

A REINVESTIGATION OF THE ACTIVITY OF
HYDROCHLORIC ACID IN THE SYSTEMS:
HYDROCHLORIC ACID-WATER-COBALT CHLORIDE
OR NICKEL CHLORIDE

By

FRANK P. DYER

Bachelor of Science

Oklahoma A. and M. College

Stillwater, Oklahoma

1953

Submitted to the Faculty of the Graduate School of
the Oklahoma Agricultural and Mechanical College
in partial fulfillment of the requirements
for the degree of
MASTER OF SCIENCE
June, 1955

OKLAHOMA
CENTRAL & MECHANICAL COLLEGE
LIBRARY
AUG 9 1955

A REINVESTIGATION OF THE ACTIVITY OF
HYDROCHLORIC ACID IN THE SYSTEMS:
HYDROCHLORIC ACID-WATER-COBALT CHLORIDE
OR NICKEL CHLORIDE

Thesis Approved:

Tom E. Moore

Thesis Adviser

Earl H. Gibmore

Robert Mawhin

Dean of the Graduate School

ACKNOWLEDGEMENT

The author shall always be indebted to Dr. Thomas E. Moore whose patient guidance throughout the course of this research has been of inestimable value.

Also the author is very grateful to Dr. Earl H. Gilmore for his considerate advice and helpful hints.

The help and inspiration given by the graduate students during the investigation is greatly appreciated.

The Research Foundation is sincerely thanked for the financial aid given in the form of a fellowship under the Air Force Contract No. A.F. 18(600)478.

TABLE OF CONTENTS

	Page
I. INTRODUCTION.	1
Purpose, Background and Scope of Problem.	1
Means of Determination of Activity.	5
Solvent Extraction	5
E.M.F. Measurements.	6
Literature Survey	10
Solvent Extraction	10
E.M.F. Measurements.	10
II. EXPERIMENTAL.	12
SOLVENT EXTRACTION.	12
Equilibration and Apparatus.	12
Analysis and Apparatus	13
A Typical Experiment	13
E.M.F. MEASUREMENTS	15
Bridge Circuit	15
Temperature Control.	15
Cells Employed	16
Preparation of Solutions	16
Electrodes	20
Hydrogen Electrode	20
Silver-Silver Chloride Electrode	21
A Typical Experiment	22

Chemicals	23
III. EXPERIMENTAL RESULTS	24
Preliminary Test	24
Solvent Extraction	24
E.M.F. Measurements	24
Tables	25
The System $\text{CoCl}_2\text{-H}_2\text{O-HCl}$	25
The System $\text{NiCl}_2\text{-H}_2\text{O-HCl}$	31
Graphs	37
IV. DISCUSSION OF RESULTS	41
Solvent Extraction	41
Comments about Results	41
Difficulties Encountered	41
Precision	43
E.M.F. Measurements	44
Results of Experiments	44
General Comments	44
Electrode Test	46
Conclusions	48
V. SUMMARY	49
VI. BIBLIOGRAPHY	51

INTRODUCTION

BACKGROUND, PURPOSE AND SCOPE OF PROBLEM

In 1952, Guereca (1) reported his work in determining the mean activity coefficients of hydrochloric acid in the systems cobalt chloride-water-hydrochloric acid and nickel chloride-water-hydrochloric acid. Guereca did the work by an E.M.F. method (2,3) employing the cell $H_2/HCl(m_1)CoCl_2$ or $NiCl_2(m_2)/AgCl-Ag$. The physical construction of the cell can be found in Guereca's Thesis (1). Twelve series of solutions were investigated, eight containing the salt, cobalt chloride, and four containing the salt, nickel chloride. Each series consisted of a number of solutions containing hydrochloric acid at a fixed molal concentration, water and cobalt chloride or nickel chloride. The concentration of the latter salts varied from a molality of a few tenths to nearly saturation. The hydrochloric acid in the different series ranged from 0.04 molal to 10.6 molal.

Garwin and Hixson (4) had previously studied the solvent extraction of these systems by 2-octanol in which hydrochloric acid was shown to be an extraction-promoting agent. As a consequence of this work Guereca's purpose in studying these systems was to discover some of the principles governing the extraction process. He hoped also that the determination of the activity coefficient of hydrochloric acid in the presence of cobalt chloride and nickel chloride would add some knowledge to the field of concentrated electrolyte mixtures.

In 1954 Gootman (5) reported his comprehensive investigation of activity in hydrochloric acid-water-nickel chloride or cobalt chloride mixtures.

A large part of Gootman's work covered the same ranges in concentration as the prior work of Guereca.

Gootman used the gas transpiration method (6) to determine the partial pressures of the volatile components in the systems. By making use of the relations $P_a = N_a P$, $P_b = N_b P$, etc. (1)

where P_a = partial pressure of component a

N_a = mole fraction of component a

P = total pressure

the partial pressure of each component of the gaseous mixture was calculated from an experimental knowledge of P and N_a , N_b , N_c . A graphical integration of the Gibbs-Duhem equation (5) was performed and the activity of the nonvolatile component, namely the cobalt chloride or nickel chloride, was obtained.

Gootman, like Guereca, made this study in order to further correlate extraction data with aqueous-phase solute activities. It was also felt that the work would be an important contribution to the thermodynamics of concentrated solutions.

The mean activity coefficients of hydrochloric acid as obtained by both Gootman and Guereca are shown plotted against molality of salt in Fig. 1. The data taken from these two investigations are listed in the section of tables and graphs.

As can be seen from Fig. 1 the results obtained by vapor pressure measurements are quite different from the results obtained by E.M.F. measurements. In the lower concentration range the E.M.F. results lie above the vapor pressure results, and the relative positions of the $\text{NiCl}_2\text{-HCl}$ and

$\text{CoCl}_2\text{-HCl}$ curves are inverted in the two investigations, as the salt concentration increases the vapor pressure curve for the system containing nickel chloride crosses the E.M.F. curve in every case except in the 10 series where the low solubility of the nickel chloride stops the curve short of crossing. The E.M.F. curves are concave toward decreasing activity coefficient whereas the vapor pressure curves are either concave toward increasing activity coefficient or almost straight lines.

It was these extreme and unexplained differences that brought about the present research. It was decided to reinvestigate the systems by a method other than E.M.F. or vapor pressure and if necessary to repeat the E.M.F. experiments. By doing the E.M.F. experiments again it was thought that the results of Guereca might be duplicated and that some satisfactory explanation for the observed difference between the E.M.F. and vapor pressure results could be given.

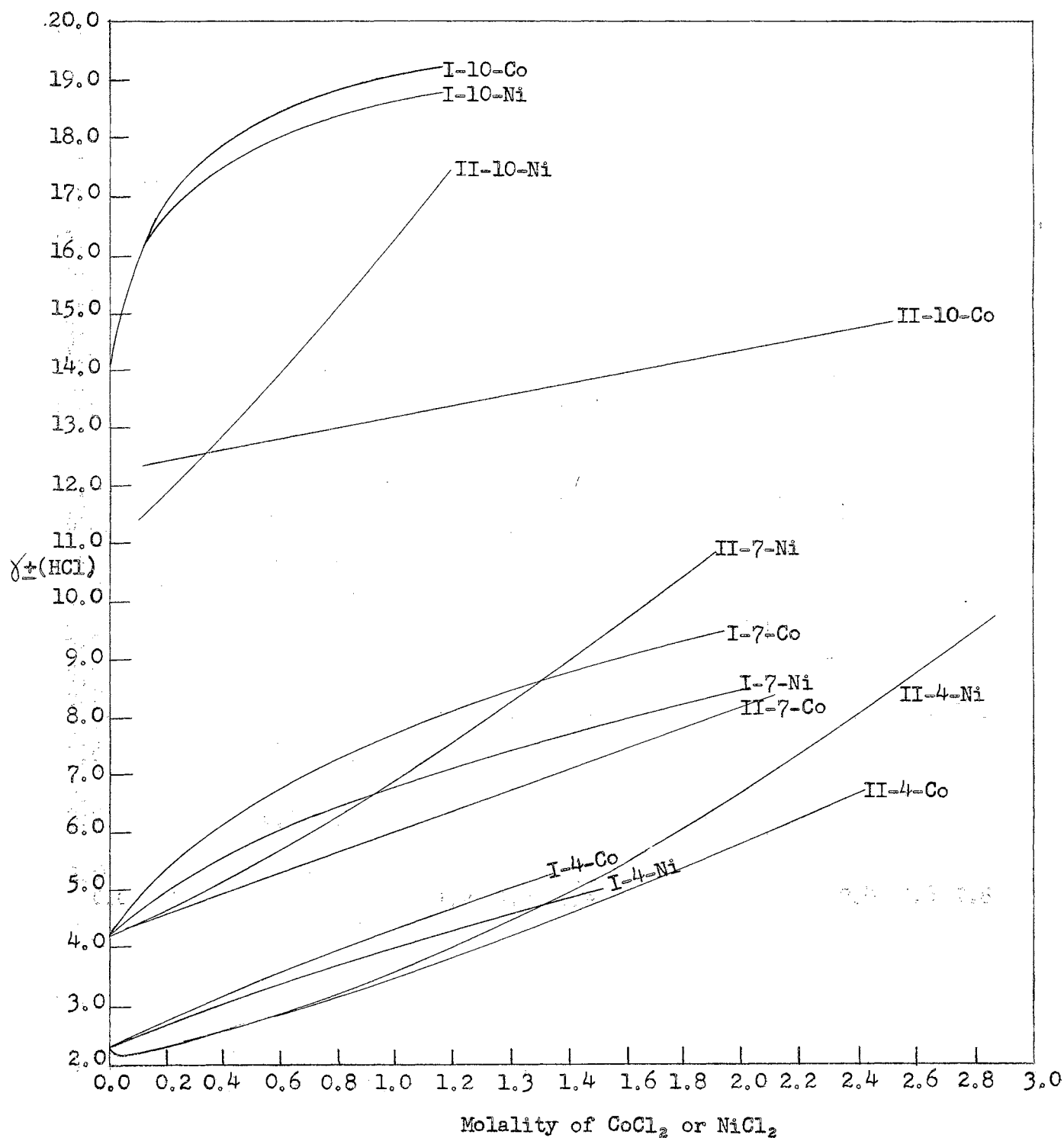


Fig. 1.- Activity coefficients of hydrochloric acid in salt solutions. I, Guereca's results; II, Gootman's results; 4, 4.84 molal HCl; 7, 7.00 molal HCl; 10, 10.6 molal HCl; Ni, system with NiCl_2 ; Co, system with CoCl_2 .

