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THERMODYNAMIC PROPERTIES OF DILUTE AQUEOUS HYDROCHLORIC ACID SOLUTIONS AT ELEVATED TEMPERATURES FROM ELECTROMOTIVE FORCE MEASUREMENTS

A DISSERTATION

Submitted to
The Graduate Council
of
The University of Tennessee
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Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

by

Richard Stiles Greeley

May, 1959

DISCLAIMER

May 22, 1959

To the Graduate Council;

I am submitting herewith a dissertation written by Richard Stiles Greeley entitled "Thermodynamic Properties of Dilute Aqueous Hydrochloric Acid Solutions at Elevated Temperatures from Electromotive Force Measurements." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Major Professor

We have read this dissertation
and recommend its acceptance:

Accepted for the Council:

Dean of the Graduate School

To Lorie

for her patience, encouragement, and understanding.

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CHAPTER I

INTRODUCTION

A. Reasons for Undertaking the Study

A study of the thermodynamic properties of dilute aqueous hydrochloric acid solutions at elevated temperatures by an electromotive force method was undertaken for several reasons. First, a great need for fundamental information at elevated temperatures was evident from the growing number of industries making use of aqueous solutions at elevated temperatures. Second, the use of the hydrogen electrode against the silver-silver chloride electrode in dilute hydrochloric acid solutions promised to give fundamental thermodynamic information on an important electrode system as well as on hydrochloric acid over a wide temperature range. Third, the measurements of Harned and Ehlers[1,2] from 0 to 60° and of Bates and Bower[3] from 0 to 95° allowed fairly confident extrapolation to higher temperatures for comparison with this study. Fourth, use of the Debye-Hückel theory[4] in the interpretation of the data would show whether that theory in either limiting[5] or extended[6] form would hold at elevated temperatures. And finally, the measurements could serve as a reference standard for other electrode systems and solutions.

B. Discussion of the Cell

The cell

$$\mathrm{Pt};\ \mathrm{H_2(g)},\ \mathrm{HCl}(m),\ \mathrm{AgCl};\ \mathrm{Ag} \qquad \text{(A)}$$

was investigated over the concentration range 0.005 to 1.0 m HCl, the temperature range 25 to 275°, and at hydrogen pressures of about one atmosphere. The cell reaction was assumed to be:

$$\frac{1}{2}\mathrm{H_2} + \mathrm{AgCl} = \mathrm{HCl} + \mathrm{Ag} \qquad \text{(A)}$$

and the corresponding Nernst equation for the measured electromotive force E is then

$$E = E^{\circ} - 2.3026\,\frac{2RT}{F}\log m_{\pm}\,\gamma_{\pm} + 2.3026\,\frac{RT}{2F}\log f_{H_2}. \qquad (1)$$

Here E° is the standard potential of the silver-silver chloride electrode at any temperature assuming that the standard potential of the hydrogen electrode is zero at that temperature, R is the gas constant, T is the absolute temperature, F is the faraday, $m_{\pm}$ is the mean molality of the solution, $\gamma_{\pm}$ is the mean ionic activity coefficient of hydrochloric acid in the solution, and f_{H_2} is the fugacity of hydrogen over the solution. No attempt was made to define or measure E° at a high temperature in relation to E° at 25° or any other standard temperature.

The use of the mean molality $m_{\pm}$ in equation (1) was necessary because silver chloride is appreciably soluble at elevated temperatures and makes a significant contribution to the ionic strength of the solution. Since the solution was saturated with silver chloride at all times the mean molality was defined as follows:

$$m_{\pm} \equiv (m_{H^+}\, m_{Cl^-})^{1/2} = \left[(m_{HCl})(m_{HCl} + s_{AgCl})\right]^{1/2} \qquad (2)$$

where m_{HCl} is the molality of the hydrochloric acid and s_{AgCl} is the solubility of silver chloride in the solution.

C. Previous Investigations

The only previous investigation of cell (A) at temperatures above 100° was that of Roychoudhury and Bonilla[7]. Their purpose was to determine the suitability of a hydrogen electrode and a silver-silver chloride electrode for acidity determinations at temperatures up to 250° and total pressures up to 600 psig. Therefore they studied only two hydrochloric acid solutions, 0.00100 N and 0.01689 N, at several hydrogen pressures and hence did not obtain any thermodynamic quantities. They observed an effect of hydrogen pressure on the electromotive force not in accord with the Nernst equation (1) which they attributed to an effect of hydrogen on the silver-silver chloride electrode. Lietzke[8] interpreted their data and showed that there was reasonable agreement between their measured values of <u>E</u> and values calculated by extrapolation of the data of Harned and Ehlers[2] at temperatures as high as 150°.

The pioneering work in extending the study of cell (A) to higher temperatures was that of Harned and Ehlers[1,2] which covered the range 0 to 60° with solutions 0.004 to 4 <u>m</u>. Since the present study included solutions more concentrated than those studied by Bates and Bower[3], <u>i.e.</u>, 0.2, 0.5, and 1.0 *m*, the data of Harned and Ehlers were used for comparison in these cases. Åkerlöf and Teare[9] studied cell (A) at hydrochloric acid molalities from 3 to 16 *m* and their results were in agreement with those of Harned and Ehlers in the region where the measurements overlapped. Janz and Taniguchi[10] have reviewed the extensive work done in developing silver-silver halide electrodes.

The most extensive investigation of cell (A) in terms of the number of cells studied over a wide temperature range was that of Bates and Bower[3]. They determined the thermodynamic quantities $\underline{E}^o$, $\gamma\pm$, $\bar{\underline{L}}_2$ (the relative partial molal heat content), and $\bar{\underline{J}}_2$ (the relative partial molal heat capacity) at 0 to 95° from measurements on solutions 0.001 to 0.12 *m*. Their results were in good agreement with those of Harned and Ehlers[2] except for a surprising 0.18 mv. discrepancy in $\underline{E}^o$ at 25°. This discrepancy has been discussed by Taniguchi and Janz[11] and explained by them on the basis of a slight difference in thermal strain of the silver-silver chloride electrodes. As noted above, the data of Bates and Bower could be extrapolated with reasonable confidence to higher temperatures and therefore their experimental and mathematical procedures were followed in the present study whenever feasible.

There have been several investigations of other electrode systems and solutions at elevated temperatures. Lietzke and Vaughen[12] studied the cell:

$$\text{Ag; AgCl, HCl(m), Hg}_2\text{Cl}_2\text{; Hg} \qquad \text{(B)}$$

from 25 to 200° and found that hydrolysis of the mercurous chloride at low acid concentrations and high temperatures prevented the cell from giving the electromotive force calculated from heat capacity data. Lietzke and Stoughton[13] studied the cell:

$$\mathrm{Ag};\ \mathrm{Ag_2SO_4},\ \mathrm{H_2SO_4}(\underline{m}),\ \mathrm{Hg_2SO_4};\ \mathrm{Hg} \qquad \text{(C)}$$

from 25 to 200° and found again that hydrolysis of the mercurous salt occurred at low acid concentrations. Vaughen and Lietzke[14] studied the effect of dissolved silver sulfate on the activity of sulfuric acid solutions from 25 to 140° using the cell:

$$\mathrm{Pt};\ \mathrm{PbO_2},\ \mathrm{PbSO_4},\ \mathrm{H_2SO_4}(\underline{m}),\ \mathrm{Ag_2SO_4};\ \mathrm{Ag} \qquad \text{(D)}$$

and observed reproducible potentials which were linear functions of the temperature at each sulfuric acid concentration. Myers[15] studied the antimony electrode against the silver-silver chloride electrode in buffered solution up to 200° under nitrogen at a total pressure of 2000 psi. The results were reproducible but showed irregularities perhaps due to the formation of different salt hydrates with differing solubilities as the temperature was raised. Pražák[16] used the silver-silver chloride electrode at temperatures to 200° in an autoclave to study corrosion phenomena. Connection to the main body of the solution was <u>via</u> a saturated sodium chloride salt bridge contained in a tube filled with corundum powder. He found that the potential of this combination <u>versus</u> a platinum wire in saturated sodium chloride solution decreased only about ten millivolts in going from 25 to 200°.

The Canadian Aviation Electronics Company Ltd. has developed a commercial pH meter for use up to 200°[17]. The meter uses a Beckman high temperature glass electrode as the pH sensitive electrode and a saturated calomel electrode maintained at 25° as the reference electrode. Lietzke and Tarrant[17] have used this meter for measurements on hydrochloric acid, sulfuric acid, and uranyl sulfate solutions. Marburger, Anderson, and Wigle at Argonne National Laboratory have developed a similar device[18].

It is apparent that relatively little work has been done in the field of high temperature electromotive force measurements in aqueous solutions. With the possible exceptions of the silver-silver sulfate electrode, which suffers by the large solubility of silver sulfate[14,19], and the lead-lead dioxide electrode, no thermodynamic reference electrode besides the silver-silver chloride electrode has been found for use at elevated temperatures. As for hydrogen ion-sensitive electrodes, glass electrodes as well as other types that may be developed will have to be calibrated against solutions standardized using the hydrogen electrode.

D. Fundamental Constants

Appendix I contains a list of the fundamental constants used in the calculations throughout this study. They were taken from the recent work by Cohen, Crowe, and Dumond[20]; the only major change from constants used by previous investigators being in the ice-point temperature, 273.1500°K rather than 273.16°K, as recommended by the Tenth General Conference on Weights and Measures, October 1954[21]. However this actually represents no significant change in the calculated results. Also given in Appendix I are S_o, that part of the Debye-Hückel limiting slope that involves fundamental constants (limiting slope = $S_o/(D^3T^3)^{1/2}$), and the equations used for calculating the dielectric constant and the density of water as a function of temperature. The former was given by Åkerlöf and Oshry[22] and the latter by Lietzke[23]. The Åkerlöf and Oshry equation gives values of the dielectric constant at high temperatures significantly different from the equation of Wyman and Ingalls[24] used by previous investigators. The Lietzke equation for the density of water was obtained by fitting the density of water from 0 to 300° to a quadratic function of the centigrade temperature by the method of least squares.

CHAPTER II

EXPERIMENTAL DETAILS

A. Introduction

The experimental apparatus used in this investigation was designed to contain the aqueous hydrochloric acid solution and about one atmosphere of hydrogen at temperatures from 25 to 275° and to permit measurement of the temperature and pressure of the system and the electromotive force between a hydrogen and a silver-silver chloride electrode in the solution. Corrosion of the container and insulation of the electrode leads were the two major problems involved.

At the outset it was decided to keep the apparatus as simple as possible with the ultimate aim of determining the electromotive forces to an accuracy of a few tenths of a millivolt over the temperature range. With this in mind a static system was used in order to avoid problems involved in bubbling hydrogen through a system containing water vapor at pressures up to 100 atm. and to avoid mechanical and electrical difficulties in trying to rock, vibrate, or stir the system. The idea of a high temperature solution sampling device was also discarded. A general schematic diagram of the apparatus is shown in Figure 1.

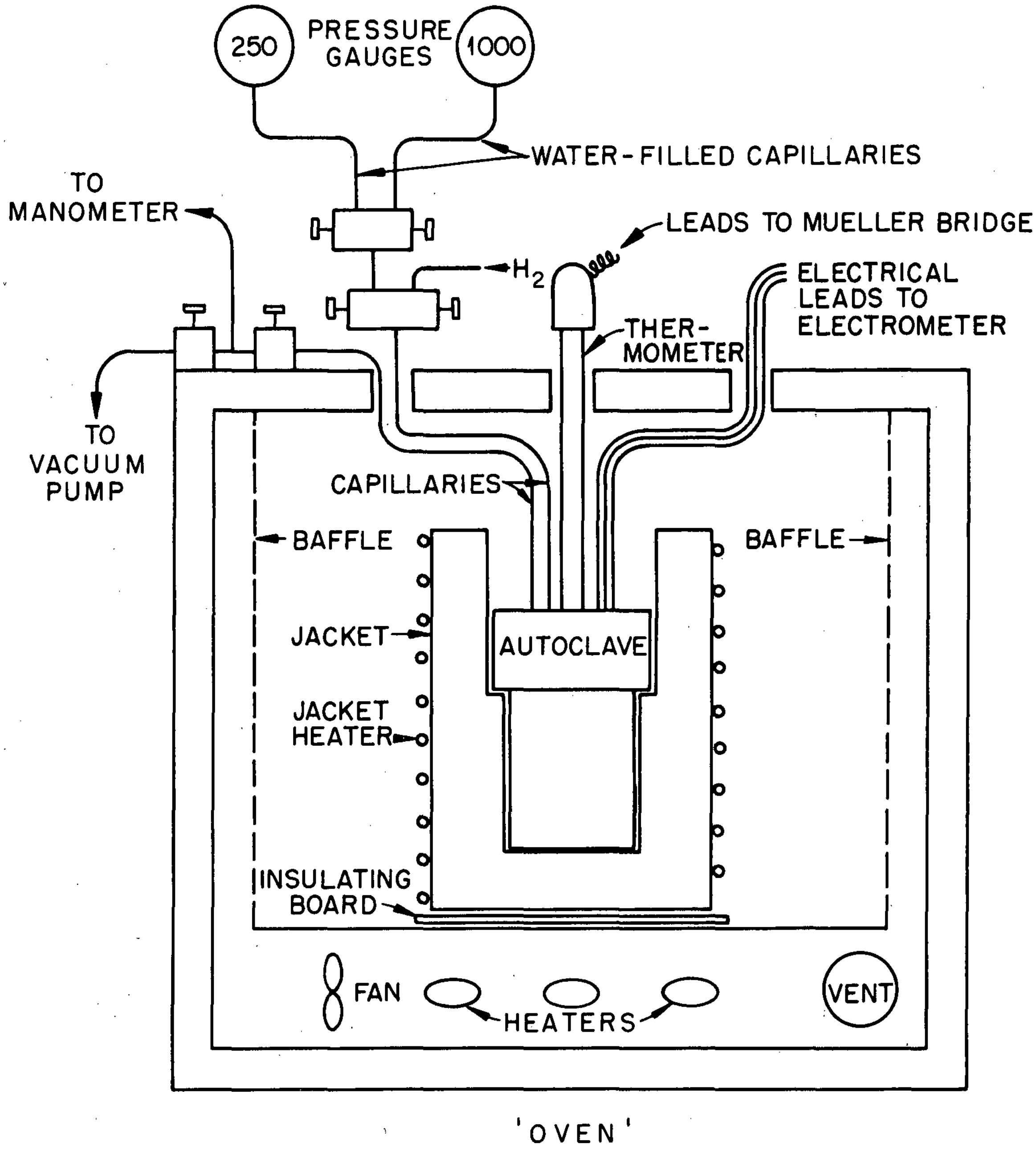

Figure 1. General Schematic Diagram of the Apparatus Used to Measure Electromotive Forces at Elevated Temperatures.

B. The Autoclave

1. The Autoclave Body

The autoclave assembly is shown in detail in Figure 2. The body was machined from a bar of type 347 stainless steel to final dimensions 3-1/2-in. dia. O.D., 2-in. dia. I.D., 6-1/4-in. high, 3/4-in. wall thickness. The mechanical properties of the stainless steel and the other materials used in the apparatus are listed in Table I. As may be calculated, the body was sufficiently strong to withstand the vapor pressure of the solutions used plus the hydrogen pressure at temperatures well above those contemplated, but it was not strong enough to withstand the hydraulic pressure of the solution had the autoclave been filled too full.

2. The Liner and Interliner

The primary containment vessel for the solution was a cylindrical liner made of fused silica for corrosion resistance. It fitted snugly into a Teflon interliner which in turn fitted snugly into the stainless steel autoclave body. The Teflon interliner, having a relatively high coefficient of thermal expansion, expanded as the autoclave was heated and filled the space between the steel body and the quartz liner completely so as to prevent condensation of water vapor between the liner and the body. A lip on the Teflon interliner served as a gasket for sealing the autoclave head to the autoclave body. The total volume of the autoclave available for solution and vapor was 160 ml.; and, allowing

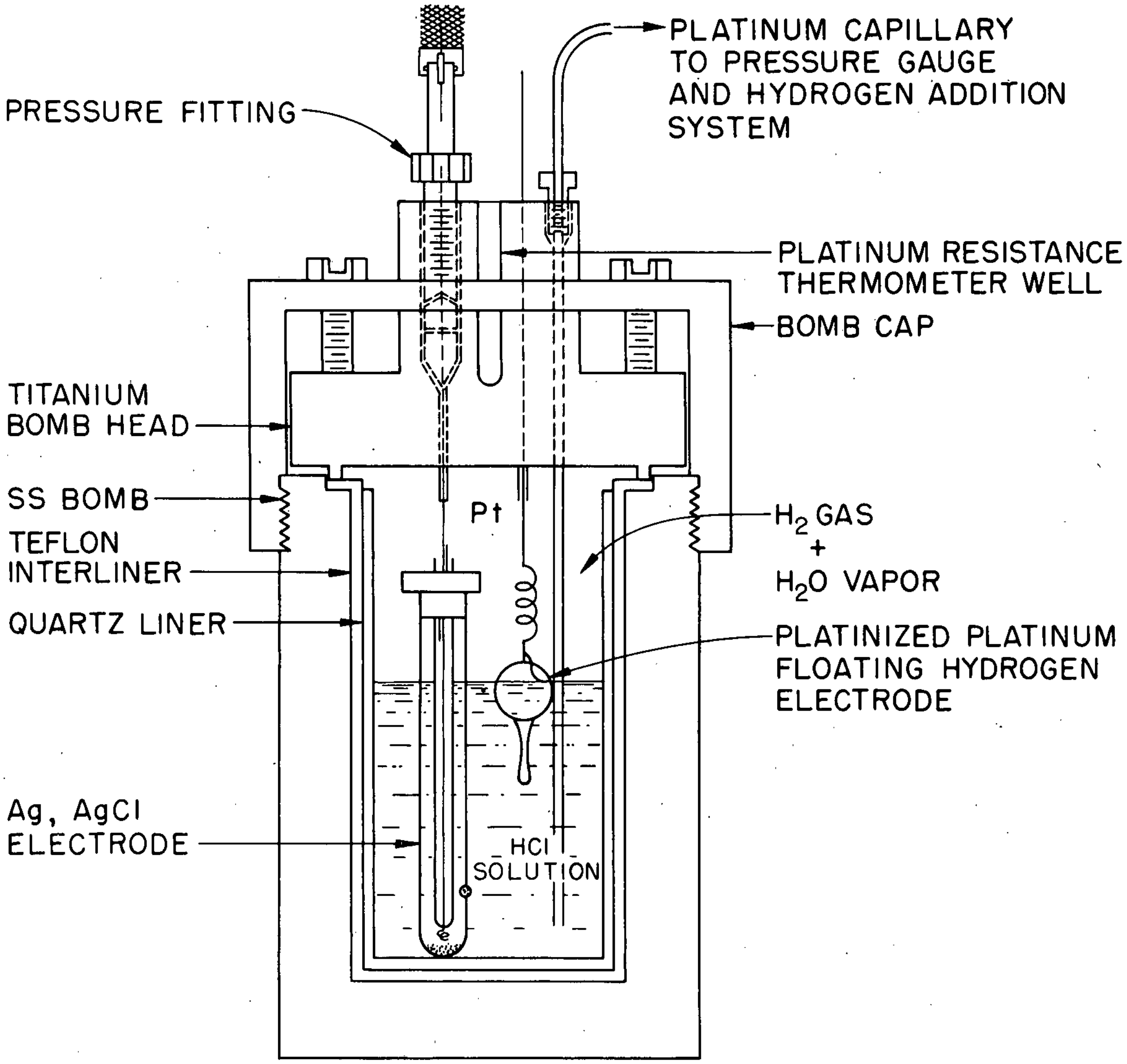

Figure 2. Autoclave Assembly for Determining Activities of Hydrochloric Acid Solutions at Elevated Temperatures.

TABLE I

MECHANICAL, THERMAL, AND ELECTRICAL PROPERTIES OF MATERIALS USED IN AUTOCLAVE

	Tensile Strength (psi)		Modulus of Elasticity (psi)	
	25°	300°	25°	300°
Type 347 SS[a]	90×10^3	68×10^3	29×10^6	25×10^6
Titanium[a, b]	58×10^3	28×10^3	16×10^6	14×10^6
Platinum[a, c]	24×10^3	18×10^3	21×10^6	-
Fused Silica[a]	-	-	12×10^6	-
Teflon[d]	2.0×10^3	0.34×10^3	0.065×10^6	0.008×10^6

TABLE I

MECHANICAL, THERMAL, AND ELECTRICAL PROPERTIES OF MATERIALS USED IN AUTOCLAVE (CONTINUED)

	Thermal Expansion Coefficient $^{o}C^{-1}$	Thermal Conductivity $(cal/cm^2/cm/^{o}C/sec)$	Electrical Resistivity (ohm-cm)
	25 to 300°	25°	25°
Type 347 SS[a]	1.8×10^{-5}	0.05	11×10^{-6}
Titanium[a, b]	9.0×10^{-6}	0.06	55×10^{-6}
Platinum[a, c]	8.9×10^{-6}	0.17	11.4×10^{-6}
Fused Silica[a]	0.5×10^{-6} [e]	0.0024	10×10^{6} [f]
Teflon[d]	120×10^{-6}	0.0006	$> 10^{15}$

[a] Values from T. Lyman, Ed., "Metals Handbook", 1948 Edition, The American Society for Metals, Cleveland, Ohio (1948).

