acid-water-salt systems. The experimental procedure employed was a dynamic gas saturation method based on the passage of a known amount of air through the solution and an analysis of the absorbed acid vapors. His data shows that the addition of either copper chloride or ammonium chloride to a hydrochloric acid-water mixture lowers the partial pressure of the hydrochloric acid, whereas the addition of titanium tetrachloride, cupric chloride, stannic chloride, stannous chloride, or lithium chloride raises the partial pressure of the acid. This he interprets as indicating the formation of the following compounds: $2CuCl \cdot HCl$ and $NH_4Cl \cdot nHCl$, where n varies with the temperature. Yannakis[28] in agreement with Morosov found that the addition of lithium chloride to an hydrochloric acid solution raises the total pressure, whereas cupric chloride lowers the total vapor pressure.

Several investigators[29-36] measured the activity coefficient of hydrochloric acid in the presence of lithium, sodium, barium, cerium, aluminum, calcium, strontium, magnesium, ammonium, or lanthanum chlorides by electromotive force methods. However, the results of these investigations are not directly applicable to the hydrochloric acid-water-nickel chloride or cobalt chloride system since the measurements were made on solutions which were dilute in both hydrochloric acid and salt, and the activity of only one component, hydrochloric acid, was measured. The results may be summarized by the statement made in Harned and Owen[7] "... at a given ionic strength and acid concentration, the activity coefficient of a strong acid is greater in the solution of a salt, of a given valence type, which in the pure solvent possesses the greater activity coefficient."

From an experimental viewpoint, the field of the thermodynamics of ternary salt systems is almost unexplored. In the absence of suitable reversible electrodes, one is faced with the problem of using the Gibbs-Duhem equation to obtain salt activities. Little could be found on the theoretical treatment of such solutions, but the reader is referred to the following three papers for development of the important relations.

Most recently McKay[37] published a theoretical discussion on activities and activity coefficients in ternary systems in which he outlined an approach based on cross-differentiation of the Gibbs-Duhem equation; e.g.,

$$\left(\frac{\partial \ln a_1}{\partial m_2}\right)_{m_1} = \left(\frac{\partial \ln a_2}{\partial m_1}\right)_{m_2} \tag{16}$$

where a = activity

m = molality

from which relations of the type

$$\left(\frac{\partial \ln a_1}{\partial \ln a_2}\right)_{m_1} = -\left(\frac{\partial m_2}{\partial m_1}\right)_{a_2} \tag{17}$$

are obtained. Although in ternary systems it is possible to calculate the activity of two components from a knowledge of the activity of the third component, by means of relations of the type mentioned above, the method is limited by the path of the integration. If a_2 is the experimentally measured activity, then the integration of equation (17) proceeds at constant m_1 and no knowledge is gained about the variation of a_1 with m_1. Integration along a sufficiently large number of such paths will lead to the desired results, however. It is apparent, therefore, that more experimentally determined activities are necessary than in the case where each experiment yields data from which the activity of two components can be calculated as was done in this research.

Darken[38] has also considered this matter and has developed relations for evaluation of the partial molal free energies of all the components of a ternary system from information about the partial molal free energy of only one of them but at all compositions again the number of measurements required is very large which is the disadvantage of all such approaches.

Nowotny and Orlicek[39] discuss the integration of the ternary Gibbs-Duhem equation from experimentally determined values of the slope of the total pressure curve as a function of two volatile components. The method is laborious and is best suited to systems consisting of two highly volatile components.

Since during the course of this investigation vapor pressure measurements were made on the binary systems hydrochloric acid-water, cobalt chloride-water, and nickel chloride-water, a brief review of the literature values of the activities in these binary systems follows. The activity of both hydrochloric acid and water in aqueous solutions of hydrochloric acid has been determined by various methods by several investigators. In 1919, Bates and Kirshman[40] determined the partial pressure of hydrochloric acid above its aqueous solution at both 25° and 30° using a comparative gas transpiration method. The hydrochloric acid vapors were absorbed in dilute sodium hydroxide solution. Dunn and Rideal[41] determined the activity of hydrochloric acid by a distillation method. Over the range from 3.5 to 5.3 molar, their results are about 15% higher than those of Bates and Kirshman. Dobson and Mason[42] have determined both the water and hydrochloric acid activities at 25° using the dynamic method. Criticism of their results arises from their method of absorption which involved the passage of the saturated vapors through 97% sulfuric acid to absorb the water vapor followed by passage through an aqueous sodium carbonate solution to absorb the hydrochloric acid. The solubility of hydrochloric acid in 97% sulfuric acid is 14 grams per 100 grams solution. Results of Gahl[43] and Dolezalek[44] are discordant and were not accepted by Zeisberg[45] in his 1925 compilation of the partial pressure of hydrochloric acid and water above their binary solutions.

In addition to the data of Bates and Kirshman and Dunn and Rideal Zeisberg relied most heavily on the electromotive force data of Harned[48] and the distillation data of Hulett and Bonner[47] and Roscoe and Dittmar.[48] Since 1925 several investigators[49-54] have determined the activity of hydrochloric acid in its aqueous solution by electromotive force, freezing point and solubility methods. However, the usefulness of this data for comparison purposes depends partly upon the accuracy of 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. No more recent measurements have been made of the vapor pressure of hydrochloric acid in aqueous solutions.

The activity of both nickel chloride and cobalt chloride in their aqueous solutions has been calculated from the water activities by integration of the Gibbs-Duhem equation. The water activities in the cobalt chloride-water system were determined isopiestically at 25° by Robinson[55] up to 2 molal in cobalt chloride and by Robinson and Brown[56] up to 4 molal. A comparison of the water activities in aqueous cobalt chloride at 25° and 30° can be seen in Figure 10 in a later section of the thesis. Pearce and Eckstrom[57] using a dynamic gas transpiration method have determined the activity of water in aqueous nickel chloride solutions at 25° up to saturation and Robinson and Stokes[58] have determined water activities in aqueous nickel chloride solutions at 25° up to 2.8 molal.

EXPERIMENTAL

APPARATUS

Preliminary Experiments

In 1950, construction of an apparatus for the measurement of the partial pressures of both hydrochloric acid and water in ternary mixtures was undertaken in these laboratories by Mr. Russell Ring.[59] This apparatus, modeled after one by Pearce and Snow,[21] consisted of three principal sections; namely, one for gas generation and measurement, one for gas saturation, and one for absorption of vapors. Since this same apparatus was used in some preliminary experiments, a brief description of the apparatus follows.

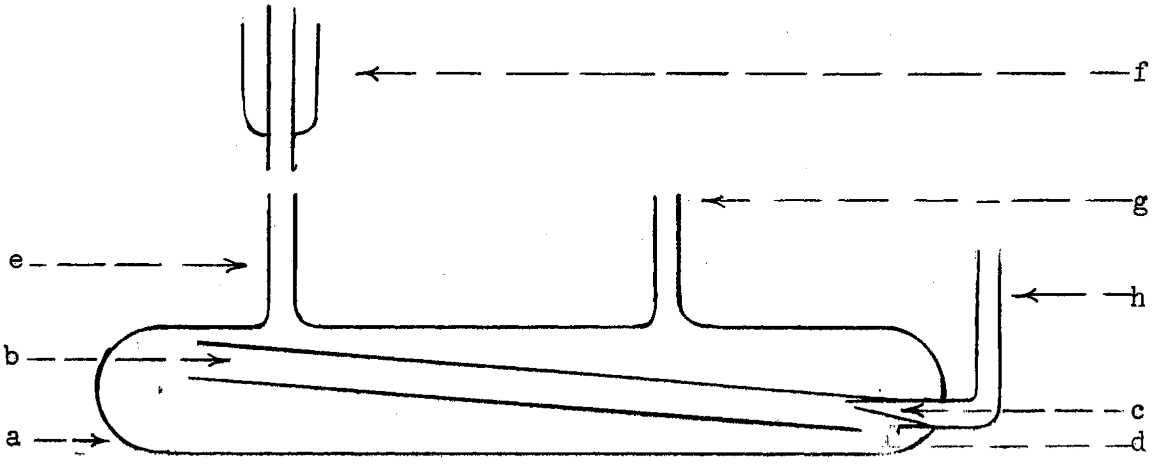
Generation and Measurement of Gas. In the first experiments, hydrogen and oxygen were generated by the electrolysis of a 25% solution of sodium hydroxide using electrolytic nickel sheet for electrodes and four six-volt storage batteries for power. Upon discovery of cathodic black deposits, which on analysis proved to be nickel, this type of gas generator was abandoned in favor of one employing platinum gauze electrodes and 20% sulfuric acid as the electrolyte. The top of the cells and the electrodes were sealed with picein wax.

By placing a copper coulometer in series with the electrolysis cells, the moles of hydrogen and oxygen generated were calculated from the weight of the copper electrode before and after an experiment and Faraday's law.[60] However, because of the inaccuracy of this type coulometer, a silver coulmeter was substituted as soon as available.

Saturation of Gas. The generated gas was saturated with the vapors of the volatile components in the solution by passing the gas through a presaturator followed by passage through a train of eight saturators.

FIGURE 1

SATURATOR



a. 38 x 300-mm. test tube

b. 10-mm. flow tube

c. 2-mm. jet opening

d. 15-mm. hole

e. 8-mm. filling tube

f. mercury seal

g. 8-mm. exit tube

h. 8-mm. entrance tube

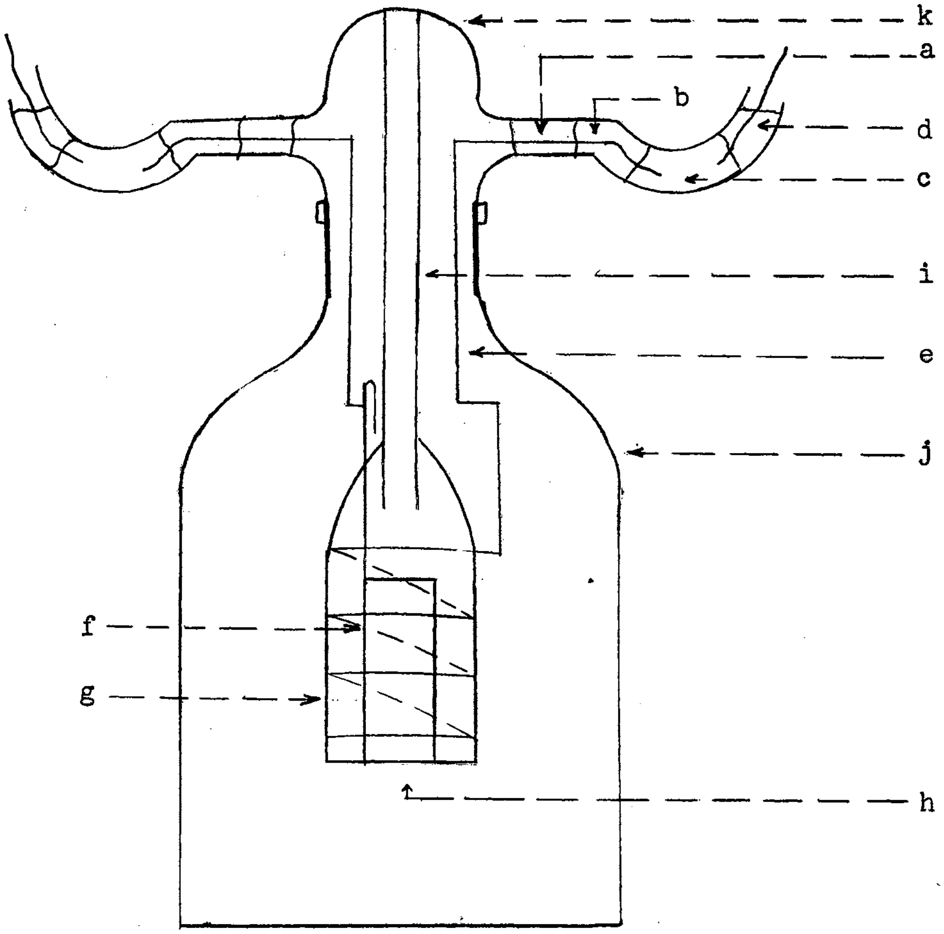
The saturators were of the type of Bichowsky and Storch[61] and are shown in Figure 1. These were each made from a 38 x 300-mm. pyrex test tube a, into one end of which a 10-mm. pyrex tube b was sealed at an inclined angle. Tube b contained within it a 7-mm. bubbling tube drawn down to a 2-mm. jet tip c. A hole d of approximately 15-mm. diameter was blown in the inclined tube, the front edge of the hole being about 8-mm. behind the jet opening. After the saturators were filled through tube e, they could be closed off by placing a lead-weighted inverted cup into the mercury seal f. All connections in the train were made by the use of ball-and-socket joints. The saturators were kept at constant temperature by immersion in a constant-temperature bath controlled by a Thermocap capacitor-type electronic relay and heated by a 75-watt light bulb.

Absorption of Vapors. The exit vapors of hydrochloric acid and water were absorbed by passing the gas saturated with the vapors first through an absorber containing magnesium perchlorate to absorb the water and then through one containing Ascarite to absorb the hydrochloric acid. The absorbers were prepared by cutting off the curved portions of U-shaped 150-mm. glass-stoppered drying tubes and sealing the two straight portions together.

Since the original apparatus constructed by Ring[59] did not give consistently satisfactory results, several changes were made in an attempt to get it functioning properly. The construction of an all-glass type of gas generation cell was undertaken in order to eliminate gas leakage, which was a possible source of error with the old type generation cell. The new type cell, shown in Figure 2, was contained in a 500-ml. glass-stoppered pyrex bottle j. The platinum gauze cathode f was supported by a pyrex rod h that was fastened across the bottom on a pyrex tube g. This in turn was supported by flanges from a glass tube i. The anode e was a piece of 26-gauge platinum wire wrapped around the

FIGURE 2

GAS GENERATOR



All-Glass Type

a. glass seal

b. silver chloride seal

c. mercury seal

d. wax seal

e. platinum wire anode

f. platinum gauze cathode

g. shield

h. support for cathode

i. 8-mm. pyrex tube

j. 500-ml. pyrex g.s. bottle

k. 24/40 standard-taper joint

tube g. The electrolyte in early experiments was a 20% solution of sulfuric acid, but in later work a 20% solution of potassium bisulfate was used in an attempt to avoid production of ozone. The platinum leads were brought out of the cells through consecutive seals of glass a, silver chloride b, mercury e, and wax d.

Further improvements in the experimental technique included:

(1) The placing of a bell jar cover over the coulometer, so as to protect it and the silver nitrate solution from impurities.

(2) Raising the temperature of the presaturator to 50° in order to insure saturation.

(3) Removal of all ball-and-socket joints and sealing together the glass joints to prevent leakage.

(4) Construction of controlled-temperature air bath to house the absorbers, so as to minimize errors caused by variations in temperature and humidity when the absorbers were weighed. Activated alumina desiccant was kept in the air bath.

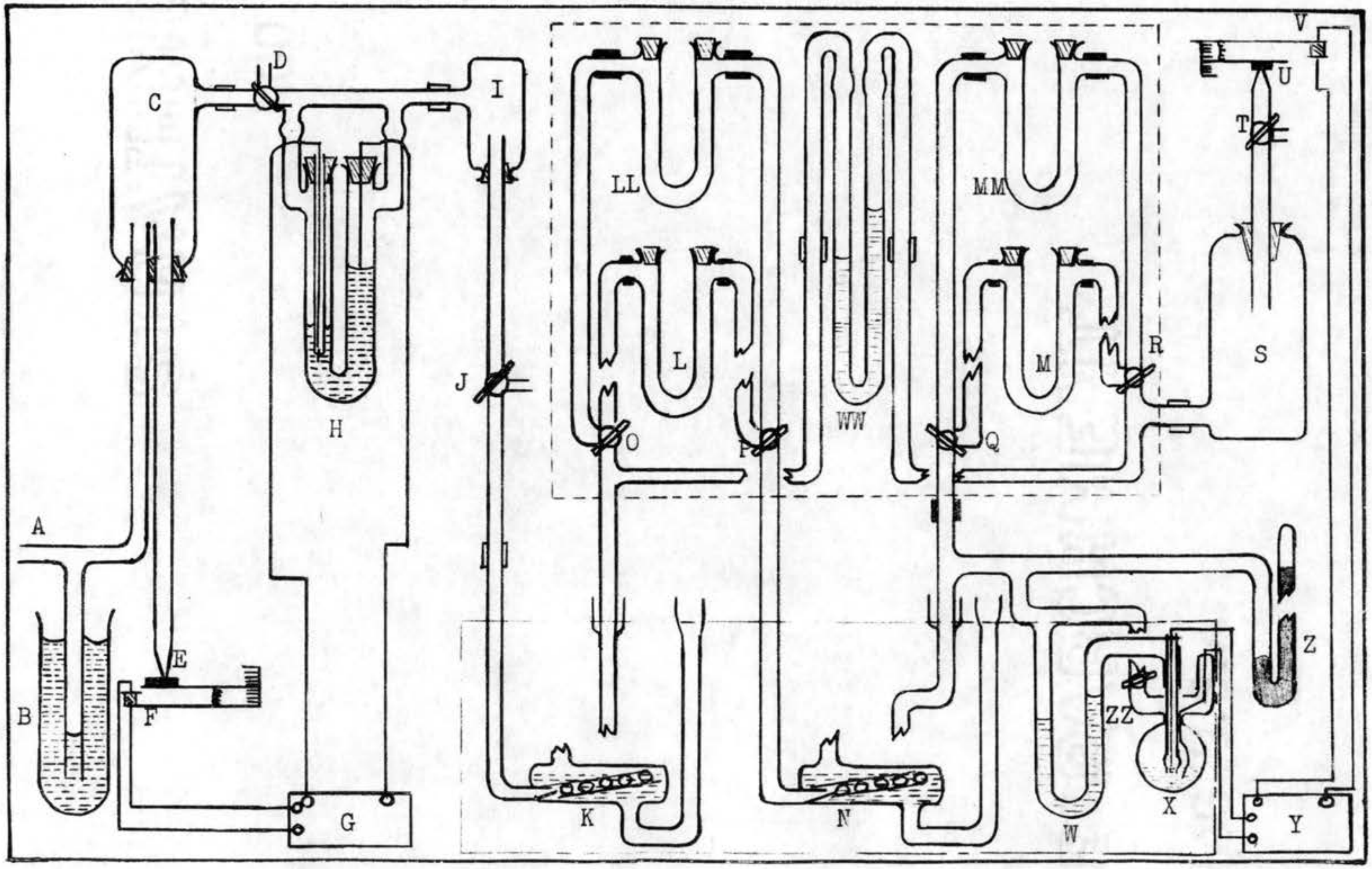
However, even after taking all of the above-mentioned precautions the results obtained for the vapor pressure of pure water at 30° were continually 20-25% below the literature values.[45] The discovery of black deposits on the cathodes showed that a side reaction was taking place and that quantitative generation of hydrogen and oxygen was not occurring. Therefore, it was decided to discontinue work on this apparatus and look for one which did not require electrolytic production of the flow of carrier gas.

Final Apparatus.

The type of apparatus finally selected, shown in Figure 3, was adapted from one described by Bechtold and Newton.[62] This apparatus

FIGURE 3

APPARATUS FOR VAPOR PRESSURE MEASUREMENT



Explanation of Symbols in Figure 3

A.	gas inlet
B.	test tube safety valve
C.	one-liter aspirator bottle
D.	three-way stopcock
E.	valve
F.	solenoid
G.	Cenco-Gilson electronic relay
H.	pressure regulating device
I.	one-half-liter aspirator bottle
J.	three-way stopcock
K.	set of six saturators
L.	water absorber
LL.	dummy absorber for water
M.	hydrochloric acid-water absorber
MM.	dummy absorber for hydrochloric acid-water
N.	set of six saturators
O.	three-way stopcock
P.	three-way stopcock
Q.	three-way stopcock
R.	three-way stopcock
S.	two-liter aspirator bottle
T.	three-way stopcock
U.	valve
V.	solenoid
W.	U-shaped mineral oil trap
WW.	differential manometer
X.	flask-type pressure regulator
Y.	Cenco-Gilson electronic relay
Z.	barometer
ZZ.	two-way stopcock
■	surgical tubing connection
⊟	tygon tubing connection
---	temperature-controlled air bath
—-—	temperature-controlled water bath

does not depend on the production by electrolysis of a known amount of gas since one can calculate the quantity of carrier gas by first passing it through a set of saturators containing a liquid such as distilled water whose vapor pressure is known and relating the weight of water picked up by the carrier to the vapor pressure and mole fraction (see page 55). This apparatus for descriptive purposes can be divided into three main divisions: namely, the pressure control and measuring system, the gas saturation mechanism, and the absorption apparatus.

Pressure Control and Measuring System. The pressure in the system was controlled both at the input and output sections of the apparatus. The make-and-break U-shaped conductivity apparatus H functioned as a device to open the valve when the pressure exceeded the desired value. The conducting liquid in the U-tube was concentrated sulfuric acid while the contacting leads were made of 26-gauge platinum wire. This system activited a Cenco-Gilson electronic relay G which in turn controlled a battery-powered solenoid F that opened and closed a valve E. The solenoid and valve mechanism were adapted from the parts of the vibrator of an automobile radio by attaching to the movable arm a piece of sponge rubber to act as the plug for closing the valve.

An excape valve leading into a test tube of water B was placed in the system as a precautionary measure against sudden surges of gas or blockage in other parts of the apparatus.

The pressure control apparatus for the exhaust gas was similar to the one described above except for the use of a 500-ml. round-bottom flask conductivity-type regulator in the place of a U-tube. The sulfuric acid in the flask was isolated from the system by a U-shaped trap W containing mineral oil. Normally the valve was open but when the pressure dropped too low, the valve was closed by a relay and a solenoid operated valve identical with that used on the input system.

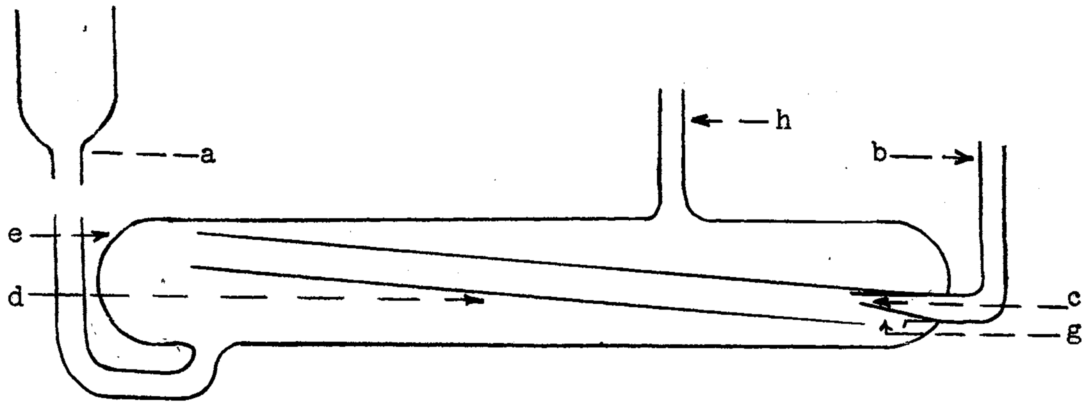
The pressure at the second set of saturators was measured by means of a mercury barometer as shown in Figure 3. A differential manometer S employing dibutyl phthalate as the manometric liquid was placed in the system so that the pressure at the first bank of saturators could be calculated.

Gas Saturation Apparatus. The carrier gas, nitrogen, was saturated by passage through a set of six saturators, the first five being of the type shown by the top drawing of Figure 4. These were similar to those used by Ring[59] except for the tubes added to permit filling of the saturators. The sixth saturator is shown by the bottom drawing of Figure 4. This saturator was made from a 38 x 300-mm. test tube to which was attached an entrance tube b, exit tube h, and filling tube a. A shield f, added to prevent condensation of vapors in the exit tube at the point where the tube passed out of the water bath, was heated by nichrome wire coil.

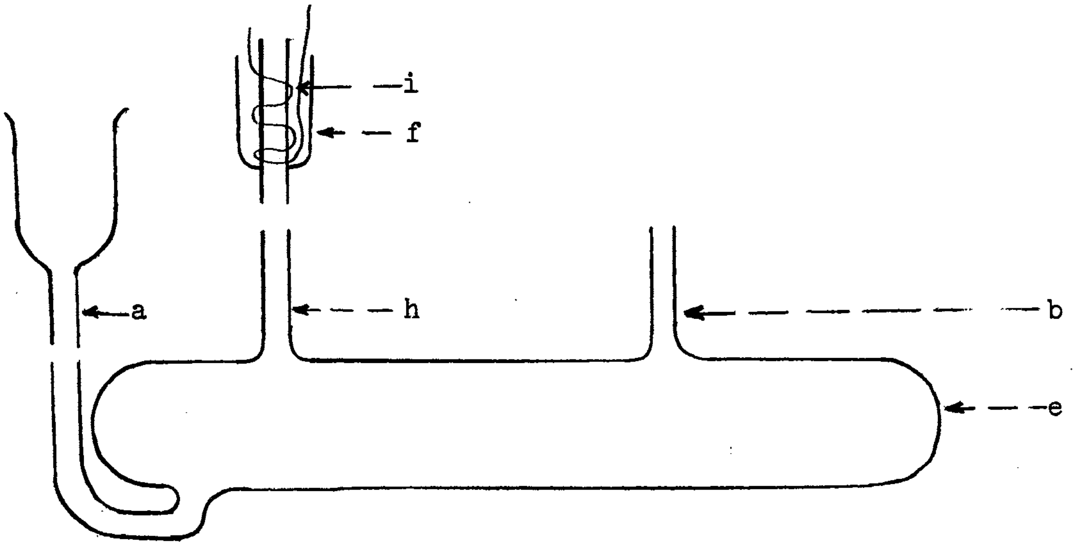
Absorption Apparatus. Upon leaving the saturators the gases passed through 150-mm U-shaped absorption tubes packed with absorbent. Anhydrous magnesium perchlorate was used as the absorbent for water while a mixture of magnesium perchlorate and sodium hydroxide dried on asbestos was used as the absorbent for the mixed vapors of water and hydrochloric acid. The absorption tube (Figure 5) for the mixed vapors was packed with sodium hydroxide-impregnated asbestos f in about two-thirds of its length and at the exit end, this was followed by a half-inch packing of magnesium perchlorate d. After cotton c had been placed in both ends to insure the mechanical stability of the packed material, rubber stoppers b

FIGURE 4

SATURATORS



Flowing Bubble Type



Surface Flow Type

a. 8-mm. filling tube

b. 8-mm. entrance tube

c. 2-mm. jet opening

d. 10-mm. flow tube

e. 38 x 300-mm. pyrex test tube

f. 22-mm. shield

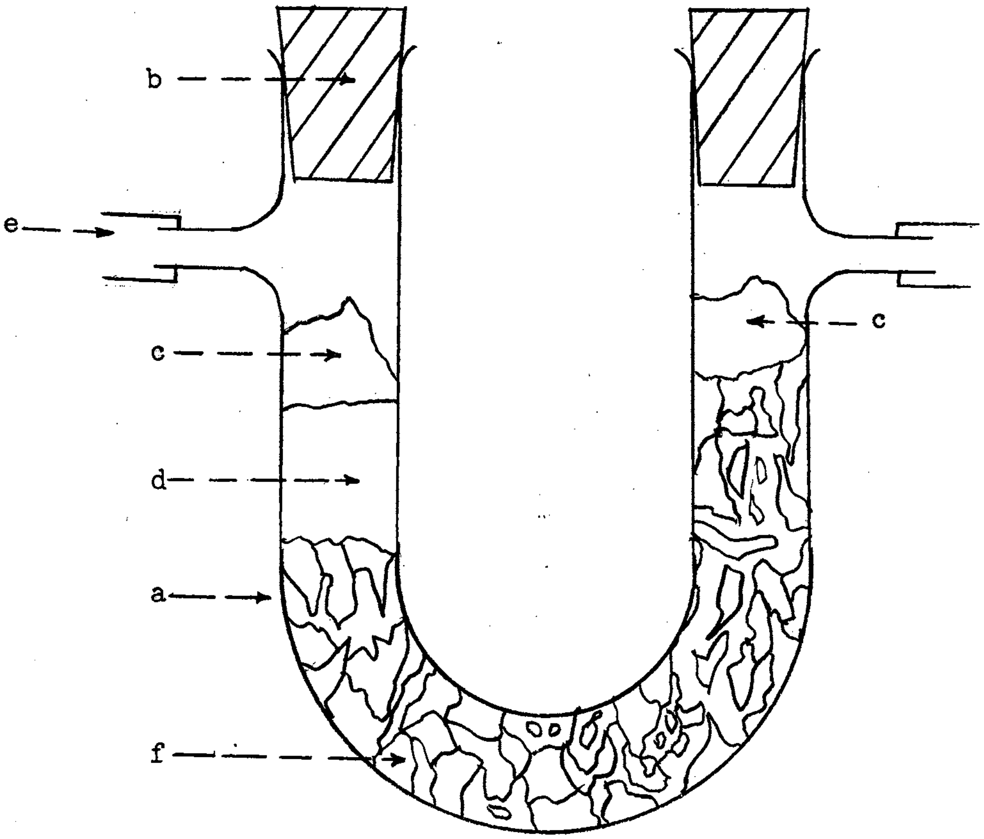
g. 15-mm. hole

h. 8-mm. exit tube

i. nichrome wire heating coil

FIGURE 5

ABSORBER



Asbestos-Packed Type

a. 150-mm. U-shaped drying tube

b. rubber stopper

c. cotton

d. magnesium perchlorate

e. surgical tubing cap

f. sodium hydroxide-asbestos absorbent

were used to close the tube and these in turn were sealed tightly to the glass by Fisher Sealit wax. When not in use, surgical tubing caps e were placed over the entrance and exit tubes. The mixture of sodium hydroxide and asbestos was prepared by adding a solution of approximately 0.8 molar carbonate-free[63] sodium hydroxide to Gooch filter-quality asbestos in a 100-ml. beaker and evaporating to dryness at 130°. At least a fourfold excess of sodium hydroxide over that calculated to be required for an average length experiment was added in order to insure complete absorption of the hydrochloric acid vapors.