MEANS OF DETERMINATION OF ACTIVITY

Solvent Extraction

The method of partition with benzene as presented by Such and Tomlison (7) was used as a third independent method for the determination of the mean activity coefficient of hydrochloric acid in the systems cobalt chloride or nickel chloride-water-hydrochloric acid.

The expression

$$\log \left(\frac{M^t}{a_{\text{HCl}}} \right) = 3.393 - 2973T^{-1} \quad (2)$$

where M^t = total concentration of hydrochloric acid in the benzene phase expressed as molality

a_{HCl} = activity of the hydrochloric acid in the aqueous phase

T = absolute temperature

is the equation used by Such and Tomlison to calculate the activity of hydrochloric acid at various temperatures. If T is set equal to 30° C., the temperature at which the author's work was done, the equation becomes

$$\log \left(\frac{a_{\text{HCL}}}{M^t} \right) = 6.418 \quad (3)$$

It has been shown (7) that over the molality range of 7.2×10^{-6} to 2.73×10^{-1} in benzene the activity coefficient of hydrogen chloride is unity, and that the activity of the hydrogen chloride in the benzene phase is proportional to the activity of the hydrogen chloride in the aqueous phase.

By means of equation 2 hydrochloric acid activities were calculated from the data obtained in this research, and the experimentally determined activities were found to be only slightly lower than those determined by Gootman. The extraction-determined activities, if multiplied by a factor of 1.12, agreed exactly with the activities (see Fig. 7) determined by vapor pressure measurements within the experimental precision of the extraction experiments. Since the constant in equation 2 was determined empirically for binary mixtures of hydrochloric acid and water, it is not surprising that the same constant would not be applicable to these ternary systems, especially in the concentrated ranges. Equation 3 was modified empirically to fit the data on the ternary systems. Equation 4

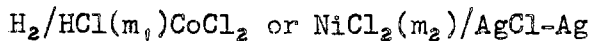
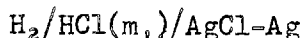
$$\log \left(\frac{a_{\text{HCl}}}{M_t} \right) = 6.448 \quad (4)$$

is equivalent to multiplying the activities determined by equation 3 by 1.12. However, regardless of which equation is used to calculate the activities, there is no question but that the results of this research completely confirm those obtained by the vapor pressure method of Gootman rather than those of Guereca.

E.M.F. Measurements

Since the results of the benzene extraction experiments failed to agree with E.M.F. measurements of Guereca, it seemed important to be able to reproduce Guereca's results. The E.M.F. measurements were accordingly made in as nearly the same manner as possible. A few modifications in the experimental procedure of Guereca were instituted; however, these will be discussed in a later section.

The fundamental equations of the cells



are

$$E \text{ corr.} + 2 k \log m = E^\circ - 2 k \log \gamma_{\pm} \quad (5)$$

$$E \text{ corr.} + k \log m_1(2M_2 + m_1) = E^\circ - 2 k \log \gamma_{\pm} \quad (6)$$

respectively,

where $E \text{ corr.}$ = observed E.M.F. corrected for pressure

$k = 0.06006$ at 30° C.

$E^\circ = 0.21912$ at 30° C. (3).

From the experimental values of $E \text{ corr.}$ and the molality m the mean activity coefficients can be calculated.

Vapor Pressure Correction.- The fundamental equation 6 can be put into the form

$$E^\circ - \frac{RT}{F} \ln a_{\text{H}^+} a_{\text{Cl}^-} = \left[E_p - \frac{RT}{2F} \ln p_{\text{H}_2} \right] = E \text{ corr.}$$

For dilute solutions of hydrochloric acid the correction factor takes the form

$$\frac{RT}{2F} \ln \frac{760}{P_B - p_{\text{H}_2\text{O}}} \quad (7)$$

and for concentrated solutions

$$\frac{RT}{2F} \ln \frac{760}{P_B - p(\text{H}_2\text{O} + \text{HCl})}$$

Guereca (1) points out that the vapor pressure of HCl becomes of consequence

for computation of the correction factor (equations 7,8) only at molalities greater than 4 m. For the concentrated solutions the data for the correction factor as taken from Gureca is listed in the following table and is plotted for interpolation in figure 2. More accurate values of p_{HCl} are tabulated by Gootman (5).

TABLE 1
t = 30° C.

<u>Corrected Barometric Pressure</u>	<u>Correction Factor (volts x 10⁵)</u>
$m_0 = 4.8428$ (15.2% HCl), $P(\text{H}_2\text{O} + \text{HCl}) = 24.0$ mm.	
760	42
755	51
750	60
745	69
740	78
735	87
730	96
$m_0 = 6.975$ (20.3% HCl), $P(\text{H}_2\text{O} + \text{HCl}) = 20.0$ mm.	
760	35
755	44
750	53
745	62
740	71
735	80
730	89
$m_0 = 10.7$ (28.0% HCl), $P(\text{H}_2\text{O} + \text{HCl}) = 22.0$ mm.	
760	38
755	47
750	56
745	65
740	74
735	83
730	93

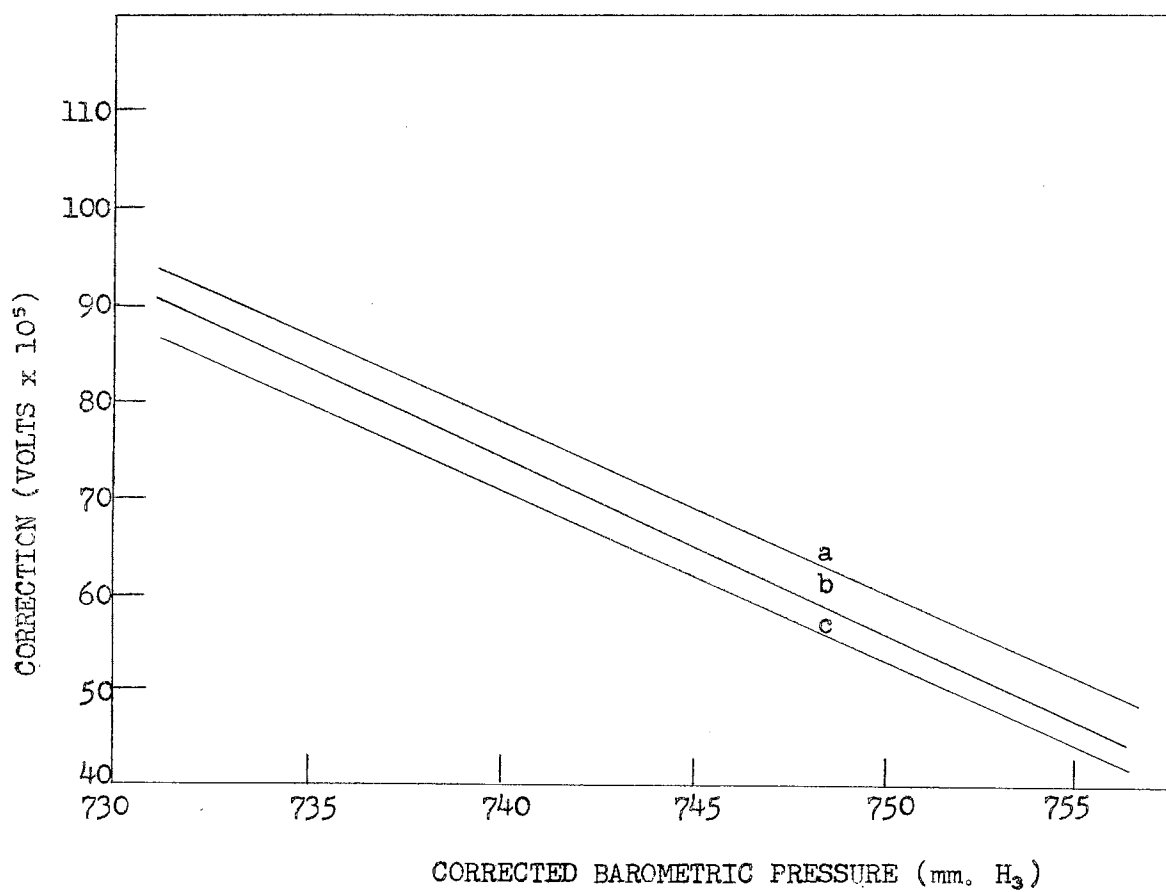


Fig. 2.- Correction factor for hydrogen electrode.
a, 4.842 molal HCl; b, 10.7 molal HCl; c, 6.975 molal HCl.

LITERATURE SURVEY

Solvent Extraction

The principle of employing liquid-liquid distribution measurements in the determination of activity coefficients of solutes in aqueous solutions has long been used for nonelectrolytes (8), but little use has been made of the principle with electrolytic mixtures.

In their article Such and Tomlison (7) gave a literature survey dating from the work of Wynne-Jones (9) to 1948 on the partition of HCl between water and benzene. Also given was a summary of their own data and all previous work. The method was used by Such and Tomlison to determine the activity of hydrochloric acid in aqueous phosphoric acid solutions. The data compiled by those authors shows about a 10% variation.