[b] Commercially pure.

[c] Annealed.

[d] Values from R. C. Doban, C. A. Sperati, and B. W. Sandt, Soc. Plastics Engrs Journal 11, 1955.

[e] Mean value up to shrink temperature.

[f] At 700°C.

for a 1/2-in. vapor space at 275° and the expansion of the solution, 91 ml. of solution was used in every test.

Corrosion of the silica liner and other silica parts was measured during several tests to ensure that the rate was low enough to be neglected as a source of error. Table II is a list of the weight losses of fused silica electrode holders immersed in dilute hydrochloric acid solution during tests for the temperature ranges shown. The ratio of the area of the electrode holders to the total area of fused silica exposed to solution was used to calculate the total amount of corrosion that occurred during the test. The total loss in weight is listed in the last column of Table II. It can be seen that most of the corrosion occurred at 275° and that the total weight losses even for the tests that went to 275° were small. For these reasons it is believed that the corrosion of the silica produced no significant effect on the measurements.

The Teflon interliner was also a possible source of contamination since it was observed previously at this Laboratory that Teflon evolves low molecular weight material at temperatures as low as 150°[25]. To avoid this difficulty, the interliners were pretreated by heating to 275° in a trial run before use in an actual test.

The silica liner-Teflon interliner arrangement was completely satisfactory. It was found that a single Teflon interliner could be used indefinitely to 200° and for three or four tests to 275°. One of the silica liners cracked during a test at 275° but a second liner was

TABLE II

CORROSION OF FUSED SILICA IN DILUTE HYDROCHLORIC ACID

HCl Conc.	Temperature Span	Weight Loss, mg.[a, b]		Total Loss of Weight
m	°C	Holder No. 1	Holder No. 2	mg.
0.0075	25 to 225	-0.2	0.0	0.3
0.01	25 to 275	-2.8	-4.2	12
0.025	25 to 275	-8.1	-1.6	17
0.1	25 to 275	-1.4	-2.9	7.4
0.2	25 to 250	-0.9	0.0	1.5
0.2	25 to 275	-4.4	-4.5	15
1.0	25 to 200	-2.0	-	3.4

[a] Area of each holder was 14 in^2. Total area of fused silica exposed to solution was roughly 48 in^2.

[b] Total length of each test was about 36 hr.

used for the remainder of the tests without difficulty.

3. The Autoclave Head and Fittings

The autoclave head was machined from commercially pure titanium. The head is shown in some detail in Figure 3 and represents extensive development work. The reason for the development work was to achieve a design which would allow the following: 1) evacuation of the vapor space, 2) bubbling of hydrogen through the solution at the start of a test, 3) complete sealing off of the vapor space during a test to prevent condensation of vapor in any crevice or recess, 4) connection of the solution with the pressure gauges*, 5) insulation of the leads to two silver-silver chloride electrodes and one hydrogen electrode, and 6) connection of the leads to shielded cables attached to the electrometer.

The first four criteria were met by installing a special valve directly in the autoclave head. As may be seen in Figure 3, the valve stem opened down so that the vapor space could be evacuated through the stainless steel capillary tube connected to a 1/16-in. dia. hole leading to the space around the lower portion of the valve stem. Hydrogen was also vented through this line during the initial bubbling. A mercury manometer was connected to the stainless steel capillary in order to determine the initial pressure in the system very accurately. When the system was ready for the test to begin the valve was closed upward

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*The solution rather than the vapor space was connected to the pressure gauges since condensation of vapor might have occurred in cooler regions of the connecting tubing.

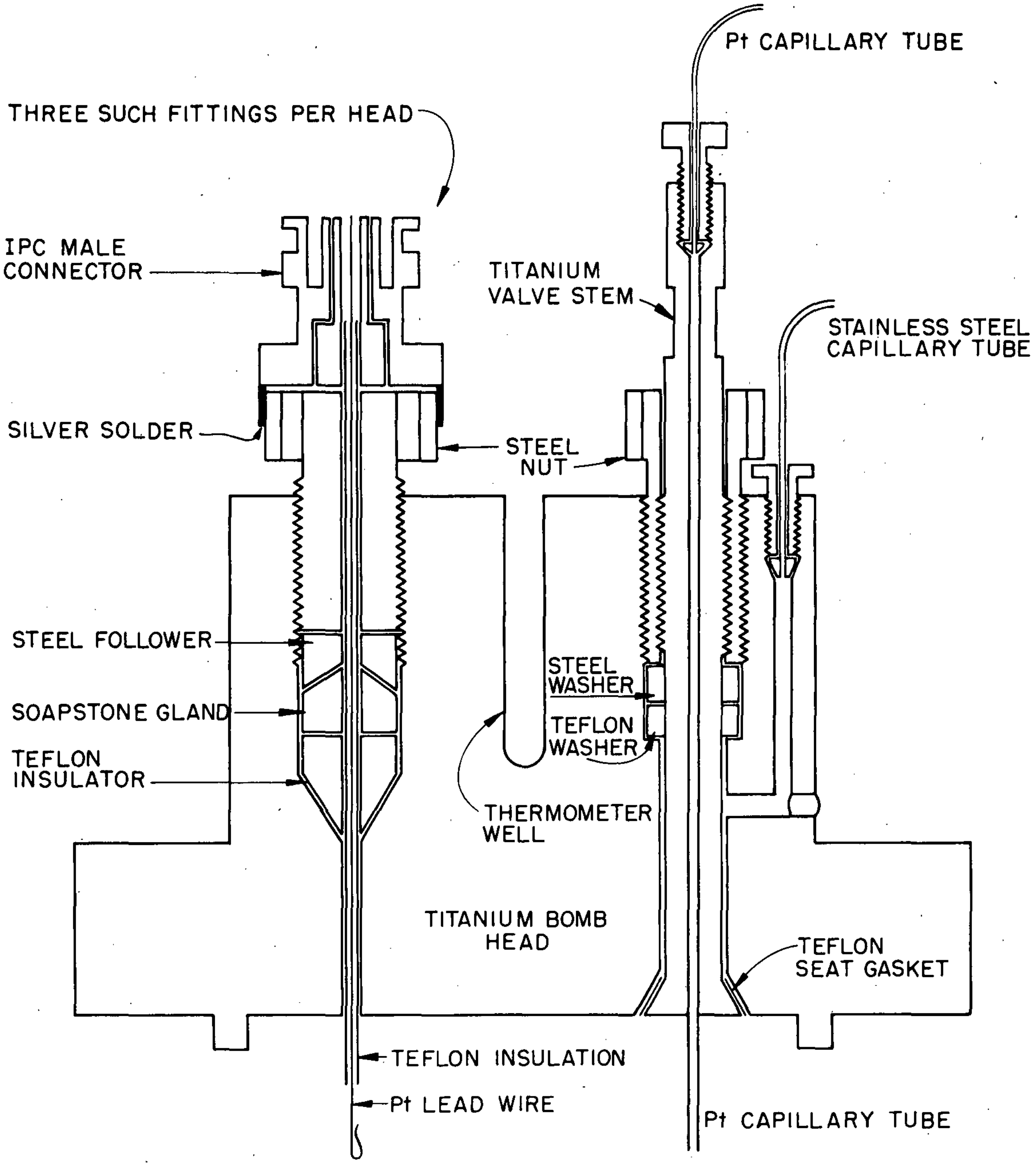

Figure 3. Titanium Bomb Head for Use with Autoclave Assembly Shown in Figure 2.

against a Teflon seat gasket and the test chamber was completely isolated except for the platinum capillary tube leading to the pressure gauges. This tube was installed right through the center of the special valve stem and was sealed in at the top of the valve stem with a Teflon gasket and a steel nut. The platinum capillary tube connected at its other end to a two-way, two-stem Autoclave valve* mounted outside of the oven. Prior to the start of a test hydrogen could be passed down the tube to bubble through the solution. Then, to make the test, the hydrogen supply was shut off at the valve on top of the oven and the other valve opened to water-filled, stainless steel capillary lines connected directly to the pressure gauges (see Figure 1). As the temperature and pressure of the solution were increased, the residual hydrogen in the platinum capillary tube was compressed but there always was a bubble of hydrogen which prevented the hydrochloric acid solution from being forced up into the stainless steel valve and capillary system.

The fifth and sixth criteria were met as follows. Stout 18 gauge platinum lead wires for the three electrodes were inserted in Teflon "spaghetti" of such a size that a snug fit was made with the holes provided through the autoclave head. Teflon cones were then slipped over the "spaghetti" and backed up with crushable soapstone cones. Finally a steel pressure cone was slipped on and the steel pressure nut tightened down. The nut was lubricated with a Vaseline-zinc dust mixture to

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*Type 1005, Autoclave Engineering Co., Erie, Pa.

prevent galling with the titanium head. This seal needed retightening after the first thermal cycle but then held vacuum- and pressure-tight to 800 psig. A Teflon insulated, snap-lock IPC* fitting was silver soldered to the steel pressure nut and a matching female fitting was silver soldered to wire-braid covered, Teflon insulated copper wire so that convenient connections between the platinum lead wires and the copper wires leading to the electrometer were made. Since the platinum-copper connections were all at the same temperature inside the oven there was no thermocouple effect. The electrodes were connected to the stout platinum lead wires by firm crimping.

The titanium autoclave head was resistant to corrosion by the vapor above the acid solutions under all conditions except during the tests with 0.5 and 1.0 m HCl. Above 200° with the former and 150° with the latter solution an increase in pressure with time at constant temperature was noticed which clearly was due to corrosion of the titanium. The extent of the reaction was followed by the change of pressure and electromotive force with time and the results corrected as discussed below in Chapter III, Section A. On opening the autoclave after the two tests in which corrosion occurred a white deposit, determined spectrographically to be TiO_2, was found on the titanium. Therefore the corrosion reaction was assumed to be:

$$Ti + 2H_2O \rightarrow TiO_2 + 2H_2 \ . \qquad (E)$$

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*Industrial Products Co., Danbury, Conn.

Agreement was obtained between the observed pressure increase and the pressure increase calculated from the change in solution concentration due to the loss of water in accordance with reaction (E).

Therefore, with the exception noted in the above paragraph, the titanium autoclave head gave excellent service. It was held pressure tight onto the autoclave body during thermal cycles by eight steel lugs supported in a stainless steel cap screwed onto the autoclave body. The lugs acted on a Belleville spring washer designed so that the expansion and contraction of the Teflon gasket (the lip on the Teflon interliner) with temperature was matched by compression and expansion of the spring[26]. The design of the washer is given in Appendix II*.

C. The Electrodes

1. The Hydrogen Electrode

The hydrogen electrode is illustrated in Figure 4. It was made, at the suggestion of Mrs. Loretta Greeley**, to float at the surface of the solution in order to come quickly into equilibrium with the hydrogen in the vapor phase. A 1-in. length of 24 gauge platinum wire was attached to a projection on a fused silica float with fine 40 gauge platinum wire.

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*The author wishes to thank Dr. W. C. Waggener of Oak Ridge National Laboratory for suggesting the use of the Belleville spring washer.

**The author wishes to thank his wife for this and several other very valuable suggestions.

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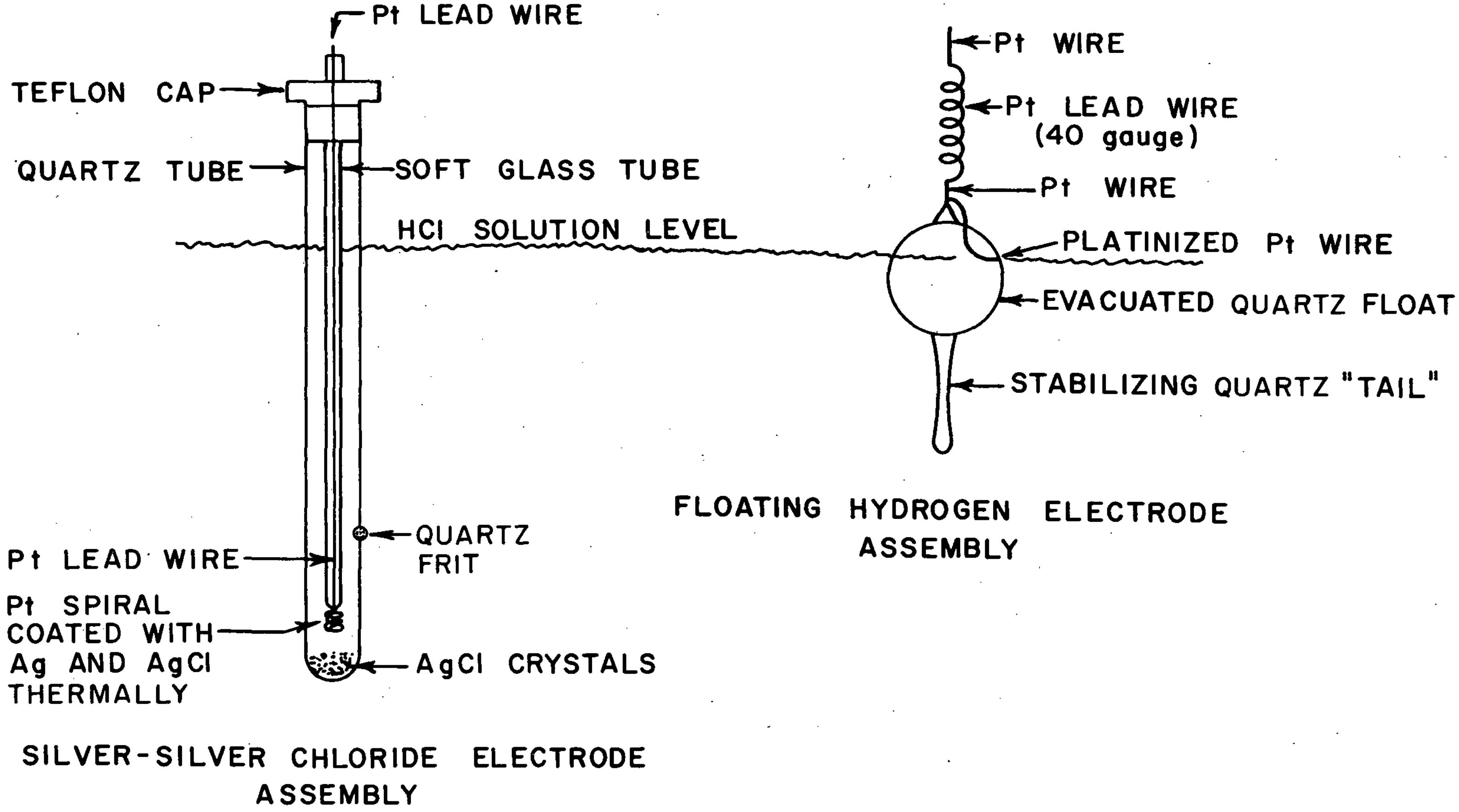

Figure 4. Electrode Assemblies for Use in Determining Activities of Hydrochloric Acid Solutions at Elevated Temperatures.

Another fine platinum wire was welded onto the 24 gauge wire in order to connect it with the platinum lead wire in the autoclave head. The platinum was platinized as directed by Bates[27]. On several occasions the floating electrode was compared with a foil electrode prepared in the usual way[28] in dilute hydrogenated hydrochloric acid, and the two types of electrodes exhibited the same potential to within ± 0.02 mv.

In preliminary high temperature tests in which the hydrogen and silver-silver chloride electrodes were immersed in the solution with no intervening barrier, the platinized platinum became covered with a deposit of silver. The deposit was shown to be silver by dissolving it in dilute nitric acid and precipitating a white salt with a few drops of hydrochloric acid. The white salt darkened on exposure to light and was undoubtedly silver chloride. The deposit of silver most probably came from reduction of silver ion in solution by hydrogen. The silver ion came from the relatively large solubility of silver chloride at high temperatures. Anderson[29] observed this phenomenon at very low hydrochloric acid concentrations at 25° and showed that the deposit did not affect the operation of the hydrogen electrode. The only effects in the present study were the change in hydrochloric acid concentration and the accompanying change in hydrogen pressure according to the reaction:

$$\frac{1}{2} H_2 + AgCl \rightarrow Ag + HCl \ . \qquad (F)$$

Since the hydrochloric acid concentration could not be determined after each electromotive force measurement, as was possible in Anderson's case, it was desired to prevent the reaction from occurring. Therefore, a silica tube was placed around each silver-silver chloride electrode in later tests. A sintered silica disk sealed into the side of the tube provided a connection between the solution inside the tube and the main body of electrolyte. This prevented the deposition of silver on the hydrogen electrode. However reaction (F) still occurred, presumably on the silver-silver chloride itself, and this reaction caused the major error in the results.

The hydrogen electrode was replatinized before each test.

2. The "Bates"-type Silver-Silver Chloride Electrode

The first type of electrode used was a completely "thermal" type[30] but will be called a "Bates"-type since his procedures were followed as closely as possible[31]. The electrode is illustrated in Figure 4. A six-inch length of 30 gauge platinum wire was sealed into a four-inch length of 1/8-in. dia. O.D. soft glass tubing. The end of the wire protruding from the seal was wound into a helix, cleaned in hot concentrated nitric acid and in conductivity water, and then coated with a paste of silver oxide and silver chlorate in a 7:1 mixture by weight. The electrode was then heated five minutes in a muffle furnace at 550°. After cooling, the coating and heating were repeated. Finally the electrode was coated a third time and heated seven minutes.

The heating produced a white intimate mixture of finely divided silver and silver chloride completely covering the platinum helix. The intimate mixture of silver and silver chloride was desired in order to prevent the electrode from becoming deficient in silver chloride at high temperatures where the solubility of silver chloride becomes appreciable.

Six electrodes were prepared simultaneously, and after cooling they were immersed in hydrochloric acid of the same composition as that to be used in the test and interconnected. The solution was heated to 75° and allowed to cool overnight as suggested by Ashby, Cooke and Datta[32]. The next day the electrodes were intercompared. With few exceptions all electrodes were within ±0.05 mv. of each other. Two electrodes reading within 0.02 mv. of the average were chosen for the experiment and fastened onto the platinum leads through the autoclave head. A Teflon cap allowed the silica tube to be fitted over the electrode.

Taniguchi and Janz[11] have investigated the causes of variation in the potential of "thermal-electrolytic" electrodes and found that freshly-made electrodes were positive with respect to electrodes in equilibrium with the solution. The cause, however, was due to concentration polarization during electrolytic chloridization and hence would not be a factor in the present study using completely thermal electrodes. A more serious question is that of "thermal strain" which they said occurred on cooling of the electrodes after heating and which introduced variations in potential of -0.08 to +0.05 mv. These variations were permanent. For this reason the electrodes used in this study were given the added treatment of being heated in solution to 75° while interconnected. This appeared to remove practically all variation in potential of one electrode from another, perhaps because at the higher temperature the electrolytic reaction between interconnected electrodes having initially different potentials occurred rapidly. Also the solubility of silver chloride was higher at the higher temperature and any silver chloride in a higher free energy state could have more easily dissolved and reprecipitated in the lowest free energy state. For these same reasons the electrodes were handled with extreme care after equilibration to prevent mechanical shocks from introducing new strains.

It was found that dilute hydrochloric acid attacked the soft glass electrode holder at 250°. Therefore this type of electrode was used only in the first series of experiments that went just to 200°. At the end of a test the two electrodes were again compared with the four that had not been used. The agreement was in all cases within ± 0.2 mv. New electrodes were made for each test in the first series.

3. The "North"-type Silver-Silver Chloride Electrode

At the suggestion of Mr. Gerald North the silver-silver chloride electrode was modified as follows: 1) the soft glass holder was omitted, 2) a stouter platinum wire (18 gauge) was used as the electrode base, and 3) the wire was coated its entire length with silver oxide and silver chlorate paste. The heating schedule was the same as for the "Bates"-

type electrode. The base wire was long enough so that it was run through the autoclave head and served as the lead wire as well. Only one pair of these electrodes was made and they were used for the entire second series of experiments covering the range 25 to 275°. The thermal cycling and successive dissolution and reprecipitation of silver chloride on the electrode apparently improved the characteristics of the electrode, if anything, and with due care being taken to avoid mechanical shock the results at all temperatures in common with the first series were entirely comparable.

As noted above, a silica tube containing a sintered silica disk was placed around the electrode. The disk was of such porosity that it took fifteen to twenty minutes for solution to come to the same level inside as outside the tube. Excess solid silver chloride was always placed inside the silica tube to ensure that the solution was saturated with silver chloride at every temperature.

D. The Autoclave Jacket, the Oven, and the Temperature Controls

The autoclave was placed inside a large, cylindrical, aluminum jacket having 2-to 2-1/2-in. thick walls. A resistance heating wire was wrapped around the jacket to provide an additional 1000 watts of power to aid in changing temperatures rapidly. The wire heater was otherwise not used. Two inches of glass wool and asbestos insulation was put on top of the autoclave inside the jacket.