Temperature Control System. All of the saturators, the round-bottom flask which housed the pressure-regulating device for the exit gases, and the U-shaped tube containing the mineral oil were kept in a constant-temperature water bath maintained at 30.00° ± 0.02° by a mercurial thermoregulator which activited a Cenco-Gilson electronic relay. The thermometer used was graduated in 0.05° divisions and standardized against a thermometer (Number 90794) calibrated by the Bureau of Standards.

The differential manometer and the absorption tubes were enclosed in a constant-temperature air bath maintained at 38.0° ± 0.2° by a mercurial thermoregulator which controlled a Fisher electronic relay. A 250-watt heater and fan were used to obtain the desired temperature in the enclosure of the air bath.

Auxiliary Heating System. The exit tubes from the saturators (Figure 4) were heated by means of nichrome wire heating elements controlled manually by a Powerstat variac. The purpose of these heaters was to prevent condensation of the vapors in those parts of the tube not enclosed by the constant-temperature baths. In order to protect the rubber connections from the heat, they were insulated with asbestos tape.

PROCEDURES

Vapor Pressure Measurements.

The saturators, rinsed with distilled water and dried at 120°, were allowed to cool while air was drawn through them. Having been assembled as in Figure 3, and filled with the desired solution, the saturators were sealed with neoprene stoppers and Fisher Sealit wax. After the water bath had been filled, its temperature adjusted to 30° and the auxiliary heating system put in operation, the flow of nitrogen was started through A while the dummy absorbers LL and MM were in the circuit. After having been in the air bath at least three hours and wiped with a dry chamois cloth, absorbers L and M were weighed on a type DLB Ainsworth chainomatic balance (Number 14806) having a sensitivity of ± 0.0001 gram. The absorbers weighed approximately fifty grams each. When the input and exhaust pressures had been satisfactorily adjusted, stopcocks O, P, Q, and R were turned to lead the flow of gas through the weighed absorbers. Barometer Z and manometer S were now read. Just prior to the termination of the experiment, these pressures were again read, and then stopcocks O, P, Q, and R turned back to their original positions. The absorbers L and M were now reweighed, completing the experiment.

Analytical Methods.

Analysis for Chloride in Absorbers. After completion of an experiment, the contents of the sodium hydroxide absorber were placed in a 600-ml. beaker and the absorber was rinsed first with distilled water, then with 25% perchloric acid and finally several times with distilled water. After complete neutralization to a phenolphthalein endpoint with 25%

perchloric acid, the solution was analyzed for chloride potentiometrically[64] employing an indicating silver electrode, made from a 2 in. x 1/2 in. x 1/16 in. piece of electrolytic sheet silver, and a saturated calomel half-cell as a reference electrode. The saturated calomel half-cell was isolated from the unknown solution by a 400-ml. beaker containing one molar ammonium nitrate and contacts were made using agar-ammonium nitrate bridges. During the titration the solution was continually stirred by means of a Magna-Stir magnetic stirrer.

Analysis for Nickel. Nickel analysis was carried out electrolytically as described by Kolthoff and Sandell.[65] When check analyses by a different method were desired, nickel was determined gravimetrically as nickel dimethylglyoxime.[66] In solutions of low nickel concentration, i.e. 10^{-2} to 10^{-4} molar, nickel was determined polarographically[67] employing a Sargent Model XXI polarograph. Reduction of the nickel ion occurred at the dropping mercury electrode, and a mercury pool was used as the reference electrode.

Analysis for Cobalt. The percentage of cobalt in the various solutions was determined in one of several ways. In the absence of any interfering salts, a sample of the solution was evaporated to dryness at 130°[68] and brought to constant weight. If this method was not applicable, cobalt was determined electrolytically by a method[69] analogous to the one previously described for nickel. In solutions of low cobalt concentration, the cobalt concentration was determined either polarographically[70] by a method similar to the one already described for nickel or amperometrically by precipitation with α-nitroso-β-naphthol.[71]

Analysis for Chloride Ion. In addition to the method described on page 29 for the determination of chloride ion in the absorbers, solutions having a relatively high chloride content were analyzed for chloride gravimetrically as silver chloride.[72]

Preparation and Standardization of Solutions.

Hydrochloric Acid Solutions. Hydrochloric acid of a predetermined molality was prepared by mixing C. P. concentrated hydrochloric acid and water in a calculated ratio to get the approximate molality. Then by successive additions of small quantities of either water or acid followed each time by analysis by an acid-base titration with sodium hydroxide to a phenolphthalein endpoint, the concentration of the solution was adjusted to the desired molality.

Ternary Mixtures. The ternary mixtures, hydrochloric acid-water-cobalt or nickel chloride, were prepared in one of two ways. Method one involved the addition of anhydrous cobalt or nickel chloride which had previously been dried, pulverized, and redried at 130°, to a hydrochloric acid solution of known molality. An analysis for cobalt or for nickel readily gave the composition of this stock solution. Method two involved the mixing of water, hydrochloric acid, and the hydrated salt in small increments until a stock solution of a desired hydrochloric acid molality and near saturation with respect to the salt had been prepared. Stock hydrochloric acid solutions were prepared of the same molality as that of the hydrochloric acid found 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 a series of solutions of constant hydrochloric acid molality and varying salt molality were prepared.

Binary Mixtures. The binary mixtures, water-cobalt or nickel chloride, were prepared by addition of the anhydrous salt to water. When necessary, a small amount of dilute hydrochloric acid was added to suppress hydrolysis. The cobalt chloride solutions were analyzed by evaporation and the nickel chloride solutions by gravimetric analysis for chloride, electrolytic determination of nickel, or by both.

Sulfuric Acid Solutions. The sulfuric acid solutions used as water vapor pressure standards were prepared by dilution of concentrated sulfuric acid and analyzed by an acid-base titration[73] with sodium hydroxide to a phenolphthalein endpoint.

Saturated Solutions. All saturated solutions in the case of both the binary and ternary systems studied were prepared by periodically adding small amounts of the dry salt to the solution which was kept at 30° in a water bath. Analyzes were carried out to determine the composition of the solution phase. In the hydrochloric acid system, the cobalt concentration was determined by the evaporation procedure, whereas in the calcium, lithium and aluminum chloride systems it was determined electrolytically. Total chloride ion was then determined gravimetrically.

Analysis of Solid Phases.

Ternary Systems. In the ternary solutions the composition of solid phase was determined by the wet residue method of Schreinemakers as described by Findlay.[74] A weighed sample of wet crystals was dissolved in water, diluted to 100 ml., and analyzed. On the usual triangular graph for three-component mixtures a line was drawn through the points corresponding to the composition of the wet crystals and the concentration of the saturated solution. The intersection of this line with the cobalt chloride-water axis determined the percentage of cobalt in the solid phase.

Binary Systems. In the case of the solid phases in equilibrium with the binary solutions, samples of the solid phases were dried by crushing several times in filter paper before they were weighed and analyzed for the cation.

Extraction Studies.

Extraction studies were made on several of the ternary solutions for which activity data was obtained. The extraction was performed by adding 50 ml. of the aqueous solution to 50 ml. of 2-octanol in a ground-glass-stoppered erlenmeyer flask and shaking the mixture rapidly on an automatic shaker for one and one-half to two hours. After the phases had been allowed to settle, they were separated and the aqueous phase discarded. The octanol phase was again equilibrated with a second portion of the ternary solution. This procedure was repeated until the concentration of a new portion of the aqueous phase did not change upon equilibration with the 2-octanol. Prior to the final separation of the phases, the flask was allowed to remain in a constant-temperature water bath at $30.00^{\circ} \pm 0.05^{\circ}$ for at least twelve hours.

Immediately upon the final separation of the phases, the absorption spectrum of the octanol phase at wavelengths from 350-700 mμ. was obtained on a Beckman DU Spectrophotometer. The temperature of the cell was kept at $30.0^{\circ} \pm 0.2^{\circ}$ during the measurement. Following the back-extraction of the octanol phase into water, the resulting aqueous solution was analyzed for cobalt or nickel and total chloride. In the low-concentration region, the cobalt analysis was carried out polarographically or amperometrically, whereas at higher concentrations the evaporation procedure was followed. All nickel analyzes were made polarographically. Chloride ion determinations were made by potentiometric titrations in low-concentration regions and gravimetrically in high-concentration regions.

CHEMICALS

The cobalt chloride used in these studies was Baker's C. P. having an assay of not more than 0.08% nickel.

The nickel chloride used in the ternary system studies was for the most part Baker's C. P. grade containing less than 0.02% cobalt. It was necessary to use one five-pound batch which contained 0.5% cobalt, but this impurity was regarded as having been removed by passage of a 7 molal hydrochloric acid solution of the salt through an anion-exchange column[75] containing Dowex Number 1. Following evaporation of the hydrochloric acid from the solution, the nickel chloride was twice recrystallized from an aqueous solution. Merck reagent grade nickel chloride containing 0.2% cobalt chloride was used in the binary system study.

The hydrochloric acid, sulfuric acid, and ammonium hydroxide used were Baker's reagent grade.

Merck reagent grade perchloric acid with an assay of 0.001% chloride was used in neutralizing the sodium hydroxide in the absorbers.

Mallinckrodt Analytical Reagent potassium acid phthalate and sodium chloride were used as primary standards.

The calcium, lithium and aluminum chlorides used in the saturation studies were Merck reagent grade.

The silver nitrate in the chloride determination and the ammonium nitrate in the salt bridges was Mallinckrodt Analytical Reagent.

Mallinckrodt Analytical Reagent sodium hydroxide with an impurity of 0.010% chloride was used in preparation of the sodium hydroxide-asbestos absorbers.

Both the 2-octanol used in the extraction and the dibutyl phthalate used in the differential manometer were products of the Matheson Company. The 2-octanol was specified to be ketone-free and had an index of refraction of 1.4244.

Eimer and Amend 'Asbestos for Gooch Crucibles,' specified as free of chloride ion by washing with acid and then water, was used in the absorbers.

The magnesium perchlorate in the absorbers was a Fisher Scientific Company product. This material failed to give a qualitative test for chloride with silver ion.

DATA AND CALCULATIONS

PRELIMINARY CHECK OF APPARATUS

Sulfuric Acid-Water and Hydrochloric Acid-Water Systems

Upon completion of the apparatus already described in an earlier section measurements were first made on solutions whose vapor pressures were available in the literature[45,76] in order to compare the results obtained with the values reported. The results of such measurements on sulfuric acid solutions are presented in Table 1. Both these and all subsequent vapor pressure measurements were made at 30°. Since the partial pressure of sulfur trioxide in these solutions is negligible, it was neglected in the calculations. Measurements of the partial pressure of both hydrochloric acid and water in hydrochloric acid solutions at several molalities are listed in Table 2. In all tables, the last digit in the columns of data marked with an asterisk is retained for computational purposes. In all the tables of vapor pressure data, P_1 is the pressure at the first set of saturators and P_2 the pressure at the second set of saturators.

TABLE 1

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.)	ΔWt. in Second Absorber (g.)	p_{H_2O} (mm. Hg)	Avg. p_{H_2O} (mm. Hg)	p_{H_2O} Literature Value (mm. Hg)
1.630	1	742.2	738.2	6.00	1.0928	1.3541	0.23	1.0211	29.63	29.66	29.65
1.630	2	741.3	738.8	6.75	1.1369	1.4070	0.21	1.0617	29.69		
3.195	1	746.7	742.6	5.00	1.1146	1.3898	0.28	0.9337	26.68	26.69	26.70
3.195	2	752.5	748.4	6.42	0.9971	1.2536	0.20	0.8352	26.71		
4.713	1	749.9	745.8	4.25	0.6654	0.8334	0.20	0.4819	23.19	23.17	23.17
4.713	2	743.7	739.4	6.33	0.8940	1.1103	0.18	0.6465	23.15		

a. P_1 = Pressure at first saturators

b. P_2 = Pressure at second 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.)	ΔWt. in Second Absorber (g.)	Meq. $AgNO_3$ Used	$\bar{p}_{H_2O}$ (mm. Hg)	$\bar{p}_{HCl}$ (mm. Hg)
4.69	278	1	759.2	755.3	11.25	1.1293	1.4328	0.13	0.8569	0.0903	24.17	-----
4.69	279	2	756.2	752.4	8.75	0.8326	1.0523	0.12	0.6546	0.0843	-----	0.055
4.69	280	3	753.7	749.7	9.75	1.0478	1.3196	0.14	0.7894	0.1091	23.97	0.055
4.84	67	3	753.1	749.4	12.92	1.4725	1.8528	0.14	1.1040	0.1868	23.85	0.074
4.84	68	4	746.6	742.9	11.75	1.1905	1.4846	0.13	0.8930	0.1370	23.87	0.068
4.84	69	5	740.0	736.3	11.25	1.0784	1.3321	0.12	0.8097	0.1415	23.88	0.075
5.53	90	4	744.9	741.8	9.50	1.0242	1.2739	0.13	0.7212	0.2384	22.32	0.130
5.53	124	5	749.8	747.6	5.50	0.8650	1.0834	0.20	0.6079	0.1932	22.32	0.127
5.53	125	6	751.7	748.5	8.58	1.3879	1.7427	0.20	0.9780	0.3105	22.35	0.129
6.10	91	1	753.7	750.6	7.58	1.1338	1.4279	0.19	0.7607	0.4250	21.12	0.215
6.10	92	2	756.5	753.5	9.25	1.3516	1.7085	0.18	0.9063	0.5245	21.10	0.223
6.97	1	1	754.2	749.3	10.00	1.6670	2.1005	0.21	1.0569	1.4660	19.34	0.507
6.97	24	3	757.6	753.4	11.25	1.4362	1.8181	0.16	0.9058	1.2813	19.24	0.517
6.97	25	4	753.2	749.0	10.16	1.3672	1.7204	0.17	0.8675	1.2319	19.35	0.521
7.73	99	1	762.0	758.6	7.25	0.7342	0.9353	0.13	0.4503	1.2802	17.72	1.013
7.73	100	2	761.9	758.5	10.25	1.6224	2.0663	0.20	0.9954	2.8468	17.71	1.017
8.25	95	1	753.0	750.1	6.84	1.0395	1.3077	0.19	0.6355	2.8075	16.56	1.573
8.25	96	2	758.8	755.8	9.00	0.6733	0.8538	0.09	0.4097	1.8181	16.47	1.573
8.86	97	1	760.8	757.7	7.92	0.8340	1.0605	0.14	0.5291	3.5599	15.46	2.483
8.86	98	2	758.6	755.4	9.50	1.3144	1.6664	0.18	0.8357	5.7453	15.38	2.545
9.16	233	1	753.7	749.3	4.50	0.5621	0.7079	0.16	0.3659	2.9850	14.75	3.079

TABLE 2 - CONTINUED

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.)	ΔWt. in Second Absorber (g.)	Meq. $AgNO_3$ Used	p_{H_2O} (mm. Hg)	p_{HCl} (mm. Hg)
9.16	233a	2	750.8	746.4	4.25	0.4983	0.6248	0.15	0.3244	2.6444	14.78	3.078
9.57	102	2	757.9	754.7	8.50	1.2255	1.5522	0.18	0.8785	9.3737	14.12	4.444
9.57	103	3	755.8	752.5	5.35	0.7662	0.9675	0.18	0.5493	5.8755	14.11	4.461
10.02	118	1	756.9	753.2	4.00	0.5571	0.7047	0.18	0.4544	6.0566	13.49	6.307
10.02	119	2	757.6	753.9	4.00	0.5811	0.7357	0.18	0.4681	6.2551	13.33	6.228
10.40	287	1	750.7	746.6	3.75	0.5786	0.7256	0.19	0.5138	8.0107	12.32	8.017
10.40	288	2	751.2	747.0	4.00	0.5680	0.7126	0.18	0.5052	7.8704	12.35	8.014
10.65	126	1	756.5	753.3	4.50	0.7188	0.9085	0.20	0.7455	13.0918	11.97	10.530
10.65	127	2	755.3	752.5	4.50	0.7035	0.8879	0.20	0.7296	12.8082	11.99	10.531

CALCULATION OF ACTIVITIES

Method of Approach.

It has become the practice to relate the activity of an electrolyte in aqueous solution to its hypothetical state of an ideal solute at a stoichiometric concentration of 1 molal. In the hydrochloric acid-water mixtures under investigation each series of solutions of constant hydrochloric acid-water ratio could be then regarded as being composed of a 'mixed' solvent of hydrochloric acid and water and a solute, cobalt chloride or nickel chloride. In keeping with the convention the standard state of the salt could be selected as a 1 molal solution in the 'mixed' solvent but having the same chemical potential as at infinite dilution in that solvent. Thus each series would have a different reference state for the activity.

A more useful reference state, however, in view of the difficulty and uncertainty involved in measurements of vapor pressures in dilute solutions, seemed to be the saturated solution in each series. Even in this case, though, a different reference state for each series would be involved unless the activity of the saturated solution were related through the equilibrium solid phase to the state of an ideal 1 molal solution of the salt in aqueous solution. To do this the equilibrium vapor pressures of the hydrates and saturated solutions need to be known together with the activities of aqueous binary solutions referred to an ideal 1 molal solution. The latter data were unfortunately lacking at 30° although they were available at 25° for both nickel chloride and cobalt chloride although not up to saturation.[56,58] A search of the literature showed that while information was available to allow calculation of the partial molal heat contents of nickel chloride solutions, no corresponding data were existent for cobalt chloride, and no calculation of the change in activity of cobalt chloride solutions with temperature could be made without assumptions regarding these heat contents.

Nevertheless, it was decided to relate the salt activity in all ternary systems to the conventional standard state, i.e., a 1 molal ideal aqueous solution of the salt at the temperature of the measurements, by first relating the activity of the saturated aqueous solution of the salt at 30° to the conventional standard state at 25° and then relating all ternary system salt activities to the solid phase in equilibrium with the binary saturated solution.

Nickel Chloride. Using the value of 0.684 for the activity coefficient of nickel chloride[76] in a 1.5 molal aqueous solution at 25°, the activity of this solution was calculated at 30° (Table 3) from the equation[77]

$$\ln \frac{a_2'}{a_2} = \frac{\overline{L}_2}{R}\left(\frac{1}{T'} - \frac{1}{T}\right) \qquad (18)$$

where a_2' = activity of salt at 30°

a_2 = activity of salt at 25°

R = 1.987 cal./deg./mole

T' = 303.2° K.

T = 298.2° K.

$\overline{L}_2$ = relative partial molal heat content of solute where $\overline{L}_2$ is defined as

$$\overline{L}_2 = (\phi_h - \phi_h^{\circ})_2 + m\,\frac{d(\phi_h - \phi_h^{\circ})_2}{dm} \qquad (19)$$

where m = molality

$\phi = -Qf$ = apparent molal heat content of solute.

In Table 3 are listed all of the activities calculated for the reference states of nickel chloride.

From the data of Qf and Qf^{o} [78] at 25°, $\overline{L}_2$ was calculated to be 2598 cal. From $\overline{L}_2$ which was assumed to be constant over the temperature range from 25°, the activity of the 1.5 molal aqueous solution was calculated to be 4.622 at 30°. The activity of nickel chloride in a 1.5 molal aqueous solution at 30° having been obtained, its activity in a saturated (5.321 molal) solution was calculated by a graphical integration of the Gibbs-Duhem equation for binary systems. The integration was carried out employing two different plotting functions against the concentration term, one the h function of Lewis and Randall[5] and the other the log a_{water}. An expanded plot was carefully drawn and the area determined by a planimeter and compared to the area obtained by Simpson's rule.[79] The activities obtained by both plots were then compared. An average value of 103,900 was obtained for the activity of the saturated aqueous solution. Estimated error in the integration was of the order of 1.5%.

The activity of $NiCl_2 \cdot 6H_2O$ was computed from the relation

$$\overline{F}^{o}_{(NiCl_2 \cdot 6H_2O)} = \overline{F}_{(NiCl_2)} + 6\,\overline{F}_{(H_2O)} \tag{20}$$

where $\overline{F}^{o}_{(NiCl_2 \cdot 6H_2O)}$ refers to the equilibrium solid phase, and

both $\overline{F}_{(NiCl_2)}$ and $\overline{F}_{(H_2O)}$ to the saturated aqueous solution. Hence

$$\overline{F}^{o}_{(NiCl_2 \cdot 6H_2O)} - \overline{F}^{o}_{(NiCl_2)} - 6\overline{F}^{o}_{(H_2O)} = RT \ln a_{(NiCl_2)} + 6RT \ln \frac{p}{p^{o}} \tag{21}$$

or

$$RT \ln a_{(NiCl_2 \cdot 6H_2O)} = RT \ln a_{(NiCl_2)} + 6\,RT \ln \frac{p}{p^{o}} \tag{22}$$

where $\overline{F}^{o}_{(NiCl_2)}$ refers to the ideal 1 molal solution, $a_{(NiCl_2)}$ refers to

TABLE 3

ACTIVITIES OF NICKEL CHLORIDE REFERENCE STATES

State	$a_3(NiCl_2)$
1.5 Molal aqueous solution (25°)	4.301
1.5 Molal aqueous solution (30°)	4.622
Saturated aqueous solution (30°)	103,900
$NiCl_2 \cdot 6H_2O$	1,783[c]
$NiCl_2 \cdot 4H_2O$	8,141[c]
Saturated solution in 4.69 Molal HCl	207,500
Saturated solution in 6.86 Molal HCl	296,700
Saturated solution in 9.12 Molal HCl	406,500
Saturated solution in 10.4 Molal HCl	707,800

TABLE 4

ACTIVITIES OF COBALT CHLORIDE IN REFERENCE STATES

State	$a_3(CoCl_2)$
2.0 Molal aqueous solution (25°)	20.36
2.0 Molal aqueous solution (30°)	22.24
Saturated aqueous solution (30°)	8583
$CoCl_2 \cdot 6H_2O$	443.3[c]
$CoCl_2 \cdot 2H_2O$	42,300[c]
Saturated solution in 4.84 Molal HCl	24,090
Saturated solution in 6.97 Molal HCl	47,350
Saturated solution in 8.86 Molal HCl	154,300
Saturated solution in 10.65 Molal HCl	443,900

c = activity of hydrated salt.

the activity of the saturated solution and p to the water vapor pressure of the saturated solutions. Again p^{o} is the vapor pressure of pure water at 30°.

Since the solid phase in equilibrium with the saturated solutions in the ternary systems was in all cases the tetrahydrate the activity of this hydrate was calculated from the activity of the hexahydrate by means of the data on the equilibrium pressure between the two hydrates. Derbye and Yngve[80] give the equilibrium pressure for the reaction

$$NiCl_2\cdot 6H_2O\ (c) \rightleftharpoons NiCl_2\cdot 4H_2O\ (c) + 2H_2O\ (g) \qquad (23)$$

as 0.0196 atm. Since at equilibrium ΔF for the reaction is 0, it follows that

$$\Delta F = \overline{F}_{(NiCl_2\cdot 6H_2O)} - \overline{F}_{(NiCl_2\cdot 4H_2O)} - 2\overline{F}_{(H_2O)} = 0 \qquad (24)$$

As both hydrates are solids in their standard states we can write

$$RT \ln a_{(NiCl_2\cdot 4H_2O)} = RT \ln a_{(NiCl_2\cdot 6H_2O)} - 2RT \ln a_{(H_2O)} \qquad (25)$$

Substituting p/p^{o} for a_{H_2O} and dividing the equation by 2.303RT one obtains

$$\log a_{(NiCl_2\cdot 4H_2O)} = \log a_{(NiCl_2\cdot 6H_2O)} - 2 \log \frac{p}{p^{o}} \qquad (26)$$

where $p^{o} = 31.82$, the vapor pressure of pure water at 30°.

From this value for the activity of $NiCl_2\cdot 4H_2O$ referred to an ideal 1 molal solution in water the activity of the saturated ternary mixtures in which this hydrate was the equilibrium solid phase was calculated in a manner similar to that described for the saturated binary solution. Thus

$$\overline{F}_{(NiCl_2)} = \overline{F}^{o}_{(NiCl_2\cdot 4H_2O)} - 4\overline{F}_{(H_2O)} \qquad (27)$$

The activities in the ternary systems referred to the saturated solution can now be calculated by the graphical integration of equation (15) in which n_1/n_3 is plotted against ϕ as shown in Figure 6. The activities of the nickel chloride in the ternary systems are tabulated in Tables 5 to 8.

Cobalt Chloride. The cobalt chloride activities were calculated in an analogous manner. From the activity coefficient of 0.860 of Robinson and Brown[56] for a 2 molal aqueous solution, the activity of cobalt chloride in this solution was calculated at 25°. The literature shows that the activity coefficients of cobalt chloride and nickel chloride in aqueous solutions[76] at 25° are extremely close together up to concentrations of approximately 1 molal, and even up to 2 molal deviations between the two are of the order of 2%. Furthermore, the heats of formation of infinitely dilute solutions of the two salts[78,81] are almost identical, and since the only heat data available for cobalt chloride in aqueous solutions are the data at infinite dilution and at 0.138 molal, it was decided to calculate $\overline{L}_2$ at 25° for a 2 molal nickel chloride solution and use the value of 3196 calories for cobalt chloride.

Integration of the Gibbs-Duhem equation yielded an activity of 8583 for the saturated solution of cobalt chloride at 30°. This value is again the average of the values derived by integration of the two different plotting functions described for nickel chloride. In Table 4 are summarized the activities of cobalt chloride in its reference states.