Recently Gleuchauf, McKay and Mathinson (10) and Jenkins and McKay (11) have studied the partition of uranyl nitrate between water and organic solvents in the presence of a second nitrate. Partition laws were extended to cover systems containing a second nitrate insoluble in the organic phase. This leads to measurements of the activity coefficient of uranyl nitrate in mixed electrolytic solutions.

E.M.F. Measurements

A number of investigators (12-19) have measured the activity coefficients of hydrochloric acid in the presence of lithium, sodium, barium, cerium, aluminum, calcium, strontium, magnesium, ammonium and lanthanum

chloride by electromotive force methods. However, it has been pointed out by Gootman (5) that these systems were not directly comparable to the hydrochloric acid-water-cobalt chloride or nickel chloride systems studied in this research since the systems that had been investigated previously were much more dilute in both acid and salt.

In none of these investigations was the applicability of the E.M.F. technique regarded as open to question although no confirmation of the results by any independent method has been attempted.

EXPERIMENTAL

SOLVENT EXTRACTION

Equilibration and Apparatus

For the equilibration of the ternary systems $\text{HCl-H}_2\text{O-CoCl}_2$ or NiCl_2 with benzene, a test tube (38 x 200 mm.) was heated near the open end and drawn out to a capillary not more than 2 mm. in diameter. This capillary was then broken off having only about two inches of the capillary on the test tube. About 50 cc. of the solution to be equilibrated and 50 cc. of benzene were added to the tube through a funnel the end of which had been drawn out to fit inside the test tube capillary. After the solutions were added the tips were sealed off in a flame. The solutions were treated in this manner because no glass stoppered bottle could be found that would confine the benzene completely during agitation.

When the capillaries were sealed off the samples were placed in a constant temperature bath at $30^\circ + 0.05^\circ \text{C.}$ and shaken for 24 hours with a Burrell wrist-action model D.D. shaker. The shaking was then stopped, and the samples were allowed to sit for twelve hours. At the end of this time the tubes were opened and samples of approximately twenty grams of the benzene phase containing HCl were carefully taken out by a pipet and placed in dropping funnels which already contained weighed quantities, approximately 20 grams, of a supporting solution of potassium nitrate. The function of the supporting solution is described below. The amount of benzene-phase sample taken was determined by weighing the dropping funnels

before and after the samples were taken. The samples were shaken vigorously for 15 to 30 minutes. The phases were then allowed to separate and stand for one hour. The HCl which had been reextracted into the supporting solutions was then ready to be analyzed. It should be mentioned here that there are methods other than reextraction suitable for determining HCl in benzene (20).

Analysis and Apparatus

The method of Kolthoff and Kuroda (21) was chosen for the analysis of the extracted hydrochloric acid. A description of this method follows: the method is a potentiometric one employing silver-silver chloride electrodes. A supporting electrolyte solution consisting of aqueous 0.5N potassium nitrate is prepared. The cell consists of two bottle-type half-cells connected by a U-tube. The U-tube contains the supporting electrolyte in an agar gel. One of the half-cells is used as a reference and is filled with supporting solution saturated with silver chloride. The unknown chloride sample in its supporting solution is placed in the other half-cell and titrated with a dilute solution of silver nitrate to a zero potential. A General Electric lamp type galvanometer (sensitivity = $0.025 \mu A$) was used as a null point indicator.
scale div.

A Typical Experiment

Supporting solution (17.7047 g.) was weighed by difference into a clean dry 60 cc. dropping funnel. A sample of the benzene - HCl mixture (14.8494 g.) which had been equilibrated with a solution that was 6.993 m.

in HCl, and 2.045 m. in NiCl_2 , was weighed by difference into the dropping funnel containing the supporting solution. After this mixture had been shaken vigorously for 30 minutes and then allowed to stand one hour a weighed amount (9.5189 g.) of the supporting solution was withdrawn from the dropping funnel. This sample was titrated as described above requiring 4.895 cc. of 0.005 N silver nitrate solution. From these data one calculates the molality of the HCl in the benzene phase to be 3.066×10^{-3} m. By inserting this datum in equation 4 the activity of the HCl is calculated to be 8,850. Since

$$a_{\pm} = \gamma_{\pm} m_{\pm}, \quad (9)$$

and for HCl
$$m_{\pm} = (m_{\text{H}^+}) (m_{\text{Cl}^-})^{1/2} \quad (10)$$

$$a_{\pm}(\text{HCl}) = (a_{\text{HCl}})^{1/2} \quad (11)$$

γ_{\pm} is calculated to be 10.5.

E.M.F. MEASUREMENTS

Since the principal reason for making the E.M.F. measurements was to see if Guereca's results (1) could be reproduced, the experimental method followed was essentially that employed by Guereca. A few modifications and additions have been introduced by the author and are described where they apply in the following description of apparatus and procedure.

Bridge Circuit

A Rubicon type B potentiometer (No. 54273) was used for all measurements. The range of this instrument is from 0.0 to 1.6 volts with an accuracy of $\pm 0.01\%$. The working standard cell (1.0186 volts at 30°) was prepared by Dr. H. M. Trimble of this institution. Balancing of the circuit was detected with the General Electric Galvanometer previously mentioned.

Temperature Control

The constant temperature bath was the same large capacity (40 gallons) water bath that had been used in the preliminary experiments on the benzene extraction. Owing to the large capacity of the bath a conventional mercury thermal thermoregulator connected through a Cenco-Gilson Electronic Relay (No. 99782) to a Central Scientific 250 watt heater was sufficient to maintain a temperature of $30^\circ \pm 0.05^\circ$ with little difficulty. A Cenco thermometer (No. 19247) calibrated in $1/20^\circ$ divisions was used to measure the temperature.

Cells Employed

Only one type of cell was used. This is shown in Fig. 3.

Preparation of Solutions

Solvent (HCl - H₂O).— For the 6 series a stock solution of 7.00 molal HCl was prepared by diluting concentrated HCl until analysis showed it to be the proper concentration.

Solutions containing CoCl₂.— The solutions containing cobalt chloride were prepared as follows. The hexahydrate of cobalt chloride was dried in an oven at 130° until analysis for cobalt and chloride showed the sample to contain anhydrous cobalt chloride to within one or two tenths of a percent. In the analysis chloride was determined potentiometrically with a Fisher Titrimeter using a silver-silver chloride electrode. Cobalt was determined by evaporation of the acidified solution and weighing as CoCl₂. The total chloride was checked against the cobalt and the sum of the two was checked against the original weight of the sample. After obtaining anhydrous cobalt chloride of a satisfactory quality, samples were weighed and placed in liter bottles containing approximately 800 cc. of the 7.00 molal HCl. In this way a series of solutions having an HCl concentration of 7.00 m. and a cobalt chloride molality varying from 0.6 or 0.7 m. to near 2.0 m. The concentrations were confirmed by analysis.

Solutions containing NiCl₂.— The solutions containing NiCl₂ were prepared as follows: The hexahydrate of nickel chloride was weighed into about

800 cc. of 7.00 molal HCl until the molality of the NiCl_2 was between 0.6 and 2.0 m. The HCl concentration was of course then too low. The solution was then analyzed (1,5) and by repeated analyses and successive addition of a 16.24 m. stock solution of HCl, the HCl molality was brought to within 0.3% of 7.00 m.

Although Guereca used solutions that were 6.97 molal in HCl and in this research the solutions were 7.00 molal in HCl, it was thought that the difference would not affect the results sufficiently to invalidate comparisons of the two sets of measurements.

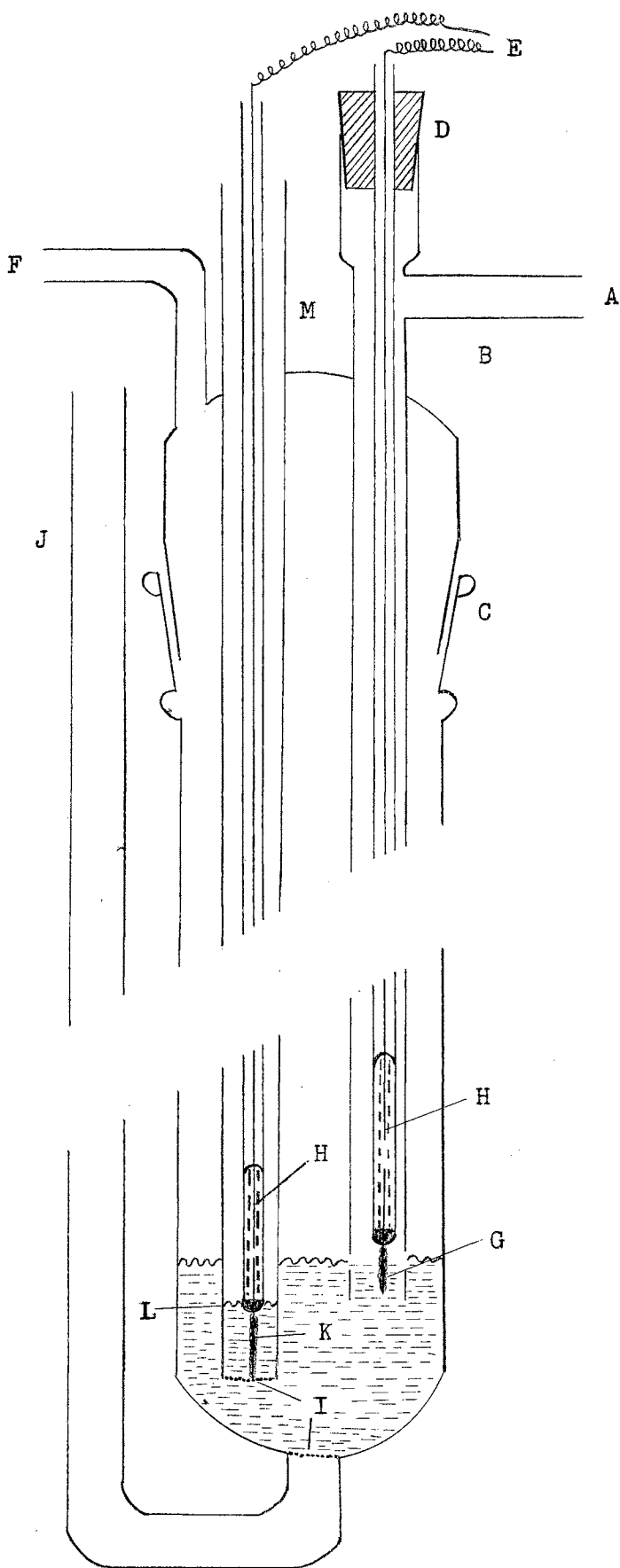


Fig. 3.- Cell used in E.M.F. Measurements

EXPLANATION OF SYMBOLS IN FIGURE 3

- A. Hydrogen gas inlet
- B. Glass tubes holding platinum electrodes
- C. Ground glass joint
- D. Cork holding hydrogen electrode
- E. Leads to Potentiometer
- F. Gas Outlet
- G. Platinized platinum spiral
- H. Mercury contacts
- I. Glass trits
- J. Tube used as hydrogen inlet to saturate solution with hydrogen
- K. Silver-silver chloride electrode on platinum spiral base
- L. Level of solution inside silver-silver chloride electrode compartment
- M. Silver-silver chloride electrode compartment

Preparation and Use of Electrodes

The electrodes were prepared and used essentially as described by Guereca.