The autoclave and jacket were placed in an electrically heated, forced-draft oven[*]. Electrical and pressure connections were run out through a hole in the top of the oven. The temperature control of the oven was modified as follows: 1) Two of the three 1500 watt heaters were connected directly to the 110 volt line through a Sola voltage regulating transformer[**]. These two heaters were either on or off; one being on at temperatures from 200 to 275° and both being on when a change in temperature was desired. 2) The third heater was sufficient to heat the oven to 175° and was connected separately to the 110 volt line through two Variac transformers. The larger one, capable of carrying 10 amp., was on continuously and was set to the proper value for the temperature desired as learned by experience. The smaller one, capable of carrying 5 amp., was controlled either full on or off by an Electron-O-Therm regulator[***] which used a nickel resistance thermometer as sensing element and a mercury switch as relay. In this way the ± 3 to 5 degree Centigrade swing in the oven temperature, obtained with the standard controls, was decreased to ± 1 degree. Within the autoclave this temperature fluctuation was smoothed out by the heat capacity of the jacket, autoclave, liners, and solution to less than that detectable with a platinum resistance thermometer, ± 0.001 degree.

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[*] Catalog No. 31240, Precision Scientific Co., Chicago, Ill.

[**] Catalog No. 30811, Sola Electric Co., Chicago, Ill.

[***] Model 141C, Technical Equipment Co., Emeryville, Calif.

E. Temperature Measurement

The temperature of the autoclave head was measured with a platinum resistance thermometer inserted in the thermowell shown in Figures 2 and 3. The reasonable assumption was made that the temperature of the head was the same as that of the vapor and solution inside the autoclave when the thermometer showed no further change of temperature with time. The thermometer had been calibrated by the National Bureau of Standards at the ice, steam, and sulfur points and the ice point was rechecked before each run.

The resistance of the thermometer was measured with a Mueller bridge and a mercury commutator*. The Mueller bridge was calibrated for internal consistency by the method given in the operating manual[33] and for accuracy by comparison with a 10 ohm resistance standard calibrated by the National Bureau of Standards. Temperatures are believed to be accurate to well within ± 0.01°.

Unfortunately the available Mueller bridge could not measure resistances equivalent to temperatures above 250°. Therefore an iron-constantan thermocouple, routinely used only for rough measurement of the autoclave temperature, was calibrated by comparison with the thermometer at 200, 225, and 250° during each run and used for the accurate temperature measurement at 275°. In these instances the temperatures were accurate only to ± 0.05°. The temperatures of the oven and jacket

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*No. 8067 Mueller Temperature Bridge, Leeds and Northrup Co., Philadelphia, Pa.

were also measured with iron-constantan thermocouples and displayed continuously on a Brown recording potentiometer[*].

F. Pressure Measurement

Pressures were measured using two precision bourdon tube gauges[**] connected directly to the solution with water-filled stainless steel capillary tubes leading to the valves and platinum capillary discussed above. One of the gauges had a range 0 to 250 psig. and a precision stated by the manufacturer to be 0.25 psi. It was used at temperatures to 200°. The other gauge had a range 0 to 1000 psig. and a stated precision of 1 psi. The gauges were calibrated after the experiments using a pneumatic dead weight tester[***]. This device was not commercially available until the end of the study. However the calibration indicated that the gauges were as accurate as the manufacturer had claimed. Because of a hysteresis which would have produced an error in mid-scale twice as large as those quoted, pressures were generally measured only after an increase in pressure. The zero shift of the gauges was well within the above stated limits, but to prevent accumulation of errors

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[*] Minneapolis Honeywell Reg. Co., Philadelphia, Pa.

[**] Gauges No. 13948 and 13949, Heise Bourdon Tube Co., Newtown, Conn.

[***] Type 6-201 Primary Pressure Standard, Consolidated Electrodynamics Corp., Pasadena, Calif.

and to take into account the weight of water within the capillaries, the pressure in the autoclave at the start of a test was measured with a mercury manometer connected to the vapor space in the autoclave as described above in Chapter II, Section B. The gauges were then set at the pressure indicated by the manometer. Pressures were converted to psi-absolute from the measured psi-gauge by means of a mercurial barometer hung next to the gauges. The barometer scale was calibrated with an accurate cathetometer and the height of the mercury column was shown to agree within better than 0.1 mm with the height of another column of triply distilled mercury above which existed a vacuum of at least 1×10^{-6} mm. Hg. as measured with a thermocouple gauge.

As a final check on the system the vapor pressure of pure, degassed water was measured to 250°. Agreement with steam tables[34,35], after considerable development of the system to its final form, was excellent and within the error limits of the gauges.

The need for accurate pressure measurement is apparent when one considers the fact that the pressure of hydrogen in the system was determined by subtracting the vapor pressure of the solution from the total pressure measured as above. To obtain an accuracy of 0.25 mv. in the electromotive force it was necessary to know the hydrogen pressure and hence the total pressure to an accuracy of 0.25 psi. in the neighborhood of 200°.

The vapor pressures of the solutions were obtained by applying Raoult's Law to the values of saturated water vapor pressure given in the steam tables. This admittedly inaccurate method was used after the vapor pressure of degassed 0.1 m HCl had been measured to 250° and found to agree with Raoult's Law within the accuracy of the gauges.

One further correction was made to the vapor pressure of the solution. This was the effect of the presence of hydrogen on the vapor pressure. Although the hydrogen pressure was only about one atmosphere, a slight correction was found to be significant. The derivation of the correction formula and a table of values are given in Appendix III.

Thus the hydrogen pressure was calculated as follows:

$$P_{H_2} = P_{total} - P_{steam} - \Delta P_R + \Delta P_H \tag{3}$$

where: P_{H_2} = calculated hydrogen pressure,

P_{total} = measured total pressure,

P_{steam} = vapor pressure of pure water from steam tables,

ΔP_R = Raoult's Law correction = $P_{steam} \left(\frac{2m}{2m + 55.56}\right)$,

m = the molality of hydrochloric acid used,

ΔP_H = hydrogen pressure correction as given in Appendix III.

No correction of pressure to fugacity was made and this fact is discussed below in Chapter IV, Section A. It is felt that the hydrogen pressures were accurate to ± 0.25 psi to 200° and ± 1 psi to 275°.

G. Electromotive Force Measurements

The electromotive force itself was measured with a vibrating reed electrometer[*] and a precision potentiometer[**], and was displayed on a Brown recorder. The precision potentiometer was used to compensate for all but 1 mv. of the cell electromotive force and the remainder was read directly from the electrometer scale. The potentiometer was calibrated for internal consistency and then used to calibrate the electrometer and recorder scales for linearity and accuracy. No corrections were found to be necessary.

Two standard cells[***] were used for standardization. Both were compared frequently with a similar cell recently compared with a standard cell at the National Bureau of Standards. Since the laboratory temperature was maintained at 25 ± 1° at all times, no temperature correction was made on the standard electromotive forces. One standard cell was used to standardize the potentiometer. The other was then connected to the electrometer and a regular electromotive force reading taken. This procedure simply showed whether all connections and adjustments were in order. In all cases the measured electromotive force agreed with the

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[*] Model 30, Applied Physics Corp., Pasadena, Calif.

[**] Type B, Rubicon Co., Philadelphia, Pa.

[***] Cat. No. 100, The Eppley Lab. Inc., Newport, R. I.

standard value within ± 0.02 mv. Twenty-four telephone-type 1-1/2 volt dry cell batteries were connected appropriately in parallel and series to give 3 volts potential to the potentiometer circuit. These dry cells were far superior to a large 6 volt wet cell battery, their rate of drift of potential being about 0.08 mv. per twenty-four hours.

The fact that the electromotive force of the second standard cell could be measured accurately was no guarantee that the potential of the cell inside the oven could be measured likewise. The vibrating reed electrometer is notorious for "ground loop" difficulties. However it is felt that these were overcome by using wire-braid covered lead wire and by insulating the autoclave and all associated tubing and wires from the oven. The autoclave was then grounded to the electrometer case. With this done, turning the oven heaters or fan on or off did not affect the potential at all. On the other hand the jacket heater caused a ten millivolt shift in the cell potential when it was in use and so no readings were taken with that heater on. Thermocouple effects between the leads were mentioned above as being negligible. The measured potentials were undoubtedly within ± 0.05 mv. of the actual cell electromotive force.

A further factor was the length of time necessary to establish equilibrium after a change of temperature. It was found that the electromotive force often came to temporary and false "constant" values when the potential appeared to change less than a few hundredths of a millivolt in an hour. The causes of this will be discussed below in Chapter III, Section A. Suffice it to say that the recorder trace was invaluable in showing slight trends and that experience soon showed the false from the true values.

H. Solutions and Materials

1. Conductivity Water

All solutions were made from conductivity water; all apparatus was given final rinsings with the same; and all chemicals were recrystallized or washed in conductivity water as deemed necessary. The conductivity water was prepared by passing laboratory distilled water through a Crystalab ion exchange column and then distilling from alkaline permanganate into a 20-l. pyrex reservoir. The water in the reservoir was protected from carbon dioxide in the atmosphere by means of a tube filled with Ascarite. The specific conductances of the two batches used were initially 5 and 8 x 10^{-7} (ohm-cm)$^{-1}$ respectively. These values increased slowly but never became greater than 1 x 10^{-6} (ohm-cm)$^{-1}$.

2. Hydrochloric Acid Solutions

The hydrochloric acid solutions were made up by weight dilutions from twice-distilled constant boiling hydrochloric acid. A fresh bottle of Baker and Adamson reagent grade concentrated hydrochloric acid was the starting material for the distillations. The procedure of Foulk and Hollingsworth[36] was followed in essence, and the final distillate fraction was collected at 741.3 mm. Hg. (corrected). The constant boiling acid was analyzed gravimetrically by the method of Kolthoff and Sandell[37] and three determinations gave a value of 20.275 percent within 0.3 parts per thousand. After correcting by 0.037 percent to account for solubility of silver chloride in the wash water and other factors according to Foulk and Hollingsworth[36], the value of 20.267 percent (<u>in vacuo</u>) compared favorably with the value 20.263 percent calculated by interpolation from the table given by Foulk and Hollingsworth[36]. The constant boiling acid was stored in a pyrex flask having a ground glass stopper.

The weight dilutions were made so as to have solutions exactly 0.005, 0.0075, 0.01, 0.025, 0.05, 0.075, 0.1, 0.2, 0.5, and 1.0 <u>m</u> HCl. Vacuum corrections were made and the weights had been previously calibrated by the transposition method given by Kolthoff and Sandell[38]. The solutions were stored in 1-l. pyrex bottles having ground glass stoppers. In order to ensure that no gross errors had been made the solutions were titrated to a <u>p</u>H 7.0 end point with standard sodium hydroxide using a Beckman Model H <u>p</u>H meter as indicator. All solutions were found to have been made accurately. The sodium hydroxide was standardized to a <u>p</u>H 8.3 end point using Baker and Adamson reagent grade potassium acid phthalate dried over Drierite. The standard sodium hydroxide solutions were also used to titrate the hydrochloric acid solutions after the tests.

3. Silver Compounds

Silver oxide was made according to the procedure given by Bates[39] and was washed twenty-five times with distilled water and ten times with conductivity water. Silver chlorate was made according to the procedure given in Inorganic Syntheses[40] and recrystallized from conductivity water. Silver chloride was made according to the procedure given by Zimmerman[41] except the starting material was Baker and Adamson reagent grade silver nitrate.

The silver oxide and silver chlorate were mixed in a 7:1 ratio by weight with a little conductivity water to give a thick paste. The paste was stored in a pyrex bottle having a ground glass stopper. The silver chloride was stored in a pyrex bottle having a Bakelite cap and was kept in a light-tight vacuum desiccator.

4. Hydrogen

Electrolytic hydrogen obtained in commercial cylinders was passed over Drierite, Ascarite, Drierite and then a platinized catalyst bed (Trade Name Deoxo) before passing through two bubble towers containing solutions identical to that under test. In this way carbon dioxide, water vapor, and oxygen were removed and the hydrogen was saturated with the vapor from the solution. Then the hydrogen was bubbled through the solution in the autoclave. Anderson[42] showed that two bubble towers were enough to pre-saturate the gas so as to prevent loss of water or acid from the test solution. The only impurity likely to be left in the hydrogen was thus nitrogen in amounts which should have caused no error.

I. Preliminary Investigations

1. Solubility of Silver Chloride

As Lietzke and Stoughton have pointed out[19], it was necessary to know the solubility of silver chloride as a function of temperature and hydrochloric acid concentration in order properly to interpret the electromotive force data. Fortunately the data of Raridon[43] became available[*]. The solubility values (s_{AgCl}) in each of the solutions Raridon used were fitted by the method of least squares[**][44] to:

$$\log (s_{AgCl})_{m_{HCl}} = a + b/T \tag{4}$$

and the resulting equations for each hydrochloric acid molality solved for the solubility at all of the temperatures of interest in this study. These values in turn were fitted at each temperature by the method of least squares to:

$$\log (s_{AgCl}) = a + b \log(m_{HCl}) + c \left[\log(m_{HCl})\right]^2 . \tag{5}$$

The values of a, b, and c at the temperatures of interest are listed in Table III as are typical values of s_{AgCl} in 0.01 m HCl.

The solubility increases markedly with temperature, and there is a minimum in the solubility at about 0.005 m HCl at each temperature. The effect of the solubility on the ionic strength of the solution at

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[*] The author would like to express his sincere thanks to Dr. Kurt A. Kraus and Dr. Richard J. Raridon for allowing the immediate use of their solubility data.

[**] The author would also like to thank Dr. M. H. Lietzke for making available a very convenient least squares code for the *ORACLE*.

TABLE III

SOLUBILITY AND SOLUBILITY PARAMETERS OF SILVER CHLORIDE IN HYDROCHLORIC ACID

Temp.	Solubility in 0.01 $\underline{m}$ HCl		Solubility Parameters[a]		
°C	Calculated[a]	Observed[b]	$\underline{a}$	$\underline{b}$	$\underline{c}$
25	6.73×10^{-7}	6.51×10^{-7}	-4.086	1.752	0.3543
60	5.42×10^{-6}		-3.447	1.555	0.3228
90	2.35×10^{-5}		-2.999	1.408	0.2968
100	3.63×10^{-5}	3.59×10^{-5}	-2.869	1.354	0.2847
125	9.84×10^{-5}	9.80×10^{-5}	-2.566	1.255	0.2673
150	2.37×10^{-4}	2.38×10^{-4}	-2.298	1.168	0.2520
175	5.17×10^{-4}	4.80×10^{-4}	-2.060	1.090	0.2383
200	1.04×10^{-3}	1.15×10^{-3}	-1.847	1.021	0.2262
225	1.94×10^{-3}		-1.656	0.9582	0.2152
250	3.43×10^{-3}		-1.482	0.9017	0.2053
275	5.76×10^{-3}		-1.323	0.8577	0.1996
300	9.20×10^{-3}		-1.180	0.8105	0.1913

[a] Constants in the equation $\log s_{AgCl} = a + b\,(\log \underline{m}_{HCl}) + c\,(\log \underline{m}_{HCl})^2$

[b] R. J. Raridon, Ph.D. thesis, Vanderbilt University, Nashville, Tennessee, (1958) p. 93.

the higher temperatures is small but certainly not negligible and it was taken into account in all calculations.

The double least squaring procedure naturally raised doubts as to the accuracy of the values calculated from the data given in Table III. Therefore several points were checked by direct observation of the disappearance of the last crystal of a weighed quantity of silver chloride in a weighed quantity of hydrochloric acid contained in a sealed silica tube as the tube was heated slowly in an air oven. Agreement was satisfactory although these experimental values were only accurate to ± 10 percent due to the small quantity of silver chloride that could be used.

2. Hydrogen Chloride Content of Vapor Phase

The fact that hydrogen chloride is present in the vapor above concentrated hydrochloric acid solutions raised the question as to the extent of such vaporization at elevated temperatures with dilute solutions. Therefore in two preliminary experiments the vapor above 0.01 and 0.1 m HCl was sampled at 200 and at 250° to determine the hydrogen chloride content.

The apparatus was essentially that already described for the electromotive force work except in place of the electrodes an 0.008-in. dia. I.D. platinum capillary tube was sealed into the autoclave head with a Teflon fitting. The end of the capillary inside the autoclave was bent up and protected by a Teflon cup from having solution splashed onto it and entrained in the vapor. The capillary was nine-feet long and passed out of the oven through a water cooling jacket. The end of the capillary outside of the oven was crimped closed. After the autoclave containing the hydrochloric acid solution was equilibrated at temperature a sample of the vapor was condensed and withdrawn simply by cutting the crimped end of the capillary. The condensate was collected dropwise in a polyethylene bottle and about 1 ml. was sent for radioactivation analysis* of chloride. Several successive samples were taken to ensure flushing of the capillary tube (total volume of the capillary was about 0.1 ml.). Then the tube was crimped again and the temperature changed.

Table IV is a list of the results. It may be seen that hydrogen chloride is in fact present in the vapor space and that the amount increases with hydrochloric acid concentration. However, it was calculated from the vapor density and volume that the total amount of hydrogen chloride in the vapor space was negligible for solutions to 0.1 m at temperatures to 250° insofar as changing the concentration of solution or influencing the pressure of the system. On the other hand the fact that 0.5 and 1.0 m HCl solutions corroded the titanium bomb head at temperatures above 200 and 150° respectively may be taken as evidence that a relatively large amount of hydrogen chloride was above those solutions. However the amount in the vapor compared to that in solution may not have been appreciable. Thus the results with those solutions are subject to

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*The author would like to thank Mr. G. W. Leddicotte and his group for performing the radioactivation analyses.

TABLE IV

THE CONCENTRATION OF HYDROGEN CHLORIDE IN THE VAPOR PHASE ABOVE DILUTE AQUEOUS HYDROCHLORIC ACID AT 200 AND 250°C

	0.01 m HCl		0.1 m HCl	
	200°	250°	200°	250°C
HCl Concentration in Vapor, micrograms/ml. condensate	13	19	160	450
HCl Concentration in Vapor, micrograms/ml. vapor	1.7	0.95	20	23
Total Amount HCl Volatilized, micrograms	61	27	720	640
Percent of Total HCl Present Volatilized	0.18	0.08	0.22	0.19
Partial Pressure of HCl (based on Perfect Gas Law), psi.	0.018	0.010	0.21	0.24

a certain error which has not as yet been determined but which is probably small in comparison to the other uncertainties in the results with those solutions.

J. General Procedure

The general procedure in making each test was as follows:

1) The autoclave containing the electrodes and solution was slipped into the jacket, the assembly was put into the oven, and all connections were made.

2) The vapor space was evacuated to less than 1 mm. Hg; hydrogen from the bubble towers (previously evacuated and purged with hydrogen) was admitted carefully; the system was re-evacuated; hydrogen was re-admitted; the process was repeated a third time; and then hydrogen was bubbled through the solution for several hours (titration of the solution before and after this procedure in several trials showed that the concentration changed less than one part per thousand).

3) When the chart record of the electromotive force showed that equilibrium was attained, the special valve in the head of the autoclave was closed, the hydrogen supply was shut off, the valves to the pressure gauges were opened, and the pressure gauges were set to agree with the manometer reading.

4) An initial reading of temperature, pressure, and electromotive force was taken; and then the temperature was raised to the next level

desired. After equilibration the second set of readings were taken and the temperature again raised.

5) After the final set of readings had been taken at the highest temperature, the oven was cooled to room temperature and another set of readings taken.

6) Finally the system was taken apart, the solution titrated, and in the first series of tests the electrodes were compared with the others not used.

In the first series of tests, conducted on seven solutions from 0.005 to 0.1 m HCl at 25, 60, 90, 125, 150, 175, and 200°, several duplicate tests were run. In one test measurements were made during both ascending and descending temperatures with good agreement between values taken at the same temperature, but otherwise measurements were made only during ascending temperatures (except for the final measurement at room temperature). Allowing for concentration changes and slight temperature differences, agreement between initial and final values at 25° averaged 0.5 mv. Therefore it appeared that the electrodes were acting reversibly over the temperature range 25 to 200°.

In the second series of tests, measurements were extended to include 225, 250, and 275° (the 60 and 90° points were generally omitted) with nine solutions from 0.005 to 0.5 m. A 1.0 m solution was measured to 200°. Since the same pair of silver-silver chloride electrodes was used throughout the second series and since the initial room temperature measurements agreed with Harned and Ehlers[2] and with Bates and Bower[3], it appeared that these electrodes also were acting reversibly over the temperature range 25 to 275°.

CHAPTER III

RESULTS

A. Experimental Data

Figure 5 is a tracing of a typical recorder chart record of one datum point. The temperature was changed as shown on the left of the figure and brought quickly from 225 to 250° with the aid of the auxiliary heaters. The temperature was allowed to level off at "$t_{obs.}$" close to but not exactly "t_{even}", in this case 250.000°. The cell electromotive force was not recorded when the auxiliary heaters were on because of the slight inductive effect. The time at which the auxiliary heaters were to be turned off in order to prevent under or over-shooting of the autoclave temperature was found by experience. As may be seen, the electromotive force fell sharply as the temperature increased. The "over-shoot" was most likely due to slow solubility of hydrogen in the unstirred system. Final "quasi-equilibrium" was reached about three hours after commencing the temperature increase at 250°. It took as long as six hours to reach this point at lower temperatures.