The activity of cobalt chloride in the saturated ternary mixtures was obtained in a manner exactly analogous to that used in the nickel chloride systems. The only difference between the two sets of calculation was that resulting from the difference in the salt hydrates. Data for the

FIGURE 6

Ø PLOTS FOR THE HCl-H_2O-$NiCl_2$ SYSTEMS

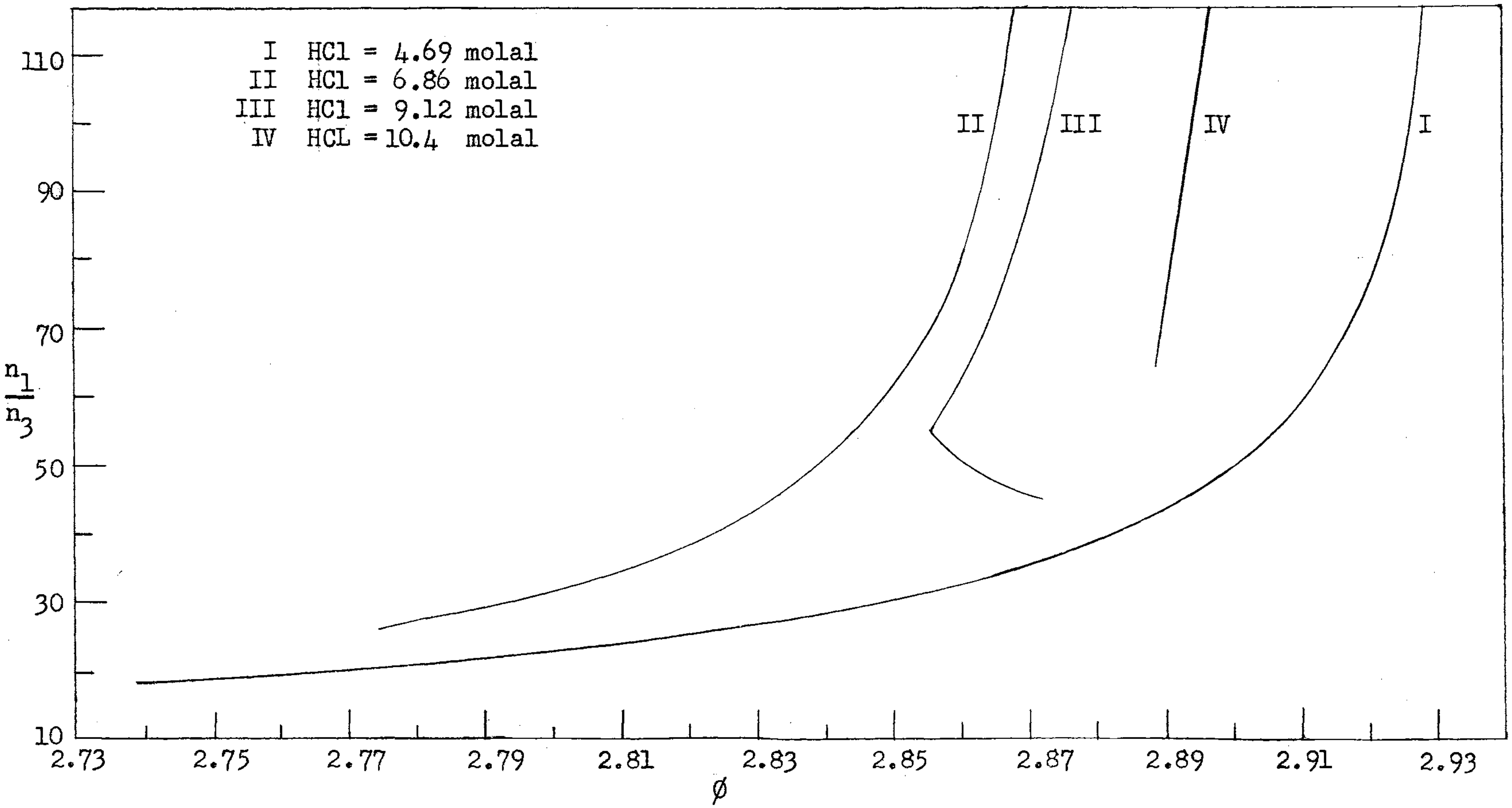


TABLE 5

ACTIVITY DATA FOR THE $NiCl_2$-HCl-H_2O SYSTEM

HCl = 4.69 Molal

Section A

HCl and H_2O Activities

$m_3(NiCl_2)$	$a_1(H_2O)^*$	$a_2(HCl)^*$	$\gamma_{\pm}(HCl)$
0.100	0.7457	110.2	2.19
0.200	0.7347	126.4	2.31
0.300	0.7234	145.9	2.43
0.400	0.7121	170.2	2.57
0.500	0.7011	199.4	2.73
0.600	0.6898	230.2	2.89
0.700	0.6785	267.5	3.06
0.800	0.6681	311.2	3.25
0.900	0.6562	359.9	3.44
1.000	0.6452	416.6	3.64
1.100	0.6335	479.8	3.85
1.200	0.6225	551.1	4.07
1.300	0.6112	629.0	4.29
1.400	0.5987	718.1	4.52
1.500	0.5889	818.6	4.76
1.600	0.5779	932.1	5.02
1.700	0.5672	1059.	5.28
1.800	0.5566	1195.	5.54
1.900	0.5459	1347.	5.82
2.000	0.5358	1517.	6.10
2.100	0.5254	1710.	6.40
2.200	0.5154	1926.	6.72
2.300	0.5063	2164.	7.05
2.400	0.4968	2427.	7.38
2.500	0.4890	2715.	7.73
2.600	0.4792	3028.	8.08
2.700	0.4708	3364.	8.43
2.800	0.4626	3709.	8.77
2.900	0.4544	4114.	9.14
3.005	0.4450	4628.	9.61

Section B

$NiCl_2$ Activities

$m_3(NiCl_2)$	$a_3(NiCl_2)^*$	$\gamma_{\pm}(NiCl_2)$
0.100	18.62	1.98
0.231	87.94	2.43
0.414	250.9	2.71
0.555	390.8	2.76
0.710	668.3	2.93
0.940	1,306.	3.18
1.115	2,237.	3.47
1.275	3,556.	3.76
1.412	5,373.	4.07
1.540	7,825.	4.38
1.664	11,080	4.70
1.791	15,270	5.00
1.916	20,590	5.29
2.030	27,280	5.55
2.133	35,620	5.93
2.227	45,930	6.27
2.326	58,520	6.61
2.421	74,060	6.96
2.532	92,700	7.16
2.643	114,900	7.59
2.761	141,100	7.88
3.005	207,500	8.45

TABLE 6

ACTIVITY DATA FOR THE $NiCl_2$-HCl-H_2O SYSTEM

HCl = 6.86 Molal

Section A

HCl and H_2O Activities

$m_3(NiCl_2)$	$a_1(H_2O)^*$	$a_2(HCl)^*$	$\gamma_\pm(HCl)$
0.100	0.5984	980.7	4.50
0.200	0.5867	1117.	4.74
0.300	0.5751	1264.	4.97
0.400	0.5641	1425.	5.21
0.500	0.5531	1605.	5.46
0.600	0.5424	1829.	5.75
0.700	0.5321	2067.	6.05
0.800	0.5217	2336.	6.34
0.900	0.5116	2624.	6.65
1.000	0.5019	2937.	6.95
1.100	0.4925	3278.	7.26
1.200	0.4833	3660.	7.59
1.300	0.4745	4080.	7.93
1.400	0.4654	4539.	8.28
1.500	0.4566	5038.	8.63
1.600	0.4478	5571.	8.98
1.700	0.4390	6129.	9.33
1.800	0.4312	6727.	9.68
1.900	0.4233	7335.	10.05
2.000	0.4161	8086.	10.42
2.100	0.4092	8826.	10.78
2.134	0.4070	9083.	10.91

Section B

$NiCl_2$ Activities

$m_3(NiCl_2)$	$a_3(NiCl_2)^*$	$\gamma_\pm(NiCl_2)$
0.100	98.75	2.71
0.233	551.3	3.53
0.338	1,462.	4.24
0.444	2,984.	4.82
0.566	5,212.	5.24
0.699	8,058.	5.53
0.804	11,650	5.86
0.895	16,140	6.22
0.991	21,660	6.54
1.086	28,300	6.84
1.182	36,120	7.11
1.276	45,270	7.37
1.366	55,850	7.63
1.453	67,970	7.89
1.525	81,890	8.18
1.593	97,830	8.47
1.660	116,000	8.77
1.735	136,700	9.04
1.807	159,900	9.31
1.883	185,800	9.56
1.956	214,600	9.82
2.035	246,500	10.05
2.134	296,700	10.40

TABLE 7

ACTIVITY DATA FOR THE $NiCl_2$-HCl-H_2O SYSTEM

HCl = 9.12 Molal

Section A
HCl and H_2O Activities

$m_3(NiCl_2)$	$a_1(H_2O)^*$	$a_2(HCl)^*$	$\gamma_{\pm}(HCl)$
0.100	0.4595	5,641.	8.15
0.200	0.4500	6,338.	8.54
0.300	0.4409	7,092.	8.94
0.400	0.4312	7,915.	9.35
0.500	0.4221	8,783.	9.75
0.600	0.4133	9,702.	10.15
0.700	0.4048	10,710	10.56
0.800	0.3969	11,830	11.00
0.900	0.3894	13,030	11.44
1.000	0.3821	14,260	11.86
1.100	0.3781	15,530	12.28
1.200	0.3765	17,000	12.72
1.227	0.3762	17,330	12.81

Section B
$NiCl_2$ Activities

$m_3(NiCl_2)$	$a_3(NiCl_2)^*$	$\gamma_{\pm}(NiCl_2)$
0.100	267,700	31.35
0.322	71,200	13.23
0.398	113,700	14.27
0.448	147,500	14.86
0.518	209,200	15.76
0.641	337,800	16.95
0.751	502,000	18.06
0.881	705,800	18.91
1.000	902,000	19.39
1.109	725,100	17.20
1.227	406,500	13.52

TABLE 8

ACTIVITY DATA FOR THE $NiCl_2$-HCl-H_2O SYSTEMS

HCl = 10.4 Molal

Section A
HCl and H_2O Activities

$m_3(NiCl_2)$	$a_1(H_2O)^*$	$a_2(HCl)^*$	$\gamma_{\pm}(HCl)$
0.100	0.3812	14,350	11.41
0.200	0.3749	15,840	11.89
0.300	0.3674	17,560	12.39
0.400	0.3583	19,450	12.93
0.500	0.3504	21,610	13.50
0.600	0.3426	23,890	14.05
0.700	0.3356	26,290	14.63
0.800	0.3303	28,400	15.09
0.856	0.3275	29,650	15.35

Section B
$NiCl_2$ Activities

$m_3(NiCl_2)$	$a_3(NiCl_2)^*$	$\gamma_{\pm}(NiCl_2)$
0.100	181,200	25.26
0.200	76,400	14.85
0.323	125,100	14.70
0.404	231,800	16.59
0.514	377,600	17.78
0.646	554,600	18.34
0.742	650,700	18.39
0.856	707,800	17.79

equilibrium water pressures of the hexahydrate and dihydrate were those listed by Derbye and Yngve.[80] The cobalt chloride activities at concentrations other than saturation (Tables 9 to 12) were calculated from the ø plots (Figure 7).

Hydrochloric Acid and Water. The water activities in the ternary mixtures (Tables 5 to 12) were calculated directly from the water partial pressure from the relation

$$a_{water} = \frac{p_a}{p^o}$$

where p_a = observed vapor pressure of water

p^o = vapor pressure of water at 30°.

By a comparison of the activity of hydrochloric acid[52] in aqueous solutions determined from electromotive force measurements over the range 4-11 molal with the partial pressure of hydrochloric acid over the same molality range, and average value of 1642 was obtained for $a_{(HCl)}/p_{(HCl)}$. Using this ratio, it was possible to calculate the activity of hydrochloric acid in the ternary mixtures (Tables 5 to 12).

<u>Experimental Data Used in Calculations.</u>

Two types of measurements were necessary in order to calculate the activity of both cobalt chloride and nickel chloride in ternary systems: vapor pressure measurements and characterization of equilibrium solid phases. The vapor pressure measurements consisted of (1) measurements of the partial pressure of water in aqueous binary solutions of cobalt chloride and nickel chloride ranging from dilute to saturated and (2) measurements of the partial pressures of both hydrochloric acid and water in ternary mixtures of cobalt chloride and nickel chloride over a range of salt concentrations up to saturation at four different but

FIGURE 7

ϕ PLOTS FOR THE HCl-H_2O-$CoCl_2$ SYSTEMS

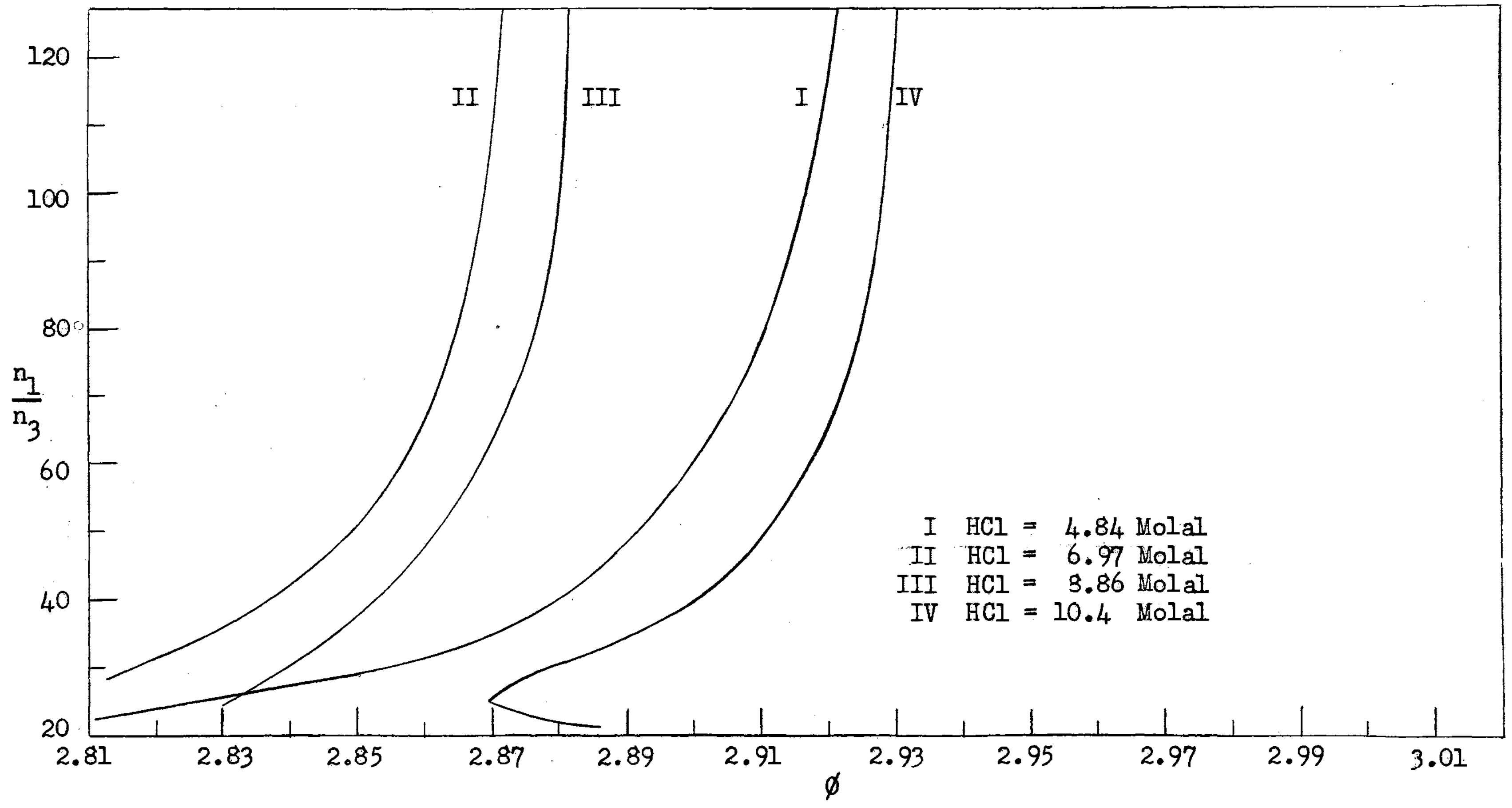


TABLE 9

ACTIVITY DATA FOR THE $CoCl_2$-HCl-H_2O SYSTEM

HCl = 4.84 Molal

Section A

HCl and H_2O Activities

$m_3(CoCl_2)$	$a_1(H_2O)^*$	$a_2(HCl)^*$	$\gamma_\pm(HCl)$
0.100	0.7379	132.9	2.33
0.200	0.7259	149.1	2.42
0.300	0.7146	168.6	2.53
0.400	0.7039	191.3	2.65
0.500	0.6933	217.2	2.77
0.600	0.6826	246.4	2.90
0.700	0.6719	277.2	3.02
0.800	0.6615	317.7	3.19
0.900	0.6508	356.6	3.33
1.000	0.6408	411.7	3.53
1.100	0.6313	465.2	3.70
1.200	0.6219	528.5	3.88
1.300	0.6125	598.2	4.08
1.400	0.6037	674.3	4.27
1.500	0.5949	755.4	4.46
1.600	0.5861	841.3	4.65
1.700	0.5773	932.1	4.83
1.800	0.5688	1028.	5.02
1.900	0.5606	1130.	5.20
2.000	0.5522	1242.	5.39
2.100	0.5440	1360.	5.57
2.200	0.5358	1487.	5.76
2.300	0.5280	1628.	5.97
2.400	0.5201	1793.	6.20
2.485	0.5138	1952.	6.44

Section B

$CoCl_2$ Activities

$m_3(CoCl_2)$	$a_3(CoCl_2)^*$	$\gamma_\pm(CoCl_2)$
0.100	20.39	2.00
0.150	10.66	1.39
0.242	46.07	1.89
0.377	137.4	2.27
0.485	229.5	2.41
0.587	385.9	2.63
0.689	596.8	2.82
0.790	869.0	2.99
0.905	1,206.	3.11
1.024	1,607.	3.21
1.149	2,075.	3.29
1.268	2,611.	3.36
1.381	3,219.	3.43
1.485	3,904.	3.51
1.585	4,677.	3.58
1.675	5,540.	3.67
1.752	6,512.	3.77
1.828	7,603.	3.86
1.901	8,824.	3.96
1.967	10,190	4.07
2.034	11,710	4.17
2.104	13,400	4.27
2.171	15,240	4.37
2.250	17,300	4.45
2.330	19,530	4.53
2.485	24,090	4.65

TABLE 10

ACTIVITY DATA FOR THE $CoCl_2$-HCl-H_2O SYSTEM

HCl = 6.97 Molal

Section A

HCl and H_2O Activities

$m_3(CoCl_2)$	$a_1(H_2O)^*$	$a_2(HCl)^*$	$\gamma_\pm(HCl)$
0.100	0.5968	959.6	4.38
0.200	0.5874	1085.	4.60
0.300	0.5776	1216.	4.80
0.400	0.5685	1354.	5.00
0.500	0.5597	1499.	5.19
0.600	0.5515	1645.	5.38
0.700	0.5436	1807.	5.57
0.800	0.5358	1974.	5.75
0.900	0.5283	2148.	5.93
1.000	0.5207	2326.	6.10
1.100	0.5138	2517.	6.28
1.200	0.5069	2715.	6.45
1.300	0.4997	2918.	6.61
1.400	0.4931	3120.	6.77
1.500	0.4865	3360.	6.95
1.600	0.4802	3600.	7.13
1.700	0.4745	3858.	7.31
1.800	0.4689	4129.	7.49
1.900	0.4632	4409.	7.67
1.950	0.4604	4555.	7.75
1.980	0.4591	4604.	7.77

Section B

$CoCl_2$ Activities

$m_3(CoCl_2)$	$a_3(CoCl_2)^*$	$\gamma_\pm(CoCl_2)$
0.100	599.1	4.88
0.363	1,824.	4.39
0.512	2,901.	4.46
0.678	4,658.	4.63
0.831	6,735.	4.77
0.969	9,167.	4.92
1.092	12,000	5.08
1.206	15,280	5.24
1.316	19,030	5.39
1.436	23,280	5.51
1.558	28,030	5.61
1.681	33,270	5.70
1.811	38,940	5.77
1.980	47,350	5.85

TABLE 11

ACTIVITY DATA FOR THE $CoCl_2$-HCl-H_2O SYSTEM

HCl = 8.86 Molal

Section **A**

HCl and H_2O ACTIVITIES

$m_3(CoCl_2)$	$a_1(H_2O)^*$	$a_2(HCl)^*$	$\gamma_{\pm}(HCl)$
0.100	0.4796	4,438.	7.44
0.200	0.4736	4,770.	7.63
0.300	0.4676	5,122.	7.82
0.400	0.4620	5,474.	8.00
0.500	0.4563	5,836.	8.17
0.600	0.4510	6,204.	8.34
0.700	0.4456	6,589.	8.51
0.800	0.4400	6,982.	8.68
0.900	0.4346	7,376.	8.84
1.000	0.4296	7,776.	8.99
1.100	0.4249	8,186.	9.14
1.200	0.4195	8,614.	9.29
1.300	0.4148	9,047.	9.45
1.400	0.4104	9,506.	9.60
1.500	0.4057	10,010	9.76
1.600	0.4013	10,530	9.92
1.700	0.3969	11,070	10.12
1.800	0.3931	11,620	10.26
1.900	0.3891	12,180	10.42
2.000	0.3853	12,740	10.57
2.100	0.3818	13,300	10.73
2.200	0.3784	13,870	10.86
2.234	0.3771	14,040	10.91

Section B

$CoCl_2$ Activities

$m_3(COCl_2)$	$a_3(CoCl_2)^*$	$\gamma_{\pm}(CoCl_2)$
0.100	3,259.	7.35
0.427	11,620	6.59
0.529	14,650	6.55
0.728	22,710	6.64
0.890	31,960	6.82
1.028	42,670	7.04
1.166	54,950	7.22
1.316	68,760	7.34
1.480	83,850	7.40
1.654	100,000	7.42
1.838	117,300	7.40
2.035	135,500	7.35
2.234	154,300	7.30

TABLE 12

ACTIVITY DATA FOR THE $CoCl_2$-HCl-H_2O SYSTEM

HCl = 10.65 Molal

Section A
HCl and H_2O Activities

$m_3(CoCl_2)$	$a_1(H_2O)^*$	$a_2(HCl)^*$	$\gamma_\pm(HCl)$
0.100	0.3733	17,510	12.29
0.200	0.3715	18,160	12.42
0.300	0.3689	18,710	12.49
0.400	0.3658	19,310	12.59
0.500	0.3627	19,970	12.69
0.600	0.3595	20,720	12.81
0.700	0.3564	21,460	12.94
0.800	0.3529	22,210	13.05
0.900	0.3498	22,990	13.16
1.000	0.3463	23,730	13.27
1.100	0.3432	24,490	13.38
1.200	0.3397	25,240	13.47
1.300	0.3363	26,000	13.57
1.400	0.3331	26,750	13.67
1.500	0.3300	27,490	13.75
1.600	0.3265	28,240	13.84
1.700	0.3234	29,000	13.92
1.800	0.3205	29,770	14.00
1.900	0.3177	30,510	14.07
2.000	0.3149	31,250	14.15
2.100	0.3127	32,020	14.22
2.200	0.3111	32,780	14.30
2.300	0.3099	33,570	14.37
2.400	0.3095	34,510	14.49
2.500	0.30890	35,920	14.68
2.594	0.3086	37,110	14.83

Section B
$CoCl_2$ Activities

$m_3(CoCl_2)$	$a_3(CoCl_2)^*$	$\gamma_\pm(CoCl_2)$
0.100	41,120	14.32
0.200	18,090	9.05
0.325	26,580	8.62
0.398	36,290	8.86
0.509	45,500	8.75
0.685	61,120	8.52
0.865	87,460	8.71
1.013	117,600	8.97
1.149	151,600	9.23
1.274	190,800	9.51
1.393	234,600	9.77
1.498	284,300	10.07
1.599	339,800	10.35
1.702	401,800	10.61
1.816	470,300	10.82
1.940	545,000	11.00
2.200	625,200	10.78
2.395	555,100	9.91
2.594	443,900	8.81

constant hydrochloric acid molalities.

Vapor Pressure. In Tables 13 to 22 are tabulated the vapor pressure data. The partial pressure was calculated from the experimental data as follows:

By the following equation the moles of nitrogen gas passed through the apparatus was calculated.

$$\frac{p^{o}}{P_1} = \frac{n_y}{n_x + n_y} \qquad (28)$$

where p^{o} = vapor pressure of pure water at 30°

P_1 = total pressure at first set of saturators

n_y = moles of water absorbed in first absorber

n_x = moles of nitrogen gas

From Dalton's law[82] and a knowledge of the number of moles of the hydrochloric acid absorbed as determined by the chloride analysis, one can calculate the partial pressure of the hydrochloric acid.

$$p_{HCl} = \frac{n_{HCl}}{n_{HCl} + n_{H_2O} + n_x} \qquad (29)$$

where p_{HCl} = vapor pressure of hydrochloric acid

n_{HCl} = moles of hydrochloric acid

n_{H_2O} = moles of water

n_x = moles of nitrogen gas

P_2 = total pressure at second set of saturators.

The partial pressure of the water was calculated similarly.