The Hydrogen Electrode.- The construction of the electrode is shown in Fig. 3. The fused platinum spiral was obtained by tightly wrapping 26 gauge platinum wire around about an inch of 22 gauge wire left protruding from the end of a glass tube. The ends of both wires were fused together.

In preparation for use, an electrode was cleaned in boiling nitric acid, and then a thin film of platinum black was deposited on it from a strongly HCl-acidified platinum chloride solution. After washing, the electrode was made the cathode in the electrolysis of a very dilute sulfuric acid solution. This treatment saturated the electrode with hydrogen causing it to come to equilibrium faster. The electrode was finally washed twice with distilled water and twice with the nickel or cobalt solution. It was then used immediately. The same electrodes were used for eight or ten experiments before they were cleaned and replated.

In making a measurement the solution was placed in the cell, the hydrogen electrode was inserted, and hydrogen (Matheson's electrolytic 99.9% pure hydrogen) which had first bubbled through two bubbling towers containing the cell solution was passed through the solution for two hours. During these two hours the hydrogen was bubbled through inlet J. (see Fig. 3). Guereca (1) had stated that he had bubbled the hydrogen through the solutions from twenty minutes to twelve hours depending on the concentration being studied. It was found in this work that bubbling for three hours was sufficient to saturate any of the solutions and that some of the solutions were saturated in an hour and a half.

Silver-Silver Chloride Electrodes.- Fused platinum spirals of the same type as the ones used for the hydrogen electrode were used in the preparation of the silver-silver chloride electrodes. These electrodes were prepared as follows: (a) The silver plating solution was made by dissolving 10 grams of potassium dicyanoargentate (I) in a liter of distilled water. Free cyanide was reduced by adding dilute silver nitrate until a faint cloud of silver cyanide became evident. After this had settled, the clear solution was decanted. It was not found necessary to add silver nitrate again. (b) The electrodes were then silver plated by electrolysis for from two to six hours at a total current of six to eight milliamperes. A salt bridge containing the plating solution was used, as suggested by Janz and Tanigrichi (22), to separate the platinum anode from the main body of the solution. After the electrodes were plated they were washed in distilled water and left in running tap water overnight. (c) "Chloridizing" was carried out in hydrochloric acid, the concentration of which varied from 0.1 N to 6 N without any apparent difference in the performance of the electrodes. The electrodes served as anodes in the chloridizing electrolysis. After the electrodes had been chloridized, they were washed for three hours and stored in a brown bottle ready for use when needed.

One set of electrodes, so prepared, was almost totally white as reported by Carmody (23). Brown (24), however, reported that he was unable to prepare white electrodes. No definite reason can be offered here for these electrodes being white; however, a slightly higher current density was used to deposit the silver and discharge the chloride. Also, in the overnight washing the tap water reached abnormally high temperatures of about 31°.

A Typical Experiment

A solution, 7.00 molal in HCl and 0.8197 molal in CoCl_2 , was placed in the cell to a level just above the gas-escape holes in the hydrogen electrode compartment (see Fig. 3). The hydrogen electrode was placed in the cell below the surface of the liquid and hydrogen was bubbled through inlet J for two hours. At the end of this time sufficient solution was aspirated into inlet tube J to allow the escape holes to be just above the surface of the solution. The hydrogen electrode was adjusted so that about two thirds of the electrode was always out of the solution. The hydrogen source was then changed to inlet A. The solution was aspirated into the silver-silver chloride electrode compartment until the level inside the compartment was an inch or so below the surface of the solution proper or until it just covered the electrode. The silver-silver chloride electrode was then inserted, the electrodes were connected to the bridge, and the bridge was balanced. The temperature of the bath was checked, and a reading was made. The electrodes were left in the solution, and readings were made over a one to two hour period. The readings taken during the first ten or fifteen minutes usually showed a downward drift. The readings then became constant and remained so for an hour or more. For $m_2 = 0.8197$, the observed E.M.F. was 0.02016 ± 0.00004 volts. The observed barometric pressure was 739.9 mm., and the observed temperature was 35.2° . The pressure correction term was calculated to be 0.00080 volts (see table 1) corresponding to E corr. equal to 0.02096 volts. By using equation 6 one calculates $\chi_{\pm} = 5.75$.

Chemicals

The cobalt chloride used was Fisher Scientific Company's reagent grade.

The nickel chloride used was Mallinckrodt's analytical reagent grade.

The hydrochloric acid used was Baker's reagent grade.

Mallinckrodt Analytical Reagent potassium nitrate was used in the preparation of the supporting solution.

The silver nitrate used in the chloride determination was Mallinckrodt's Analytical Reagent.

Matheson's high quality electrolytic 99.9% pure hydrogen was used as a source of hydrogen for the hydrogen electrodes.

Baker's reagent grade benzene was used in the extraction.

EXPERIMENTAL RESULTS

Preliminary Experiments on Binary Systems

Solvent Extraction.- Some preliminary extractions were done using binary HCl solution. It was found that the mean activity coefficient determined by this method checked with that of Akerloff and Teare (25). It was also found that the determinations could be reproduced with the accuracy reported by Such and Tomlison (5).

E.M.F. Measurements.- It was found that E.M.F. measurements on hydrochloric acid solutions gave mean activity coefficients for the binary HCl solutions which were very close to the results of Akerloff and Teare (28).

The System $\text{CoCl}_2\text{-H}_2\text{O-HCl}$ Table 2
(Guereca)

$$m_1 = 4.8428 \quad t = 30^\circ$$

$$\gamma_{\pm} = 2.207 \pm 0.001$$

$$E \text{ corr. (solvent)} = 0.09532$$

$$\gamma_{\pm} = 2.170 \text{ (Akerloff and Teare)}$$

$m_2(\text{CoCl}_2)$	$E \text{ corr.}$	γ_{\pm}	$m_2(\text{CoCl}_2)$	$E \text{ corr.}$	γ_{\pm}
0.0411	0.08987	2.431	0.8317	0.05743	3.935
0.1078	0.08393	2.690	0.8751	0.05634	3.991
0.1976	0.07887	2.909	1.087	0.05010	4.360
0.3000	0.07438	3.110	1.285	0.04429	4.741
0.3454	0.07246	3.200	1.353	0.04253	4.859
0.3785	0.07132	3.251	1.455	0.03971	5.060
0.4959	0.06752	3.425	1.498	0.03851	5.150
0.5452	0.06563	3.523	1.531	0.03783	5.195
0.5962	0.06418	3.590	1.592	0.03608	5.331 ± 0.001
0.7120	0.06076	3.762			

Table 3
(Guereca)

$$m_1 = 6.975 \quad t = 30^\circ$$

$$\gamma_{\pm} = 4.345 \pm 0.001$$

$$E \text{ corr. (solvent)} = 0.04089$$

$$\gamma_{\pm} = 4.180 \text{ (Akerloff and Teare)}$$

$m_2(\text{CoCl}_2)$	$E \text{ corr.}$	γ_{\pm}	$m_2(\text{CoCl}_2)$	$E \text{ corr.}$	γ_{\pm}
0.0194	0.03962	4.441	0.4269	0.01829	6.323
0.0228	0.03935	4.462	0.5243	0.01516	6.631
0.0512	0.03761	4.595	0.5815	0.01333	6.820
0.0819	0.03550	4.763	0.6402	0.01162	6.996
0.0998	0.03426	4.866	0.6875	0.01043	7.117
0.1097	0.03350	4.930	0.8617	0.00652	7.515
0.1133	0.03322	4.954	1.039	0.00304	7.873
0.1906	0.02829	5.387	1.214	-0.00013	8.210
0.2535	0.02505	5.682	1.400	-0.00314	8.528
0.3109	0.02260	5.911	1.502	-0.00460	8.681
0.3299	0.02180	5.987	1.688	-0.00697	8.918 ± 0.001
0.3601	0.02064	6.098			

Table 4
(Guereca)

$m_1 = 10.7$ $t = 30^\circ$

E corr. (solvent) = -0.03606

$\gamma_{\pm} = 12.35 \pm 0.001$

$\gamma_{\pm} = 11.70$ (Akerloff and Teare)

<u>$m_2(\text{CoCl}_2)$</u>	<u>E corr.</u>	<u>γ_{\pm}</u>	<u>$m_2(\text{CoCl}_2)$</u>	<u>E corr.</u>	<u>γ_{\pm}</u>
0.0105	-0.04095	13.56	0.4372	-0.05667	17.84
0.0130	-0.04139	13.67	0.4499	-0.05737	17.85
0.0314	-0.04518	14.67	0.5171	-0.05852	18.14
0.0514	-0.04740	15.28	0.7295	-0.06120	18.76
0.0937	-0.04991	15.97	0.7949	-0.06192	18.92
0.2441	-0.05407	17.06	0.8470	-0.06242	19.02
0.2794	-0.05482	17.25	0.0951	-0.06297	19.13 ± 0.001