However, the electromotive force did not stay constant but began a steady, linear decrease with time. This effect was noticed by Anderson[45] and is undoubtedly due to reaction of hydrogen with silver ion which both concentrates the solution and decreases the hydrogen

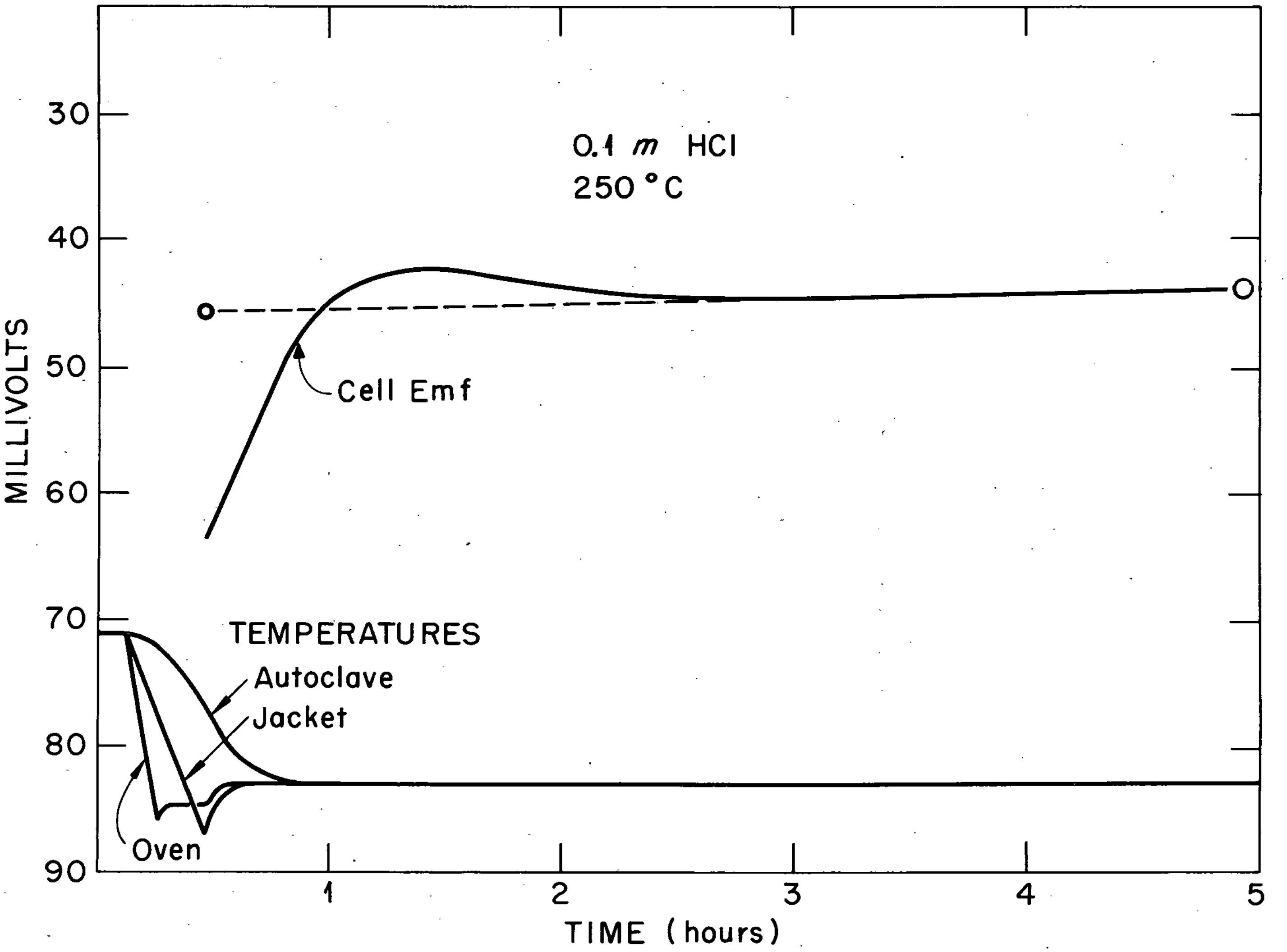

Figure 5. A Typical Recorder Trace of Electromotive Force and Temperature *versus* Time.

pressure according to reaction (F). The rate of the reaction increased with increasing temperature and with decreasing acid concentration. Once the rate had been established, the electromotive force, temperature, and pressure were measured, and the temperature increased again.

It was decided to calculate the molality of the solution for each final measurement of the electromotive force at each temperature by using the slope of the recorder trace. In this way the relatively large error in measuring the slopes and times at each temperature was thrown entirely into the value of m, the molality of the solution. The electromotive force values were not extrapolated.

The calculation of the change in molality due to reaction (F) was made according to the equations

$$\Delta m = \text{antiln} \frac{F}{2RT} \Delta E_m \tag{6}$$

$$\Delta E_m = \Delta E_{total} - \Delta E_{P_{H_2}} \tag{7}$$

$$\Delta E_{P_{H_2}} = \frac{RT}{2F} \ln \left[1 + \frac{\frac{1}{2} m_o v \left(\text{antiln} \frac{\Delta E_m}{2RT/F} - 1\right)}{P^o_{H_2} \left(\frac{V}{RT} + \frac{55.75}{K}\right)} \right] \tag{8}$$

Δm = change in molality during a measurement at constant temperature,

ΔE_m = change in emf at the temperature of interest due to change in m,

ΔE_{total} = total change in emf at the temperature of interest,

$\Delta E_{P_{H_2}}$ = change in emf due to change in hydrogen pressure,

$\underline{m}_o$ = concentration of solution at start of measurement,

$\underline{v}$ = weight of solution (kg.),

$\underline{P}^o_{H_2}$ = hydrogen pressure at start of measurement (atm.),

$\underline{V}$ = vapor volume (ml.),

$\underline{K}$ = Henry's Law Constant for hydrogen at the temperature of interest (assumed to be that for hydrogen in water).

The total change in electromotive force, $\Delta\underline{E}_{total}$, was taken to be the slope of the recorder line after "quasi-equilibrium" multiplied by the time at temperature, taken to be from the moment the auxiliary heaters were turned off until the electromotive force reading was made. These times are indicated on Figure 5 by the circles. This total change was corrected for the change due to the decrease in hydrogen pressure, $\Delta\underline{E}_{P_{H_2}}$, to give that due solely to the change in acid concentration, $\Delta\underline{E}_m$, by equation (7). The change in hydrogen pressure was measured for some points but usually it had to be calculated by iteration using a trial value of $\Delta\underline{E}_m$ in equation (8) to give a value of $\Delta\underline{E}_{P_{H_2}}$, which could give a better value of $\Delta\underline{E}_m$ from equation (7) and so forth. Finally the change in molality, $\Delta\underline{m}$, was calculated using equation (6). The perfect gas law was used in deriving equation (8) and activity coefficient corrections were neglected in equation (6), but the $\Delta\underline{m}$ values were small enough to allow these approximations.

Two further corrections were made to the molality of the solution. The first was the change in concentration due to the reaction (F) that occurred between the time a reading was taken at one temperature and the time the auxiliary heaters were turned off at the next higher temperature. This was calculated from the average of the slopes at the lower and higher temperatures multiplied by the time involved. The second was the increase in concentration due to the loss of water from solution to the vapor space. This was calculated from the vapor density of steam[46] and the vapor volume (calculated assuming that the expansion of the solutions with temperature was equal to that of pure water). Table V is a list of the total accummulated changes in concentration at each temperature, including all of the above effects.

Therefore the experimental data consisted of values of the electromotive force at temperatures slightly different from even values, at concentrations slightly different from the starting values, and at hydrogen pressures slightly different from 1 atm.

B. Treatment of the Data

In order to deal with the experimental electromotive force data it was necessary to correct them to values at exactly 1.00 atm. and exact even temperatures. The former was done by subtracting the Nernst pressure term $\frac{RT}{2F} \ln P_{H_2}$ in which the hydrogen pressure was assumed to be equivalent to the hydrogen fugacity. It was further assumed that the water vapor pressure had no effect on the hydrogen fugacity. This latter assumption will be discussed below.

The second correction (to even temperatures) could have been made

TABLE V

CHANGES IN CONCENTRATION OF HYDROCHLORIC ACID DURING TESTS

Temp. °C	Total Δ m[a]				
	0.005 m	0.0075 m	0.01 m	0.025 m	0.05 m
150	0.000033	0.000184	0.00002	0.00004	0.00009
175	0.000619	0.000553	0.00010	0.00036	0.00015
200	0.00223	0.000757	0.00030	0.00058	0.00169
225			0.00086	0.00085	0.00280
250			0.00238	0.00138	0.00379
275				0.00217	0.00591

Temp. °C	Total Δ m[a]				
	0.075 m	0.1 m	0.2 m	0.5 m	1.0 m
150	0.00013	0.00017	0.0003	0.0009	0.0020
175	0.00022	0.00029	0.0006	0.0015	0.0090
200	0.00090	0.00071	0.0009	0.0023	0.0167
225	0.00161	0.00143	0.0014	0.0035	
250	0.00692	0.00354	0.0168	0.0075	
275	0.00809	0.00543	0.0326	0.0170	

---

[a] Includes all changes up to and including the temperature of interest. Loss of water to the vapor space was also taken into consideration.

graphically but an analytical method was found which was more accurate. Figure 6 is an outline of this method. In essence, after the pressure correction was made, the electromotive forces were corrected to even molalities neglecting activity corrections. These values at each molality were then fitted to a quadratic function of the centigrade temperature by the method of least squares. The quadratic did not fit the data within the errors of measurement in all cases (the standard error of fit averaged 1.44 mv.), but the first derivative of the quadratic at each temperature was very close to the true change of electromotive force with temperature. Therefore a correction to the electromotive force for slight temperature differences was made as follows:

$$\Delta E_T = (\frac{dE}{dT})(\Delta T) = (b + 2\ ct)(t_{even} - t_{obs.}), \qquad (9)$$

where $dE/dT = (b + 2\ ct)$ was the first derivative of the quadratic equation for each molality and $\Delta T = (t_{even} - t_{obs.})$ was the temperature difference between the exact even temperature of interest and the actual temperature measured. This ΔE_T was then added to the electromotive forces corrected to 1 atm. H_2 to give the final working values of electromotive force at 1 atm. H_2, even temperatures, and observed molality.

C. Calculation of $\underline{E}^{o''}$

The further treatment of the data was similar to that used by Bates and Bower[3]. In order to make a linear extrapolation of the

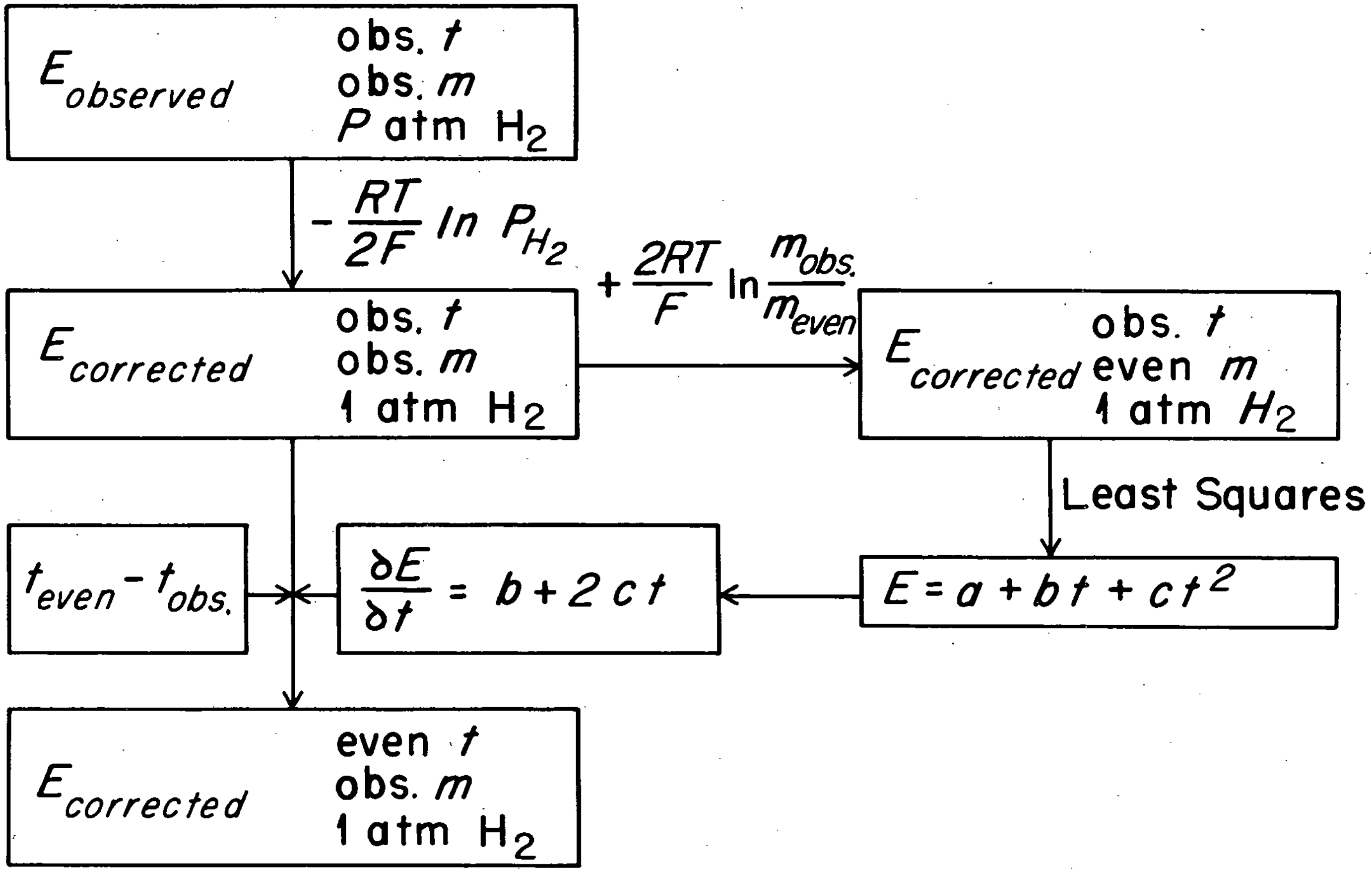

Figure 6. Method of Correction of Electromotive Force Data to 1.00 atm. Hydrogen Pressure and Even Temperatures.

electromotive forces to infinite dilution so as to evaluate $\underline{E}^{\circ}$, the standard potential of the silver-silver chloride electrode, it was necessary to put the mean ionic activity coefficient, $\gamma_{\pm}$, in proper form. The Debye-Hückel equation in extended form was used as follows:

$$\log \gamma_{\pm} = - \frac{1.8252 \times 10^{6} \sqrt{\rho_{o} I}}{(DT)^{3/2}(1 + A \sqrt{\rho_{o} I})} + BI - \log (1 + 0.03604m) + Ext' \quad (10)$$

where ρ_{o} = density of water,

$\underline{D}$ = dielectric constant of water,

$\underline{T}$ = absolute temperature,

$\underline{I}$ = ionic strength of solution = $m_{HCl} + s_{AgCl}$,

$\underline{A}$ = denominator coefficient,

$\underline{B}$ = linear term coefficient,

$\log (1 + 0.03604m)$ = corr'n from rational to practical scale,

$\underline{Ext'}$ = extended terms of Gronwall, LaMer, and Sandved[47].

Inserting equation (9) into the Nernst equation (1) and collecting all terms measureable or calculable on the left, we have defined $\underline{E}^{\circ ''}$ to be a linear function of the ionic strength as follows:

$$E^{\circ ''} \equiv E + \frac{2RT}{F} \ln m_{\pm} + 2.3026 \frac{2RT}{F} \left[\frac{-1.8252 \times 10^{6} \sqrt{\rho_{o} I}}{(DT)^{3/2}(1+A \sqrt{\rho_{o} I})} \right] + Ext$$
$$= E^{\circ} + bI \quad (11)$$

where $\underline{E}$ = emf at 1 atm. H_2 and even temperature,

$\underline{m_{\pm}}$ = mean molality of solution,

$\underline{Ext} = 2.3026 \left(\frac{2RT}{F}\right)(Ext' - \log (1 + 0.03604\, m))$,

$\underline{b} = 2.3026 \left(\frac{2RT}{F}\right)B$; $\underline{B}$ = linear term coefficient,

$\underline{A}$ = denominator coefficient.

As a first approximation $\underline{I}$ and $\underline{m}_{\pm}$ were set equal to $\underline{m}_{HCl}$, the molality of hydrochloric acid, $A\sqrt{\rho_0}$ was taken to be 1.5, and $\underline{Ext}$ was calculated using an ion size of 4.3 Ångstroms. The $\underline{E}^{o''}$ values were calculated as the tests were made and used as a guide only so that obvious errors or omissions in the data could be noticed and duplicate tests made.

For the second approximation the solubility of silver chloride, $\underline{s}_{AgCl}$, was taken into account and $\underline{A}$ was set equal to $(50.2904(DT)^{-1/2}\,\mathring{a})$ where $\underline{\mathring{a}}$ is the ion size parameter[48]. A set of $\underline{E}^{o''}$ values was calculated for all of the electromotive force values using successively 2.0, 4.3, and 6.0 Ångstroms for $\underline{\mathring{a}}$. All of these values were then plotted on large-scale graph paper *versus* ionic strength*. At this point the first tentative decision as to what data to discard was made. Arbitrarily, all points lying more than 0.5 mv. off the best straight line that could be drawn with a ruler at temperatures up to 225° and more than 2 mv. at 250 and 275° were discarded. Some of these points were later used. Then the remaining $\underline{E}^{o''}$ values for concentrations up to and including 0.1 $\underline{m}$ were fitted by the method of least squares at each temperature and for each value of $\underline{\mathring{a}}$ to

$$E^{o''} = E^{o} + bI. \qquad (12)$$

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*It is a pleasure to acknowledge the very helpful discussions that the author had with Prof. Herbert S. Harned at this stage of the work.

It was obvious that the $\underline{\mathring{a}}$ values chosen did not in most cases give the best straight lines possible.

Therefore a third calculation of $\underline{E}^{o''}$ values was made. First the electromotive force data were again inspected and all points giving $\underline{E}^{o''}$ values lying within $2\sigma_{fit}$ of the least squares line determined in the above treatment were accepted. Here σ_{fit} is the standard error of fit of the least squares line to the data[44]. Also, to rule out further arbitrariness, if all but one or two points from a test were accepted, the points at first discarded were accepted if at all possible since it was felt unlikely that electrodes giving "good" values should suddenly go "bad" and then become "good" again. Table VI is a chart of the values accepted for each test.

Furthermore, in the third calculation the $\underline{\mathring{a}}$ values were varied in 1 Ångstrom increments over wide limits at each temperature. The $\underline{Ext}$ terms corresponding to each $\underline{\mathring{a}}$ value were obtained by interpolation or extrapolation of the values previously calculated for $\underline{\mathring{a}} = 2.0$, 4.3, and 6.0. The values of $\underline{Ext}$ used are listed in Table VII. The calculations were made on a high speed digital computer such that the output of $\underline{E}^{o''}$ values for each value of $\underline{\mathring{a}}$ at each temperature up to an ionic strength of 0.1 was in proper paper tape form for use as input to the least squares code[44]. The least squares code then put out values of $\underline{E}^{o}$, $\underline{b}$, the standard errors in $\underline{E}^{o}$ and $\underline{b}$, and the standard errors of fit for each $\underline{\mathring{a}}$ at each temperature according to equation (12). Finally, the standard errors of fit were plotted *versus* $\underline{\mathring{a}}$ and that value of $\underline{\mathring{a}}$ which gave the

TABLE VI

DATA POINTS USED IN $\underline{E}^{o''}$ CALCULATIONS

Run Number	Conc. $\underline{m}$	25°	60°	90°	125°	150°	175°	200°	225°	250°	275° C
21	0.005	X[a]	X	X							
22	0.005	XX[b]									
31	0.005	XX									
20	0.0075	X	X	X	X	X	X	XX			
16	0.01	XR[c]	X	X	X	X	X	XX			
29	0.01	X			X	XX	XX	X	X	X	
17	0.025	XR	X	X	X	X	X	X			
28	0.025	XX			XX	XX	X	X	X	X	X
12	0.05	X	X	X	XX	XX	XX	XX	X	X	X
27	0.075	X			XX	XX	XX	XX	XX	XX	XX
18	0.075	XXR	XX	XX	XX	XX	XX				
33	0.1	XX			XX	XX	XX	XX	XX	XX	XX
19	0.1	XX	XX	XX	XX	X	X	X			
26	0.1							X	X	X	X

[a] One silver-silver chloride electrode of the two in the autoclave used.

[b] Both silver-silver chloride electrodes in the autoclave used.

[c] The average emf of the cell after cooling to room temperature was used.