Solid-Phase Analysis. Table 23 lists the composition of the saturated solutions in the ternary systems and Table 24 gives the composition of the corresponding equilibrium solid phases. In the binary systems

TABLE 13

VAPOR PRESSURE DATA FOR THE SYSTEM $NiCl_2$-H_2O

$m_3(NiCl_2)$	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.)	ΔWt. in Second Absorber (g.)	p_{H_2O} (mm. Hg)
0.194	156	1	754.4	750.6	7.16	0.8955	1.1288	0.16	0.8949	31.64
0.194	157	2	753.3	749.5	1.00	0.1173	0.1477	0.15	0.1166	31.45
0.518	169	1	747.4	744.0	2.00	0.2624	0.3275	0.16	0.2573	31.00
0.518	170	2	746.8	743.4	1.00	0.1270	0.1582	0.16	0.1236	30.90
0.940	162	1	753.3	749.6	2.25	0.3736	0.4699	0.21	0.3550	30.16
0.940	164	3	752.3	748.8	1.66	0.2676	0.3362	0.20	0.2543	30.16
1.180	160	1	751.5	748.0	3.66	0.5301	0.6656	0.18	0.4915	29.45
1.180	161	2	750.7	747.3	1.92	0.2810	0.3522	0.18	0.2612	29.52
1.588	158	1	755.4	752.0	3.66	0.6089	0.7685	0.21	0.5413	28.29
1.588	159	2	753.1	749.7	2.58	0.4621	0.5813	0.22	0.4135	28.47
2.284	173	1	749.3	745.0	1.58	0.1997	0.2499	0.16	0.1654	26.40
2.284	174	2	749.6	745.3	1.00	0.1320	0.1652	0.17	0.1084	26.20
2.284	175	3	750.4	746.2	9.50	1.1481	1.4392	0.15	0.9483	26.32
2.764	178	1	756.0	751.4	1.00	0.1487	0.1877	0.19	0.1144	24.55
2.764	179	2	753.8	749.3	9.75	1.4681	1.8489	0.19	1.1260	24.50
3.230	307	1	755.8	750.3	2.00	0.2792	0.3525	0.18	0.2006	22.97
3.230	308	2	754.6	749.1	1.84	0.2467	0.3110	0.17	0.1763	22.84
3.578	303	1	743.9	738.6	2.00	0.3774	0.4688	0.23	0.2557	21.70
3.578	304	2	745.1	739.9	8.25	1.3342	1.6602	0.20	0.9071	21.77
4.286	299	1	750.7	746.3	2.25	0.3678	0.4614	0.21	0.2222	19.42
4.286	300	2	748.2	743.8	2.50	0.3265	0.4080	0.16	0.1962	19.33
4.925	281	1	752.4	747.1	2.16	0.2010	0.2525	0.12	0.1071	17.17
4.925	283	3	750.6	745.0	2.00	0.1791	0.2246	0.11	0.0953	17.11
5.321	274	1	763.0	755.8	2.00	0.2480	0.3163	0.16	0.1249	16.14
5.321	275	2	763.2	756.0	2.00	0.2449	0.3123	0.16	0.1232	16.18

TABLE 14

VAPOR PRESSURE DATA FOR THE SYSTEM $CoCl_2$-H_2O

$m_3(CoCl_2)$	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.)	ΔWt. in Second Absorber (g.)	p_{H_2O} (mm. Hg)
0.224	141	1	760.0	756.9	2.58	0.5007	0.6362	0.25	0.4951	31.34
0.224	142	2	757.8	754.7	2.75	0.5637	0.7139	0.26	0.5576	31.36
0.424	135	1	756.6	753.4	3.25	0.5242	0.6628	0.20	0.5145	31.01
0.424	136	2	757.9	754.8	9.75	1.5572	1.9724	0.20	1.5221	31.00
1.006	128	1	755.9	752.5	9.08	1.2060	1.5234	0.17	1.1373	29.94
1.006	129	2	756.5	752.9	2.08	0.2927	0.3699	0.18	0.2733	29.64
1.588	131a	1	763.1	759.3	10.25	1.5637	1.9950	0.19	1.3980	28.43
1.588	132	2	763.0	758.9	3.75	0.5555	0.7084	0.19	0.4974	28.46
2.190	130	1	760.3	756.6	4.25	0.6752	0.8578	0.20	0.5644	26.65
2.190	131	2	761.3	757.5	2.84	0.4730	0.6018	0.21	0.3958	26.67
2.548	139	1	761.4	758.3	5.50	1.0005	1.2733	0.23	0.7975	25.47
2.548	140	2	759.8	756.7	8.25	1.4828	1.8832	0.23	1.1704	25.23
2.850	143	1	754.5	751.0	2.92	0.5174	0.6521	0.22	0.3986	24.64
2.850	145	3	759.5	756.0	1.75	0.2900	0.3681	0.21	0.2240	24.69
3.365	150	3	749.7	746.6	2.00	0.3863	0.4837	0.24	0.2765	23.26
3.365	151	4	748.7	745.6	1.75	0.2602	0.3254	0.19	0.1869	23.03
3.720	152	1	751.0	747.8	3.93	0.7373	0.9249	0.23	0.5024	21.88
3.720	154	3	748.7	745.0	1.00	0.1921	0.2405	0.24	0.1307	21.80
4.088	146	1	750.6	747.1	3.08	0.5722	0.7176	0.23	0.3703	20.80
4.088	147	2	752.9	749.2	2.92	0.6029	0.7584	0.26	0.3888	20.73
4.432	137	1	763.1	759.9	2.50	0.3582	0.4569	0.19	0.2195	19.73
4.432	138	2	763.4	759.9	0.84	0.1324	0.1687	0.20	0.0814	19.79
4.561	---	-	-----	-----	----	------	------	----	------	19.42[d]

[d] value obtained by extrapolation

TABLE 15

VAPOR PRESSURE DATA FOR THE SYSTEM HCl-H_2O-$NiCl_2$
m_2 (HCl) = 4.69 Molal

$m_2(NiCl_2)$	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/	ΔWt. in Second Absorber (g.)	Meq. $AgNO_3$ Used	p_{H_2O} (mm. Hg)	p_{HCl} (mm. Hg)
0.000	278	1	759.2	755.3	11.25	1.1293	1.4328	0.13	0.8569	0.0903	24.17	-----
0.000	279	2	756.2	752.4	8.75	0.8326	1.0523	0.12	0.6546	0.0843	-----	0.055
0.000	280	3	753.7	749.7	9.75	1.0478	1.3196	0.14	0.7894	0.1091	23.97	0.055
0.189	257	1	739.0	735.1	8.58	1.3231	1.6325	0.19	0.9722	0.1594	23.38	0.070
0.189	258	2	743.2	739.4	10.16	1.4642	1.8171	0.18	1.0811	0.1944	23.48	0.075
0.437	269	1	753.9	751.0	5.25	0.8579	1.0806	0.21	0.6113	0.1584	22.64	0.108
0.437	271	3	756.8	754.0	5.08	0.8196	1.0366	0.20	0.5831	0.1514	22.62	0.106
0.671	267	1	755.9	751.8	9.50	1.4440	1.8242	0.19	0.9864	0.4126	21.58	0.164
0.671	268	2	755.8	751.8	5.25	0.7606	0.9603	0.18	0.5198	0.2224	21.59	0.167
0.909	277	2	761.2	757.9	9.92	1.2702	1.6175	0.16	0.8403	0.4832	20.80	0.219
0.909	276	1	761.4	758.1	6.00	0.8056	1.0251	0.17	0.5342	0.2966	20.89	0.216
1.171	263	1	746.3	741.9	5.50	0.5658	0.7051	0.13	0.3608	0.2995	19.88	0.307
1.171	264	2	749.9	745.5	10.00	0.9675	1.2119	0.12	0.6160	0.5103	19.84	0.305
1.433	265	1	757.6	753.8	4.92	0.8502	1.0764	0.22	0.5264	0.6789	18.99	0.464
1.433	266	2	756.7	752.9	4.92	0.7960	1.0064	0.20	0.4909	0.6299	18.96	0.460
1.715	273	2	756.1	753.0	8.50	1.2642	1.5974	0.19	0.7501	1.3996	17.84	0.644
1.715	272	1	756.3	753.2	6.00	0.8041	1.0162	0.17	0.4816	0.9161	17.98	0.665
1.989	261	3	742.0	737.6	9.84	1.3182	1.6329	0.17	0.7700	2.1142	16.95	0.930
1.989	262	4	741.6	737.0	6.00	0.7681	0.9510	0.16	0.4508	1.2064	17.06	0.915
2.253	255	1	744.7	740.6	5.30	0.6350	0.7896	0.15	0.3717	1.4042	16.28	1.282
2.253	256	2	740.0	736.0	10.00	1.1684	1.4433	0.14	0.6828	2.5557	16.29	1.274
2.478	253	1	752.1	748.0	9.58	1.2478	1.5681	0.16	0.7379	3.5624	15.72	1.659
2.478	254	2	748.8	744.4	6.25	0.7669	0.9586	0.16	0.4511	2.1624	15.67	1.638
2.762	311	1	752.7	746.0	8.25	1.1224	1.4116	0.17	0.6748	4.2754	14.87	2.210
2.762	312	2	750.0	743.5	4.25	0.5060	0.6339	0.15	0.3038	1.9182	14.87	2.200
3.005	309	1	754.3	748.8	3.75	0.7133	0.8990	0.24	0.4459	3.5250	14.33	2.865
3.005	310	2	754.4	749.0	4.00	0.7599	0.9578	0.24	0.4657	3.7192	14.00	2.844

TABLE 16

VAPOR PRESSURE DATA FOR THE SYSTEM HCl-H_2O-$NiCl_2$

m_2 (HCl) = 6.86 Molal

m_3 ($NiCl_2$)	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.)	ΔWt. in Second Absorber (g.)	Meq. $AgNO_3$ Used	p_{H_2O} (mm. Hg)	p_{HCl} (mm. Hg)
0.137	35	1	756.8	751.7	7.75	1.3599	1.7200	0.22	0.8511	1.4649	18.85	0.622
0.137	36	2	757.7	752.7	9.25	1.6040	2.0312	0.22	1.0218	1.8108	19.14	0.653
0.137	37	3	746.9	742.2	8.15	1.2762	1.5918	0.20	0.7946	1.3146	19.10	0.599
0.362	47	1	748.8	744.7	8.15	1.1928	1.4919	0.18	0.7298	1.6789	18.05	0.817
0.362	48	2	741.7	736.8	7.50	0.3992	0.4942	0.07	0.2460	0.5661	18.17	0.828
0.583	41	1	749.7	744.9	7.50	1.0921	1.3676	0.18	0.6611	2.0880	17.24	1.110
0.583	42	2	747.9	742.9	8.00	1.1150	1.3928	0.17	0.6742	2.1006	17.26	1.092
0.583	43	3	744.8	739.9	8.00	1.0726	1.3340	0.17	0.6504	2.0238	17.31	1.093
0.821	38	1	753.8	749.4	9.84	1.4163	1.7837	0.18	0.8589	3.5453	16.61	1.456
0.821	39	2	751.8	747.4	7.75	0.9932	1.2474	0.16	0.6010	2.4960	16.55	1.462
0.821	40	3	752.1	747.7	8.25	0.9957	1.2511	0.15	0.6046	2.5120	16.60	1.464
0.968	52	4	744.1	740.3	8.75	1.3113	1.6293	0.19	0.7942	3.9033	16.05	1.734
0.968	53	5	744.0	740.1	4.92	0.6731	0.8363	0.17	0.4078	2.0181	16.02	1.745
1.145	54	1	744.3	740.5	5.00	0.5121	0.7607	0.15	0.3772	2.2038	15.65	2.090
1.145	55	2	745.3	749.4	8.92	1.3187	1.6505	0.19	0.8089	4.7937	15.52	2.112
1.321	44	1	741.7	737.2	9.92	1.0699	1.3247	0.13	0.6682	4.6929	14.99	2.548
1.321	45	2	745.7	741.0	7.50	0.8781	1.0935	0.15	0.5514	3.8586	15.07	2.553
1.517	63	1	751.5	747.9	5.75	0.8800	1.1046	0.19	0.5721	4.8607	14.48	3.212
1.517	64	2	752.0	748.6	9.75	1.3812	1.7353	0.18	0.8975	7.6206	14.49	3.210
1.754	199	1	752.3	747.5	4.58	0.7758	0.9752	0.21	0.5317	5.4981	13.75	4.115
1.754	200	2	750.2	744.8	9.58	1.5252	1.9113	0.20	1.0462	10.7926	13.84	4.128
1.850	315	1	755.1	748.2	4.75	0.6249	0.7883	0.17	0.4417	4.8138	13.68	4.455
1.850	316	2	754.0	747.3	5.25	0.7017	0.8839	0.17	0.4869	5.3617	13.35	4.424
2.134	313	1	746.9	740.9	3.25	0.4388	0.5472	0.17	0.3329	4.2470	13.04	5.610
2.134	314	2	746.8	741.2	2.92	0.3986	0.4972	0.17	0.2998	3.8511	12.85	5.597

TABLE 17

VAPOR PRESSURE DATA FOR THE SYSTEM $HCl-H_2O-NiCl_2$

m_2 (HCl) = 9.12 Molal

$m_3(NiCl_2)$	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.)	ΔWt. in Second Absorber (g.)	Meq. $AgNO_3$ Used	p_{H_2O} (mm. Hg)	p_{HCl}^* (mm. Hg)
0.000	233	1	753.7	749.3	4.50	0.5621	0.7079	0.16	0.3659	2.9850	14.75	3.079
0.000	233a	2	750.8	746.4	4.25	0.4983	0.6248	0.15	0.3244	2.6444	14.78	3.078
0.117	242	1	759.2	756.1	5.33	0.7847	0.9957	0.19	0.5305	4.7709	14.67	3.535
0.117	247	3	753.3	749.2	4.58	0.7377	0.9283	0.20	0.4976	4.4457	14.66	3.505
0.214	251	1	765.1	762.0	6.84	0.9960	1.2751	0.19	0.6899	6.9027	14.13	4.054
0.214	252	2	766.1	762.6	10.42	1.2588	1.6111	0.15	0.8662	8.5910	14.18	3.969
0.322	237	1	748.8	745.5	5.25	0.8769	1.0967	0.21	0.6323	6.8417	14.08	4.533
0.322	238	2	743.7	740.5	4.66	0.7860	0.9759	0.21	0.5582	6.0202	13.90	4.455
0.490	234	1	751.1	748.1	9.85	1.5787	1.9809	0.21	1.1989	14.6785	13.56	5.404
0.490	236	3	750.9	748.0	5.00	0.6937	0.8702	0.18	0.5188	6.3302	13.40	5.305
0.665	249	2	746.8	742.7	5.16	0.5746	0.7167	0.14	0.4593	6.2704	12.92	6.329
0.665	250	3	750.1	746.0	5.75	0.6593	0.8260	0.14	0.5277	7.1963	12.96	6.334
0.847	240	2	757.3	753.6	5.50	0.8050	1.0188	0.19	0.6977	10.5865	12.46	7.625
0.847	241	3	758.5	754.7	9.50	1.2142	1.5390	0.16	1.0563	15.9774	12.63	7.675
1.030	245	2	747.0	743.2	4.75	0.5462	0.6814	0.14	0.5162	8.5281	12.07	9.040
1.030	246	3	747.1	743.3	10.16	1.3961	1.7420	0.17	1.3206	21.8023	12.10	9.038
1.227	231	2	753.9	750.1	4.58	0.5714	0.7197	0.16	0.6001	10.6294	11.93	10.745
1.227	232	3	754.3	750.5	9.00	1.0470	1.3196	0.15	1.0957	19.2913	12.01	10.640

TABLE 18

VAPOR PRESSURE DATA FOR THE SYSTEM $HCl-H_2O-NiCl_2$

$m_2(HCl) = 10.4$ Molal

$m_3(NiCl_2)$	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.)	ΔWt. in Second Absorber (g.)	Meq. $AgNO_3$ Used	p_{H_2O} (mm. Hg)	p_{HCl}* (mm. Hg)
0.000	287	1	750.7	746.6	3.75	0.5786	0.7256	0.19	0.5138	8.0107	12.32	8.017
0.000	288	2	751.2	747.0	4.00	0.5680	0.7126	0.18	0.5052	7.8704	12.35	8.014
0.154	293	1	746.1	743.1	4.08	0.5728	0.7136	0.17	0.5564	9.3510	12.08	9.441
0.154	294	2	746.6	742.6	3.25	0.4343	0.5414	0.17	0.4207	7.1036	11.95	9.457
0.304	292	2	744.9	741.0	4.00	0.5424	0.6745	0.17	0.5671	10.1739	11.60	10.834
0.304	291	1	746.3	742.3	3.58	0.5069	0.6317	0.18	0.5369	9.6159	11.80	10.963
0.462	297	1	752.6	748.9	4.25	0.7513	0.9447	0.22	0.8789	16.6838	11.52	12.794
0.462	298	2	752.0	748.3	3.50	0.5971	0.7502	0.21	0.6899	13.2950	10.99	12.827
0.668	295	1	746.3	742.8	4.42	0.7794	0.9714	0.22	1.0375	21.2569	10.75	15.678
0.668	296	2	743.9	740.1	3.50	0.5849	0.2075	0.21	0.7758	15.8857	10.73	15.633
0.856	305	1	749.9	747.1	4.16	0.6982	0.8746	0.21	1.0481	22.2928	10.72	18.301
0.856	306	2	750.3	747.5	3.33	0.5246	0.6575	0.20	0.7763	16.7163	10.13	18.285

TABLE 19

VAPOR PRESSURE DATA FOR THE SYSTEM HCl-H_2O-$CoCl_2$

m_2 (HCl) = 4.84 Molal

$m_3(CoCl_2)$	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.)	ΔWt. in Second Absorber (g.)	Meq. $AgNO_3$ Used	p_{H_2O} (mm. Hg)	p_{HCl} (mm. Hg)
0.000	67	3	753.1	749.4	12.92	1.4725	1.8528	0.14	1.1040	0.1868	23.85	0.074
0.000	68	4	746.6	742.9	11.75	1.1905	1.4846	0.13	0.8930	0.1370	23.87	0.068
0.000	69	5	740.0	736.3	11.25	1.0784	1.3321	0.12	0.8097	0.1415	23.88	0.075
0.160	70	1	741.9	738.5	8.75	1.0965	1.3584	0.16	0.8044	0.1602	23.33	0.084
0.160	71	2	752.9	749.5	9.50	1.1925	1.5000	0.16	0.8728	0.1845	23.27	0.087
0.314	120	1	755.8	752.7	10.50	1.6133	2.0373	0.19	1.1502	0.2927	22.66	0.104
0.314	121	2	749.8	746.7	8.00	1.1857	1.4853	0.19	0.8442	0.2217	22.62	0.107
0.477	73	1	761.9	758.7	10.50	1.1482	1.4624	0.14	0.8019	0.2638	22.14	0.131
0.477	74	2	762.0	758.8	10.33	1.1137	1.4187	0.14	0.7799	0.2618	22.20	0.135
0.709	76	1	760.4	757.3	8.58	1.1464	1.4572	0.17	0.7709	0.3562	21.24	0.180
0.709	77	2	760.3	757.2	10.42	1.6471	2.0930	0.20	1.1190	0.5188	21.46	0.183
0.925	78	1	757.3	753.6	9.00	0.8177	1.0348	0.12	0.5364	0.3265	20.61	0.231
0.925	79	2	764.0	760.2	9.84	1.5007	1.9164	0.19	0.9871	0.6243	20.65	0.239
1.115	85	1	750.2	746.7	7.50	0.8366	1.0483	0.14	0.5379	0.3991	20.13	0.277
1.115	86	2	748.9	745.2	8.84	1.0495	1.3130	0.15	0.6760	0.5267	20.12	0.293
1.318	80	1	758.7	755.0	7.50	0.9459	1.1993	0.16	0.5921	0.6193	19.38	0.380
1.318	82	3	752.0	748.3	6.92	0.7786	0.9780	0.14	0.4889	0.5123	19.43	0.380
1.528	83	1	754.7	750.7	5.58	0.7149	0.9015	0.16	0.4404	0.5804	18.87	0.471
1.528	84	2	753.8	749.8	8.33	1.0103	1.2722	0.15	0.6218	0.8338	18.84	0.477
1.622	93	1	758.8	755.3	6.50	1.0248	1.2998	0.20	0.6251	0.9100	18.62	0.516
1.622	94	2	754.2	750.6	9.08	1.3397	1.6881	0.19	0.8149	1.2045	18.54	0.520
1.838	194	1	747.6	742.7	10.50	1.5631	1.9518	0.19	0.9459	1.7943	18.13	0.664
1.838	196	3	764.8	759.8	4.50	0.6948	0.8885	0.20	0.4153	0.7862	17.90	0.659

TABLE 19 - CONTINUED

$m_3(CoCl_2)$	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.)	ΔWt. in Second Absorber (g.)	Meq. $AgNO_3$ Used	p_{H_2O} (mm. Hg)	p_{HCl} (mm. Hg)
1.838	197	4	761.2	756.2	4.08	0.6159	0.7834	0.19	0.3675	0.7048	17.86	0.659
2.026	184	1	756.7	753.2	4.00	0.6388	0.8076	0.20	0.3800	0.8681	17.59	0.791
2.026	185	2	755.5	751.9	8.50	1.3271	1.6756	0.20	0.7872	1.8406	17.50	0.806
2.259	201	1	749.3	741.4	6.42	0.9115	1.1408	0.18	0.5347	1.5065	16.89	0.958
2.259	202	2	748.3	740.5	9.42	1.4354	1.7940	0.19	0.8437	2.3896	16.82	0.957
2.485	203	1	747.5	741.3	5.50	0.5586	0.6974	0.13	0.3287	1.1712	16.47	1.214
2.485	204	2	745.7	740.0	4.50	0.4277	0.5327	0.12	0.2479	0.8813	16.24	1.194

TABLE 20

VAPOR PRESSURE DATA FOR THE SYSTEM $HCl-H_2O-CoCl_2$

m_2 (HCl) = 6.97 Molal

$m_3(CoCl_2)$	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.)	ΔWt. in Second Absorber (g.)	Meq. $AgNC_3$ Used	p_{H_2O} (mm. Hg)	p_{HCl} (mm. Hg)
0.000	1	1	754.2	749.3	10.00	1.6670	2.1004	0.21	1.0569	1.4656	19.34	0.507
0.000	24	3	757.6	753.4	11.25	1.4362	1.8181	0.16	0.9058	1.2813	19.24	0.520
0.000	25	4	753.2	749.0	10.16	1.3672	1.7204	0.17	0.8675	1.2319	19.35	0.520
0.074	3	1	753.9	748.9	8.25	1.4520	1.8291	0.22	0.9132	1.3105	19.07	0.562
0.074	5	3	754.4	749.5	8.08	1.2956	1.6334	0.20	0.8165	1.2959	18.97	0.570
0.172	6	1	754.5	749.0	8.00	1.4077	1.7747	0.22	0.8788	1.5488	18.76	0.633
0.172	7	2	747.2	742.9	8.33	1.3910	1.7358	0.21	0.8683	1.5621	18.77	0.650
0.172	8	3	748.0	742.7	8.84	1.4907	1.8622	0.21	0.9292	1.7074	18.69	0.660
0.322	10	2	756.3	751.6	8.84	1.5261	1.9287	0.22	0.9408	1.9846	18.51	0.752
0.322	11	3	759.6	755.2	8.16	1.1152	1.4159	0.17	0.6880	1.4271	18.35	0.743
0.425	12	1	757.1	752.3	8.84	1.2320	1.5571	0.18	0.7547	1.8220	17.99	0.857
0.425	13	2	755.0	750.1	8.16	1.1617	1.4656	0.18	0.7115	1.6624	18.03	0.829
0.530	21	1	753.2	748.3	8.00	1.1956	1.4920	0.19	0.7203	1.9579	17.61	0.959
0.530	22	2	757.4	752.7	8.75	1.1874	1.5027	0.17	0.7229	1.9461	17.68	0.951
0.530	23	3	761.9	757.3	8.00	1.0102	1.2851	0.16	0.6118	1.7109	17.53	0.983
0.605	15	1	747.9	743.4	8.25	1.2910	1.6126	0.20	0.7843	2.2322	17.52	1.002
0.605	16	2	745.5	741.0	8.25	1.2857	1.6005	0.19	0.7856	2.2414	17.63	1.011
0.605	17	3	746.7	742.2	8.08	1.0433	1.3009	0.16	0.6291	1.8475	17.35	1.029
0.765	18	1	745.7	741.0	10.00	1.3789	1.7169	0.17	0.8338	2.8184	17.19	1.187
0.765	19	2	742.5	737.7	7.84	1.0424	1.2922	0.17	0.6279	2.1718	16.98	1.208
0.765	20	3	744.7	739.9	9.75	1.3403	1.6669	0.17	0.8126	2.7828	17.09	1.203

TABLE 20 - CONTINUED

$m_3(CoCl_2)$	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.)	ΔWt. in Second Absorber (g.)	Meq. $AgNO_3$ Used	p_{H_2O} (mm. Hg)	p_{HCl} (mm. Hg)
0.913	31	3	754.2	749.5	7.66	1.0511	1.3295	0.17	0.6355	2.4101	16.72	1.326
0.913	61	4	750.5	746.0	9.50	1.0364	1.2994	0.14	0.6235	2.3507	16.72	1.317
0.913	62	5	751.2	746.8	8.50	1.0059	1.2626	0.15	0.6042	2.2824	16.69	1.316
1.086	32	1	749.0	743.5	8.58	1.0236	1.2806	0.15	0.6182	2.6743	16.38	1.513
1.086	33	2	746.6	741.5	7.42	0.8828	1.1009	0.15	0.5318	2.3177	16.31	1.525
1.086	34	3	747.2	742.4	12.00	1.0692	1.3342	0.11	0.6467	2.8214	16.39	1.533
1.230	26	1	747.2	743.0	9.33	0.6122	0.7640	0.08	0.3724	1.8086	16.15	1.718
1.230	27	2	751.9	746.9	9.42	1.6385	2.0584	0.22	1.0099	4.9995	16.26	1.770
1.427	56	1	755.3	751.5	8.00	1.3284	1.6766	0.21	0.8077	4.5290	15.61	1.983
1.427	57	2	755.5	751.8	8.42	1.3372	1.6882	0.20	0.8120	4.4919	15.64	1.953
1.613	59	1	753.0	750.0	6.00	0.8402	1.0570	0.18	0.5183	3.2229	15.41	2.231
1.613	60	2	753.1	750.0	9.00	1.2197	1.5347	0.17	0.7476	4.7138	15.25	2.248
1.978	192	1	742.7	738.9	5.50	0.7726	0.9580	0.17	0.4883	3.7613	14.68	2.831
1.978	193	2	741.1	735.6	4.33	0.5072	0.6275	0.14	0.3196	2.4865	14.55	2.850

TABLE 21

VAPOR PRESSURE DATA FOR THE SYSTEM $HCl-H_2O-CoCl_2$

m_2 (HCl) = 8.86 Molal

$m_3(CoCl_2)$	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.)	ΔWt. in Second Absorber (g.)	Meq. $AgNO_3$ Used	p_{H_2O} (mm. Hg)	p_{HCl}* (mm. Hg)
0.000	97	1	760.8	757.7	7.92	0.8340	1.0605	0.14	0.5291	3.5599	15.46	2.483
0.000	98	2	758.6	755.4	9.50	1.3144	1.6664	0.18	0.8357	5.7453	15.38	2.545
0.153	122	1	745.3	742.0	9.50	1.3642	1.6981	0.18	0.8818	6.7410	15.05	2.874
0.153	123	2	743.7	740.3	5.25	0.7087	0.8801	0.17	0.4576	3.5070	15.03	2.881
0.269	104	1	756.6	753.5	4.50	0.7106	0.8984	0.20	0.4689	3.7832	15.04	3.094
0.269	105	2	756.2	753.1	7.92	1.2343	1.5600	0.20	0.8118	6.5642	14.97	3.091
0.410	108	1	752.3	748.9	8.33	1.2659	1.5912	0.19	0.8454	7.3405	14.73	3.371
0.410	109	2	750.4	747.0	5.75	0.8547	1.0715	0.19	0.5715	4.9559	14.75	3.374
0.553	114	1	751.1	747.3	8.33	1.1351	1.4242	0.17	0.7789	7.3029	14.56	3.737
0.553	115	2	749.3	745.5	5.75	0.7628	0.9548	0.17	0.5188	4.8770	14.41	3.718
0.777	106	1	755.2	752.1	4.84	0.7564	0.9544	0.20	0.5310	5.5565	14.01	4.275
0.777	107	2	751.9	748.8	4.50	0.6847	0.8601	0.19	0.4796	5.2176	13.91	4.299
0.935	110	1	752.5	748.9	4.66	0.7684	0.9662	0.21	0.5531	6.0962	13.88	4.611
0.935	111	2	753.4	749.7	9.00	1.3780	1.7345	0.19	0.9881	11.0646	13.68	4.663
1.166	112	1	757.1	753.6	5.00	0.8216	1.0395	0.21	0.6096	7.3316	13.43	5.183
1.166	113	2	755.7	752.0	4.33	0.7067	0.8924	0.21	0.5238	6.3275	13.36	5.194
1.338	116	1	752.7	749.0	5.00	0.7616	0.9576	0.19	0.5831	7.4218	13.22	5.657
1.338	117	2	754.4	750.5	9.25	1.4051	1.7714	0.19	1.0725	13.7408	13.10	5.676
1.601	133	1	762.9	759.4	5.84	0.9613	1.2261	0.21	0.7708	10.6628	12.80	6.435
1.601	134	2	761.6	757.3	9.16	1.4441	1.8382	0.20	1.1540	15.9889	12.73	6.421
1.786	301	1	739.4	736.6	4.00	0.6166	0.7611	0.19	0.5180	7.6357	12.52	7.196
1.786	302	2	737.8	735.0	3.75	0.5440	0.6701	0.18	0.4544	6.6855	12.48	7.142
2.234	289	1	754.4	750.7	4.00	0.5675	0.7152	0.18	0.5236	8.5250	12.05	8.696
2.234	290	2	752.6	749.1	3.66	0.5777	0.7261	0.20	0.5281	8.5998	11.95	8.629