Table 5
(Gootman)

HCl = 4.84 molal

$m_3(\text{CoCl}_2)$	$\gamma_{\pm}(\text{HCl})$
0.100	2.33
0.200	2.42
0.300	2.53
0.400	2.65
0.500	2.77
0.600	2.90
0.700	3.02
0.800	3.19
0.900	3.33
1.000	3.53
1.100	3.70
1.200	3.88
1.300	4.08
1.400	4.27
1.500	4.46
1.600	4.65
1.700	4.83
1.800	5.02
1.900	5.20
2.000	5.39
2.100	5.57
2.200	5.76
2.300	5.97
2.400	6.20
2.485	6.44

Table 6
(Gootman)

HCl = 6.97 molal

$m_3(\text{CoCl}_2)$	$\gamma_{\pm} \text{ HCl}$
0.100	4.38
0.200	4.60
0.300	4.80
0.400	5.00
0.500	5.19
0.600	5.38
0.700	5.57
0.800	5.75
0.900	5.93
1.000	6.10
1.100	6.28
1.200	6.45
1.300	6.61
1.400	6.77
1.500	6.95
1.600	7.13
1.700	7.31
1.800	7.49
1.900	7.67
1.950	7.75
1.980	7.77

Table 7
(Gootman)

HCl = 10.65 Molal

<u>$m_2(\text{CoCl}_2)$</u>	<u>$\gamma_{\pm}(\text{HCl})$</u>
0.100	12.29
0.200	12.42
0.300	12.49
0.400	12.59
0.500	12.69
0.600	12.81
0.700	12.94
0.800	13.05
0.900	13.16
1.000	13.27
1.100	13.38
1.200	13.47
1.300	13.57
1.400	13.67
1.500	13.75
1.600	13.84
1.700	13.92
1.800	14.00
1.900	14.07
2.000	14.15
2.100	14.22
2.200	14.30
2.300	14.37
2.400	14.49
2.500	14.68
2.594	14.83

Solvent Extraction Data

Table 8
(Dyer)HCl = 7.00 molal $t = 30^\circ$

<u>$m_2(\text{CoCl}_2)$</u>	<u>$a(\text{HCl})$</u>	<u>$\gamma_{\pm}(\text{HCl})$</u>
0.902	2020	5.72
1.14	2490	6.19
1.34	2560	6.16
1.61	3560	7.05
1.86	4220	7.50
1.99	4430	7.60

Data From E.M.F. Measurements

Table 9
(Dyer)HCl = 7.00 Molal $t = 30^\circ$

<u>$m(\text{CoCl}_2)$</u>	<u>E corr.</u>	<u>$\gamma_{\pm}(\text{HCl})$</u>
0.819	0.02096	5.75
0.985	0.01731	6.05
1.20	0.01207	6.52
1.68	0.00380	7.28
1.77	0.00250	7.46

Table 10
(Dyer)

HCl = 4.84

<u>m(CoCl₂)</u>	<u>E corr.</u>	<u>$\delta \pm$(HCl)</u>
1.54	0.04453	4.59
1.84	0.03480	5.20

Table 11
(Dyer)

HCl = 10.6 Molal

<u>m(CoCl₂)</u>	<u>E corr.</u>	<u>$\delta \pm$(HCl)</u>
0.545	-0.0362	12.0
0.740	-0.0380	12.3
1.10	-0.0398	12.5

The System $\text{NiCl}_2\text{-H}_2\text{O-HCl}$ Table 12
(Guereca) $m_1 = 4.8428$ $t = 30^\circ$

$m_2(\text{NiCl}_2)$	E corr.	$\gamma \pm$	$m_2(\text{NiCl}_2)$	E corr.	$\gamma \pm$
0.1067	0.08782	2.495	0.5461	0.06900	3.302
0.1200	0.08676	2.540	0.5784	0.06767	3.369
0.1623	0.08390	2.861	0.6627	0.06540	3.470
0.1713	0.08358	2.672	0.7075	0.06346	3.575
0.1943	0.08193	2.746	0.8061	0.06062	3.717
0.2635	0.07888	2.873	1.0048	0.05474	4.037
0.3976	0.07427	3.063	1.0232	0.05399	4.084
0.4047	0.07382	3.085	1.3586	0.04559	4.580
0.4591	0.07144	3.198	1.5097	0.04258	4.756 ± 0.001
0.5118	0.06962	3.282			

Table 13
(Guereca) $m_1 = 6.975$ $t = 30^\circ$

$m_2(\text{NiCl}_2)$	E corr.	$\gamma \pm$	$m_2(\text{NiCl}_2)$	E corr.	$\gamma \pm$
0.0103	0.04039	4.382	0.4990	0.02135	5.910
0.0250	0.03958	4.441	0.6280	0.01819	6.178
0.0765	0.03686	4.644	0.6349	0.01810	6.184
0.0882	0.03619	4.697	0.9009	0.01278	6.636
0.0966	0.03580	4.726	0.9584	0.01177	6.722
0.1650	0.03265	4.973	1.123	0.00853	7.024
0.1889	0.03159	5.058	1.214	0.00693	7.172
0.2187	0.03047	5.147	1.306	0.00533	7.323
0.3212	0.02649	5.479	1.322	0.00505	7.350
0.4799	0.02187	5.865	1.498	0.00238	7.597 ± 0.001

Table 14
(Guereca)

$m_1 = 10.7$ $t = 30^\circ$

<u>$m_2(\text{NiCl}_2)$</u>	<u>E corr.</u>	<u>$\delta \pm$</u>	<u>$m_2(\text{NiCl}_2)$</u>	<u>E corr.</u>	<u>$\delta \pm$</u>
0.0062	-0.03893	13.05	0.4867	-0.05728	17.76
0.0535	-0.04766	15.36	0.5137	-0.05766	17.85
0.0718	-0.04884	15.68	0.5395	-0.05798	17.92
0.0930	-0.04981	15.94	0.5888	-0.05857	18.05
0.1014	-0.05014	16.03	0.7222	-0.06001	18.35
0.1832	-0.05241	16.62	0.7520	-0.06034	18.42
0.4537	-0.05686	17.67	0.8185	-0.06099	18.55 ± 0.001

Table 15
(Gootman)

HCl = 4.69 Molal

$m_2(\text{NiCl}_2)$	$\gamma_{\pm}(\text{HCl})$
0.100	2.19
0.200	2.31
0.300	2.43
0.400	2.57
0.500	2.73
0.600	2.89
0.700	3.06
0.800	3.25
0.900	3.44
1.000	3.64
1.100	3.85
1.200	4.07
1.300	4.29
1.400	4.52
1.500	4.76
1.600	5.02
1.700	5.28
1.800	5.54
1.900	5.82
2.000	6.10
2.100	6.40
2.200	6.72
2.300	7.05
2.400	7.38
2.500	7.73
2.600	8.08
2.700	8.43
2.800	8.77
2.900	9.14
3.005	9.61

Table 16
(Gootman)

HCl = 6.86 Molal

$m_2(\text{NiCl}_2)$	$\gamma_{\pm}(\text{HCl})$
0.100	4.50
0.200	4.74
0.300	4.97
0.400	5.21
0.500	5.46
0.600	5.75
0.700	6.05
0.800	6.34
0.900	6.65
1.000	6.95
1.100	7.26
1.200	7.59
1.300	7.93
1.400	8.28
1.500	8.63
1.600	8.98
1.700	9.33
1.800	9.68
1.900	10.05
2.000	10.42
2.100	10.78
2.134	10.91

Table 17
(Gootman)

HCl = 10.4 Molal

<u>$m_2(\text{NiCl}_2)$</u>	<u>$\gamma_{\pm}(\text{HCl})$</u>
0.100	11.41
0.200	11.89
0.300	12.39
0.400	12.93
0.500	13.50
0.600	14.05
0.700	14.63
0.800	15.09
0.856	15.35

Solvent Extraction Data

Table 18
(Dyer)HCl = 7.00 Molal $t = 30^\circ$

<u>$m_2(\text{NiCl}_2)$</u>	<u>$a(\text{HCl})$</u>	<u>$\gamma_{\pm \text{HCl}}$</u>
0.904	2630	6.52
0.968	2850	6.76
1.15	3770	7.59
1.56	5150	8.54
1.75	6590	9.45
2.05	8850	10.5

Table 19
(Dyer)

HCl = 7.00 Molal

<u>$m_2(\text{NiCl}_2)$</u>	<u>E corr.</u>	<u>$\gamma_{\pm}(\text{HCl})$</u>
0.966	0.01100	6.82
1.14	0.00640	7.35
1.36	0.00040	8.00
1.57	-0.00570	8.80
1.65	-0.00930	9.25
2.05	-0.01729	10.29

Table 20
(Dyer)

HCl = 4.84

<u>$m_2(\text{NiCl}_2)$</u>	<u>E corr.</u>	<u>$\gamma_{\pm}(\text{HCl})$</u>
0.910	0.06451	3.44
1.43	0.04638	4.53

Table 21
(Dyer)

HCl = 10.4

<u>$m(\text{NiCl}_2)$</u>	<u>E corr.</u>	<u>$\gamma_{\pm}(\text{HCl})$</u>
0.375	-0.03503	11.7
0.741	-0.04340	13.2