TABLE VII

VALUES OF *EXT* USED IN $E^{o''}$ CALCULATIONS

Temp. °C	å Angstroms	Millivolts				
		0.005 *m*	0.0075 *m*	0.01 *m*	0.025 *m*	0.05 *m*
25	4.3	0.04	0.06	0.07	0.12	0.18
60	6.0	0.04	0.05	0.05	0.10	0.15
90	7.0	0.03	0.04	0.06	0.10	0.16
125	7.0	0.05	0.06	0.08	0.12	0.18
150	8.0	0.06	0.07	0.08	0.14	0.20
175	9.0	0.08	0.10	0.12	0.15	0.20
200	11	0.10	0.12	0.15	0.20	0.25
225	12	0.06	0.08	0.12	0.15	0.22
250	15	0.02	0.08	0.10	0.18	0.30
275	20	0.10	0.12	0.22	0.32	0.37

Temp. °C	å Angstroms	Millivolts				
		0.075 *m*	0.1 *m*	0.2 *m*	0.5 *m*	1.0 *m*
25	4.3	0.23	0.28	0.45	0.97	1.90
60	6.0	0.20	0.25	0.44	1.04	2.03
90	7.0	0.21	0.27	0.47	1.12	2.21
125	7.0	0.25	0.30	0.50	1.25	2.40
150	8.0	0.27	0.33	0.55	1.30	2.58
175	9.0	0.30	0.35	0.60	1.40	2.75
200	11	0.33	0.40	0.68	1.45	2.90
225	12	0.25	0.35	0.65	1.53	3.05
250	15	0.37	0.42	0.68	1.61	3.20
275	20	0.47	0.54	0.80	1.69	3.36

lowest standard error of fit was taken to be the correct value. A typical fit of $E^{\circ\prime\prime}$ values is illustrated in Figure 7. Typical plots of σ_{fit} *versus* $\mathring{a}$ are shown in Figure 8. The value of $\mathring{a}$ at 275° was obtained by extrapolation of $\mathring{a}$ values at lower temperatures since the errors were too large to give a meaningful value of $\mathring{a}$ at that temperature.

D. Determination of E° and B

Having assigned the value of $\mathring{a}$ at each temperature, the values of E° and B became established. Table VIII is a list of the values of E°, B, their standard errors, $\mathring{a}$, and the standard error of fit at each temperature of interest from 25 to 275°. Figure 9 is a plot of the values of $\mathring{a}$ and B *versus* temperature.

The values of E° from 25 to 200° were fitted to a quadratic function of the centigrade temperature by the method of least squares to give the equation and values shown in Table IX. The standard error of fit was 0.19 mv., very satisfactorily within the errors of measurement. Also shown in Table IX are the measured values taken from Table VIII, the values measured by Bates and Bower[3] at the National Bureau of Standards, and values calculated by extrapolating the data of Bates and Bower in two different ways (see Chapter IV, Section B).

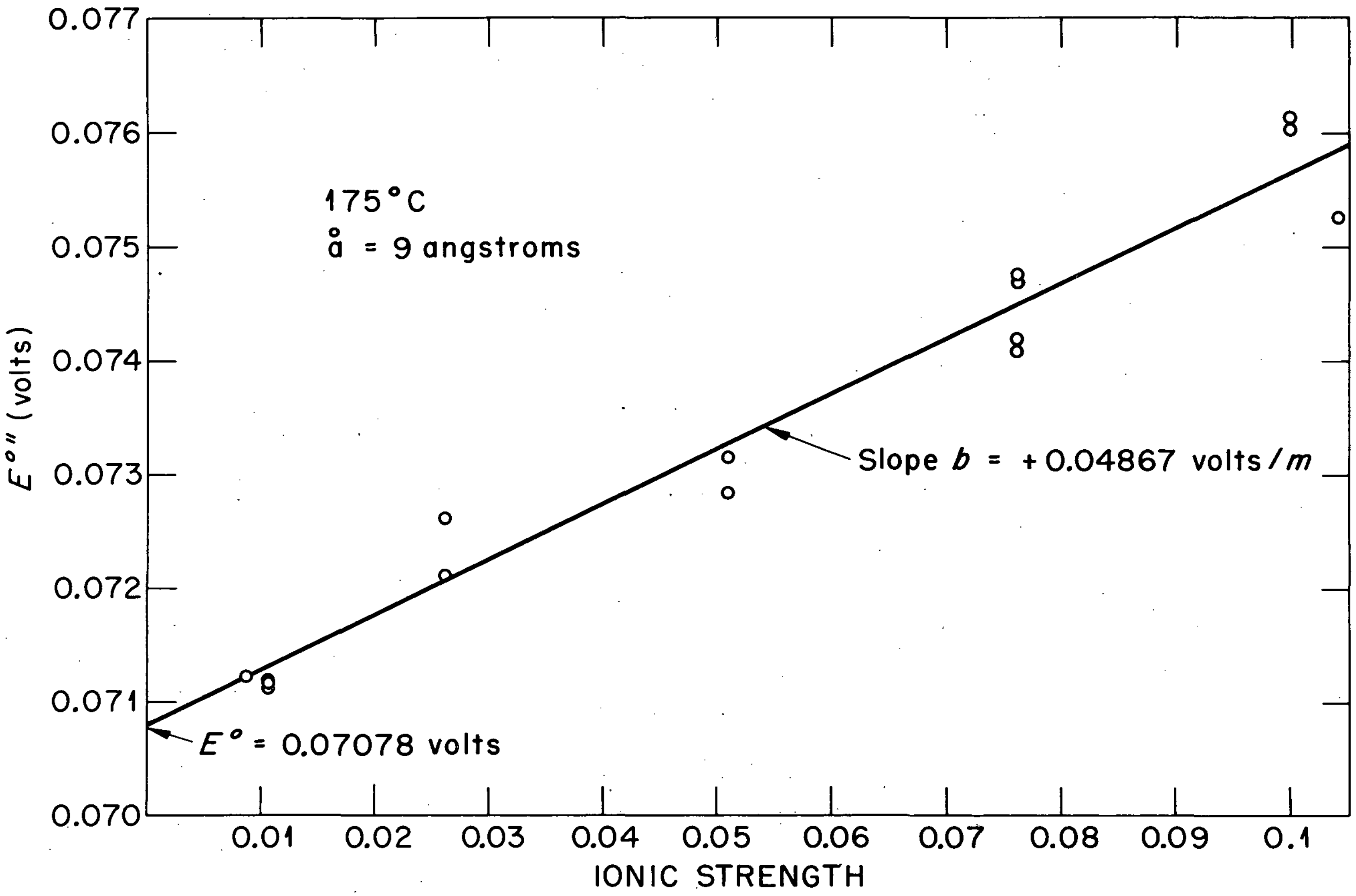

Figure 7. Typical Least Squares Fit of $E^{o''} = E^{o} + bI$.

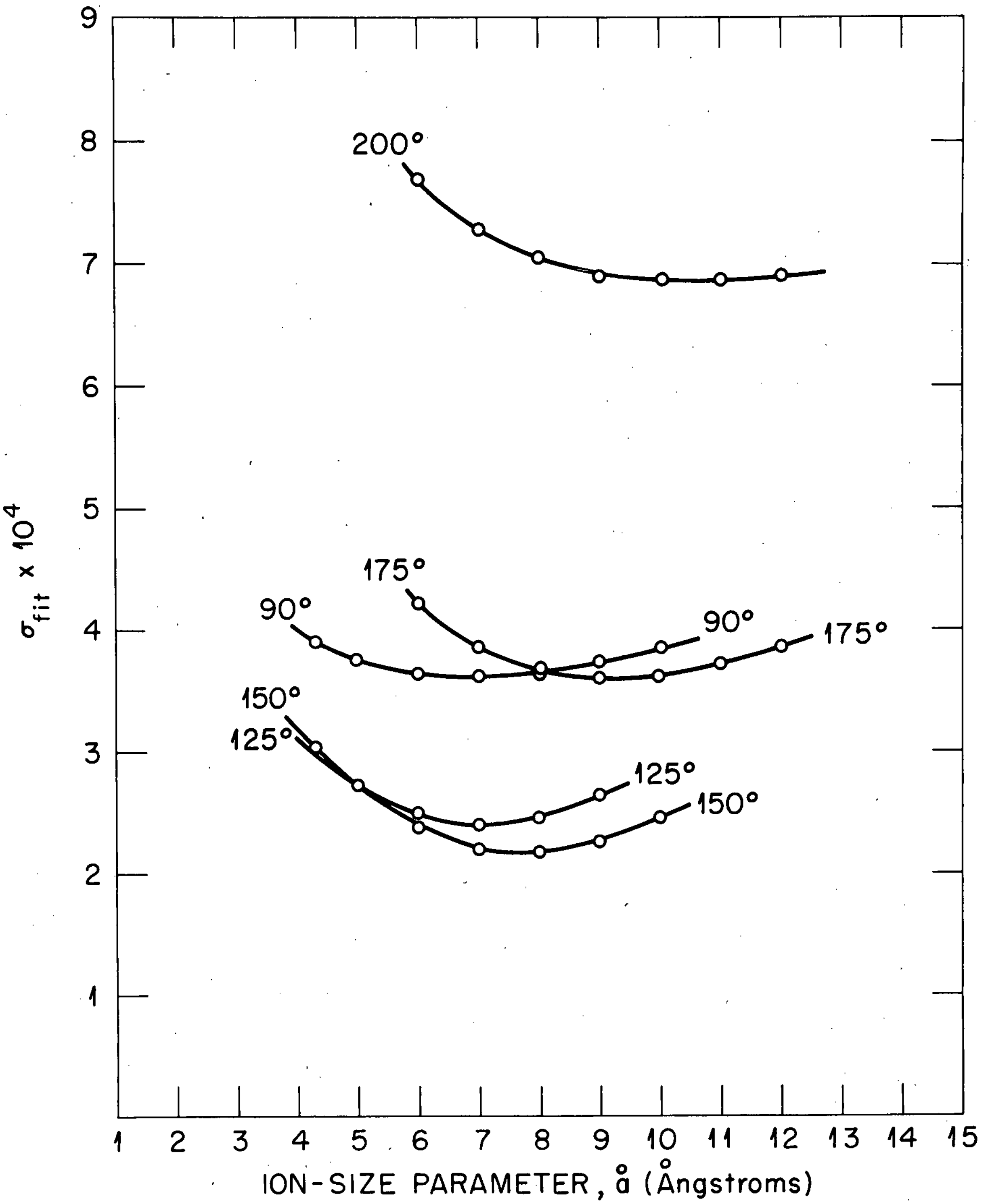

Figure 8. Standard Error of Fit *versus* Ion-Size Parameter for the Equation $E^{o''} = E^{o} + bI$ at 90, 125, 150, 175, and 200°C.

TABLE VIII

VALUES OF $\underline{E}^{\circ}$, $\overset{\circ}{\underline{a}}$, AND $\underline{B}$ FROM LEAST SQUARES FIT OF $E^{\circ''} = E + bI$

Temp. °C	$\overset{\circ}{\underline{a}}$ Angstroms	$\underline{E}^{\circ}$ volts	$\sigma_{\underline{E}^{\circ}}$[a] millivolts	$\underline{B}$ m^{-1}	$\sigma_{\underline{B}}$[a] millivolts	σ_{fit}[a] millivolts
25	4.3	0.22233	0.08	+0.152	0.011	0.22
60	6.0	0.1968	0.23	-0.025	0.028	0.41
90	7.0	0.1696	0.20	-0.125	0.023	0.36
125	7.0	0.1330	0.14	-0.116	0.013	0.23
150	8.0	0.1032	0.10	-0.250	0.010	0.21
175	9.0	0.0708	0.17	-0.274	0.015	0.36
200	11	0.0348	0.30	-0.422	0.024	0.68
225	12	-0.0051	0.34	-0.578	0.020	0.29
250	15	-0.054	2.16	-1.1	0.12	2.57
275	20	-0.090	4.74	-0.95	0.23	3.89

[a] σ = standard error.

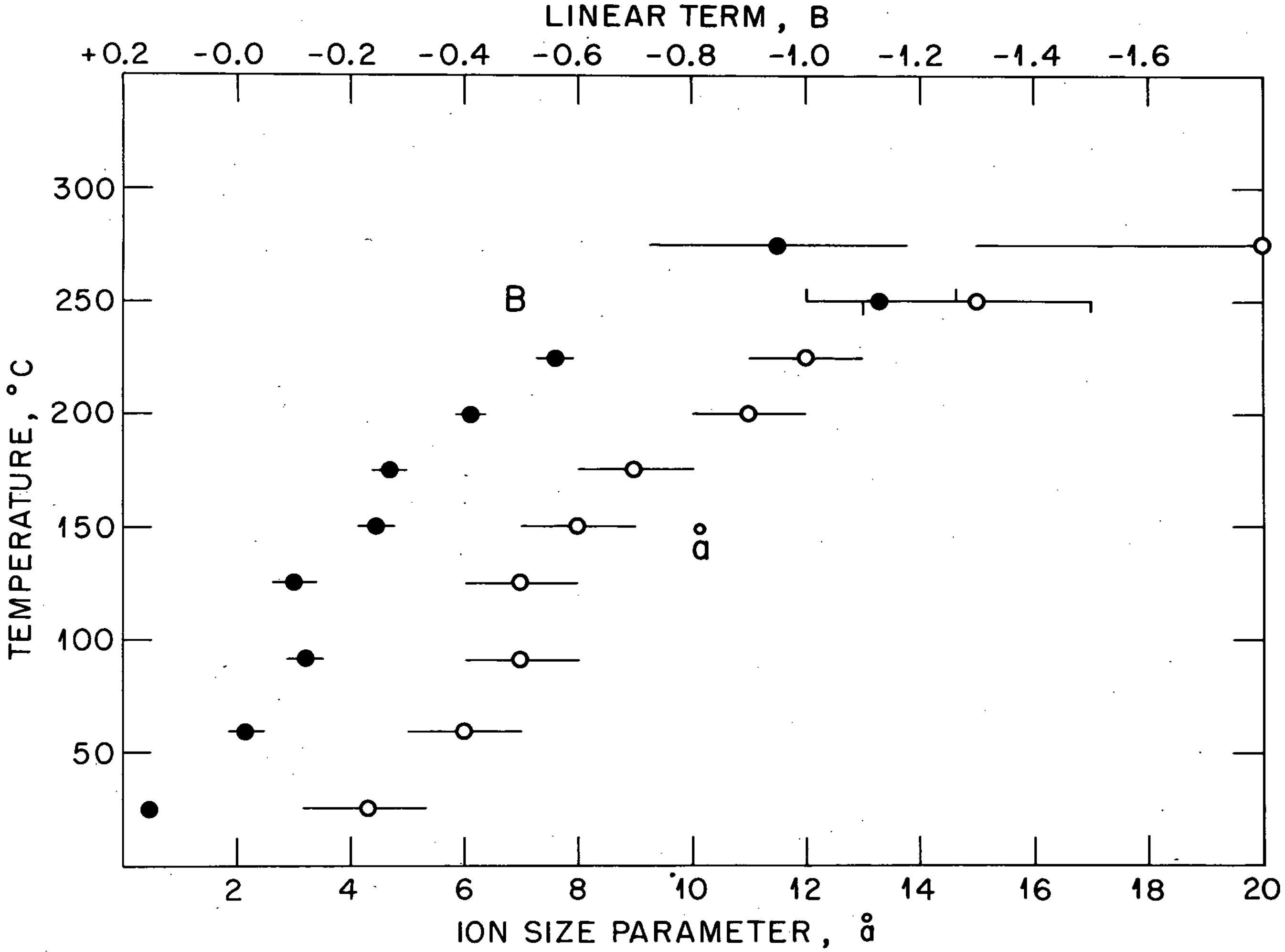

Figure 9. Values of the Ion-Size Parameter, $\overset{\circ}{a}$, and the Linear Term Coefficient, B, *versus* Temperature.

TABLE IX

STANDARD ELECTRODE POTENTIAL OF THE SILVER - SILVER CHLORIDE ELECTRODE

Temp.	E^o, volts				
°C	Measured	Equation I[a]	Bates[b]	Equation II[c]	Equation III[d]
25	0.22233	0.22242	0.22234	0.22225	0.22232
60	0.19676	0.19654	0.19649	0.19654	0.19648
90	0.1696	0.1697	0.1695	0.1696	0.1696
125	0.1330	0.1330		0.1324	0.1331
150	0.1032	0.1033		0.1020	0.1040
175	0.0708	0.0706		0.0685	0.0725
200	0.0348	0.0349		0.0319	0.0387
225	-0.0051	-0.0038		-0.0080	0.0028
250	-0.054	-0.045		-0.051	-0.035
275	-0.090	-0.090		-0.097	-0.075
300		-0.138		-0.146	-0.117

---

[a] $E^o = 0.23735 - 5.3783\ 10^{-4}t - 2.3728\ 10^{-6}t^2$ based on measured values from 25 to 200°. $\sigma_{fit} = 0.19$ millivolts.

[b] R. G. Bates and V. E. Bower, J. Research Natl. Bur. Standards 53 283, (1954).

[c] $E^o = 0.23683 - 5.2004 \times 10^{-4}\ t - 2.5241 \times 10^{-6}\ t^2$ based on Bates[b].

[d] $E^o = -0.06864 - 0.0037345\ T \log T + 0.010217\ T$ based on Bates[b].

E. Activity Coefficients

1. Molalities up to and including 0.1

The mean ionic activity coefficients of hydrochloric acid at concentrations up to 0.1 m were readily determined from equation (10) once the values of $\overset{\circ}{a}$ and B were known. These values are tabulated in Table X. The activity coefficients from 25 to 200° were fitted to quadratic functions of the centigrade temperature by the method of least squares and the constants of these equations are listed in Table XI.

2. Molalities from 0.2 to 1.0

It was observed that the plots of $E^{o''}$ versus I showed marked curvature above 0.1 m. Obviously the linear relation between $E^{o''}$ and E^{o} was not holding true at the higher concentrations, as expected. Therefore, following Harned and Ehlers[2], a quadratic term was added:

$$E^{o''} = E^{o} + b'I + d\,I^{2}. \qquad (13)$$

$E^{o''}$ values for the concentrations 0.2, 0.5, and 1.0 were calculated using the $\overset{\circ}{a}$ values previously found. Then equation (13) was fitted by the method of least squares using all of the data previously chosen from 0.005 to 1.0 m. The values of B' and D are listed in Table XII where $B' = -\left[F/(2.3026)(2)(RT)\right] b'$ and $D = -\left[F/(2.3026)(2)(RT)\right] d$. Then activity coefficients were calculated from the equation:

$$\log \gamma_{\pm} = -\frac{1.8252 \times 10^{6} \sqrt{\rho_{o} I}}{(DT)^{3/2}\,(1 + A\sqrt{\rho_{o} I})} + \text{Ext} + B'I + DI^{2}. \qquad (14)$$

TABLE X

MEAN IONIC ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID, $\gamma_{\pm}$

m	25°	60°	90°	125°	150°	175°	200°C
0.001	0.9655	0.963	0.960	0.955	0.949	0.939	0.925
0.002	0.9522	0.949	0.946	0.940	0.934	0.926	0.915
0.005	0.9284	0.924	0.920	0.912	0.906	0.898	0.889
0.0075	0.9149	0.910	0.905	0.896	0.889	0.882	0.862
0.01	0.9044	0.899	0.893	0.884	0.876	0.869	0.860
0.02	0.8754	0.868	0.861	0.849	0.840	0.833	0.824
0.025	0.8650	0.857	0.849	0.837	0.826	0.819	0.810
0.05	0.8310	0.819	0.807	0.794	0.779	0.772	0.760
0.075	0.8109	0.795	0.780	0.765	0.746	0.739	0.724
0.1	0.7972	0.776	0.758	0.744	0.720	0.714	0.694
0.2	0.7632	0.742	0.723	0.694	0.668	0.661	0.637
0.5	0.7540	0.730	0.695	0.665	0.631	0.601	0.567
1.0	0.8061	0.761	0.714	0.655	0.615	0.577	0.535

m	225°	250°	275°C
0.001	0.904	0.87	0.85
0.002	0.898	0.87	0.85
0.005	0.875	0.85	0.84
0.0075	0.859	0.84	0.83
0.01	0.846	0.82	0.82
0.02	0.808	0.78	0.78
0.025	0.793	0.76	0.77
0.05	0.738	0.69	0.71
0.075	0.698	0.63	0.66
0.1	0.663	0.58	0.62
0.2	0.606	0.57	0.68
0.5	0.609	(0.58)	(0.60)
1.0	-	-	-

TABLE XI

CONSTANTS OF QUADRATIC EQUATIONS EXPRESSING LOG $\gamma_{\pm}$ AS A FUNCTION OF TEMPERATURE

HCl Conc.	Constants[a]			σ_{fit}
m	a	b	c	
0.005	-3.165×10^{-2}	-1.854×10^{-5}	-3.870×10^{-7}	0.0001
0.01	-4.202×10^{-2}	-5.125×10^{-5}	-3.287×10^{-7}	0.0002
0.02	-5.499×10^{-2}	-9.286×10^{-5}	-2.755×10^{-7}	0.0005
0.05	-7.558×10^{-2}	-1.765×10^{-4}	-2.143×10^{-7}	0.0010
0.075	-8.501×10^{-2}	-2.352×10^{-4}	-2.065×10^{-7}	0.0015
0.1	-9.136×10^{-2}	-2.914×10^{-4}	-2.076×10^{-7}	0.0026
0.2	-1.022×10^{-1}	-5.206×10^{-4}	-2.442×10^{-7}	0.0058
0.5	-1.140×10^{-1}	-2.931×10^{-4}	-1.880×10^{-6}	0.002
1.0	-6.731×10^{-2}	-1.047×10^{-3}	$+1.811 \times 10^{-6}$	0.003

[a] Constants in the equation $\log \gamma_{\pm} = a + bt + ct^2$

TABLE XII

VALUES OF B' AND D FROM LEAST SQUARES FIT OF $E^{o''} = E^{o} + b'I + dI^2$

Temp. °C	B'[a] m^{-1}	$\sigma_{B'}$[b]	D[c] m^{-2}	σ_{D}[d]	σ_{fit}[e] millivolts
25	-0.130	0.0059	-0.0026	0.006	0.25
60	-0.040	0.012	-0.042	0.012	0.51
90	0.029	0.014	-0.077	0.014	0.64
125	0.036	0.011	-0.060	0.011	0.69
150	0.139	0.018	-0.149	0.018	0.96
175	0.213	0.012	-0.210	0.012	0.64
200	0.357	0.021	-0.325	0.022	1.04
225	0.599	0.036	-0.955	0.064	0.73
250	1.18	0.15	-2.01	0.27	3.43
275	0.91	0.24	-1.77	0.44	4.31

[a] $B' = \frac{-F}{4.6052\ RT} b'$

[b] $\sigma_{B'}$ = Standard error in B'

[c] $D = \frac{-F}{4.6052\ RT} d$

[d] σ_{D} = Standard Error in D

[e] σ_{fit} = Standard Error of Fit

However, since there were so few experimental points above 0.1 m, the quadratic did not fit well and the activity coefficients calculated by equation (14) will not be listed. Therefore activity coefficients were also calculated directly from the experimental electromotive force values according to:

$$\log \gamma_{\pm\text{meas.}} = \frac{F}{(2.3026)(2)RT}(E^{o} - E) - \log m_{\pm} \qquad (15)$$

where the E values were the averages of all the measurements made at that concentration and temperature and were corrected to even molalities by the term $\frac{2RT}{F} \ln \frac{m_{\text{obs.}}}{m_{\text{even}}}$ where necessary. These values are the ones given in Table X for concentrations 0.2, 0.5, and 1.0 m.