TABLE 22

VAPOR PRESSURE DATA FOR THE SYSTEM $HCl-H_2O-CoCl_2$

m_2 (HCl) = 10.65 Molal

$m_3(CoCl_2)$	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.)	ΔWt. in Second Absorber (g.)	Meq. $AgNO_3$ Used	p_{H_2O} (mm. Hg)	p_{HCl}* (mm. Hg)
0.000	126	1	765.5	753.3	4.50	0.7188	0.9085	0.20	0.7455	13.0918	11.97	10.530
0.000	127	2	755.3	752.5	4.50	0.7035	0.8879	0.20	0.7296	12.8081	11.99	10.531
0.119	176	1	754.9	751.9	3.25	0.4869	0.6140	0.19	0.5183	9.3172	11.77	11.055
0.119	177	2	754.6	750.9	3.16	0.4648	0.5859	0.18	0.4938	8.8674	11.76	11.024
0.376	165	1	750.6	747.0	3.84	0.6180	0.7749	0.20	0.6950	12.8401	11.75	11.984
0.376	166	2	748.0	744.3	3.58	0.5714	0.7137	0.20	0.6299	11.5919	11.62	11.708
0.547	168	2	746.6	742.6	3.33	0.4249	0.5299	0.16	0.4918	9.3132	11.46	12.623
0.547	198	3	754.5	749.5	3.92	0.6310	0.7954	0.20	0.7251	13.6328	11.55	12.433
0.741	171	1	748.1	744.7	3.25	0.4766	0.5956	0.18	0.5774	11.2236	11.28	13.561
0.741	172	2	747.4	744.0	3.33	0.4707	0.5875	0.18	0.5683	11.0246	11.30	13.491
1.015	180	1	749.5	745.9	3.25	0.4773	0.5976	0.18	0.6093	12.1828	11.04	14.677
1.015	181	2	748.4	744.8	3.42	0.4747	0.5933	0.17	0.6036	12.0873	10.96	14.656
1.177	182	1	756.2	759.7	3.20	0.5029	0.6385	0.20	0.6639	13.4922	10.91	15.421
1.177	183	2	759.0	755.3	3.08	0.4967	0.6298	0.20	0.6548	13.4086	10.65	15.526
1.376	186	1	752.6	749.0	3.84	0.6463	0.8127	0.21	0.8944	18.5906	10.68	16.512
1.376	187	2	749.2	745.6	3.16	0.5133	0.6423	0.20	0.7026	14.6026	10.57	16.336
1.589	188	1	747.2	744.9	4.25	0.7303	0.9112	0.21	1.0416	22.0731	10.34	17.370
1.589	189	2	744.5	742.2	3.25	0.5357	0.6659	0.20	0.7647	16.1270	10.52	17.305
2.380	319	1	749.0	742.0	2.84	0.4023	0.5033	0.18	0.6751	15.0116	10.01	21.198
2.380	320	2	747.7	741.0	2.75	0.3771	0.4710	0.17	0.6262	14.0171	9.64	21.142
2.594	317	1	753.5	748.2	3.00	0.4250	0.5351	0.18	0.7605	17.1936	9.92	22.981
2.594	318	2	752.4	747.1	3.00	0.1991	0.2502	0.08	0.3528	7.9808	9.80	22.792

TABLE 23

COMPOSITION OF SATURATED SOLUTIONS AND EQUILIBRIUM SOLID PHASES

LIQUID PHASES

$CoCl_2$-H_2O-HCl System

m_2(HCl)	% $CoCl_2$	% H_2O	% HCl
4.84	21.52	66.70	11.77
6.97	17.05	66.19	16.76
8.86	17.98	61.97	20.05
10.65	19.51	57.93	22.56

$NiCl_2$-H_2O-HCl System

m_2(HCl)	% $NiCl_2$	% H_2O	% HCl
4.69	24.97	64.12	10.91
6.86	18.12	65.52	16.36
9.12	10.68	67.15	22.17
10.4	7.45	67.17	25.38

WET SOLID PHASES

$CoCl_2$-H_2O-HCl System

m_2(HCl)	% $CoCl_2$	% H_2O	% HCl
4.84	44.45	51.09	4.47
6.97	43.22	51.08	5.70
8.86	46.32	49.04	4.54
10.65	48.28	40.78	10.94

$NiCl_2$-H_2O-HCl System

m_2(HCl)	% $NiCl_2$	% H_2O	% HCl
4.69	45.81	49.09	5.10
6.86	48.36	45.48	6.16
9.12	60.59	37.69	1.72
10.4	36.42	51.12	12.46

TABLE 24

CHARACTERIZATION OF SOLID PHASES

$CoCl_2$-H_2O-HCl System

m_2(HCl)	% $CoCl_2$	% $CoCl_2$ in $CoCl_2 \cdot nH_2O$	n
4.84	58.2	54.6	6
6.97	56.2	54.6	6
8.86	54.8	54.6	6
10.65	75.2	78.3	2

$NiCl_2$-H_2O-HCl System

m_2(HCl)	% $NiCl_2$	% $NiCl_2$ in $NiCl_2 \cdot nH_2O$	n
4.69	65.2	64.3	4
6.86	66.3	64.3	4
9.12	64.4	64.3	4
10.4	63.5	64.3	4

the solid phase in equilibrium with the saturated nickel chloride contained 54.3% nickel chloride as compared with a calculated value of 54.5% for $NiCl_2 \cdot 6H_2O$. In the cobalt chloride-water system the percentage of cobalt chloride in the solid phases was 54.0% as compared to a calculated value of 54.6% for $CoCl_2 \cdot 6H_2O$.

EXTRACTION STUDIES

In Tables 25 and 26 are summarized the data for the extraction of cobalt chloride and nickel chloride from hydrochloric acid solutions by 2-octanol.

TABLE 25

EXTRACTION DATA FOR THE $HCl-H_2O-NiCl_2$ SYSTEM

HCl = 6.86 Molal

$m_3(NiCl_2)$ Aqueous Phase	$m_3(NiCl_2)$ Octanol Phase	$m_2(HCl)$ Octanol Phase
1.517	0.00464	2.367
1.321	0.00409	2.319
1.145	0.00367	2.238
0.968	0.00291	2.142
0.821	0.00236	1.996
0.583	0.00159	1.940
0.362	0.00074	1.775
0.137	0.00045	1.673

TABLE 26

EXTRACTION DATA FOR THE $HCl-H_2O-CoCl_2$ SYSTEM

HCl = 6.97 Molal

$m_3(CoCl_2)$ Aqueous Phase	$m_3(CoCl_2)$ Octanol Phase	$m_2(HCl)$ Octanol Phase
1.613	0.195	2.285
1.427	0.162	2.185
1.230	0.111	2.129
1.086	0.104	2.105
0.913	0.0677	2.013
0.765	0.0548	1.913
0.605	0.0287	1.900
0.530	0.0159	1.801
0.425	0.0132	1.668
0.322	0.00858	1.821
0.172	0.00641	1.667
0.074	0.00629	1.395

SOLUBILITY OF COBALT CHLORIDE IN SALT SOLUTIONS

In Table 27 are listed the data on the solubility of cobalt chloride in aqueous solutions of lithium chloride, calcium chloride, and aluminum chloride along with identification of the equilibrium solid phase.

TABLE 27

SOLUBILITY DATA AND CHARACTERIZATION OF SOLID PHASES

$CoCl_2$-H_2O-LiCl System

m_2(LiCl)	m_3($CoCl_2$)	% $CoCl_2$	% $CoCl_2$ in $CoCl_2 \cdot nH_2O$	n
1.341	4.036	49.0	54.6	6
2.539	3.469	51.0	54.6	6
4.125	3.130	52.5	54.6	6
5.554	2.870	54.0	54.6	6
8.070	2.686	53.5	54.6	6
10.370	2.936	75.0	78.3	2
11.175	2.904	76.0	78.3	2
11.986	2.882	78.0	78.3	2

$CoCl_2$-H_2O-$CaCl_2$ System

m_2($CaCl_2$)	m_3($CoCl_2$)	% $CoCl_2$	% $CoCl_2$ in $CoCl_2 \cdot nH_2O$	n
0.185	4.211	59.0	54.6	6
1.372	3.474	53.5	54.6	6
1.944	3.163	55.0	54.6	6
3.469	2.465	53.0	54.6	6
3.864	2.136	53.5	54.6	6
4.065	2.126	56.0	54.6	6
4.687	2.113	56.5	54.6	6
5.533	2.411	76.0	78.3	2
6.689	2.090	76.0	78.3	2
7.742	1.859	76.0	78.3	2

$CoCl_2$-H_2O-$AlCl_3$ System

m_2($AlCl_2$)	m_3($CoCl_2$)	% $CoCl_2$	% $CoCl_2$ in $CoCl_2 \cdot nH_2O$	n
1.168	3.198	51.0	54.6	6
1.459	2.424	55.0	54.6	6
2.229	1.549	54.5	54.6	6
2.688	1.300	56.0	54.6	6

DISCUSSION OF RESULTS

ACCURACY OF MEASUREMENTS

Before discussing the relative activities of water, hydrochloric acid, cobalt chloride and nickel chloride in ternary mixtures or their relation to the extraction of cobalt chloride and nickel chloride from hydrochloric acid solutions into 2-octanol, some estimate of the probable accuracy of the data is in order. One way of doing this would be to compare the results obtained with those found by other investigators for comparable binary systems.

Sulfuric Acid-Water.

It can be seen from Table 1 that the experimental values of the average partial pressure of the water agree within 0.1% with the values of the partial pressure of water over sulfuric acid solutions calculated from the osmotic coefficients of Stokes.[76] The measurements were reproducible with less than 0.1% error.

Hydrochloric Acid-Water.

Figure 8 was constructed by first drawing a smooth curve through the experimental data on the partial pressures of hydrogen chloride obtained in this investigation (designated by circles) and then plotting (squares) the data of the I. C. T. compilation by Zeisberg.[45] In Figure 9 a similar comparison is made of the data obtained for the partial pressure of water above hydrochloric acid solutions with those of Akerlof and Teare[52] and the compilation by Zeisberg.[45] These two figures indicate that in addition to their being reproducible as shown in Table 2, the measurements of both the hydrogen chloride and water partial

FIGURE 8

VAPOR PRESSURE OF HCl IN THE HCl-H_2O SOLUTIONS

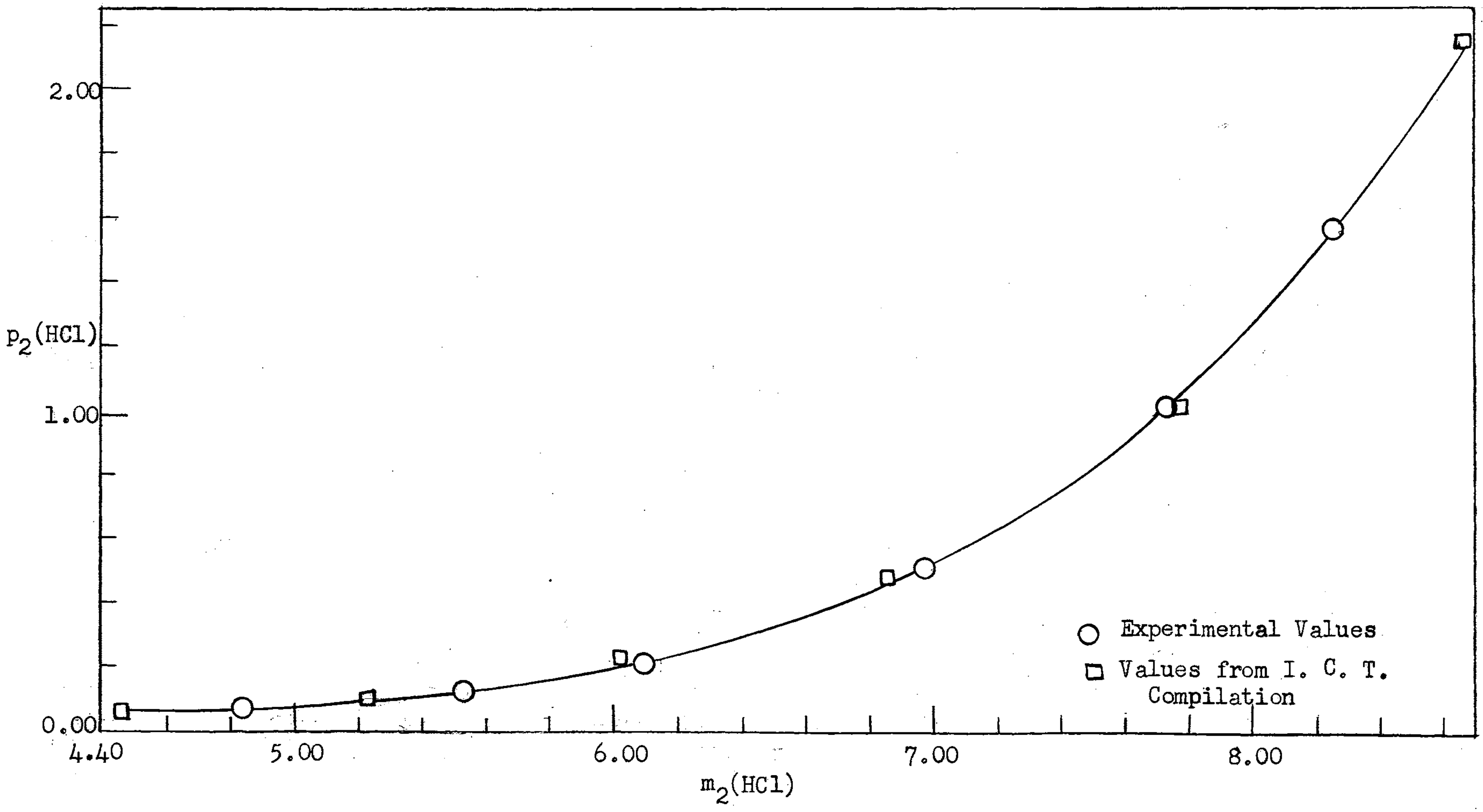
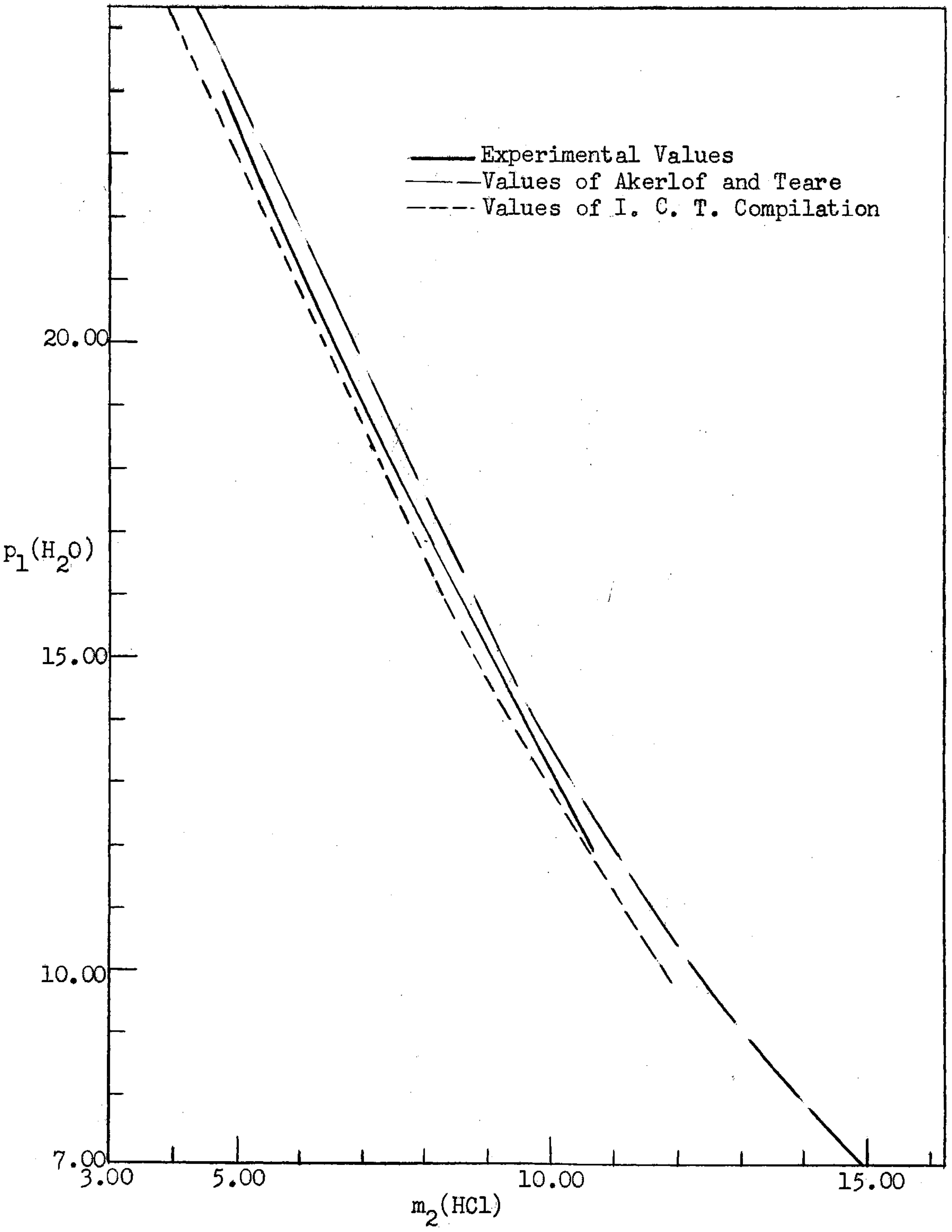


FIGURE 9

VAPOR PRESSURE OF H_2O IN THE $HCl-H_2O$ SOLUTIONS



pressures agree with literature values obtained by several independent methods.

Nickel Chloride-Water

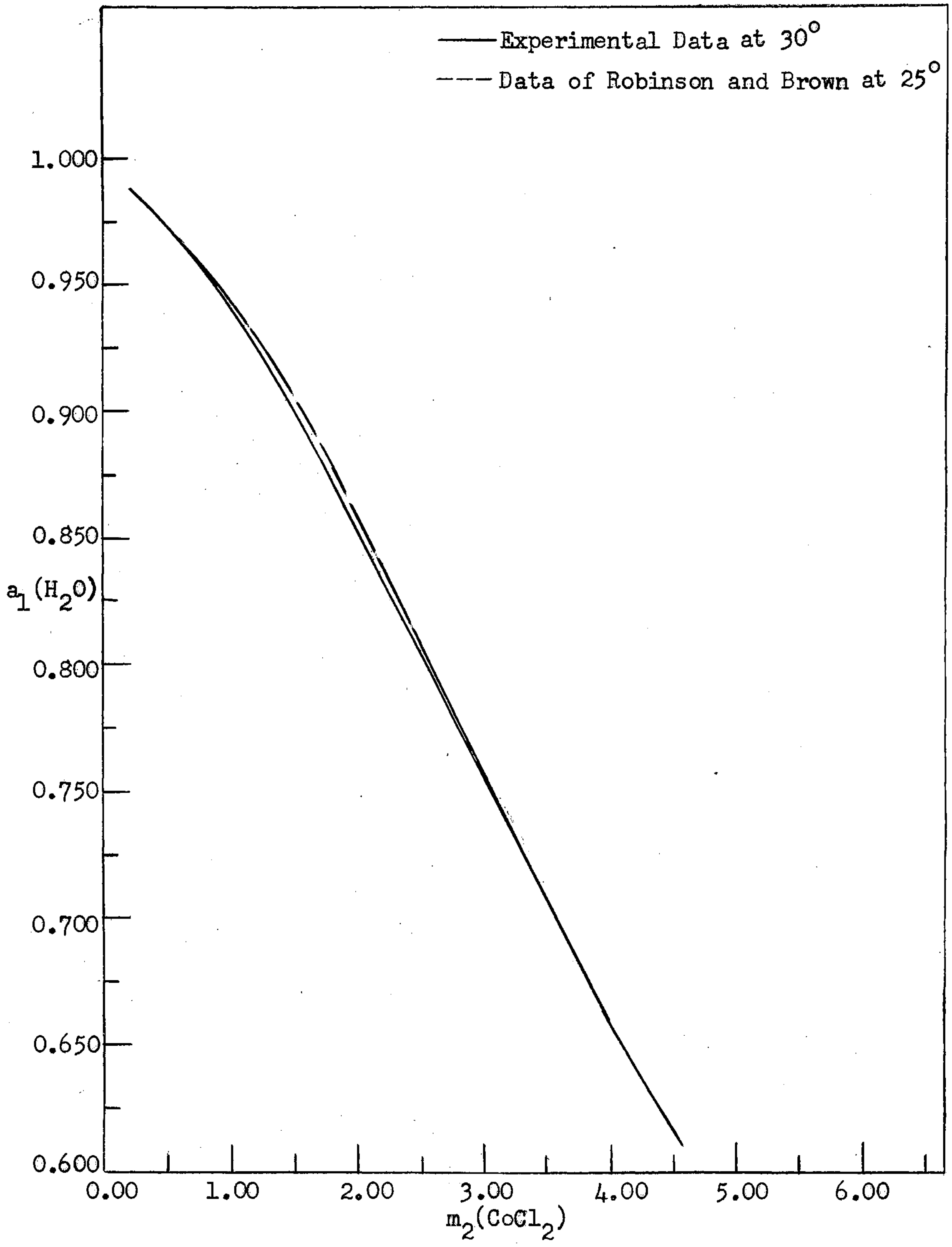
Although no data were available at 30° for the vapor pressure of water over nickel chloride solutions, two investigators had measured this quantity at 25°. A calculation of the effect of temperature on the vapor pressure of water indicated that the change in log $a_{(H_2O)}$ from 25° to 30° should be smaller than the scatter of the experimental measurements and hence imperceptible. Accordingly a plot of log $a_{(H_2O)}$ against salt concentration was made for these data at 30°, the data of Pearce and Eckstrom[57] at 25°, and those of Robinson and Stokes[58] at 25°. The data of Robinson and Stokes were found to lie on the curve drawn through the experimental points while those of Pearce and Eckstrom deviated somewhat from the experimental curve in the range from 1.8 to 3.0 molal. The latter workers had used a gas transpiration method employing electrolytic gas generation whereas Robinson and Stokes had used the isopiestic technique.

Cobalt Chloride-Water.

Figure 10 shows a comparison of the water activities in aqueous solutions of cobalt chloride determined isopiestically at 25° by Robinson and Brown[56] and by the gas transpiration method at 30° in our laboratories. Using the value of $\overline{L}_{(H_2O)}$ calculated for the nickel chloride-water system one again calculates that the water activity over the temperature range from 25° to 30° should not vary appreciably. In agreement with this it can be seen from the figure that within the experimental error ($\pm$ 0.2%) for these measurements, the results from both investigations are almost identical.

FIGURE 10

ACTIVITY OF H_2O IN $CoCl_2$-H_2O MIXTURES AT 25° AND 30°



Hydrochloric Acid-Water-Cobalt Chloride or Nickel Chloride.

Since as stated earlier, no prior investigations have been made of activities in the ternary systems being studied, data were lacking for comparison with the experimentally determined partial pressure. Nonetheless, one can calculate the average error in reproducibility of the data. In Table 28 one sees that in only two cases is the average deviation from the average greater than 1% and in most cases the deviation is less than 0.5%. The accuracy in the HCl molalities is ± 0.01 for the three lower series in the presence of both $NiCl_2$ and $CoCl_2$ and ± 0.1 for the 10 molal series.

TABLE 28

DEVIATIONS IN VAPOR PRESSURE MEASUREMENTS

System	Average Deviation from Average Value in P_{HCl}	Average Deviation from Average Value in P_{H_2O}
4.69 HCl + $NiCl_2$	± 0.76%	± 0.24%
6.86 HCl + $NiCl_2$	± 0.58%	± 0.39%
9.12 HCl + $NiCl_2$	± 0.46%	± 0.35%
10.4 HCl + $NiCl_2$	± 0.17%	± 1.12%
4.84 HCl + $CoCl_2$	± 1.23%	± 0.23%
6.97 HCl + $CoCl_2$	± 0.86%	± 0.31%
8.86 HCl + $CoCl_2$	± 0.31%	± 0.32%
10.65 HCl + $CoCl_2$	± 0.36%	± 0.60%

Solid Phase Analysis.

The solid phase in equilibrium with aqueous cobalt chloride at 30° was found to be the hexahydrate, in agreement with the literature.[83] In the case of aqueous nickel chloride, however, it was found that the hexahydrate was the equilibrium phase at 30° although Boye[84] had reported 28.8° as the transition temperature of the hexahydrate to the tetrahydrate. Repeated experiments gave the same result, and in at least one experiment the solid phase had remained in contact with the solution for a period of three weeks. Derbye and Yngve,[80] who measure the dissociation pressures for the equilibria

$$NiCl_2 \cdot 6H_2O \text{ (c)} \rightleftharpoons NiCl_2\ 4H_2O \text{ (c)} + 2H_2O \text{ (g)} \qquad (30)$$

$$NiCl_2 \cdot 4H_2O \text{ (c)} \rightleftharpoons NiCl_2 \cdot 2H_2O \text{ (c)} + 2H_2O \text{ (g)} \qquad (31)$$

gave 35.25° for the transition temperature of the hexahydrate to the tetrahydrate, which is in agreement with the results of this investigation.

In the ternary systems involving hydrochloric acid, the solid phases were found to be those reported by Seidell.[85]

COMPONENT ACTIVITIES IN TERNARY SYSTEMS

According to the Gibbs-Duhem equation all of the component activities are related to each other and to their concentrations while their magnitudes are determined by the chemical interactions occurring within the system. It is, therefore, impossible to ascribe the variations in any one activity to a single component as is possible in the case of binary systems. In the following discussions apparent relationships are pointed out and an explanation is suggested where a reasonable one seems possible , although not all of the results found appear to have simple explanations. This should not be surprising since in the case of binary salt-water systems the variations in activity of the salt are by no means well understood, expecially in concentrated solutions.