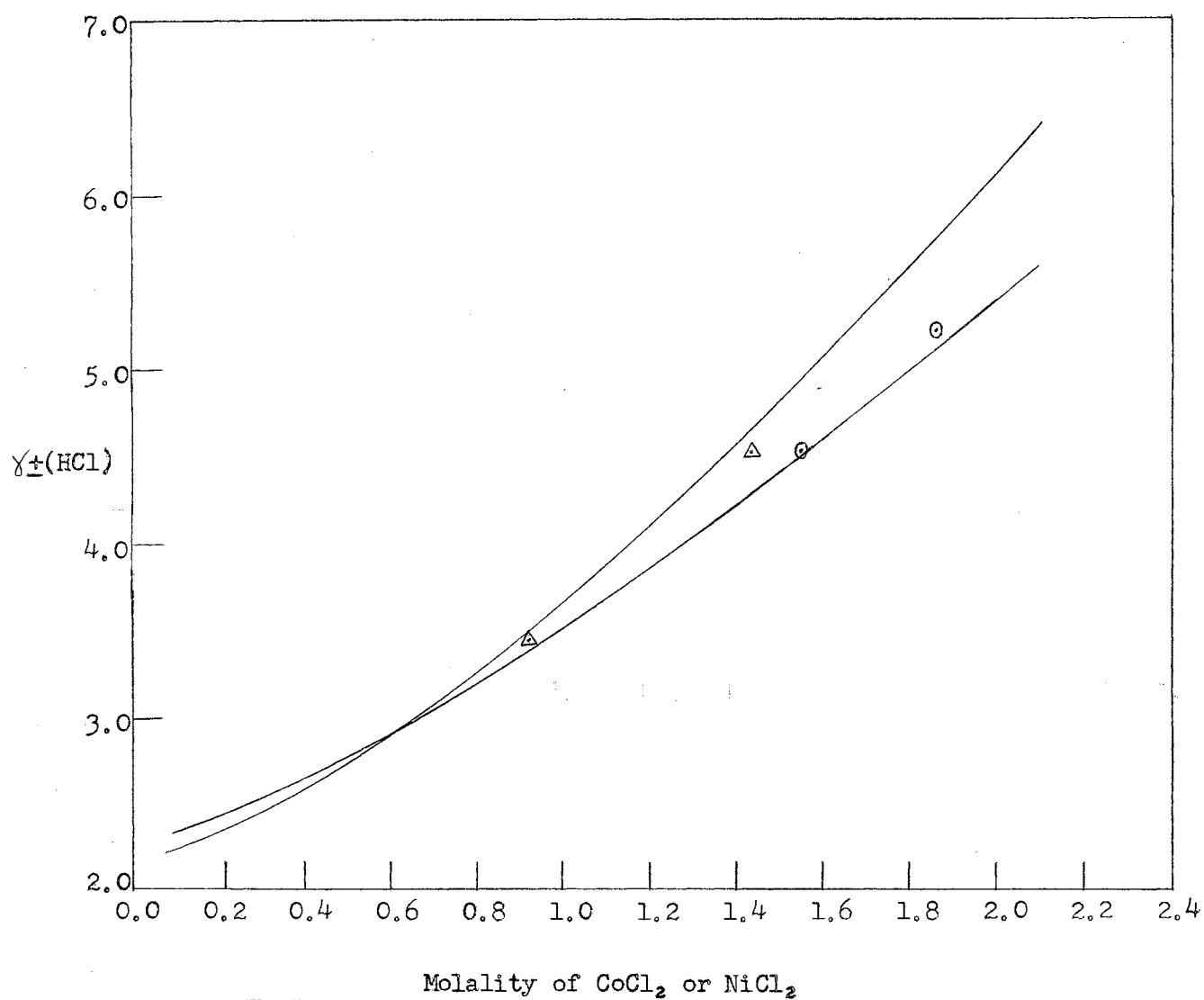


Fig. 4.- Activity coefficient of hydrochloric acid in salt solutions. HCl molality = 4.84; Smoothed curves are Gootman's data. Δ , E.M.F. data for system with NiCl_2 ; \odot , E.M.F. data for system with CoCl_2 .

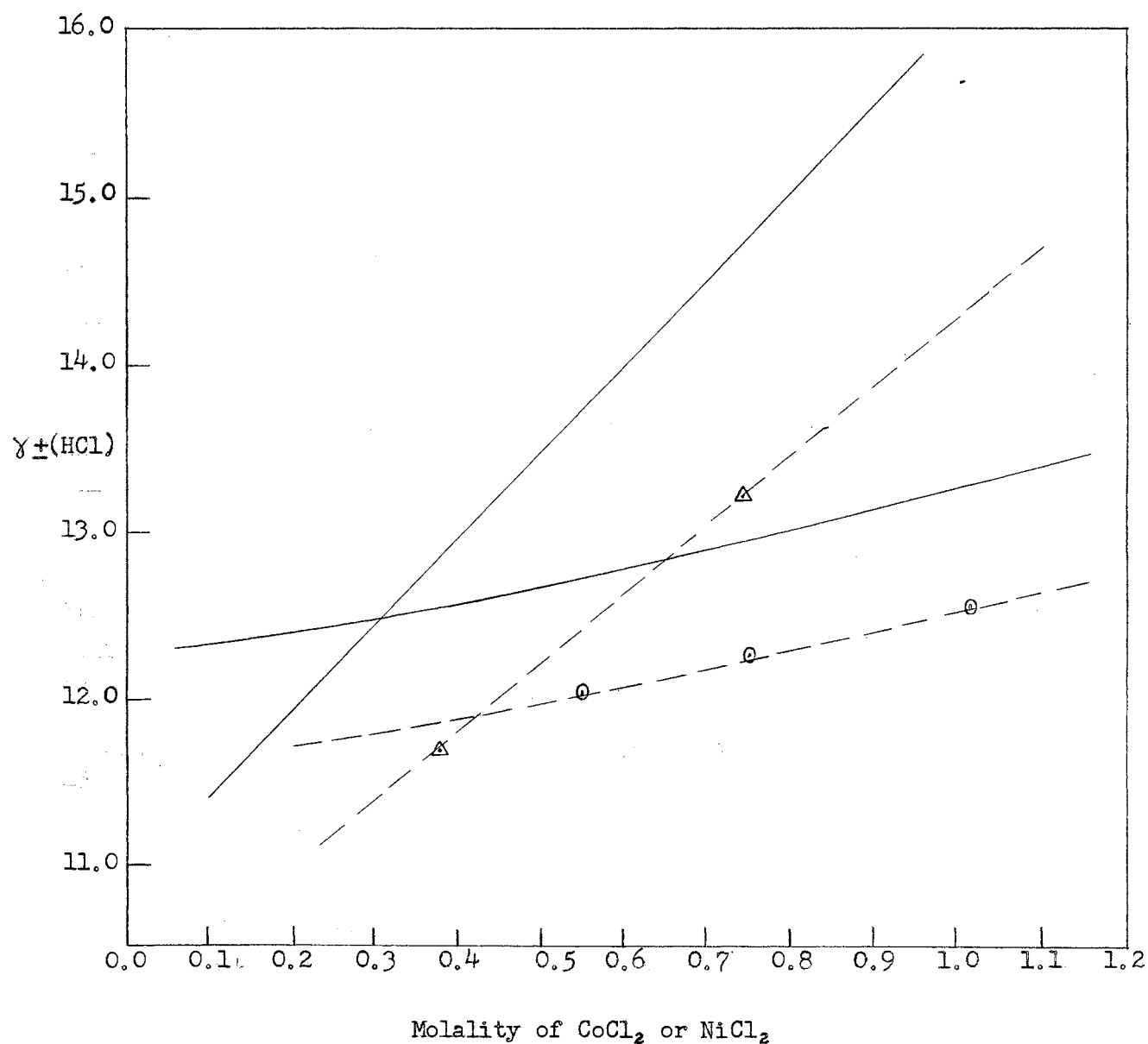


Fig. 5.- Activity coefficient of hydrochloric acid in salt solutions. HCl molality = 10.6; Smoothed curves are Gootman's data. Δ , E.M.F. data for system with NiCl_2 ; \circ , E.M.F. data for system with CoCl_2 ; Dotted lines are drawn to show that E.M.F. data is parallel to vapor pressure data.