F. Calculation of pH

The pH of a solution has no exact thermodynamic basis but must be operationally defined. The definition is usually made so as to be both convenient for measurement and as close to the "thermodynamic" value as possible. Bates[49] describes the procedure and has listed a number of standard solutions whose pH values up to, in some cases, 95° have been defined and agreed upon. He lists also 0.1 m HCl as a supplementary standard. Therefore it was considered appropriate to extend the temperature range of the operationally defined pH scale using the present measurements on dilute hydrochloric acid.

The non-thermodynamic assumption that may be made is that the single ion activity coefficient of the hydrogen ion and chloride ion are equal and equivalent to the mean ionic activity coefficient. This is the Guggenheim assumption[50]. Values of the pH calculated on this basis are listed in Table XIII.

The pH values for 0.1 m HCl fit in with the values listed by Bates[51] and may be considered to be an extension to higher temperatures of the supplementary standard scale of pH values. These values may be used to calibrate pH meters and electrodes for use with other systems.

G. The Relative Partial Molal Heat Content

The relative partial molal heat content, $\bar{L}_2$, is defined by:

$$\bar{L}_2 = -\,4.6052\,RT^2\left(\frac{\partial \log \gamma\pm}{\partial T}\right)_{m,P}. \tag{16}$$

The change in activity coefficient with temperature was determined by taking the first derivative of the quadratic equations given in Table XI. Then $\bar{L}_2$ was calculated by equation (16). The values at several molalities are listed in Table XIV and are illustrated in Figure 10.

H. The Relative Partial Molal Heat Capacity

The relative partial molal heat capacity is defined by:

$$\bar{J}_2 = \left(\frac{\partial \bar{L}_2}{\partial T}\right)_{m,P}. \tag{17}$$

Values of $\bar{J}_2$ calculated from the second derivative of the activity coefficient quadratic equations are listed in Table XV and are illustrated in Figure 11.

TABLE XIII

VALUES OF THE pH OF HYDROCHLORIC ACID SOLUTIONS

m	25°	60°	90°	125°	150°	175°	200° C
0.001	3.02	3.02	3.02	3.02	3.02	3.03	3.04
0.002	2.72	2.72	2.73	2.73	2.73	2.73	2.74
0.005	2.33	2.34	2.34	2.34	2.35	2.35	2.36
0.0075	2.16	2.17	2.17	2.17	2.18	2.18	2.20
0.01	2.04	2.05	2.06	2.06	2.06	2.06	2.07
0.02	1.75	1.76	1.77	1.77	1.78	1.79	1.79
0.025	1.66	1.67	1.68	1.68	1.69	1.70	1.71
0.05	1.38	1.39	1.40	1.41	1.42	1.43	1.44
0.075	1.21	1.23	1.24	1.25	1.27	1.28	1.30
0.1	1.09	1.11	1.13	1.14	1.17	1.18	1.20
0.2	0.82	0.83	0.84	0.86	0.88	0.88	0.90
0.5	0.42	0.44	0.46	0.48	0.50	0.52	0.55
1.0	0.09	0.12	0.15	0.18	0.20	0.21	0.23

m	225°	250°	275° C
0.001	3.0	3.1	3.1
0.002	2.7	2.8	2.8
0.005	2.4	2.4	2.4
0.0075	2.2	2.2	2.2
0.01	2.1	2.1	2.1
0.02	1.8	1.8	1.8
0.025	1.7	1.8	1.7
0.05	1.5	1.5	1.5
0.075	1.3	1.4	1.4
0.1	1.2	1.4	1.3
0.2	0.92	0.98	0.93
0.5	0.51	0.53	0.51

TABLE XIV

VALUES OF THE RELATIVE PARTIAL MOLAL HEAT CONTENT OF HYDROCHLORIC ACID

Temp.	$\bar{L}_2$ (calories)						
°C	0.005 $\underline{m}$	0.01 $\underline{m}$	0.02 $\underline{m}$	0.05 $\underline{m}$	0.1 $\underline{m}$	0.2 $\underline{m}$	0.5 $\underline{m}$
25	30.8	55.1	86.7	152	246	433	315
60	66.0	92.1	128	205	321	558	526
90	107	133	172	260	397	681	762
125	167	193	234	334	498	843	1110
150	221	246	288	395	580	973	1400
175	283	306	348	462	669	1110	1740
200	355	374	416	537	767	1270	2140

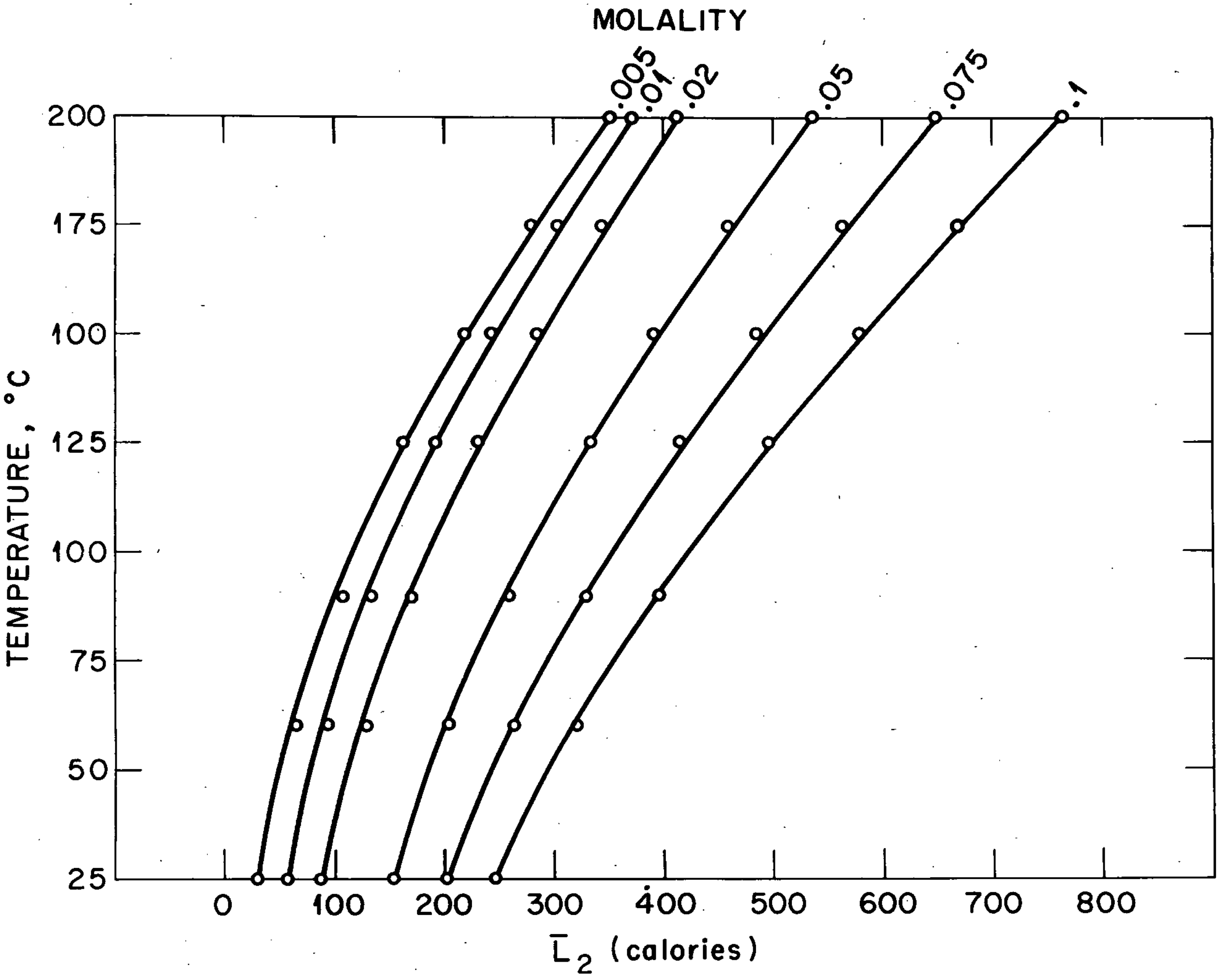

Figure 10. The Relative Partial Molal Heat Content of Hydrochloric Acid *versus* Temperature.

TABLE XV

VALUES OF THE RELATIVE PARTIAL MOLAL HEAT CAPACITY OF HYDROCHLORIC ACID

Temp.	$\bar{J}_2$ (calories)						
°C	0.005 *m*	0.01 *m*	0.02 *m*	0.05 *m*	0.1 *m*	0.2 *m*	0.5 *m*
25	0.83	0.90	1.0	1.4	2.0	3.3	5.2
60	1.2	1.2	1.3	1.7	2.4	3.9	7.0
90	1.5	1.5	1.6	2.0	2.7	4.3	8.7
125	2.0	1.9	2.0	2.3	3.1	5.0	11
150	2.3	2.2	2.3	2.6	3.4	5.4	13
175	2.7	2.6	2.6	2.8	3.8	5.9	15
200	3.1	2.9	2.9	3.2	4.1	6.4	17

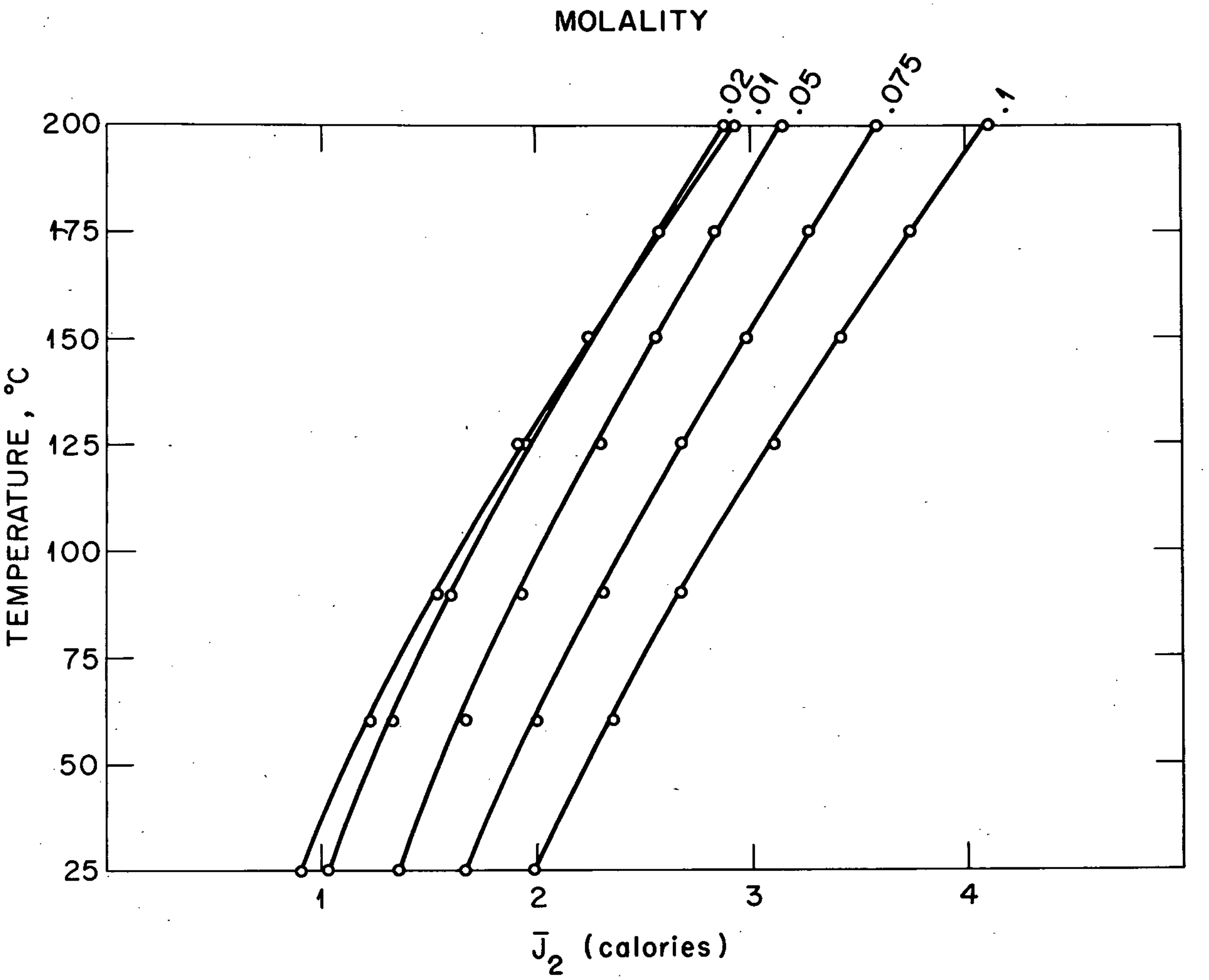

Figure 11. The Relative Partial Molal Heat Capacity of Hydrochloric Acid *versus* Temperature.

I. Smooth Values of E

For the purpose of comparison with previous and possible future work, smooth values of the electromotive force of cell (A) up to 0.1 m HCl were calculated from the E^o and B values determined above. These values are listed in Table XVI.

TABLE XVI

SMOOTHED VALUES OF THE ELECTROMOTIVE FORCE OF CELL A AT ONE ATMOSPHERE HYDROGEN PRESSURE

m	E_{smooth} (volts)						
	25°	60°	90°	125°	150°	175°	200°
0.001	0.57904	0.5953	0.6036	0.6063	0.6014	0.5897	0.5698
0.002	0.54415	0.5565	0.5617	0.5620	0.5571	0.5474	0.5308
0.005	0.49838	0.5055	0.5063	0.5023	0.4952	0.4846	0.4689
0.0075	0.47830	0.4831	0.4820	0.4758	0.4674	0.4559	0.4407
0.01	0.46411	0.4672	0.4648	0.4571	0.4478	0.4354	0.4185
0.02	0.43017	0.4295	0.4238	0.4124	0.4007	0.3859	0.3673
0.025	0.41932	0.4174	0.4107	0.3982	0.3856	0.3701	0.3508
0.05	0.38576	0.3802	0.3705	0.3543	0.3396	0.3215	0.3002
0.075	0.36619	0.3587	0.3473	0.3290	0.3132	0.2936	0.2713
0.1	0.35228	0.3435	0.3310	0.3112	0.2948	0.2742	0.2514
0.2	0.31891	0.3063	0.2906	0.2685	0.2499	0.2264	0.2025
0.5	0.27245	0.2546	0.2357	0.2085	0.1872	0.1630	0.1373
1.0	0.23340	0.2124	0.1907	0.1616	0.1361	0.1076	0.0767

m	225°	250°	275°C
0.001	0.5422	0.504	0.474
0.002	0.5067	0.471	0.443
0.005	0.4474	0.415	0.390
0.0075	0.4183	0.387	0.363
0.01	0.3970	0.366	0.342
0.02	0.3447	0.314	0.290
0.025	0.3277	0.297	0.272
0.05	0.2758	0.246	0.219
0.075	0.2463	0.218	0.189
0.1	0.2261	0.200	0.168
0.2	0.1754	0.147	0.108
0.5	0.0966	0.056	0.020

CHAPTER IV

DISCUSSION

A. Error Analysis

1. Measured Quantities

The errors in directly measurable quantities were probably no greater and in many cases much less than errors in calculated quantities. The most accurate measurement was undoubtedly that of temperature, the error in which can be conservatively set at ±0.01° up to 250° and ±0.05° at 275°[*]. The electromotive force measurements were subject to errors in standardization, as well as thermocouple, inductive, and non-equilibrium effects and the errors were estimated to be about ±0.05 mv. at 25°, ±0.1 mv. at 60 to 90°, ±0.2 mv. at 125 to 200°, and ±0.5 mv. at 225 to 275°. Pressure measurements, as was stated, were accurate to ±0.25 psi. to 200° and ±1 psi. at 225 to 275°. The initial hydrochloric acid concentrations were certainly known to within 0.1 per cent and the final titrations had an error no greater than that. On the other hand the solubility of silver chloride was determined to within only a few per cent.

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[*] Errors are listed as ranges within which the true value would be expected to lie. This is not based on a detailed statistical analysis but on a consideration of the factors entering into the measurement.

2. Calculated Quantities

a. Solution Molality. As noted above, the quantity having the largest error in the calculations was that of the molality at the time of measuring the electromotive force. The molality was in error primarily due to the errors involved in measuring the slopes of the electromotive force *versus* time curve and in determining the length of time to ascribe to each slope. A check on the calculation at each temperature during a test was obtained by adding up all the changes in molality and comparing the result with the value obtained by titrating the solution after the run. In the first series of tests (which went to 200°) the total change in molality averaged 5 per cent and the agreement between calculated and titrated concentrations averaged 0.6 per cent In the second series (which went to 275°) the changes averaged 12 per cent and the agreement between calculated and titrated concentration averaged 2.4 per cent. The errors in the concentrations were equivalent to errors in the electromotive forces averaging 0.5 mv. in the first series and 2.2 mv. in the second series. Of course these errors occurred to a greater extent the higher the temperature and the lower the concentration.

b. Hydrogen Fugacity. The errors involved in calculating the hydrogen pressure have been discussed above. It would appear that the errors in the pressure gauges were larger than errors in the steam tables, the use of Raoult's law, or the correction of steam pressure for the presence of hydrogen. Therefore errors of ±0.25 psi. and ±1 psi., equivalent to ±0.25 mv. and ±1 mv. in the electromotive force, were likely up to 200° and from 225 to 275° respectively.

Now the assumption that the hydrogen pressure was equivalent to the hydrogen fugacity introduced a possible further error. Hainsworth, Rowley, and MacInnes[52] found that, for the hydrogen-calomel cell, hydrogen acted as a perfect gas insofar as the electromotive force was concerned at pressures as high as 100 atm. at 25°. The data of Deming and Shupe[53] and more recently Holley, Worlton, and Zeigler[54] show that pure hydrogen at 1 to 2 atm. has a fugacity equal to its pressure within 0.1 percent at temperatures to 300°. However the effect of the large excess of water vapor on the hydrogen fugacity at the higher temperatures was a definite consideration*. Gillespie[55] gives a thermodynamic equation for the fugacity of a gas in a gas mixture:

$$RT \ln f = \int_0^P \left(\bar{v} - \frac{RT}{P}\right) dP + RT \ln PX \qquad (18)$$

where f = the fugacity desired,

$\bar{v}$ = partial molal volume of gas in the mixture,

P = total pressure of mixture,

X = mole fraction of the gas in the mixture.

The last term on the right in equation (18) is the Lewis and Randall[56]

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*The author would like to thank Prof. George Scatchard for helpful information on this point.

approximation (except P should be f^o, the fugacity of the pure gas at the same total pressure). The integral may be calculated from the equation of state of the mixture, if it is known. Unfortunately no data on either the fugacity of hydrogen in steam or the equation of state of hydrogen-steam mixtures was found. The various sets of data on such mixtures[57-61] are not extensive enough to permit calculation of the fugacity or the equation of state at the temperatures of interest to this study. Therefore recourse was made to the various methods of estimating the coefficients of equations of state of gas mixtures from the equations of state of the pure gases.