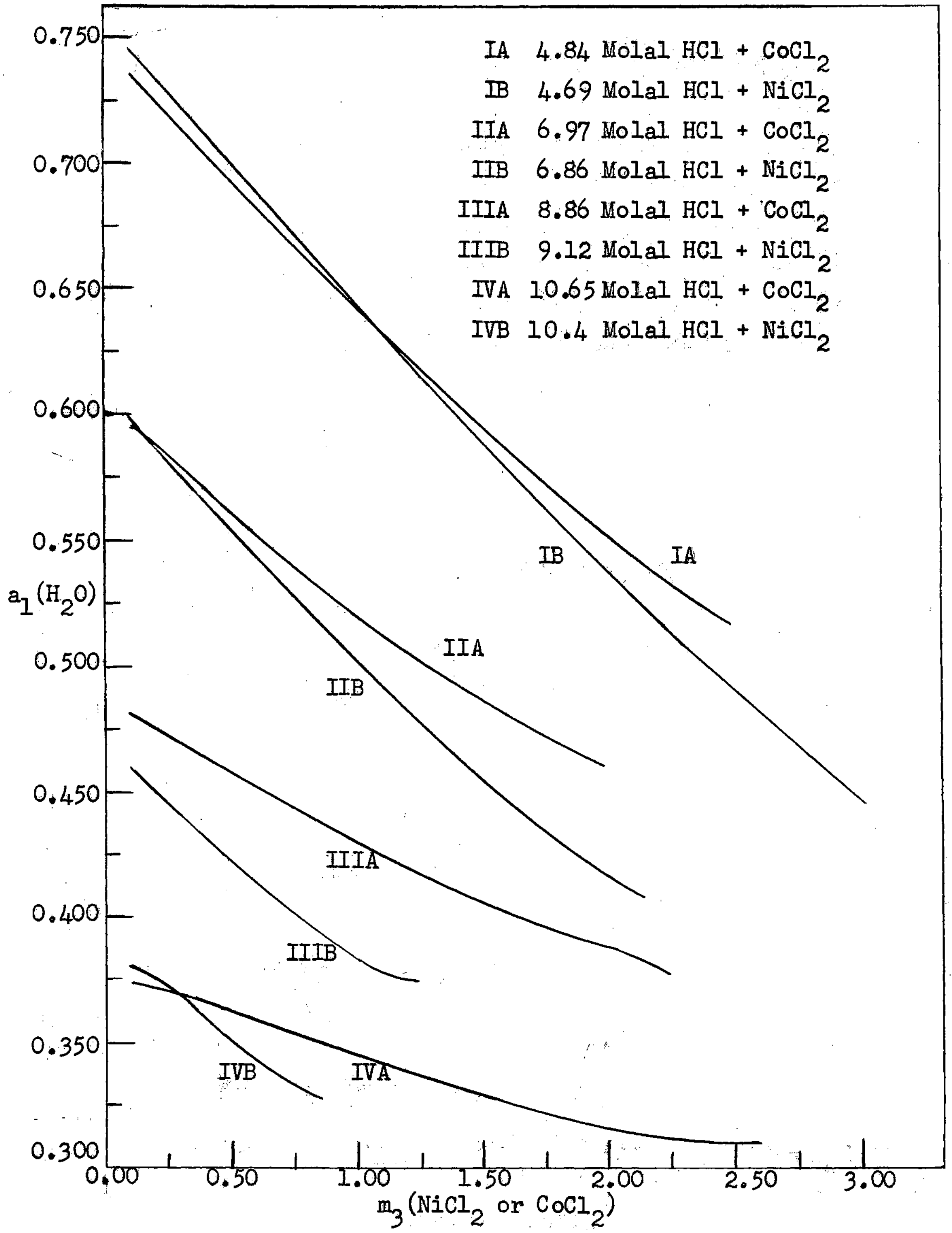
Water.

Qualitatively the effect of the addition of either cobalt chloride or nickel chloride to hydrochloric acid-water mixtures is to decrease the water activity. This decrease can be generally attributed to a removal of 'free' water from the solution by the hydration of the added ions.[86] Examination of the curves (Figure 11) representing the water activity as a function of salt concentration shows the following behaviors of the water activity:

(1) At constant hydrochloric acid concentration the addition of nickel chloride lowers the water activity to a far greater degree than does cobalt chloride at the same salt concentration. This relative effect is in the same direction as that observed in binary solutions of these salts and has been postulated as being due to the more pronounced

FIGURE 11

ACTIVITY OF H_2O IN THE HCl-H_2O-$NiCl_2$ or $CoCl_2$ SYSTEMS



complexing tendency of cobalt chloride compared to nickel chloride.[87,88]

Furthermore, the lowering of the water activity is relatively smaller in concentrated hydrochloric acid solution than in dilute solutions. A leveling off of the curves at the concentrated end of the 9.12 molal hydrochloric acid plot for nickel chloride and of the 10.65 molal hydrochloric acid plot for cobalt chloride can be observed.

(2) At constant salt concentration the addition of hydrochloric acid lowers the water activity, but the amount of lowering is not a sensitive function of the salt concentration and is only slightly less at high salt concentrations than in pure hydrochloric acid.

Hydrochloric Acid.

The addition of cobalt chloride or nickel chloride to hydrochloric acid solutions increases the activity of the hydrochloric acid as shown in Figure 12. It has been generally found that although a minimum may occur in solutions dilute with respect to salt and hydrochloric acid, the acid activity rises rapidly as the salt concentration increases.[7] This behavior has been observed for the systems under investigation by electromotive force measurements.[89] It seems plausible that the addition of salt should result in the tying up of water causing an increase in the effective molality or activity of the acid. The environment of the ions of hydrochloric acid is doubtless altered considerably by the presence of the highly hydratable ions of cobalt or nickel.

Reference to Figure 12 shows that the relative effects of cobalt chloride and nickel chloride differ as follows:

(1) At constant hydrochloric acid concentration the activity of the activity of hydrochloric acid increases much more rapidly with increasing nickel chloride concentration than with cobalt chloride. This

FIGURE 12

ACTIVITY OF HCl IN THE HCl-H_2O $NiCl_2$ or $CoCl_2$ SYSTEMS

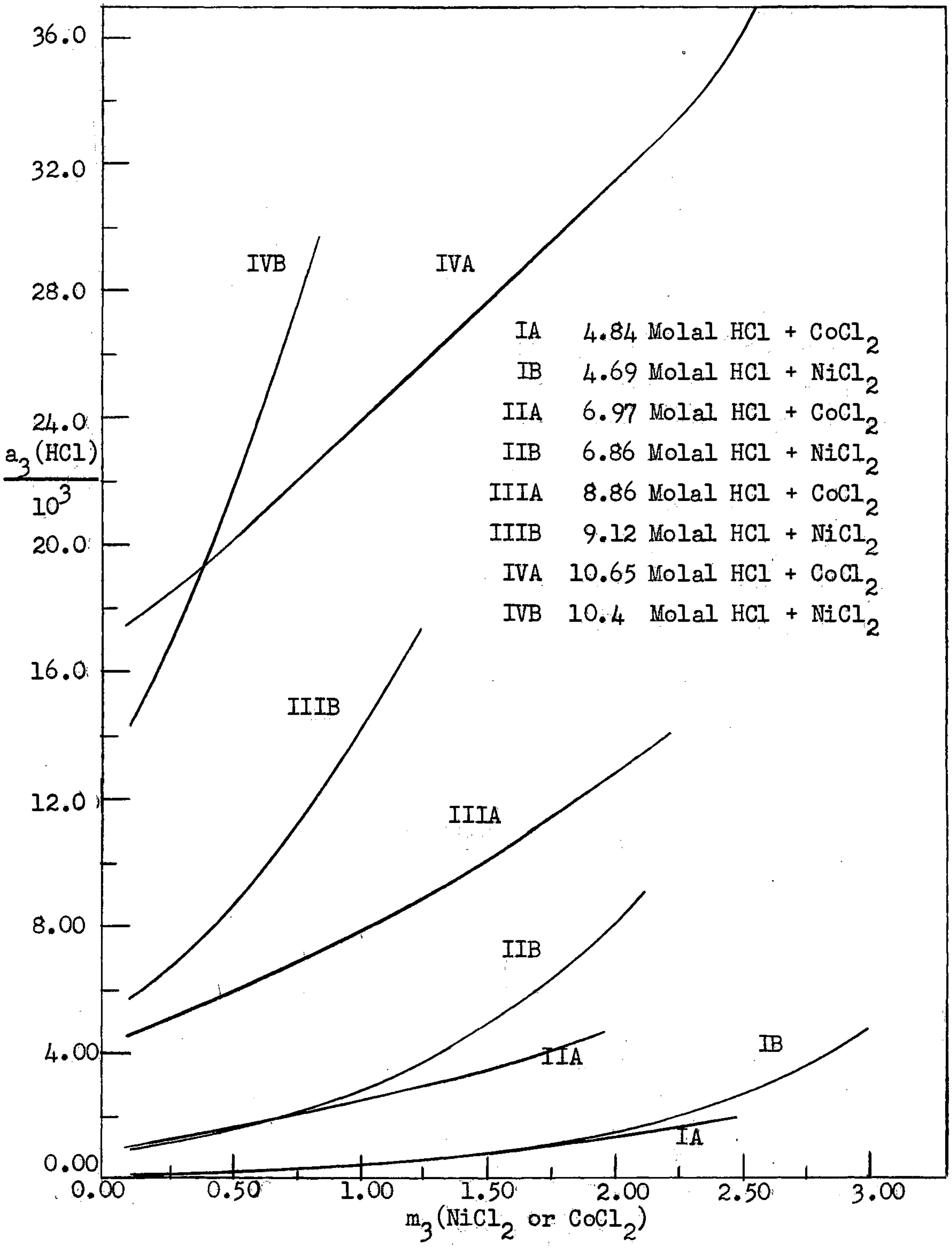
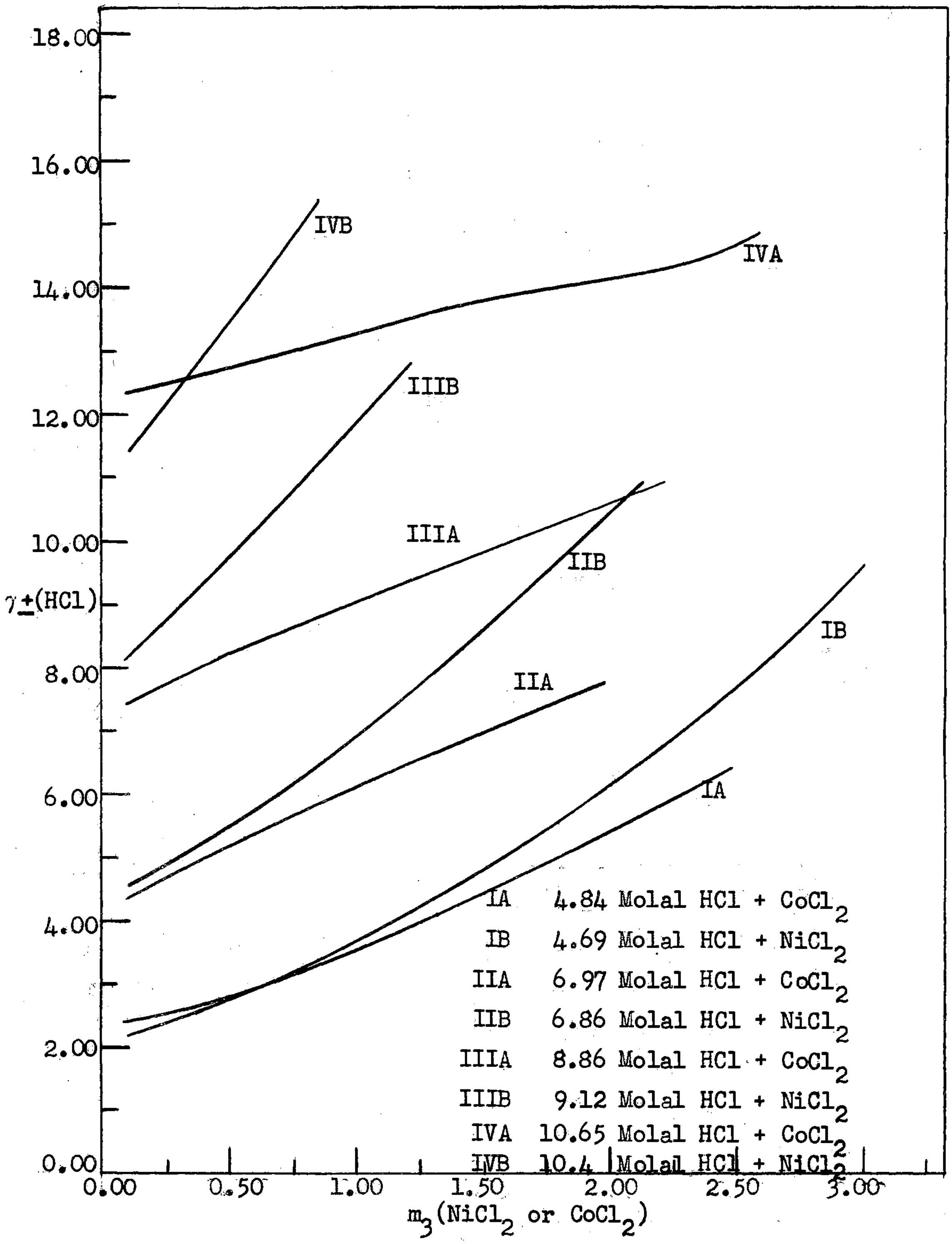


FIGURE 13

ACTIVITY COEFFICIENTS OF HCl IN THE $HCl-H_2O-NiCl_2$ or $CoCl_2$ SYSTEMS



effect is more pronounced in solutions of high hydrochloric acid concentration. The relative effects of cobalt chloride and nickel chloride agree qualitatively with the generalization of Harned and Owen[7] stated earlier '...that at a given ionic strength and acid concentration, the activity coefficient of a strong acid is greater in the solution of a salt, of a given valence type, which in the pure solvent possesses the greater activity coefficient' but does not agree with the results of the measurements of Guereca[89] on these systems.

A relation which has been found to hold in mixtures of strong electrolytes[7] is

$$\log \gamma_A = \log \gamma_{A(o)} + \alpha m_B \tag{32}$$

where γ_A refers to the activity coefficient of electrolyte A in mixtures of ionic strength μ containing electrolyte B at molality m_B, $\gamma_{A(o)}$ is the activity coefficient of electrolyte A alone in aqueous solution at ionic strength μ, and α is a constant at constant μ.

This equation has been verified in many instances for hydrochloric acid in halide solutions at moderate ionic strengths (ca. 6). When the experimental data were substituted into this equation by letting electrolyte A be hydrochloric acid and electrolyte B be the salt several points of interest were found reemphasizing the differences between cobalt chloride and nickel chloride in hydrochloric acid solution. For example, at constant ionic strength (Table 29) the values of α were found to be constant over the range of ionic strengths for which these calculations could be made only for nickel chloride solutions. Harned and Mason[35] had found that $\log \gamma_{\pm(HCl)}$ varied in a linear manner with the hydrochloric acid concentration in the presence of aluminum chloride at low ionic strength ($\mu = 1$), and the results obtained for nickel chloride-

TABLE 29

DATA ON HARNED'S CONSTANT

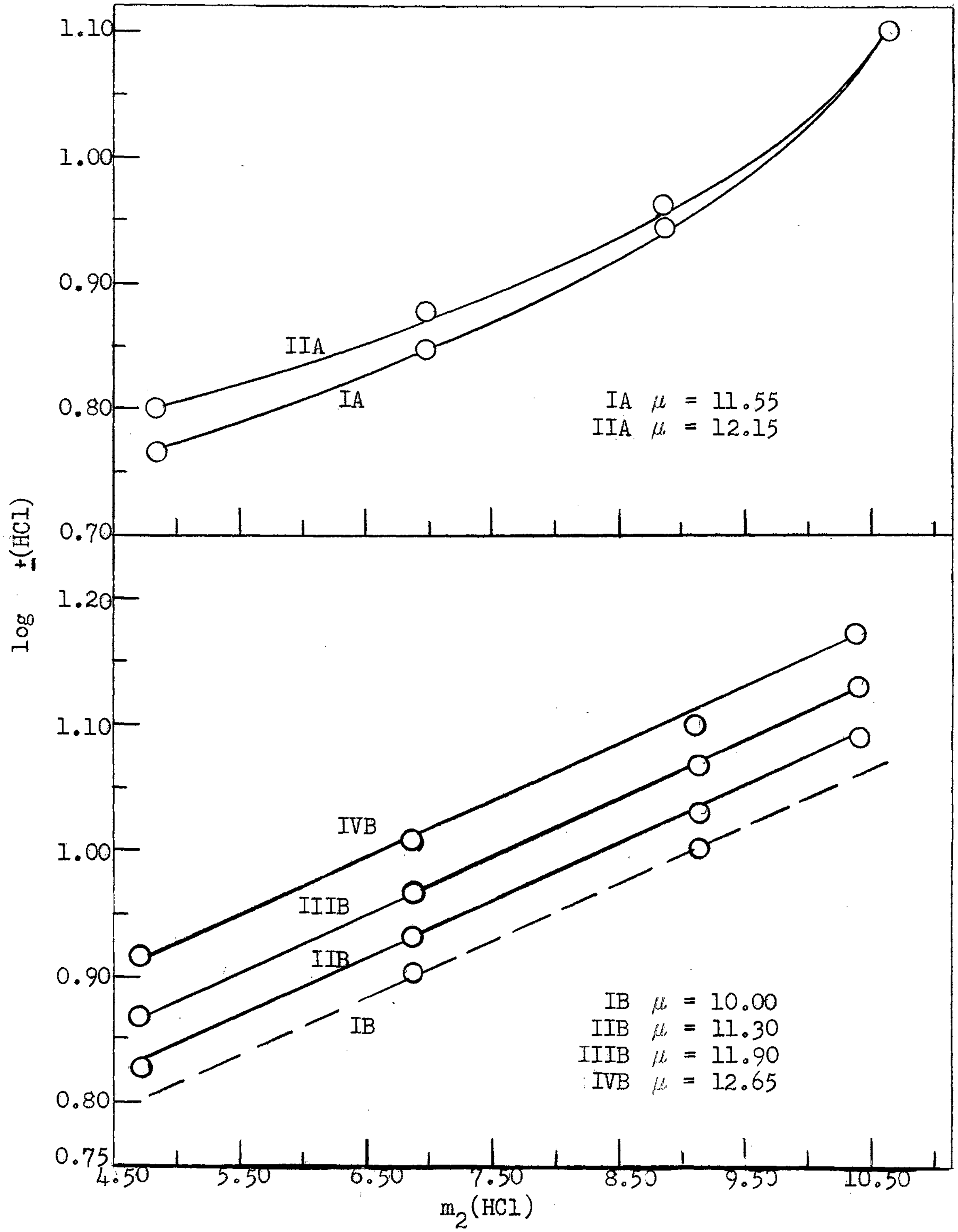
Ionic Strength	m_2(HCl)	m_3($NiCl_2$)	α
11.3	10.4	0.30	0.147
11.3	9.12	0.73	0.148
11.3	6.86	1.48	0.138
11.3	4.69	2.20	0.141
11.9	10.4	0.50	0.139
11.9	9.12	0.93	0.141
11.9	6.86	1.68	0.139
11.9	4.69	2.40	0.138
12.65	10.4	0.75	0.141
12.65	9.12	1.18	0.149
12.65	6.86	1.93	0.140
12.65	4.69	2.65	0.136
Ionic Strength	m_2(HCl)	m_3($CoCl_2$)	
11.55	10.65	0.30	0.222
11.55	8.86	0.90	0.241
11.55	6.97	1.53	0.212
11.55	4.84	2.24	0.177
12.15	10.65	0.50	0.241
12.15	8.86	1.10	0.239
12.15	6.97	1.73	0.206
12.15	4.84	2.44	0.174

hydrochloric acid mixtures (Figure 14) are in agreement with their observations. The lines corresponding to different ionic strengths were parallel. At ionic strength of 1.0 the dotted line is drawn through the only two experimental points available. In the case of cobalt chloride-hydrochloric acid mixtures (Figure 14) a nonlinear relation was found. Because of the solubility limitations this relation could not be tested over a wider range of ionic strengths.

Further examination of the data showed that at constant hydrochloric

FIGURE 14

VARIATION OF LOG $\gamma_{\pm}$(HCl) WITH HCl MOLALITY AT CONSTANT IONIC STRENGTHS



acid concentration and varying salt concentration γ for cobalt chloride-hydrochloric acid mixtures was practically constant at each hydrochloric acid concentration for a range of salt molalities but increased with hydrochloric acid concentration. There appeared to be a slight increase in α with increasing salt concentration. The corresponding data for nickel chloride-hydrochloric acid solutions showed α to be independent of both hydrochloric acid and nickel chloride concentration within experimental error.

Harned's rule is by no means universally applicable to all electrolyte mixtures and would not be expected to hold for a solute such as cobalt chloride which has been shown[88] by independent experimental evidence to complex with hydrochloric acid. By contrast nickel chloride may conform more closely to a relation of this type since its interactions with hydrochloric acid are more likely to be closer to those of a solute like aluminum chloride. Recently Glueckauf, McKay, and Mathieson[25] have investigated the activity of uranyl nitrate in sodium nitrate mixtures by an organic solvent partition technique and report that although the values of log $\gamma_{\pm(UO_2(NO_3)_2)}$ vary linearly with sodium nitrate molality, there are theoretical reasons why log $\gamma_{\pm(NaNO_3)}$ should not be a simple linear function of the uranyl nitrate concentration. It might be remarked that the experimental scatter in their values of α is as great as those found in this investigation.

It was not possible to verify equation (32) for the case where electrolyte A is the salt and electrolyte B the acid since the salt does not exist in aqueous solutions at the ionic strengths of the mixtures and hence log $\gamma_{B(0)}$ has no meaning.

(2) At constant salt concentration reference to Figure 12 shows

that the relative increase in hydrochloric acid activity with hydrochloric acid concentration is greater in solutions of high salt concentration.

Nickel Chloride and Cobalt Chloride

The activity of cobalt or nickel chloride in aqueous hydrochloric acid is obviously determined by the magnitude and variation in the partial pressures of the water and hydrochloric acid as shown by equation

$$\int_{\phi}^{\phi'} \frac{n_1}{n_3} \, d\phi = - \int_{a_3}^{a_3'} d \ln a_3 \qquad (33)$$

where ϕ is given by equation

$$\phi = \ln p_1 + \frac{n_2}{n_1} \ln p_2 \qquad (34)$$

Calculation of the probable error in the final salt activity is exceedingly involved; however, it seems worthwhile to point out the concentration ranges in which the calculation is most reliable.

Considering only the error in ϕ introduced by constant experimental errors Δp_1 and Δp_2 one calculates the approximate percentage error in ϕ as

$$\frac{\Delta\phi}{\phi} = \frac{\Delta p_1}{p_2} \cdot \frac{1}{\phi} + \frac{n_2}{n_1} \left(\frac{\Delta p_2}{p_2} \right) \cdot \frac{1}{\phi} \qquad (35)$$

The factor n_2/n_1 is small in dilute solutions so that the error introduced by errors in p_2 are relatively unimportant compared to errors in p_1. As a matter of fact, the magnitude of the activity of the salt at low acid concentration (< 5 molal) is determined largely by the water partial pressure and in extremely low acid concentration, one would need more precise experimental methods such as the isopiestic technique of Robinson and Sinclair[20] for the water pressures and electromotive force methods for the hydrochloric acid in order to observe the effect of the acid on the salt activity.

Equation (35) shows that the accuracy in determining ϕ is greatest for large values of ϕ. In these experiments the magnitude of ϕ decreased with increasing salt concentration. Since the error in ϕ is inversely related to the values of p_1 and p_2, this error will be the smallest for the largest values of these quantities. The value of p_1 increases with decreasing salt concentration and acid concentration while p_2 increases with increasing acid and salt concentrations.

From equation (33) ln a_3 depends upon the evaluation of the integral in the left member of the equation. Since n_1/n_3 asymptotically approaches infinity, the accuracy in the evaluation of the integral decreases with increasing values of this ratio, i.e., at the lower salt concentrations.

The results obtained in the activity measurements and the calculated values of the activity coefficients for both cobalt chloride and nickel chloride are presented graphically in Figures 15 to 18. It is apparent that the behavior of the activity and activity coefficients of both salts in high and in low hydrochloric acid is markedly different. As before the results can be compared best at constant hydrochloric acid but varying salt concentration and at constant salt but varying acid concentration as follows:

(1) At the two lowest hydrochloric acid concentrations the activities of both salts rise regularly with increasing salt concentration. A striking difference is observed (Figure 15) between the shapes of the curves of the two salts. The activity of the nickel chloride at any salt concentration is higher than that of cobalt chloride at the same salt concentration. These differences become most pronounced at high salt