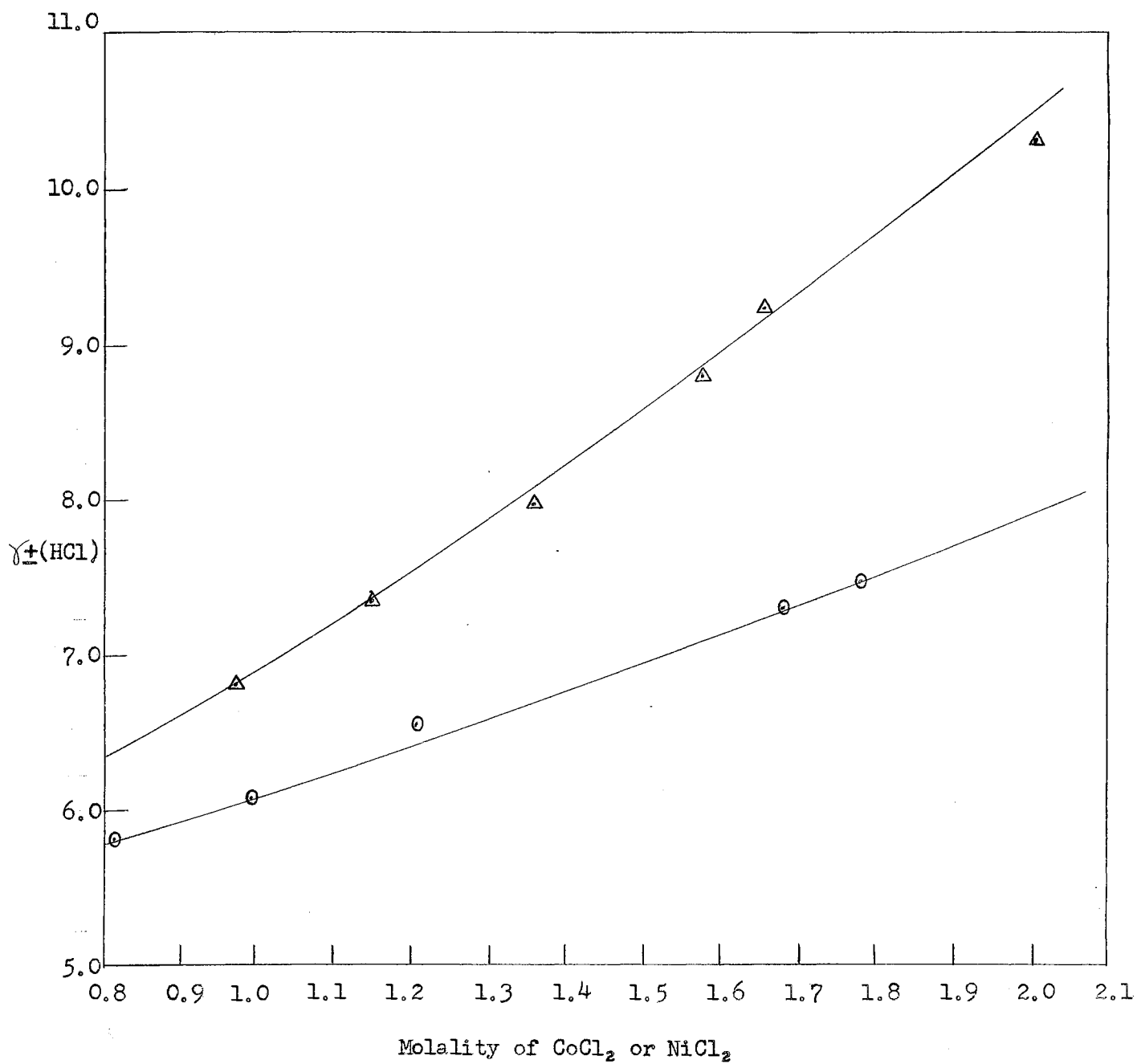


Fig. 6.- Activity coefficient of hydrochloric acid in salt solutions. HCl molality = 7.00; Smoothed curves are Gootman's data. Δ , E.M.F. data for system with NiCl_2 ; \circ , E.M.F. data for system with CoCl_2 .

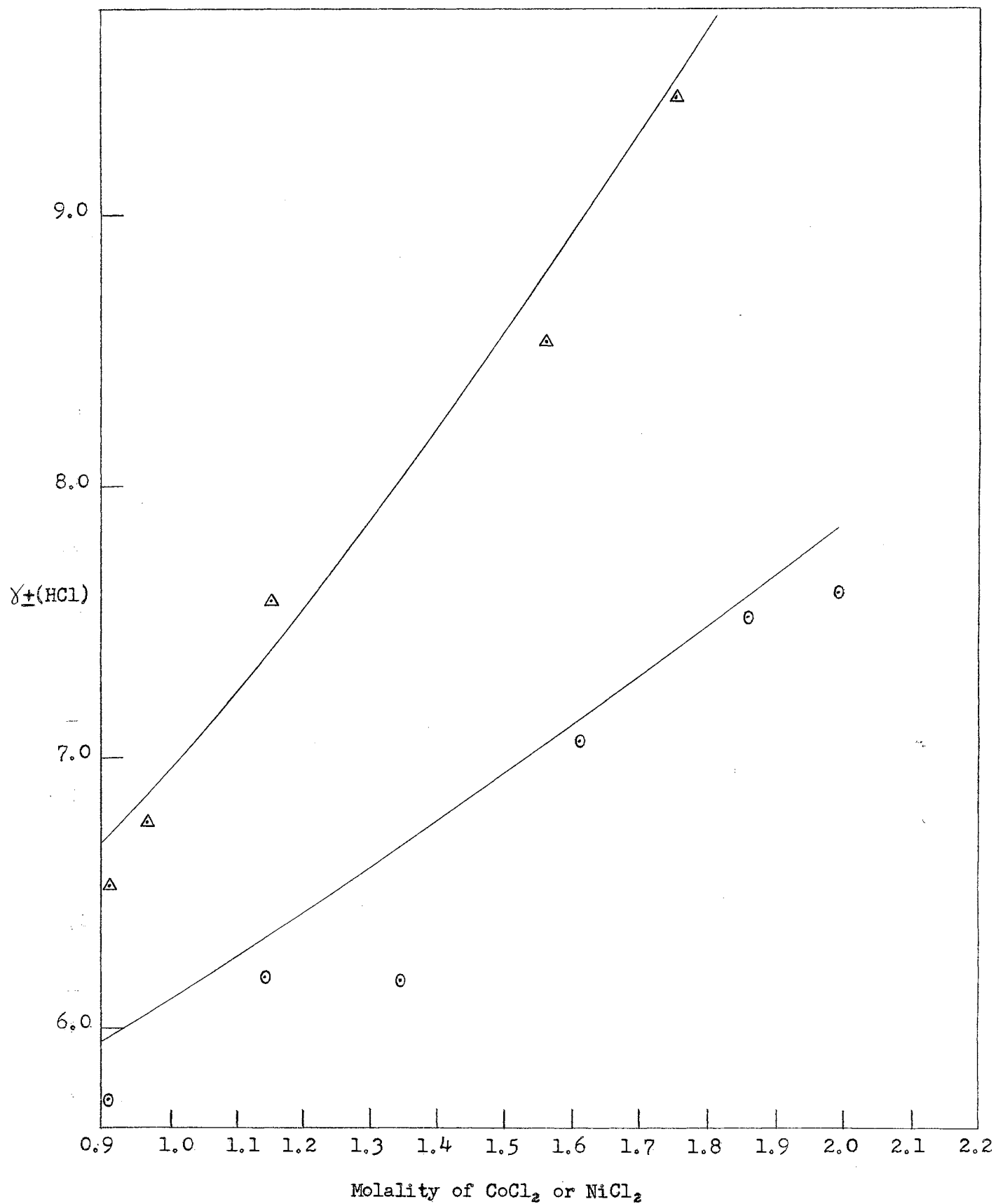


Fig. 7.- Activity coefficient of hydrochloric acid in salt solutions. HCl molality = 7.00; Smoothed curves are Gootman's data. Δ , solvent extraction data for system with NiCl_2 ; \circ , solvent extraction data for system with CoCl_2 .

DISCUSSION OF RESULTS

SOLVENT EXTRACTION

Comments About Results

The solvent extraction method for determining hydrochloric acid activity was used only with the series that was seven molal in HCl.

As was mentioned earlier the results of this work were in good agreement with the values determined through vapor pressure measurements. This fact then led to an attempt to reproduce Guereca's E.M.F. measurements. Before discussing the results obtained from the E.M.F. measurements, it seems advisable to discuss some of the difficulties encountered in applying the solvent extraction procedure.

Difficulties Encountered

Experimental.— The principal difficulty encountered arose in connection with equilibration of the solution with benzene. Such and Tomlison (7) did not say how they managed to shake one liter samples for periods of one to three days. It is to be assumed they used either a water bath for constant temperature and thereby shook the samples occasionally by hand or an air bath in conjunction with some type of large mechanical shaking device. In either case the large size of the samples would present a problem.

In this work it was first decided to equilibrate 200 ml. samples of HCl solutions in 250 ml. ground-glass stoppered bottles by shaking the

samples occasionally by hand. This method did not give satisfactory results. It was not known whether the samples leaked water through the ground glass joints or whether the time of shaking was insufficient for complete equilibration.

To test the adequacy of the length of shaking, a shaking apparatus was constructed by which 500 ml. samples could be shaken. Ground glass stoppered bottles were again chosen. The samples were large enough to permit one to make a number of analysis over a period of days after they presumably had been equilibrated.

In the equilibration the samples were shaken 24 hours and allowed to stand 12 hours before a sample was taken. It was found that this method gave, for the hydrochloric acid solutions, results which were in agreement with Such and Tomlison and that the same results could be obtained with the same sample over a period of days.

However, it was found that there was a slight leakage of benzene and solution around the glass stoppers, and there was doubt raised as to whether or not one could completely trust the results from a very high percentage of samples, especially if the glass stoppers had been used a number of times. As a result of this lack of trust in the first results, the methods of sealing small samples in tubes as previously described was adopted.

Theoretical.- As can be seen in figure 7 the constant used in equation 4 does not apply exactly to both the system containing cobalt chloride and the system containing nickel chloride. This fact is to be expected

because the equation was empirically adjusted to fit the data on the system containing nickel chloride. One would suspect that, since these are very concentrated solutions and the salt concentrations vary widely, the right member of the equation would not be strictly a constant. This work does not attempt to deal theoretically with this partition law, but as was pointed out earlier the work does agree with the vapor pressure measurements in showing that the "nickel curve" lies above the "cobalt curve", and that the two curves are both concave upward.

Precision

From this standpoint the mean activity coefficients for HCl listed by Akerloff and Teare could be reproduced by the solvent extraction method with a precision of about five percent.

E.M.F. MEASUREMENTS

Results of Experiments

General Comments.- A few experiments were performed on the 10 and 4 series (see Figs. 4,5). The solutions used for these experiments were some that had been prepared by Gootman. The solutions had been stored in screw cap liter bottles for approximately two years. The caps after being screwed on had been sealed with paraffin. As can be seen from figure 5 the results for the 10 series lie below but paralleled to the vapor pressure measurements. Since the vapor pressure of the hydrochloric acid becomes appreciable at these concentrations, it was thought that some of the hydrochloric acid had escaped during the two years of storage in spite of the seemingly good seals on the bottles.

Only four experiments were done with the 4 series. Good agreement between these results and the vapor pressure measurements was obtained.

It had been anticipated that the work of Guereca would be reproduced, and that the cause for the difference between the vapor pressure and E.M.F. results might be traced to a failure of the cell $H_2/HCl(m_1)CaCl_2$ or $NiCl_2(m_2)/Ag-AgCl$ to act in a reversible manner in the systems under study. The good agreement with the vapor pressure results actually found was therefore surprising and efforts were made to reproduce the experimental conditions and results of Guereca.