Hildebrand and Scott[62] give the following equation for gases that have equations of state in the virial form:

$$\ln f = \ln Xf^o + \frac{P\Delta}{RT}(1-X)^2 \qquad (19)$$

where f^o = the fugacity of the pure gas at the same total pressure,

and $\Delta = 2B_{12} - B_1 - B_2$,

B_{12} = second virial coefficient of the mixture,

B_1 = second virial coefficient of pure gas 1,

B_2 = second virial coefficient of pure gas 2.

Guggenheim[63] gave essentially the same equation for "slightly imperfect binary gas mixture", i.e., ones for which the virial coefficients above the second are negligible. Hildebrand and Scott[64] pointed out that for such gases the second virial coefficients are related to the Van der Waals constants a and b by:

$$B = b - \frac{a}{RT}\,, \tag{20}$$

and then

$$\Delta = \frac{(a_1^{1/2} - a_2^{1/2})^2}{RT}\,. \tag{21}$$

Guggenheim showed that for gases that obey the principle of corresponding states*[65]:

$$B_{12} = \left(\frac{1}{2}\,V_1^{*1/3} + \frac{1}{2}\,V_2^{*1/3}\right)^3 \phi \; \frac{T}{(T_1^* \, T_2^*)^{1/2}} \tag{22}$$

where V_1^* = characteristic volume of pure substance 1,

V_2^* = characteristic volume of pure substance 2,

T_1^* = characteristic temperature of pure substance 1,

T_2^* = characteristic temperature of pure substance 2,

ϕ = a function for all such gases and mixtures.

Guggenheim gave a plot of ϕ so that B_{12} values could be obtained[66]. Various other methods for calculating B_{12} from B_1 and B_2 have been proposed, particularly using the Bridgeman-Beattie[67] equation of state.

Unfortunately, as Stockmayer pointed out[68], steam is not a gas that can be treated in this way. He gave a method for calculating the second virial coefficient of steam and other polar gases using the

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*A substance obeys the principal of corresponding states if the interaction energy w of two molecules a distance r apart can be represented by $w = u\frac{e^*}{r^*}\,r$ where e^* is an energy and r^* is a length characteristic of the molecule and u is the same function for all the molecules concerned.

empirical equation of state for steam given by Keyes, Smith, and Gerry[69]:

$$B = B_o - \frac{A}{RT} e^{D/T^2} \qquad (23)$$

Then Stockmayer split the coefficients A and D up into two parts, the first depending only on the intermolecular force common to all kinds of molecules and the second depending on the dipole moment of the molecule. Expressing the intermolecular potential energy by

$$u = -Kr^{-6} - u^2 r^{-3} g \qquad (24)$$

where K = constant,

r = intermolecular distance,

u = dipole moment,

g = orientation factor,

he was able to calculate the terms B_o, A and D for steam and carbon dioxide. He then calculated the values of the coefficients for the mixture by taking the geometric mean of the values for the pure gases except for B_o which he took as:

$$(B_o)_{\text{mixture}} = \frac{1}{8}\left(B_{o_{H_2O}}^{1/3} + B_{o_{CO_2}}^{1/3}\right)^3 . \qquad (25)$$

The calculation of B_{12} fitted the experimental data for the carbon dioxide-steam system of Gerry[70] fairly well. However, in applying the treatment to nitrogen-steam equilibria Stockmayer found that at high temperatures (about 200^o) Dalton's law gave better agreement with the experimental data! Since hydrogen-steam mixtures are probably more nearly like nitrogen-steam mixtures than carbon dioxide-steam mixtures, Stockmayer's method was not tried.

Instead, in order to get an idea of the magnitude of the error, equations (19) and (21) of Hildebrand and Scott[62] were used; the Van der Waals a constant being available for hydrogen and water[71]. A detailed calculation was made for one temperature, viz., 200°. An average value of the hydrogen pressure was taken, 1.600 atm., and the fugacity found to be 1.642 atm. The corresponding error in the electromotive force due to neglecting this effect would have been +0.56 mv. on this basis (i.e., the electromotive force at 1 atm. should have been calculated to be 0.56 mv. lower).

Therefore the error is in the range of being significant, although at present there is no way of being sure of its absolute magnitude. Furthermore, the $\ln X f^{\circ}$ term alone in equation (19) would give a fugacity lower than the observed pressure whereas addition of the Δ term results in a fugacity higher than the observed pressure, i.e., the two terms tend to cancel each other. Smith and Katz[72], in reviewing the data on the solubility of hydrogen in water, found that the $\ln X f^{\circ}$ term generally was adequate to represent the fugacity of hydrogen in the vapor phase. They referred to a thermodynamic relationship derived by Krichevsky and Kasarnovsky[73] for the solubility of gases in water which utilized the Lewis and Randall approximation and successfully interpreted the data for hydrogen and for nitrogen. It should be realized that since the electromotive force data at each temperature were taken at about the same hydrogen and total pressure, the error in neglecting fugacity corrections would affect both $\underline{E}$ and $\underline{E}^{o}$ in the same way and hence $\gamma_{\pm}$ which depends on $\underline{E}-\underline{E}^{o}$ would not be affected.

c. Mean Molality and Ionic Strength. Errors in other calculated quantities were not significant in comparison with the above. These other quantities included the mean molality and the ionic strength of the solution. Values of these quantities are given in Tables XVII and XVIII. Even though the solubility of silver chloride was known only to a few percent, the errors in $m_{\pm}$ and $\underline{I}$ were at most ± 0.5 and 1.0 percent respectively in 0.005 $\underline{m}$ HCl at 200°, and much less than this at higher molalities. Thus the largest error in the electromotive force would have been about 0.25 mv. at 200°.

Another consideration involving the solubility of silver chloride, however, is that complexes involving species such as $AgCl_2^-$ are known to exist in hydrochloric acid solution[74]. Therefore the values of the mean molality and ionic strength are stoichiometric quantities, and the activity coefficients derived therefrom are stoichiometric activity coefficients and are not the activity coefficients of the actual species involved. If the latter were desired, the stability constants for the various complex ions and indeed the nature of the complex ions themselves would have to be known. These have not as yet been determined at the temperatures of interest to this study.

TABLE XVII

VALUES OF THE MEAN IONIC MOLALITY, $\underline{m}_{\pm}$, OF HYDROCHLORIC ACID SOLUTIONS SATURATED WITH SILVER CHLORIDE

$\underline{m}$	25°	60°	90°	125°	150°C
0.001	0.001000	0.001003	0.001014	0.001058	0.001137
0.002	0.002000	0.002003	0.002011	0.002049	0.002118
0.005	0.005000	0.005002	0.005011	0.005046	0.005110
0.0075	0.007500	0.007503	0.007511	0.007547	0.007613
0.01	0.01000	0.01000	0.01001	0.01005	0.01012
0.02	0.02000	0.02000	0.02001	0.02006	0.02014
0.025	0.02500	0.02500	0.02502	0.02506	0.02515
0.05	0.05000	0.05001	0.05002	0.05009	0.05020
0.075	0.07500	0.07501	0.07503	0.07511	0.07525
0.1	0.1000	0.1000	0.1000	0.1001	0.1003
0.2	0.2000	0.2000	0.2001	0.2002	0.2005
0.5	0.5000	0.5001	0.5002	0.5006	0.5012
1.0	1.000	1.000	1.001	1.001	1.003

$\underline{m}$	175°	200°	225°	250°	275°C
0.001	0.001286	0.001529	0.00188	0.00236	0.00299
0.002	0.002255	0.002494	0.00287	0.00340	0.00414
0.005	0.005241	0.005479	0.00587	0.00648	0.00733
0.0075	0.007746	0.007990	0.00840	0.00903	0.0995
0.01	0.01026	0.01050	0.0109	0.0116	0.0126
0.02	0.02030	0.02058	0.0211	0.0218	0.0229
0.025	0.02532	0.02562	0.0261	0.0269	0.0281
0.05	0.05042	0.05080	0.0514	0.0524	0.0538
0.075	0.07552	0.07597	0.0767	0.0778	0.0795
0.1	0.1006	0.1011	0.102	0.103	0.105
0.2	0.2010	0.2018	0.203	0.205	0.207
0.5	0.5021	0.5037	0.506	0.509	0.513
1.0	1.004	1.007	1.01	1.02	1.02

TABLE XVIII

VALUES OF THE IONIC STRENGTH, I, OF THE HYDROCHLORIC ACID SOLUTIONS SATURATED WITH SILVER CHLORIDE

m	25°	60°	90°	125°	150° C
0.001	0.001001	0.001006	0.001028	0.001119	0.001293
0.002	0.002001	0.002005	0.002023	0.002098	0.002243
0.005	0.005001	0.005005	0.005021	0.005091	0.005223
0.0075	0.007501	0.007505	0.007522	0.007594	0.007728
0.01	0.01000	0.01001	0.01002	0.01010	0.01024
0.02	0.02000	0.02001	0.02003	0.02012	0.02028
0.025	0.02500	0.02501	0.02503	0.02513	0.02530
0.05	0.05000	0.05001	0.05005	0.05018	0.05041
0.075	0.07500	0.07502	0.07506	0.07523	0.07551
0.1	0.1000	0.1000	0.1001	0.1003	0.1006
0.2	0.2000	0.2000	0.2001	0.2005	0.2010
0.5	0.5000	0.5001	0.5004	0.5012	0.5024
1.0	1.000	1.000	1.001	1.003	1.005

m	175°	200°	225°	250°	275° C
0.001	0.001653	0.002337	0.00355	0.00557	0.00895
0.002	0.002542	0.003110	0.00412	0.00580	0.00855
0.005	0.005494	0.006004	0.00690	0.00839	0.0108
0.0075	0.008001	0.008512	0.00941	0.0109	0.0132
0.01	0.01052	0.01104	0.0119	0.0134	0.0158
0.02	0.02060	0.02118	0.0222	0.0238	0.0263
0.025	0.02564	0.02625	0.0273	0.0290	0.0315
0.05	0.05084	0.05161	0.0529	0.0549	0.0579
0.075	0.07604	0.07695	0.0785	0.0808	0.0842
0.1	0.1012	0.1023	0.104	0.107	0.110
0.2	0.2020	0.2035	0.206	0.210	0.215
0.5	0.5043	0.5073	0.512	0.518	0.527
1.0	1.009	1.014	1.02	1.03	1.05

However, no error in the activity coefficients or standard potentials is incurred because of this consideration since it actually involves only a choice of standard state.

d. Junction Potentials. The cell (A) is ordinarily referred to as a cell "without liquid junction". However, in the present case the solubility of silver chloride became appreciable as the temperature increased and so there was a definite liquid junction at the quartz frit which divided the silver-silver chloride electrode compartment (saturated with silver chloride) from the main body of the solution. The potential across this junction was not measured. It could be calculated if the transference numbers or mobilities of silver ion and chloride ion were known or if the ratio of the equivalent conductances of hydrochloric acid with and without silver chloride were known at the temperatures of interest, but such is not the case. Therefore it was assumed to be small and negligible in relation to the other effects noted above, particularly since the concentration of hydrochloric acid was in all cases much larger than the concentration of dissolved silver chloride.

e. Smoothed Values of E. The final error was in the smoothing of the electromotive force values to even temperatures. As noted previously the greatest error in this step was not over 0.1 mv. The larger errors occurred when the observed temperature was far from the even temperature desired.

3. Reproducibility of Results

The final test of the random errors inherent in a procedure is the ability to make duplicate tests and reproduce the results. A number of duplicate tests were made in this study. Table XIX is a list of the differences between the results for each molality for duplicate tests. The observed electromotive forces were corrected to 1 atm. hydrogen pressure and even temperatures. Then the difference between the values at the same temperature and concentration for duplicate tests was entered in the table. No correction was made for slight differences in concentration between the tests since these differences were quite small. In order to estimate the effect of random errors, a term called the "emf variation" (similar to but not the same as the standard deviation) was defined:

$$\sigma_e = \sqrt{\frac{\sum r^2}{n}} = \sqrt{\frac{\sum \left|E_1 - E_2\right|^2}{2n}} \qquad (26)$$

where $\underline{r} = \underline{E}_{ave.} - \underline{E}$ at each temperature,

$\underline{n}$ = number of $\underline{r}$ values,

$\underline{E}_{ave.}$ = average of the two emf's at that temperature,

$\underline{E}$ = one of the emf's at that temperature,

and the summation is carried out for both emf's at all of the temperatures studied in the duplicate runs. The σ_e's at each temperature agree well with the σ_{fit} values obtained in the least squares fitting of $\underline{E}^{o''}$.

TABLE XIX

REPRODUCIBILITY OF ELECTROMOTIVE FORCES IN DUPLICATE RUNS

Temp. °C	$\lvert E_1 - E_2 \rvert^a$							
	0.005 m	0.01 m	0.025 m	0.05 m	0.075 m	0.1 m	σ_e^b	σ_{ls}^c
25	0.06	0.17	0.02		0.51	0.04	0.17	0.22
60				0.68				0.41
90				0.63				0.36
125		0.59	0.14	0.54	0.16	0.39	0.29	0.23
150		0.42	0.92	0.48	0.25	0.51	0.40	0.21
175		0.09	0.56	0.30	0.58	1.21	0.47	0.36
200		0.47	0.18	1.45		1.05	0.66	0.68
σ_e^b		0.28	0.35	0.55	0.29	0.55	0.30	
						Overall σ_σ	0.40	0.39

[a] $\lvert E_1 - E_2 \rvert$ = absolute value of difference between emf values of duplicate runs at the same temperature and concentration.

[b] $\sigma_e = \sqrt{\dfrac{\sum \lvert E_1 - E_2 \rvert^2}{2n}}$; n = number of $\lvert E_1 - E_2 \rvert$ values.

[c] $\sigma_{ls} = \sqrt{\dfrac{\sum r^2}{n-2}}$ where r = difference between observed point and the least squares line, and n = number of data points.

[d] $\sigma_\sigma = \sqrt{\dfrac{\sum \sigma^2}{n}}$ where n = number of values.

It can be seen from the overall σ_σ that as far as random errors go, the electromotive force data are accurate to about ±0.4 mv. to 200°. Duplicate tests were not made at higher temperatures.

On the other hand, reproducibility of results does not ensure that there were no systematic errors. However, the difference in procedure between the first and second series and the fact that the results could be used interchangeably indicate that systematic errors in the procedure were minimized. Systematic errors introduced by the assumptions made in the calculations were discussed above and the following error analysis does not consider them.

4. Derived Quantities

The errors in quantities derived from the measured and calculated quantities may be obtained statistically by defining the error of the derived quantity to be the square root of the sum of the squares of the errors of the quantities making up the derived quantity (assuming all quantities were weighted equally) divided by the number of quantities. According to this definition the overall error in $E^{\circ''}$ is ±0.5 mv. to 225°, ±2.2 mv. at 250°, and ±5 mv. at 275°.

The standard error in E° was obtained in the least squaring of the $E^{\circ''}$ values to a straight line. The ionic strength was assumed to be known exactly and the scatter of $E^{\circ''}$ values used to calculate the standard errors in both E° and B (the linear term coefficient) according to the usual least squares procedure. Actually the errors in

I would not affect the results greatly. However the choice of the ion-size parameter $\overset{\circ}{a}$, which depended on making the standard error in the fit of the line to the data a minimum, was certainly no better than ±1 Ångstrom and in fact at 250° and 275° the choice of $\overset{\circ}{a}$ was quite arbitrary. It should be realized that due to the small number of $E^{\circ''}$ values entering into the least squaring at higher temperatures, one bad value could skew the line and several accidentally close values could give a false picture of the error. The latter undoubtedly occurred at 225° where the σ_{fit} was much lower than at 200°. The errors in E°, B, and σ_{fit} are listed in Table VIII.

The errors in $\gamma_{\pm}$ were calculated from the errors in the difference $(E^{\circ} - E)$ and in $m_{\pm}$ and also from the errors in I, $\overset{\circ}{a}$, and B. The two results showed that the mean ionic activity coefficients are good to ±0.005 to 225° in solutions no greater than 0.2 m. At higher concentrations the error is ±0.01 and at higher temperatures the errors are ±0.02 (250°) and ±0.05 (275°).

The errors in the smoothed values of E should be less than the errors in either the measured E or $E^{\circ''}$. The standard errors in E° were used to estimate the error in E_{smooth} to be ±0.2 mv. up to 225°, ±2 mv. at 250° and ±4 mv. at 275°.

The errors in $\bar{L}_2$ and $\bar{J}_2$ are of a different sort since they depend on the function used to fit the activity coefficient data. The quadratic equations calculated for log $\gamma_{\pm}$ did fit the data within the above calculated error to 200° (see the σ_{fit} values in Table XI) and so it may be presumed that the first and second derivatives are as accurate as first and second derivatives can ever be. This has been taken to be ±10 percent for $\bar{L}_2$ and ±30 percent for $\bar{J}_2$. However, in looking at Figure 11 a discrepancy is seen in that above 150° the curves for 0.01 and 0.02 m cross over. Actually $\bar{J}_2$ should go to zero as m goes to zero. Therefore taking the second derivative appears to be too drastic a step in this case. On the other hand Gucker and Schminke[75] reported from calorimetric measurements that at 25° at concentrations below 0.1 m the partial molal heat capacity $\overline{Cp_2}$ increased very sharply. If their low concentration data were accurate, the $\overline{J_2} = \overline{Cp_2} - \overline{Cp_2{}^o}$ could actually increase at lower concentrations. However the results of Harned and Ehlers[2] and Bates and Bower[3] as well as the results given here do not show this at 25°, and Rossini[76] was inclined to disregard the anomoly entirely.

B. Comparison with Previous Investigators

1. Low Temperatures

Table XX is a list of the values of E_{smooth}, $\gamma\pm$, $\bar{L}_2$, and $\bar{J}_2$ from this investigation and from Harned and Ehlers[2], Bates and Bower[3], Covington and Prue[77], Lietzke[78], and Gucker and Schminke[75]. The agreement is seen to be satisfactory. Part of the difference in E_{smooth} and $\gamma\pm$ between this study and that of Bates and Bower at 90° was the

TABLE XX

COMPARISON OF RESULTS WITH THOSE OF PREVIOUS INVESTIGATORS

Temp.	HCl Conc.	$\gamma_\pm$				
°C	m	Greeley[a]	Bates[b]	Harned[c]	Covington[d]	Lietzke[e]
25	0.005	0.9284	0.9283	0.9285	0.9280	0.9277
	0.01	0.9044	0.9045	0.9048	0.9037	0.9030
	0.05	0.8310	0.8308	0.8304	0.8285	0.8216
	0.1	0.7972	0.7967	0.7964		0.7775
	0.2	0.7632		0.7667		0.7304
	1.0	0.8061		0.8090		0.6254
60	0.005	0.924	0.925	0.924		0.926
	0.01	0.899	0.900	0.899		0.900
	0.05	0.819	0.823	0.817		0.822
	0.1	0.776	0.783	0.781		0.783
	0.2	0.742		0.744		0.741
	1.0	0.761		0.754		0.653
90	0.005	0.920	0.920			0.921
	0.01	0.893	0.893			0.895
	0.05	0.807	0.810			0.814
	0.1	0.758	0.765			0.775
	0.2	0.723				0.734
	1.0	0.714				0.649

[a] Values measured in this study.

[b] See reference 3 in text.

[c] See reference 2 in text.

[d] See reference 77 in text.

[e] See reference 78 in text.

TABLE XX

COMPARISON OF RESULTS WITH THOSE OF PREVIOUS INVESTIGATORS (CONTINUED)

Temp.	HCl Conc.	E_{smooth} (volts)		
°C	m	Greeley[a]	Bates[b]	Harned[c]
25	0.005	0.49838	0.49840	0.49841
	0.01	0.46411	0.46412	0.46416
	0.05	0.38576	0.38579	0.38587
	0.1	0.35228	0.35233	0.35239
	0.2	0.31891		0.31871
	1.0	0.23340		0.23328
60	0.005	0.5054	0.5052	0.5049
	0.01	0.4672	0.4669	0.4667
	0.05	0.3802	0.3797	0.3797
	0.1	0.3435	0.3428	0.3425
	0.2	0.3063		0.3055
	1.0	0.2124		0.2123
90	0.005	0.5063	0.5063	
	0.01	0.4648	0.4648	
	0.05	0.3705	0.3703	
	0.1	0.3310	0.3304	
	0.2	0.2906		
	1.0	0.1907		

TABLE XX

COMPARISON OF RESULTS WITH THOSE OF PREVIOUS INVESTIGATORS (CONTINUED)

Temp. °C	HCl Conc. m	$\bar{L}_2$ (calories)			$\bar{J}_2$ (calories)			
		Greeley[a]	Bates[b]	Harned[c]	Greeley[a]	Bates[b]	Harned[c]	Gucker[f]
25	0.005	30.8	42	37; 45[h]	0.83	0.53	0.9;1.1[h]	
	0.01	55.1	54	46; 63	0.90	0.88	1,2;1.5	
	0.05	152	113	120;130	1.4	1.9	2.1;3.1	
	0.1	246	177	160;175	2.0	3.0	2.9;3.8	2.4
	0.2	433		238;242	3.3		3.7;4.8	3.4
	1.0	778[g]		626;611			7.5;8.1	7.5
60	0.005	66	63	90; 79	1.2	0.69	1.1	
	0.01	92	90	117;108	1.2	1.2	1.4	
	0.05	205	234	238;219	1.7	2.6	2.6	
	0.1	321	295	300;295	2.4	4.1	3.5	
	0.2	558		414;395	3.9		4.3	
	1.0	842		944;900			8.6	
90	0.005	107	86		1.5	0.84		
	0.01	133	130		1.5	1.5		
	0.05	260	269		2.0	3.1		
	0.1	397	400		2.7	5.1		
	0.2	681			4.3			
	1.0	870						

[f] Calorimetric values. See reference 75 in text.