FIGURE 15

ACTIVITY OF $NiCl_2$ AND $CoCl_2$ IN THE $HCl-H_2O-NiCl_2$ or $CoCl_2$ SYSTEMS

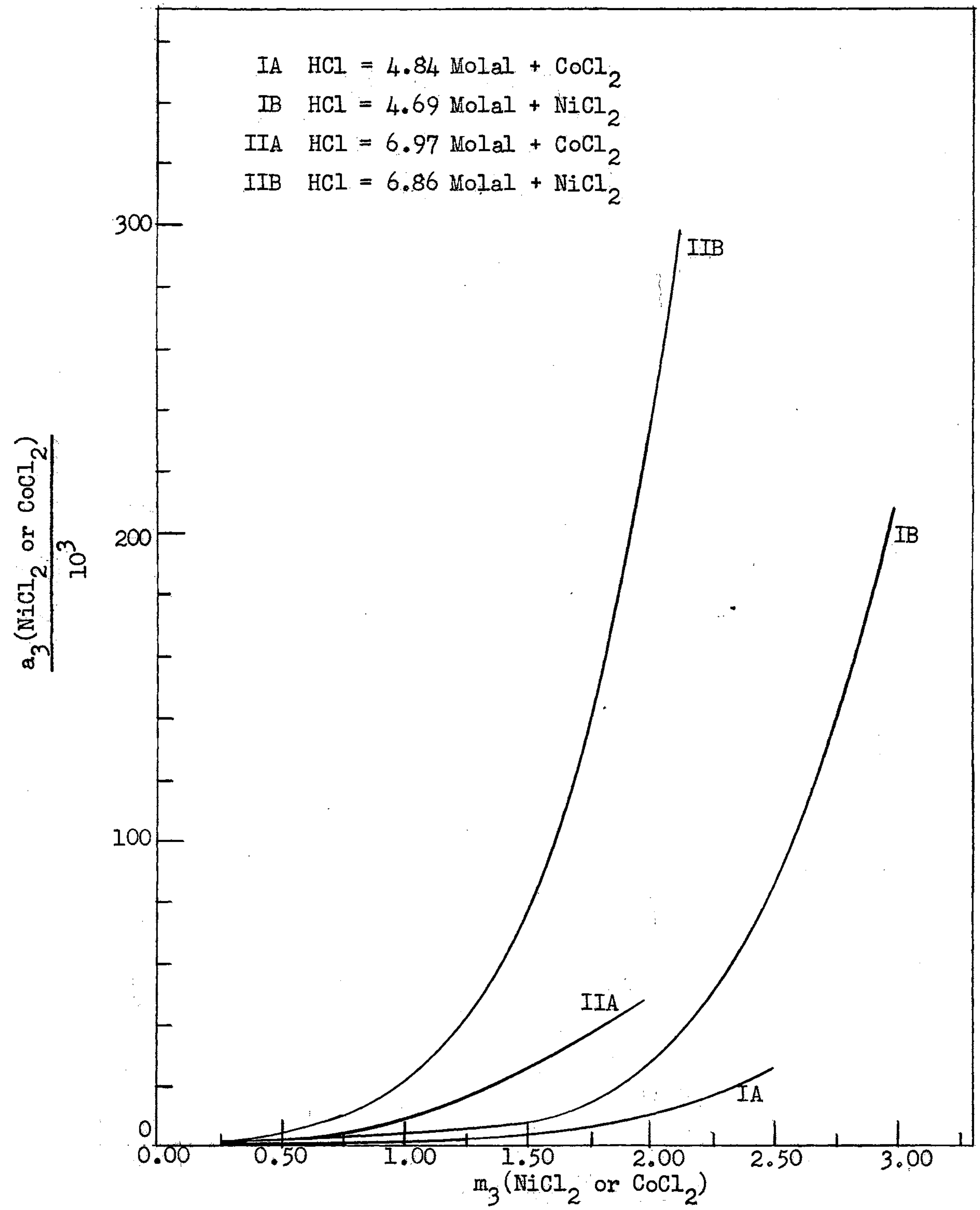


FIGURE 16

ACTIVITY OF $NiCl_2$ AND $CoCl_2$ IN THE $HCl-H_2O-NiCl_2$ or $CoCl_2$ SYSTEMS

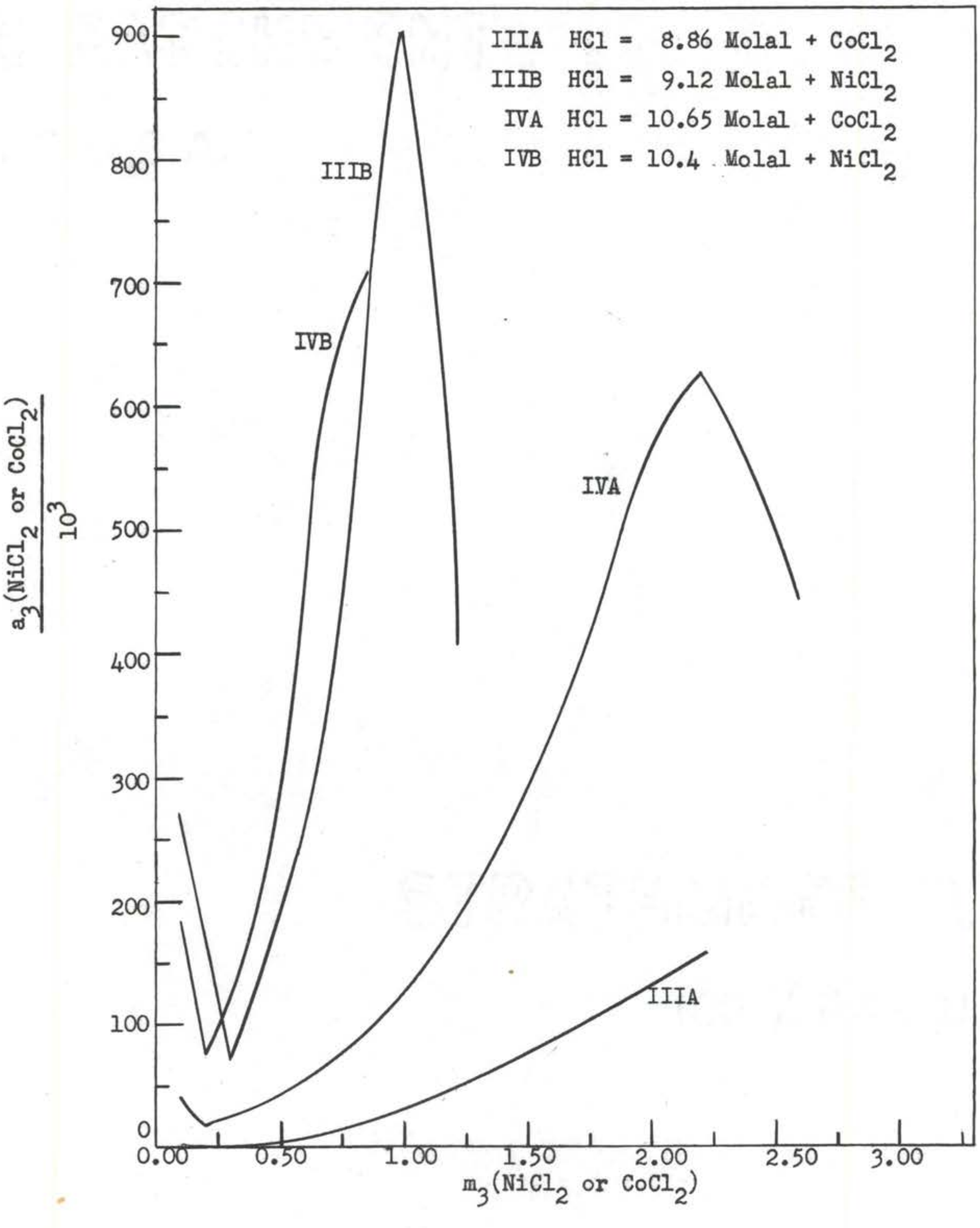


FIGURE 17

ACTIVITY COEFFICIENTS OF $NiCl_2$ IN THE $HCl-H_2O-NiCl_2$ SYSTEMS

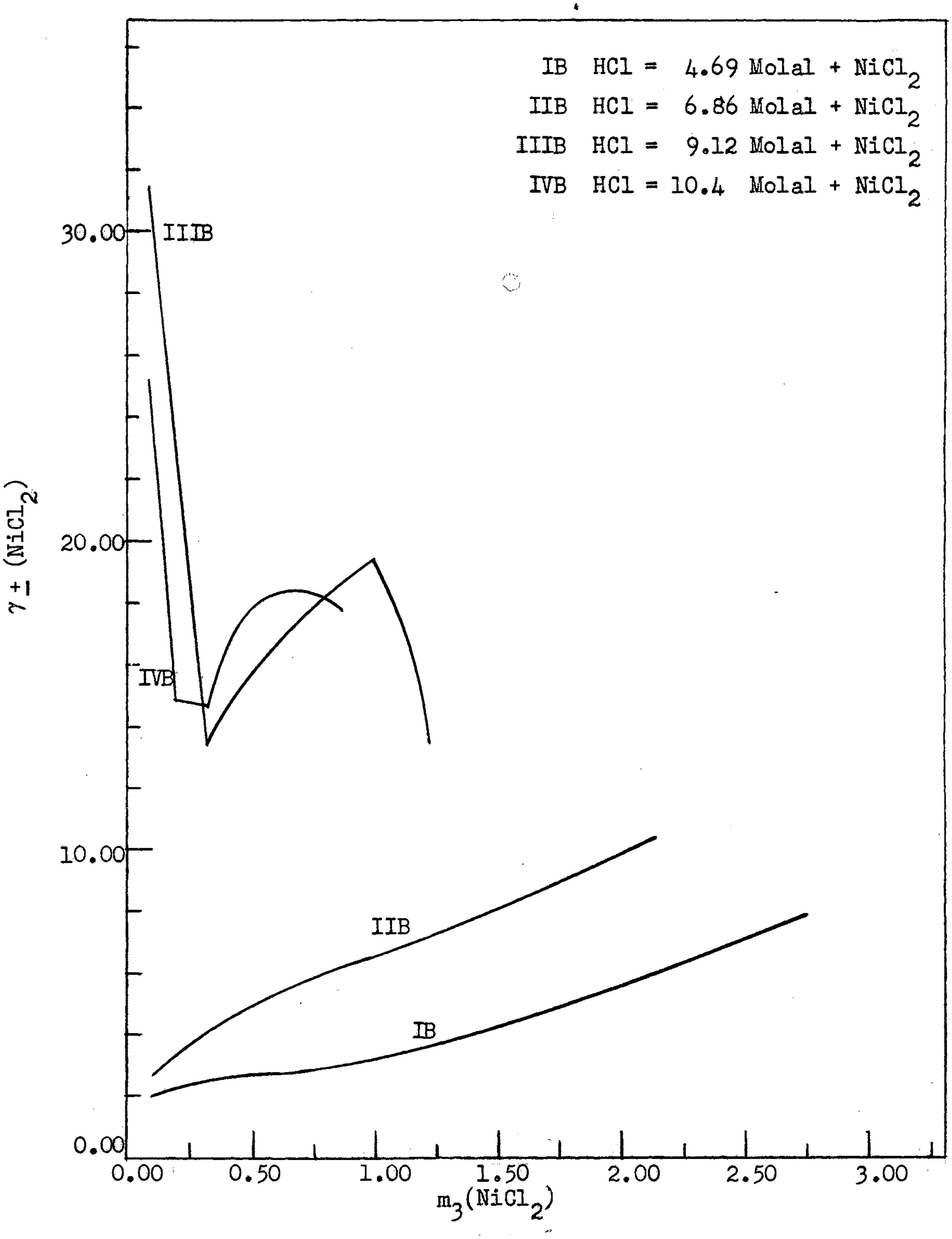
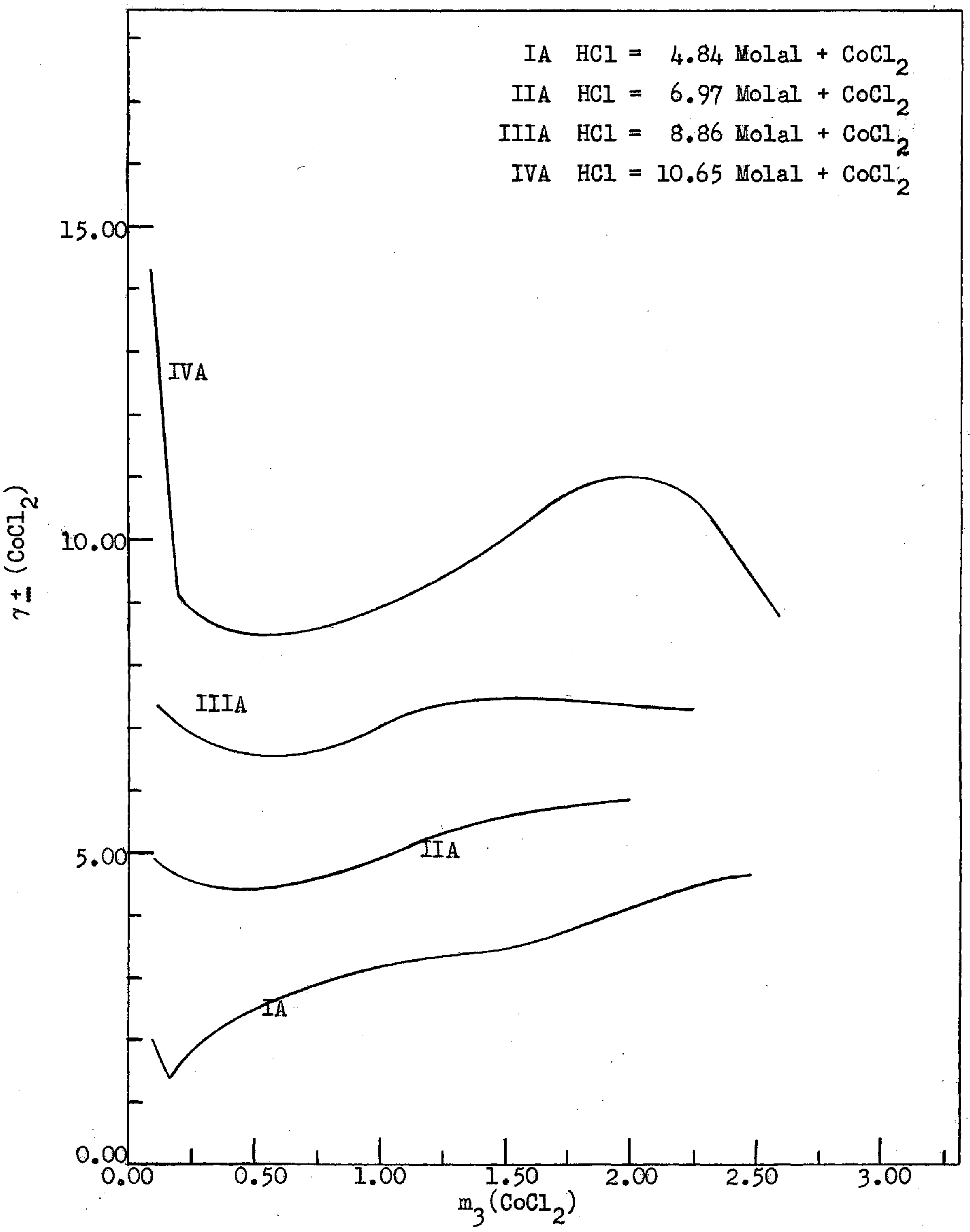


FIGURE 18

ACTIVITY COEFFICIENTS OF $CoCl_2$ IN THE $HCl-H_2O-CoCl_2$ SYSTEMS



molality.

The curves IIIB, IVA, and IVB in Figure 16 show unexpected maxima and minima not found in the curves of the activities at lower acid concentration on curve IVA. There is no reason to doubt the real existence of these changes in slope although no explanation for this behavior is apparent.

The maxima in IVA and IIIB arise from the leveling off of the decrease in water activity in the corresponding solutions (Figure 11) while at the same time the hydrochloric acid activity is rapidly increasing (Figure 12). The minima observed in the low salt region of curves IIIB, IVA, and IVB appear to be beyond experimental error although the steep slope of ϕ plot at these salt concentrations conceivably could introduce a serious error in the integral. It seems significant that only a single point in each curve lies above the minimum.

The corresponding activity coefficient curves for nickel chloride (Figure 17) and cobalt chloride (Figure 18) show the same irregularities and relations already mentioned above.

(2) At constant salt concentrations (Figures 19 and 20) both salts have sharply rising activities with increasing hydrochloric acid concentration although in the case of nickel chloride the activity does not change greatly until the hydrochloric acid concentration is about 7 molal.

In summarizing the variations in the activities of each of the components in the several ternary mixtures studied, no chemical explanation of the detailed features of the activity curves can be given by the author. In a general way the effect of stronger interaction between cobalt chloride and hydrochloric acid than between nickel chloride and hydrochloric acid causes a relatively smaller increase in both

FIGURE 19

ACTIVITY OF $NiCl_2$ IN THE $HCl-H_2O-NiCl_2$ SYSTEMS
AT CONSTANT $NiCl_2$ CONCENTRATIONS

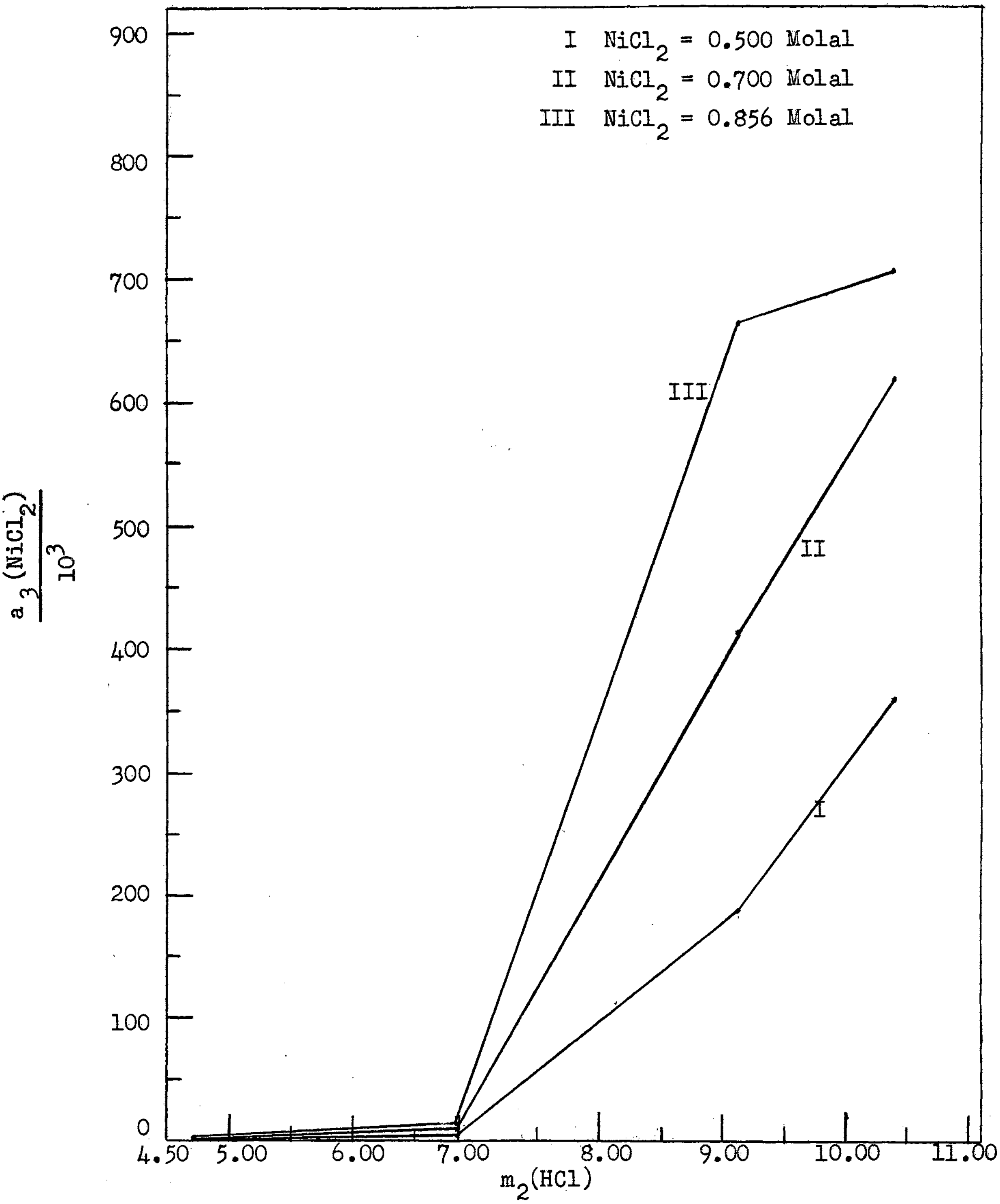
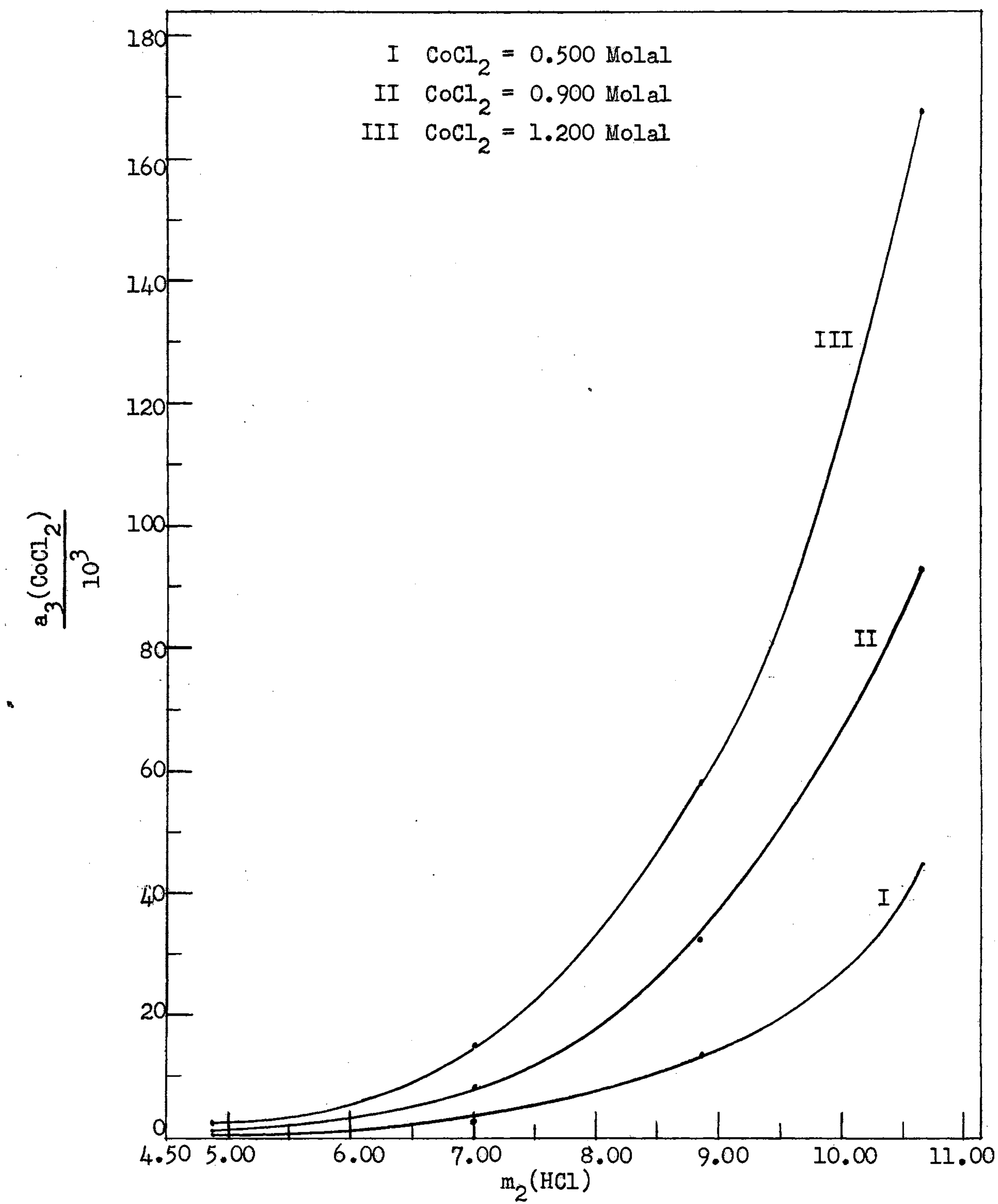


FIGURE 20

ACTIVITY OF $CoCl_2$ IN THE HCl-H_2O-$COCl_2$ SYSTEMS
AT CONSTANT $CoCl_2$ CONCENTRATIONS



hydrochloric acid and salt activity and a smaller decrease in the water activity.

EXTRACTION STUDIES

Efforts to correlate the extraction of cobalt chloride and nickel chloride from aqueous hydrochloric acid solutions by 2-octanol with their activities in the aqueous phase resulted in a failure to find a direct correlation. In fact the extraction of cobalt chloride from 7 molal hydrochloric acid solutions exceeded that of nickel chloride (Figures 21 and 22) even though the activity of the nickel chloride was the higher. Such a result does not seem surprising in view of the more extensive complexing of cobalt chloride by other chlorides in octanol compared to nickel chloride.[87,88]

Attempts to study this extraction at higher acid concentration resulted in a chemical attack of the octanol by the hydrochloric acid. A probably reaction is

$$ROH + HCl \rightleftharpoons RCl + HOH \qquad (36)$$

From the distribution data and the activity data numbers proportional to the activity coefficients of both salts and hydrochloric acid were calculated for the octanol solutions.

The equations employed in making these computations were

$$a_{(\text{salt in water})} = k \cdot m_{(\text{salt in octanol})} \qquad (37)$$

$$a_{(\text{HCl in water})} = k' \cdot m_{(\text{HCl in octanol})} \qquad (38)$$

It was necessary to assume negligible mutual solubility of the two solvents although in reality this assumption is not entirely valid. McKay[37] has discussed how to correct for the effects due to the mutual solubility of the solvents. It should be pointed out that the