There were as previously mentioned, a few differences in the author's experimental method and Guereca's experimental method. The differences were: (1) Guereca bubbled hydrogen through the solution and over the platinum black electrode for a period of time sometimes as long as twelve hours whereas in this work the time of saturation with hydrogen never exceeded two hours; (2) Guereca used a medium porosity glass frit in the silver-silver chloride electrode compartment. A fine porosity frit was used in this work; (3) Guereca aspirated the solution into the silver-silver chloride electrode compartment to a height above the solution in the rest of the cell. In this work the solution was aspirated into this compartment only sufficiently to cover the electrode. The possible results of these changes have been considered and are discussed below.

Guereca's calculations were first checked and found to be correct. It was not considered reasonable that Guereca might have made a consistent error in preparing his solutions which could have inverted the relative positions of the cobalt and nickel curves. It was therefore thought that some experimental factor had operated to make one or both of his electrodes irreversible.

As can be seen from figure 1 the effect must operate so as to cause the activity coefficient of the HCl in the cobalt chloride series to lie above the activity coefficient of the HCl in the nickel chloride series contrary to the vapor pressure results. The factor must also operate to cause the curves to be concave downward. Furthermore, the effect must be such that the E.M.F. curve of the nickel chloride system crosses the vapor pressure curve of the same system; i.e., the factor must, in effect, reverse

its effect on the electrodes at and beyond some particular concentration. A series of tests on the electrodes were accordingly made in an effort to discover what this factor might possibly be.

Electrode Test.- It has been pointed out that two of the differences between the author's and Guereca's experimental methods involved the use of a medium frit on the silver-silver chloride electrode compartment rather than a fine porosity frit and the aspiration of the solution into this compartment to a level higher than the remainder of the solution.

It was reasoned that these two factors might over a period of a few hours allow silver ions to diffuse into the cell, and be discharged at the hydrogen electrode (3), thereby causing that electrode to operate irreversibly. The importance of this factor was tested in two ways: first, by deliberately introducing solid silver chloride into the cell, and second, by replacing the fine frit with a medium one, aspirating the solution in the compartment to a level above the bulk of the solution proper, and allowing it to stand until it was evident that some silver ion had diffused into the cell. It was found that silver ion did diffuse in a period of 5 or 6 hours. However, since not all medium frits are of the same porosity, Guereca's may have been of a lower porosity than this one.

The silver chloride had the effect of reducing the observed E.M.F. by a large factor. This change was in the right direction in the more dilute solutions for both systems and was in the right direction for all concentrations for the cobalt chloride. However the effect did not lead to the observed reversal in the magnitude of the activity values obtained by the

two methods in the nickel chloride system, if the concentration of nickel chloride was increased. However, the E.M.F. measurements, after the introduction of the silver chloride, were so unstable that it was impossible to obtain a value that had much meaning. This factor was regarded as probably not being the one responsible for the difference between Guereca's and Gootman's work.

Some experiments were tried in which hydrogen was bubbled through the cell and over the hydrogen electrode for from 12 to 24 hours before making a measurement. Care was taken to insure that no silver chloride was in the cell. It was found that the observed E.M.F. was still approximately the same as it had been without the extended saturation period.

Since the effect was reversed for the nickel chloride at higher concentrations it was considered possible that some factor specific to the cobalt and nickel ions might be the cause of the anomaly. A few experiments were carried out in which the hydrogen electrode had been first nickel plated or cobalt plated. It was found, however, that the nickel or cobalt dissolved off the electrode after it was placed in the strongly acid solution and that after the solution was saturated with hydrogen, the correct E.M.F. was obtained.

CONCLUSIONS

Although none of the electrode test experiments gave any definite clues as to what may have caused the anomalous results obtained by Guereca, it seems inescapable that some unrecognized experimental factor in the construction of his cells and electrodes must be responsible for the high internal consistency of his data and at the same time cause that data to be in error. Had there been large fluctuations in his E.M.F. values there would have never been the misplaced confidence in his results nor any occasion for this investigation.

However, it can confidently be said that the cell used in this study can be used to measure HCl activities in ternary systems involving cobalt and nickel.

Perhaps the most important result from the investigation is the confirmation of the HCl activity values obtained by the vapor pressure method through the use of two additional independent methods. It is rarely in chemical research that results are checked by several independent methods. The established reliability of the E.M.F. method in such solutions validates the extension of measurements to dilute solutions where vapor pressure measurements can not be made.

SUMMARY

Efforts were made to discover the reason for the differences which exist between the electromotive force investigation by Guereca (1) and the vapor pressure investigation by Gootman (5).

The mean activity coefficients of hydrochloric acid in the systems hydrochloric acid-water-cobalt chloride and hydrochloric acid-water-nickel chloride were determined by a liquid extraction method and by an electromotive force method.

In the liquid extraction experiments the hydrochloric acid was extracted into benzene. With knowledge of the equilibrium concentrations of the hydrochloric acid in the benzene and aqueous phases the mean activity coefficients of the hydrochloric acid could be calculated.

In the electromotive force experiments the mean activity coefficients of hydrochloric acid were determined by the use of the cell $H_2/HCl(m_1), CoCl_2$ or $NiCl_2(m_2)/AgCl-Ag$.

The principal work was concerned with the series that had a 7.00 molal hydrochloric acid concentration. The cobalt chloride and nickel chloride concentrations were varied from about 0.8 to 2.0 molal. A limited number of experiments were performed on two other series; one 10.6 molal, the other 4.84 molal in hydrochloric acid.

It was found that both the results from the liquid extraction and the E.M.F. method agreed well with the vapor pressure results obtained by Gootman(5). Attempts were made to reproduce the E.M.F. results

obtained by Guereca (1), but none of the experiments were successful in this respect. It was therefore concluded that some unrecognized experimental factor in the construction of Guereca's cells and electrodes must be responsible for the high internal consistency of his data and at the same time cause his data to be in error.

Never the less the reliability of the E.M.F. method in such solutions was confirmed making it possible to use this method in solutions in which the hydrochloric acid is too dilute to give a measureable vapor pressure.

BIBLIOGRAPHY

1. Guereca, Ph. D. Thesis, Okla. A. and M. College, 1952.
2. Mac Innes, Principles of Electrochemistry, p. 148-150, Reinhold Publishing Co., New York, 1939.
3. Harned and Owen, The Physical Chemistry of Electrolytic Solutions, 2nd. Ed., Reinhold Publishing Co., New York, 1950.
4. Garwin and Hixson, Ind. Eng. Chem. 41, 2298-2310 (1949).
5. Gootman, Ph. D. Thesis, Okla. A. and M. College, 1954.
6. Pearce and Snow, J. Phys. Chem., 31, 231-41 (1927).
7. Such and Tomlison, J. Soc. Chem. Ind., 67, 110 (1948).
8. Long and Bergen, J. Phys. Chem. 58, 166-68 (1954).
9. Wynne-Jones, J. Chem. Soc., 1930, 1064.
10. Gleuckauf, McKay and Mathieson, J. Chem. Soc., 1949, 5299-302.
11. Jenkins and McKay, Trans. Faraday Soc., 50, 107-19 (1954).
12. Duboux and Vuilleumier, Helv. Chim. Acta., 25, 1319-28 (1942).
13. Hawkins, J. Am. Chem. Soc., 54, 4480-7 (1932).
14. Duboux and Rochat, Helv. Chim. Acta., 22, 161-83 (1939).
15. Harned and Brumbaugh, J. Am. Chem. Soc., 44, 2729-48 (1922).
16. Harned, J. Am. Chem. Soc., 48, 326-42 (1926).
17. Randall and Breckenridge, J. Am. Chem. Soc., 49, 1435-45 (1927).
18. Harned and Mason, J. Am. Chem. Soc., 53, 3377 (1931).
19. Hawkins, J. Am. Chem. Soc., 54, 4480-7 (1932).
20. Jenson, U.S. 2,645,563 July 14, 1953.
21. Kolthoff and Kuroda, Anal. Chem. 23, 1304 (1951).

22. Janz and Tanigrichi, Chem. Rev., 53, 397-438 (1953).
23. Carmody, J. Am. Chem. Soc., 51, 2901 (1929).
24. Brown, J. Am. Chem. Soc., 52, 646 (1934).
25. Akerloff and Teare, J. Am. Chem. Soc., 52, 1855 (1937).

VITA

Frank F. Dyer
candidate for the degree of
Master of Science

Thesis: A REINVESTIGATION OF THE ACTIVITY OF HYDROCHLORIC ACID IN
THE SYSTEMS: HYDROCHLORIC ACID-WATER-COBALT CHLORIDE OR
NICKEL CHLORIDE

Major: Physical Chemistry

Biographical and Other Items:

Born: November 18, 1931, Webbers Falls, Oklahoma

Undergraduate Study: Oklahoma Agricultural and Mechanical
College

Graduate Study: Oklahoma Agricultural and Mechanical College,
Stillwater, Oklahoma, 1952-1954

Experience: Graduate Fellowship, Chemistry Department, Okla-
homa A. and M. College

Member: Phi Lambda Upsilon, Pi Mu Epsilon, American Chemical
Society

Date of Final Examination: November, 1954

THESIS TITLE: A REINVESTIGATION OF THE ACTIVITY OF
HYDROCHLORIC ACID IN THE SYSTEMS:
HYDROCHLORIC ACID-WATER-COBALT CHLORIDE
OR NICKEL CHLORIDE

AUTHOR: Frank F. Dyer

THESIS ADVISER: Dr. Thomas Edwin Moore

The content and form have been checked and approved by the author and thesis adviser. The Graduate School assumes no responsibility for errors either in form or content. The copies are sent to the bindery just as they are approved by the author and faculty adviser.

TYPIST: M. A. Miner