FIGURE 21

EXTRACTION OF $CoCl_2$ INTO 2-OCTANOL FROM 6.97 MOLAL HCl

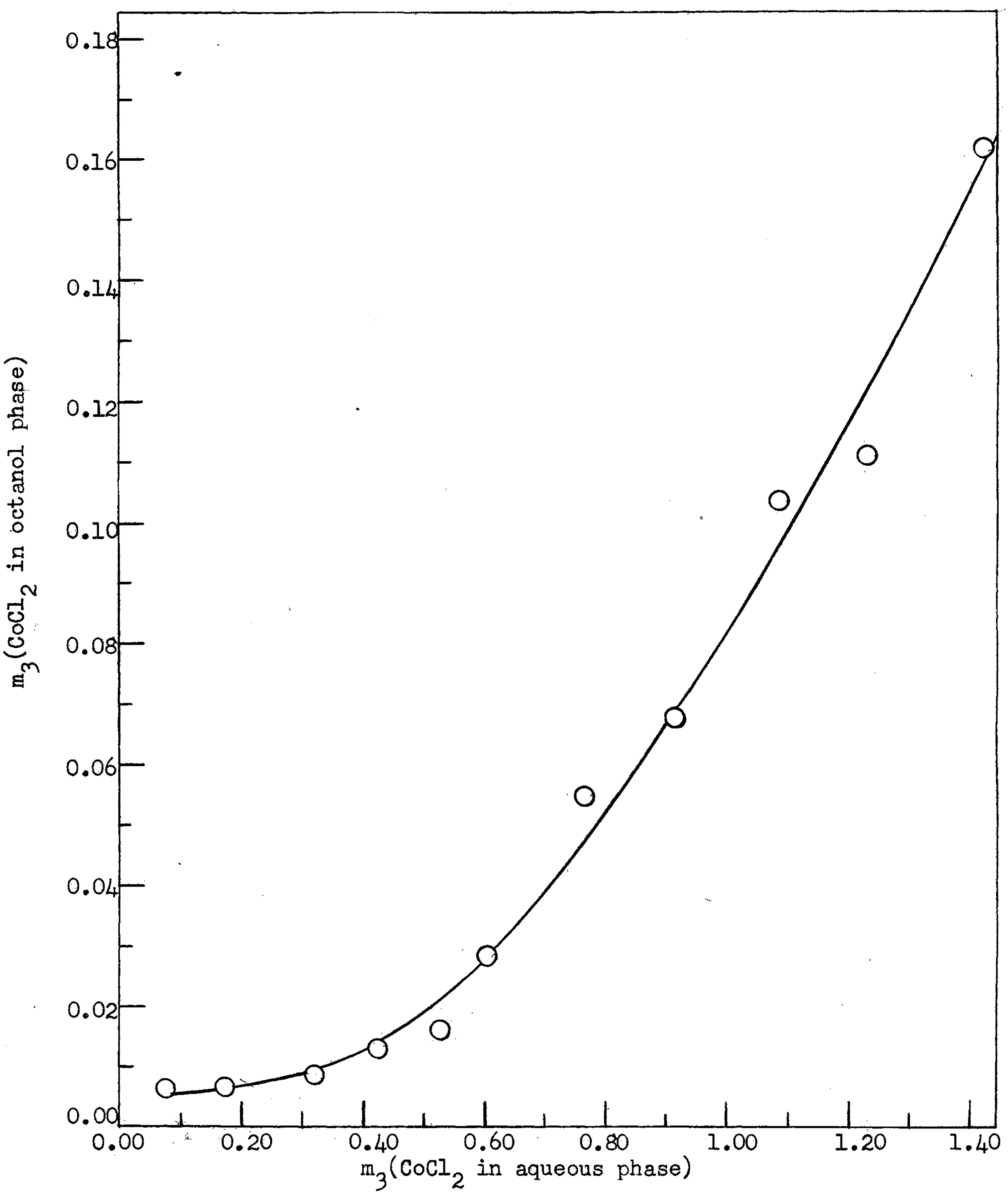


FIGURE 22

EXTRACTION OF $NiCl_2$ INTO 2-OCTANOL FROM 6.86 MOLAL HCl

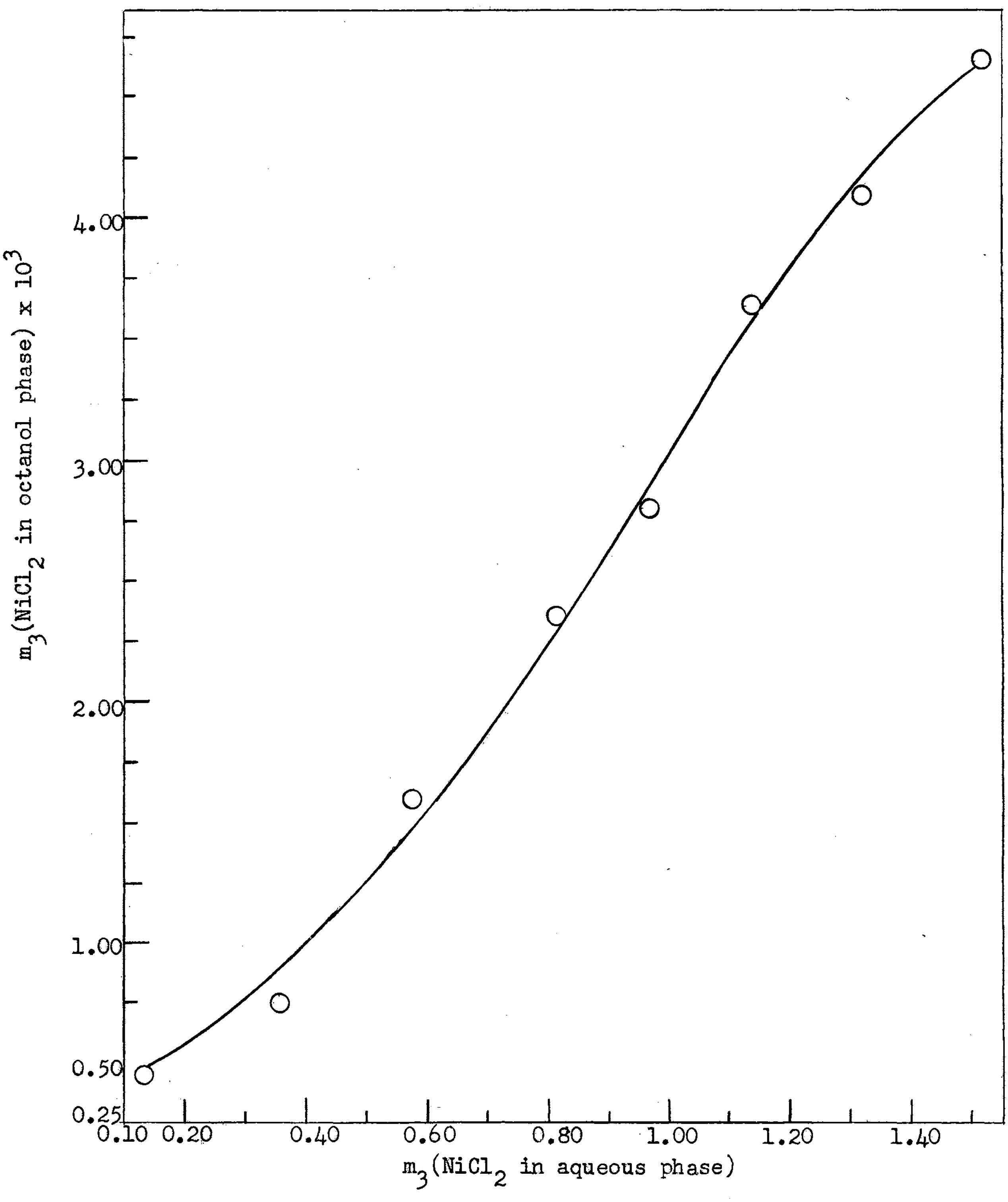


FIGURE 23

EXTRACTION OF HCl INTO 2-OCTANOL FROM 6.97 MOLAL HCl IN THE PRESENCE OF $CoCl_2$

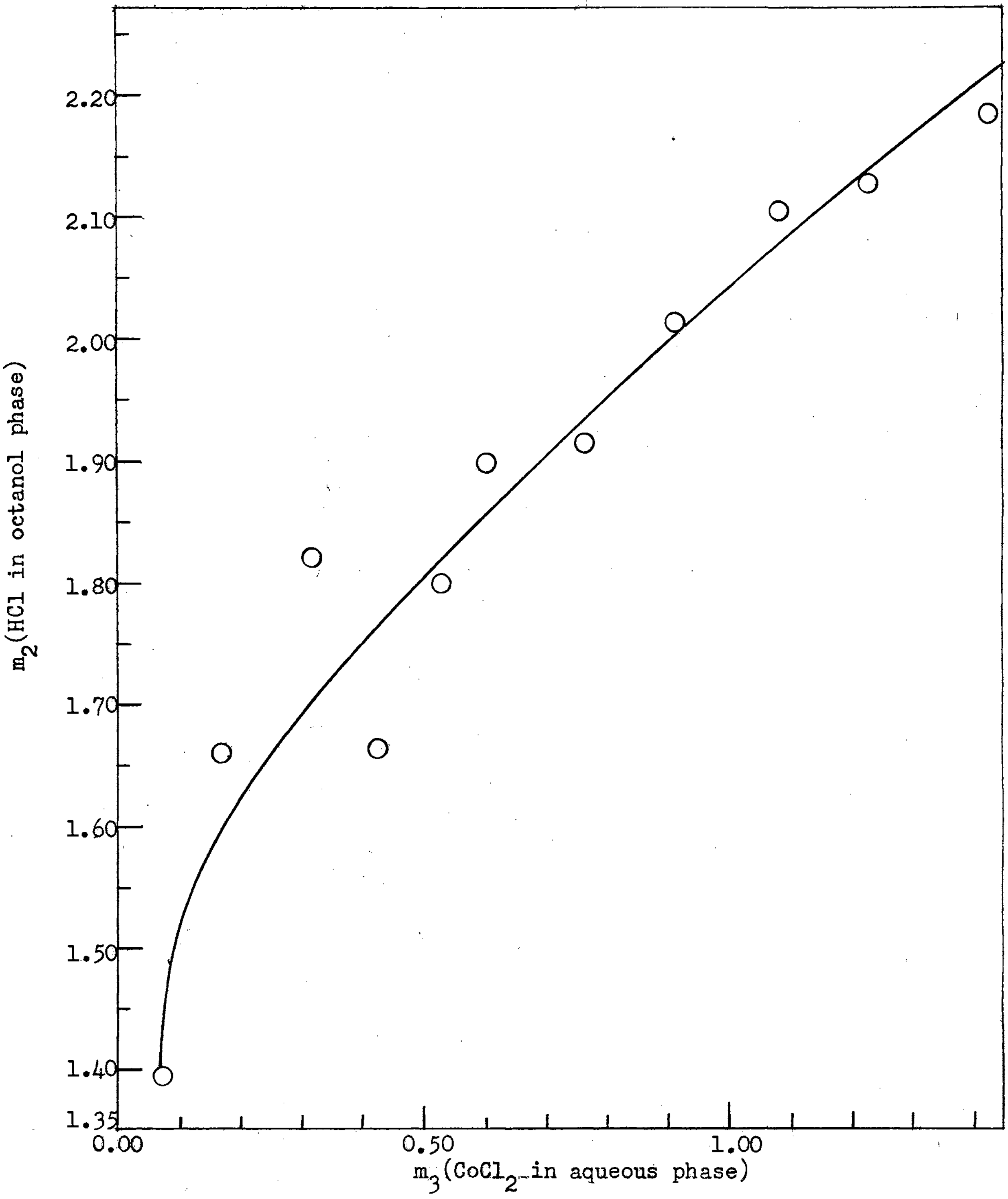
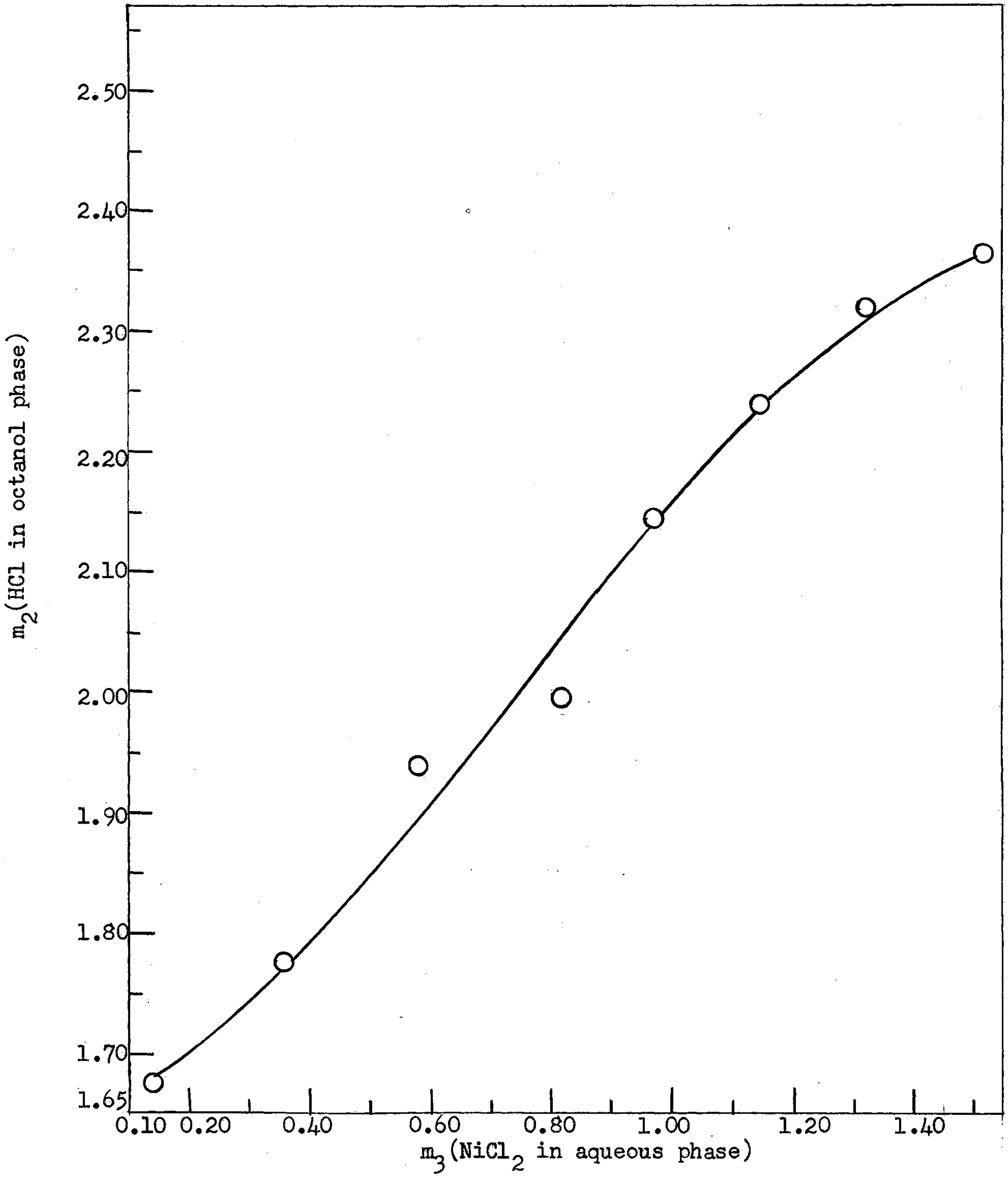


FIGURE 24

EXTRACTION OF HCl INTO 2-OCTANOL FROM 6.86 MOLAL HCl IN THE PRESENCE OF $NiCl_2$



proportionality factors in equation (37) are different for cobalt chloride and nickel chloride because of the difference in the standard reference states of the solutes.

Figures 25 and 26 show the results of such calculations. The observed slower increase in the amount of hydrochloric acid extracted compared to the increase in the aqueous phase hydrochloric acid activity can be attributed to a rising activity coefficient of hydrochloric acid in octanol with increasing salt concentration. The minimum found for the cobalt chloride activity in the octanol phase has been observed in the case of other readily extractible salts in octanol such as nickel perchlorate or zinc chloride. Nachtrieb and Fryxell[26] in the only other study of the activity of a transition metal halide in concentrated hydrochloric acid concluded that 'the abnormal extraction of ferric chloride by isopropyl ether is the result of low activity coefficients in the ether phase.' It seems that good extractibility can generally be correlated with low activity coefficients in the nonaqueous phase.

FIGURE 25

ACTIVITY COEFFICIENTS OF HCl IN THE 2-OCTANOL PHASE

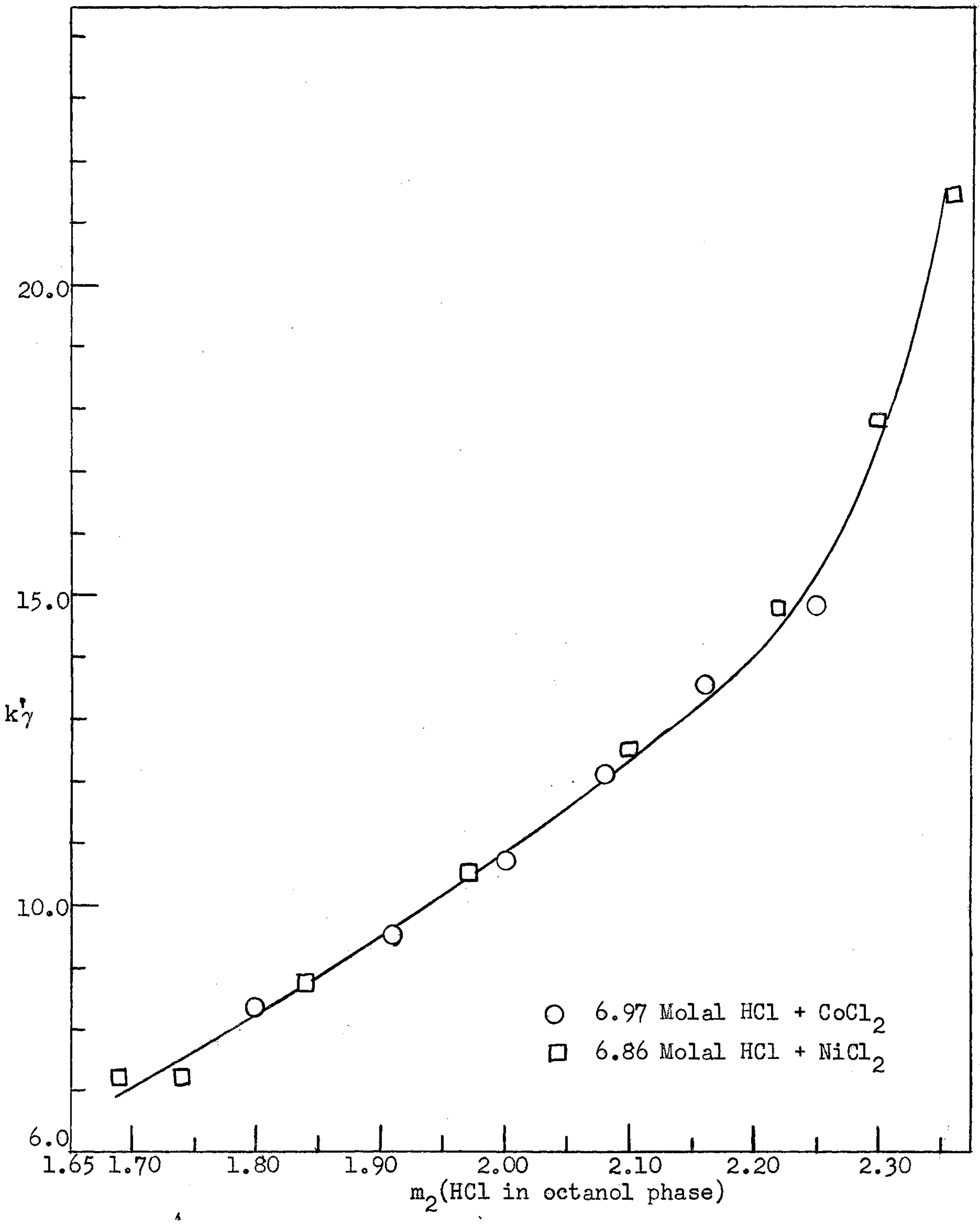
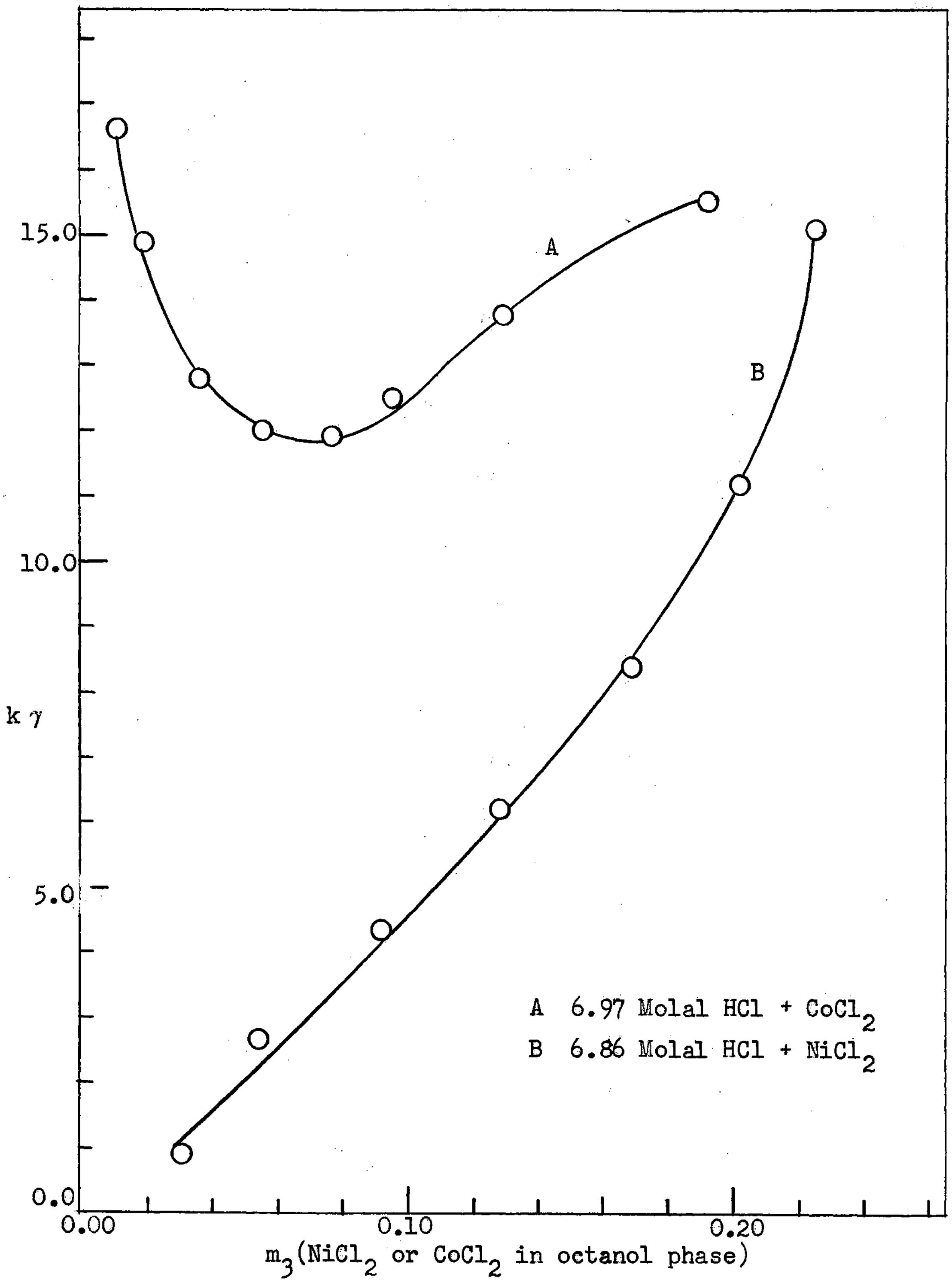


FIGURE 26

ACTIVITY COEFFICIENTS OF $NiCl_2$ AND $CoCl_2$ IN THE 2-OCTANOL PHASE



SOLUBILITY STUDIES

If one considers the equilibrium in saturated solutions of cobalt chloride containing other salts in which the same hydrate is the equilibrium solid phase, one has the following relation for the chemical potentials

$$\overline{F}(\mathrm{CoCl_2 \text{ in solution}}) + n\overline{F}(\text{water in solution}) = \overline{F}(\mathrm{CoCl_2 \cdot nH_2O}) \quad (39)$$

This shows that the activities of cobalt chloride in such solutions are related to the partial pressures of water in the solution by

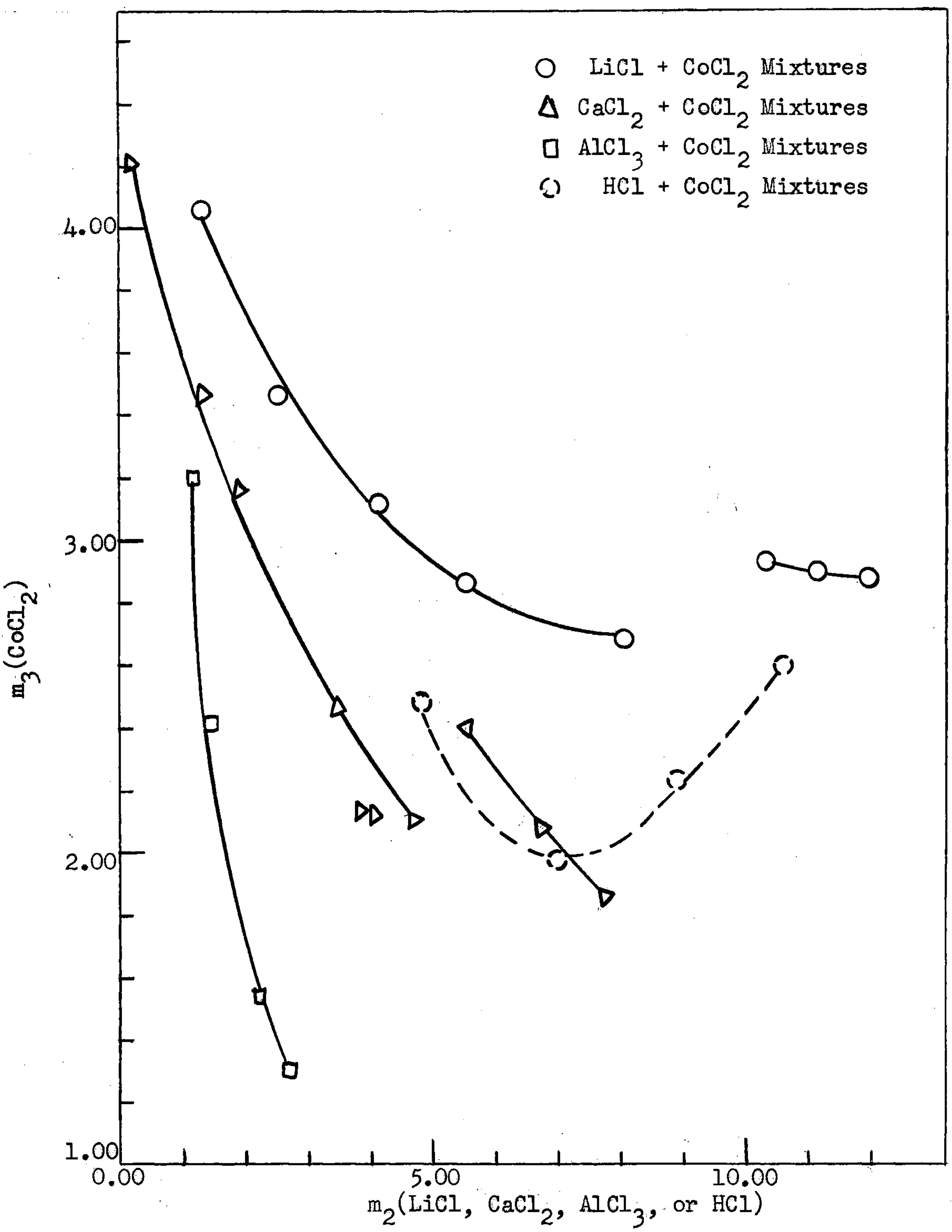
$$\log \frac{a}{a'} = n \log \frac{p'}{p} \quad (40)$$

where the a's are cobalt chloride activities in the saturated solutions and the p's are the water vapor pressures. The primed and unprimed terms refer to two different solutions in equilibrium with the same hydrate.

The solubility of cobalt chloride in solutions containing lithium chloride, calcium chloride, or aluminum chloride has been determined over a range of concentrations of these salts (Figure 27). Since no values of the water vapor pressure have been determined as yet, the relative activities cannot be ascertained.

FIGURE 27

SOLUBILITY OF $CoCl_2$ IN THE PRESENCE OF OTHER CHLORIDES



SUMMARY

By means of a comparative gas-transpiration apparatus the partial pressures of the two volatile components hydrochloric acid and water in ternary mixtures of hydrochloric acid-water-nickel or cobalt chloride were measured at 30°. The salt concentration was varied from 0.1 molal to saturation at several constant but different hydrochloric acid molalities. In the case of cobalt chloride the hydrochloric acid molalities in the four series were 4.84, 6.97, 8.86, 10.65 whereas in the nickel chloride solutions the hydrochloric acid molalities were 4.69, 6.86, 9.12, and 10.4.

In addition to a calculation of the activities of hydrochloric acid and water from their partial pressures, the activity of the third component, nickel chloride or cobalt chloride, was calculated by an integration of the Gibbs-Duhem equation. The salt activities at different hydrochloric acid molalities were related through the activity of the equilibrium solid phases. Solubility studies in the systems water-cobalt chloride and lithium chloride, calcium chloride, or aluminum chloride were carried out over a range of promoting salt concentrations.

From the results of the activity determinations the extraction experiments, and the solubility studies, it was found that:

(1) The partial pressures of hydrochloric acid and water in the binary system hydrochloric acid-water agree within 1.0% with the accepted literature values. In the aqueous binary systems of nickel chloride and cobalt chloride, the water activities agreed with those calculated from

literature values at 25°.

(2) The composition of the solid phases in equilibrium with solutions of nickel chloride and cobalt chloride, both in the presence and absence of hydrochloric acid, were determined and the results agreed in general with those reported for these solutions; viz.,

(a) The solid hydrate in equilibrium with cobalt chloride in solutions of 4.84, 6.97, and 8.86 molal hydrochloric acid in each case was the hexahydrate whereas the dihydrate was the equilibrium solid phase for the 10.65 molal hydrochloric acid solutions.

(b) The tetrahydrate was the solid phase in equilibrium with all hydrochloric acid-nickel chloride saturated solutions studied.

(c) In the aqueous binary systems the hexahydrates were the equilibrium solid phases.

(3) Although the extraction of cobalt chloride into 2-octanol from aqueous hydrochloric acid solutions far exceeded that of nickel chloride the activity of nickel chloride in aqueous hydrochloric solutions was greater than that of cobalt chloride in corresponding solutions.

(4) In general the salt activity increased with either increasing salt concentration or increasing hydrochloric acid concentration. However at 9.12 molal hydrochloric acid in the presence of nickel chloride and at 10.65 molal hydrochloric acid in the presence of cobalt chloride maxima were observed in the activity function.

(5) The activity coefficient of cobalt chloride in the octanol phase in equilibrium with 6.97 molal aqueous hydrochloric acid solutions of cobalt chloride went through a minimum on increasing octanol-phase salt concentration. By contrast the activity coefficient of nickel chloride in the octanol phase in equilibrium with 6.86 molal hydrochloric

acid solutions of nickel chloride steadily increased with increasing nickel chloride concentration.

(6) The addition of nickel chloride to the hydrochloric acid solutions both lowered the water activity and raised the hydrochloric acid activity to a greater extent than did cobalt chloride. Although the hydrochloric acid activities in the case of nickel chloride were found to obey Harned's rule, in the case of cobalt chloride solutions this rule was not followed.

(7) The solubility of cobalt chloride in the presence of varying concentrations of lithium chloride, cobalt chloride, or aluminum chloride was measured at 30°. It was found that in solutions having the same molality of a second electrolyte such as lithium chloride, cobalt chloride, or aluminum chloride the solubility of cobalt chloride was least in solutions of the salt of the highest charge type and greatest in the solution of the lowest.

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VITA

Ernest Allen Gootman
candidate for the degree of
Doctor of Philosophy

Thesis: DETERMINATION OF ACTIVITIES IN HYDROCHLORIC ACID-WATER-NICKEL CHLORIDE OR COBALT CHLORIDE MIXTURES

Major: Inorganic Chemistry

Biographical and Other Items:

Born: May 9, 1929, at Chelsea, Massachusetts

Undergraduate Study: Worcester Polytechnic Institute, 1946-1947; University of Miami, 1947-1949

Graduate Study: University of Miami, 1949-1951; O. A. M. C., 1951-53

Experiences: Graduate Assistant, University of Miami, 1949-1951; Research Fellow, O. A. M. C., 1951-53

Member of American Chemical Society, Phi Lambda Upsilon, and Associate Member of The Society of Sigma Xi.

Date of Final Examination: July, 1953.

THESIS TITLE: DETERMINATION OF ACTIVITIES IN HYDROCHLORIC ACID-WATER-NICKEL CHLORIDE OR COBALT CHLORIDE MIXTURES

AUTHOR: ERNEST ALLEN GOOTMAN

THESIS ADVISER: Dr. Thomas E. Moore

TYPIST: Louise Gardels