[g] Calorimetric value at 1.0m is 550 cal. (J. M. Sturtevant, *J. Am. Chem. Soc.* 62, 584 (1940).

[h] Harned gave values calculated in two ways.

choice of 7 Ångstroms for $\mathring{a}$ rather than 6 Ångstroms and the inclusion of the solubility of silver chloride which begins to become significant. Lietzke's values for $\gamma_\pm$ were calculated from an equation of the form:

$$\log \gamma_\pm = -\left(\frac{\rho}{D^3T^3}\right)^{1/2} \frac{S_o\sqrt{I}}{1 + a'\sqrt{I}} \quad . \qquad (27)$$

Naturally his values at the higher concentrations fall off since he did not include the BI term. The agreement between $\bar{L}_2$ and $\bar{J}_2$ values of the different investigators is within reason considering the temperature ranges covered by each.

The agreement with the data of Bates and Bower is particularly valuable since their study was over a wider temperature range than any previous to this one and they used many more cells at each temperature. Furthermore their methods and electrodes were enough different to minimize still further the chance that unknown systematic errors were occurring. What is vitally needed now is a non-electromotive force measurement of $\gamma_\pm$ at the higher temperatures.

2. High Temperature

a. Extrapolations. The E^o values of Bates and Bower[3] were extrapolated in two ways. The first was by fitting their measured values to a quadratic function of the centigrade temperature and the second was by fitting their measured values to an equation of the form:

$$E^o = a + b\,T \log T + cT^2. \qquad (28)$$

Extrapolated values calculated by each equation are listed in Table IX along with the results from this study. It can be seen that the present results fall between the values extrapolated in the two different ways.

The extended equation for $\gamma_{\pm}$ of Harned and Ehlers[2] was fitted by Lietzke[79] to their data at 0.1 and 1.0 m at 25° and at 60° to give the following equation:

$$\ln \gamma_{\pm} = \frac{-4.1779 \times 10^{6}\sqrt{m}}{(DT)^{3/2}} \left(\frac{1}{1 + 50.30\, \mathring{a}(DT)^{1/2}\sqrt{m}}\right) + (b-b't)m + (d-d't)m^{2} - \ln(1 + 0.01802\,\nu m) \qquad (29)$$

where $\mathring{a} = 4.3$ $\qquad d = 0.0161$

$b = 0.3201$ $\qquad d' = 0.0000735$

$b' = 0.01075$ $\qquad \nu = 2$

and D was calculated from the Wyman equation[24].

This equation was then solved at 10° intervals from 0 to 300°C for several molalities from 0.001 to 4 m. The values so obtained were used throughout this study for comparison as the work progressed. Table XXI is a list of some of the values which may be compared with the values measured in the present study. It can be seen that agreement is generally better than 1 per cent up to 200°.

b. Experimental Data of Roychoudhury and Bonilla. As discussed previously, the only other high temperature measurements of cell (A) were by Roychoudhury and Bonilla[7]. The electromotive forces for their conditions have been calculated using the E^{o} and $\gamma_{\pm}$ values of the present study. The results are listed in Table XXII. The agreement is within

TABLE XXI

COMPARISON OF MEASURED $\gamma_{\pm}$ VALUES WITH VALUES CALCULATED BY EXTRAPOLATION FROM THE DATA OF HARNED

Temp. °C	0.01 m		0.05 m		0.1 m		1.0 m	
	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.
90	0.893	0.889	0.807	0.803	0.758	0.760	0.714	0.708
150	0.876	0.869	0.779	0.768	0.720	0.717	0.615	0.610
200	0.860	0.854	0.760	0.743	0.694	0.686	0.535	0.543
250	0.82	0.85	0.69	0.73	0.58	0.68	(0.59)[a]	0.50

[a] Value calculated from equation (14) in text.

TABLE XXII

COMPARISON OF THE DATA OF ROYCHOUDHURY AND BONILLA FOR CELL (A) WITH THE RESULTS OF THE PRESENT INVESTIGATION

Temp. °C	Mean Molality $m_\pm$	Log $\gamma_\pm$ interpolated[a]	Total Pressure psia.	H_2 Pressure atm.	E Calc[b] volts	E Meas[c] volts	Δ $E_C - E_M$ mv.
24	0.01695	-0.0535	14.7	0.970	0.4381	0.4398	- 1.7
			115	7.80	0.4644	0.4603	+ 4.1
			265	18.0	0.4751	0.4730	+ 2.1
			615	41.8	0.4859	0.4797	+ 6.2
80	0.01696	-0.0593	115	7.33	0.4654	0.4665	- 1.1
			265	17.53	0.4787	0.4820	- 3.3
100	0.01698	-0.0620	265	17.0	0.4765	0.4810	- 4.5
			615	40.8	0.4906	0.4860	+ 4.6
150	0.01707	-0.0702	115	3.11	0.4324	0.4450	-12.6
			265	13.3	0.4589	0.4683	- 9.4
			615	37.1	0.4776	0.4801	- 2.5
200	0.01746	-0.0785	265	2.67	0.3996	0.4322	-32.6
			615	26.5	0.4464	0.4684	-22.0
250	0.01811	-0.1015	615	2.57	0.3581	0.3935	-35.4

[a] Interpolated values from Table X.

[b] Calculated from the E^o values of the present investigation and the data given in the table according to the equation:

$$E = E^o - \frac{2RT}{F} \ln m_\pm \gamma_\pm + \frac{RT}{2F} \ln P_{H_2}.$$

[c] Measured by Roychoudhury and Bonilla[7].

about 5 and 10 mv. at 100° and 150° respectively and is perhaps satisfactory considering the fact that they waited only an hour for equilibrium at each temperature and that they took into account neither the solubility of silver chloride nor the reaction of hydrogen with silver ion. However the difference from the calculated value becomes 35 mv. at 250° and is in the opposite direction from that calculated by Lietzke[8].

Roychoudhury and Bonilla cross-plotted their data in order to determine the effect of hydrogen pressure on the electromotive force at constant temperature and found a discrepancy from the theoretical equation:

$$\Delta E_{P_{H_2}} = \frac{RT}{2F} \ln \frac{P_2}{P_1} . \qquad (30)$$

This discrepancy was attributed to an effect of hydrogen on the silver-silver chloride electrode. Lietzke[8] noted that at high temperatures and pressures hydrogen electrode sites might become established on the silver-silver chloride electrode thereby lowering its potential relative to the hydrogen electrode. Roychoudhury and Bonilla stated that they observed a 7.6 mv. difference at 25° between a silver-silver chloride electrode in a cell through which hydrogen was bubbling and a silver-silver chloride electrode in a connecting cell kept free of hydrogen.

Posey[80] has given an equation for the observed potential, V, of an electrode upon which two electrode processes are occurring:

$$V = \frac{RT}{\lambda F} \ln \left[\frac{(i_1^o)^{1/2} e^{+\frac{\lambda F}{2RT} V_1^o} + (i_2^o)^{1/2} e^{+\frac{\lambda F}{2RT} V_2^o}}{(i_1^o)^{1/2} e^{-\frac{\lambda F}{2RT} V_1^o} + (i_2^o)^{1/2} e^{-\frac{\lambda F}{2RT} V_2^o}} \right] \qquad (31)$$

where $\underline{i}_1^o$ = exchange current of reaction 1,

$\underline{i}_2^o$ = exchange current of reaction 2,

$\underline{V}_1^o$ = potential of electrode 1 in the absence of process 2,

$\underline{V}_2^o$ = potential of electrode 2 in the absence of process 1,

λ = number of charges transferred across the electrode interface during the charge transfer step (assumed here to be 1).

The exchange current is the rate of the reaction involved in the particular electrode process, here

(1) $1/2\ H_2 \rightleftharpoons H^+ + e^-$ (G)

(2) $AgCl + e^- \rightleftharpoons Ag + Cl^-$. (H)

In the present case if process (1), the hydrogen electrode reaction (G), occurs at an appreciable rate on the silver-silver chloride in comparison to process (2), the observed potential $\underline{V}$ will be different from the thermodynamically expected potential $\underline{V}_1^o$. Since Anderson[81] found that a platinized platinum electrode covered with finely divided silver still gave the same potential as a fresh platinized surface, it would appear that process (1) can readily occur on a silver surface. Hence the possibility that process (1) occurs on the finely divided silver of the silver-silver chloride electrode is entirely within reason. The question to be answered is, "What are the relative rates of process (1) and (2) on each electrode?"

Now the exchange currents may be measured in the following way. If a small current is passed between the silver-silver chloride and a working electrode in hydrochloric acid free of hydrogen, the current may be expressed as:

$$i = i_2^o \left[e^{+\frac{V}{\phi+}} - e^{-\frac{V}{\phi-}} \right] \tag{32}$$

where i_2^o = the desired exchange current of process (2),

$\underline{V}$ = potential change occurring upon the passage of current versus a suitable reference electrode (e.g., calomel),

$\phi+$ = function of asymmetry of charge barrier which can be assumed to be symmetrical so that $\phi+ = \frac{RT}{2F}$,

$\phi-$ = function of asymmetry of charge barrier which can be assumed to be symmetrical so that $\phi- = \frac{RT}{2F}$.

Expanding the exponentials for small $\underline{V}$:

$$i \cong i_2^o \left(\frac{1}{\phi+} + \frac{1}{\phi-}\right) V \tag{33}$$

and

$$\frac{dV}{di} \cong \frac{RT}{i_2^o F} . \tag{34}$$

Therefore a plot of $\underline{V}$ <u>versus</u> $\underline{i}$ would yield the exchange current of process (2). Then a similar measurement could be made of the exchange current of process (1) on silver using a finely divided silver electrode in sulfuric acid unsaturated with respect to silver sulfate in the presence of hydrogen. These measurements would have to be made at several temperatures up to 200° and would at least indicate the magnitude of the effect.

Another possible explanation for the difference between calculated and observed pressure dependence of the potential is similar to the above in that any deposited silver on the hydrogen electrode undergoing an exchange reaction with silver ion in solution would not respond to changes in hydrogen pressure. This possibility could be checked by measuring the effect of hydrogen pressure with both a clean platinized platinum surface and one with silver deposited on it.

Actually it is not possible to be entirely sure that the pressure anomaly noted by Roychoudhury and Bonilla is real. The difference between their data and the values calculated from the present study are larger than the pressure discrepancy. However further work, particularly along the lines of small current polarization measurements, is definitely needed.

C. Applicability of Debye-Hückel Equation

The Debye-Hückel equation in extended form was found to be entirely applicable over the range of temperatures studied. Straight lines were obtained for $\underline{E}^{o''}$ *versus* $\underline{I}$ that were well within the limits of experimental error and which readily allowed extrapolation to infinite dilution. However the magnitude of the ion-size parameter, $\underline{\mathring{a}}$, found to give the best fit of the data has been brought into question*. The value determined at 200°, 11 Ångstroms, and the extrapolated value at 275°, 20 Ångstroms, are so large as to suggest that $\mathring{a}$ in these cases is simply a convenient constant at each temperature and bears no relationship to ion size. Lietzke and Stoughton[82] found that when the denominator term in the Debye-Hückel expression for the activity coefficient was set equal to $(1 + A_s\sqrt{I})$ better agreement with experiment was obtained than with the full expression $(1 + 50.29\ \mathring{a}\ (DT)^{-1/2}\sqrt{\rho I})$ for solubility calculations up to 200° where A_s was independent of temperature. Harned and Ehlers[2] observed that $\mathring{a}$ did not change by more than 0.4 Ångstroms from 0 to 60° and their method of calculation of $\mathring{a}$ was probably more sensitive than that of Bates and Bower[3] which was the same as used in this study. Therefore an equation of slightly different form than equation (2) used here might give $\mathring{a}$ values more nearly representing an "ion size". Such an equation might involve a term in $m \ln m$ suggested by Fuoss[83] or a power series in $m^{1/2}$ as given by Harned and Owen[84].

The relationship between $\mathring{a}$ and the linear term coefficient B was investigated since, as may be seen in Figure 9, the two vary in the same way with temperature. Table XXIII is a list of $B/\mathring{a}$ values and shows that the ratio of B to $\mathring{a}$ is not constant and goes through a minimum at 250°. If these very rough values can be believed, this would

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*The author would like to acknowledge the interest of Prof. R. M. Fuoss in this discussion.

TABLE XXIII

VALUES OF THE DEBYE - HÜCKEL LINEAR TERM DIVIDED BY THE ION-SIZE PARAMETER

Temp. °C	$B/\mathring{a}$ (m-Ångstrom)$^{-1}$
25	+0.035
60	-0.004
90	-0.018
125	-0.017
150	-0.031
175	-0.030
200	-0.038
225	-0.047
250	-0.076
275	-0.047

indicate that perhaps B (or $\mathring{a}$) involves the DT product since it too goes through a minimum near 250°.

In calculating the activity coefficient for the higher concentrations the quadratic term Dm^2 was used. Here D is certainly just an empirical constant. The errors in fitting the data with this term included were large but were due to the paucity of data above 0.1 m.

Therefore the Debye-Hückel extended equation can be used to calculate the mean ionic activity coefficients of hydrochloric acid up to 0.1 m over the temperature range 25 to 275° with an accuracy equivalent to that in the electromotive force data using the empirical $\mathring{a}$ and B constants given in Table VIII. The activity coefficients from 0.2 to 1.0 m can be calculated using the equation extended further to include the quadratic term from the empirical constants B and D listed in Table XII with somewhat less accuracy.

D. Conclusion

The errors as listed above were somewhat higher than the goal set for the work, *viz.*, ±0.1 mv., but appear to be reasonable insofar as meeting the other objectives of the study. In particular it has been shown that the silver-silver chloride electrode can be used as a reference electrode at elevated temperatures. The agreement with previous investigations and with extrapolated data lend support to the validity of the work. On the other hand measurement of activity coefficients, the standard free energy of reaction (A), and the other quantities of interest by non-electromotive force methods must be made to check the validity of the underlying assumptions.

CHAPTER V

SUMMARY

Electromotive force measurements have been made of the cell

$$\text{Pt}; H_2(g), HCl(\underline{m}), AgCl; Ag$$

from 25 to 200° and in some cases to 275° using hydrogen pressures of about 1 atm. and hydrochloric acid concentrations from 0.005 to 1.0 *m*. The potentials observed were corrected to exactly 1 atm. by means of the Nernst equation, assuming that the fugacity of hydrogen was equivalent to the pressure of hydrogen, and to exactly even temperatures by adding the temperature difference times the slope of the quadratic equation representing the change in electromotive force *versus* temperature. It was necessary to correct the concentration of hydrochloric acid for changes occurring during the test due to the reduction of silver ion by hydrogen. This correction was made from the slope of the electromotive force *versus* time at constant temperature. The mean molality and ionic strength of the solution were calculated assuming that the solution was saturated with silver chloride and that all of the chloride in solution existed as free chloride ion. Junction potentials were assumed to be insignificant.

The mean ionic activity coefficient of hydrochloric acid was written in the form of the Debye-Hückel extended equation and the resulting expression substituted into the Nernst equation. Rearrangement of the latter gave a term $\underline{E}^{o''}$ as a linear function of the ionic strength of the solution where $\underline{E}^{o''}$ was the collection of all terms measureable or calculable. The ion size parameter in the Debye-Hückel part of $\underline{E}^{o''}$ was chosen so as to make the standard error of fit of the $\underline{E}^{o''}$ values to a straight line a minimum for solutions of concentration up to 0.1 m. Extrapolation of the line to infinite dilution gave values of $\underline{E}^{o}$, the standard potential of the silver-silver chloride electrode (assuming the standard potential of the hydrogen electrode to be zero at each temperature) which fitted the following equation to within 0.19 mv. to 200°:

$$E^{o} = 0.23735 - 5.3783 \times 10^{-4}t - 2.3728 \times 10^{-6}t^{2} \text{ volts.}$$

The Nernst equation was then solved for the mean ionic activity coefficient of hydrochloric acid at the temperatures and concentrations of interest. pH values for the same solutions and temperatures were calculated assuming that the activity coefficient of chloride ion was equivalent to the mean ionic activity coefficient. Finally, the mean ionic activity coefficients were fitted to quadratic functions of the centigrade temperature over the range 25 to 200° at each concentration and these equations differentiated to give the relative partial molal heat contents. A second differentiation gave the relative partial molal heat capacities.

The overall error in the reproducibility of the electromotive forces was about ±0.5 mv. up to 225°, probably ±2 mv. at 250°, and

±5 mv. at 275°. Agreement with previous investigators at temperatures below 100° was satisfactory, both with the electromotive forces and with the derived quantities. Agreement with the single investigation at high temperatures was within the probable error of the other investigation.

On the other hand it was shown that several assumptions made in the calculations could have caused systematic errors in the results. These were (1) assuming the hydrogen fugacity to be equivalent to the hydrogen pressure; (2) neglecting junction potentials; and (3) neglecting the possibility that the hydrogen-hydrogen ion exchange current on the silver-silver chloride electrode could have been significant in relation to the chloride-silver chloride exchange current. The maximum error attributable to effect (1) was estimated as less than 1 mv. at 200°. The errors for effects (2) and (3) are unknown.

The Debye-Hückel extended equation was shown to express the data satisfactorily although the ion size parameter appeared to be simply an adjustable parameter.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc. 54*, 1350 (1932).
2. H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc. 55*, 2179 (1933).
3. R. G. Bates and V. E. Bower, *J. Research Natl. Bur. Standards 53*, 283 (1954).
4. P. J. W. Debye and E. Hückel, *Physik. Z. 24*, 185 (1923).
5. H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 3rd ed., Reinhold Publishing Corp., New York, N. Y., 1958, p. 64
6. *Ibid.*, p. 67.
7. R. N. Roychoudhury and C. F. Bonilla, *J. Electrochem. Soc. 103*, 241 (1956).
8. M. H. Lietzke, *J. Am. Chem. Soc. 77*, 1344 (1955).
9. G. C. Åkerlöf and J. W. Teare, *J. Am. Chem. Soc. 59*, 1855 (1937).
10. G. J. Janz and H. Taniguchi, *Chem. Revs. 53*, 397 (1953).
11. H. Taniguchi and G. J. Janz, *J. Electrochem. Soc. 104*, 123 (1957).
12. M. H. Lietzke and J. V. Vaughen, *J. Am. Chem. Soc. 77*, 876 (1955).
13. M. H. Lietzke and R. W. Stoughton, *J. Am. Chem. Soc. 75*, 5226 (1953).
14. J. V. Vaughen and M. H. Lietzke, *J. Am. Chem. Soc. 79*, 4266 (1957).
15. C. M. Myers with C. F. Bonilla, Senior Research Thesis in Chemical Engineering, Johns Hopkins University (1947); (referred to by R. N. Roychoudhury and C. F. Bonilla, *op. cit.*, p. 241).
16. V. Pražák, *Werkstoffe u Korrosion 9*, 524 (1958).
17. M. H. Lietzke and J. R. Tarrant, "Preliminary Report on the Model 904 High Temperature pH Meter", Oak Ridge National Laboratory Publication ORNL CF-57-11-87, November 21, 1957.

18. W. H. Marburger, K. Anderson, and G L. Wigle, Argonne National Laboratory Publication ANL-5298, July 1954.

19. M. H. Lietzke and R. W. Stoughton, *J. Am. Chem. Soc.* *79*, 2067 (1957).

20. E. R. Cohen, K. M. Crowe, and J. W. M. Dumond, "The Fundamental Constants of Physics", Interscience Publishers, Inc., New York, N. Y., 1957.

21. E. C. Crittenden, *Science* *120*, 1007 (1954).

22. G. C. Åkerlöf and H. I. Oshry, *J. Am. Chem. Soc.* *72*, 2844 (1950).

23. Private Communication from M. H. Lietzke, 1958.

24. J. Wyman, Jr., and E. N. Ingalls, *J. Am. Chem. Soc.* *60*, 1182 (1938).

25. Private Communication from W. C. Waggener, 1957.

26. J. O. Almen and A. Laszlo, *Trans. Am. Soc. Mech. Engrs.* *58*, 305, (1936).

27. R. G. Bates, "Electrometric *p*H Determinations", John Wiley and Sons, Inc., New York, N. Y., 1954, p. 167.

28. *Ibid.*, p. 166.

29. N. J. Anderson, Ph.D. Thesis, University of Chicago, Chicago, Ill. (1945), p. 16.

30. C. K. Rule and V. K. LaMer, *J. Am. Chem. Soc.* *58*, 2339 (1936).

31. R. G. Bates, *op. cit.*, p. 204.

32. W. C Ashby, A. R. Cooke, and S. C. Datta, *Biochem. J.* *56*, 190 (1954).

33. "Directions for No. 8067 Mueller Temperature Bridge", Direction Book 77-2-0-2, Leeds and Northrup Co., Philadelphia, Pa.

34. N. S. Osborne, H. F. Stimson, E. F. Fioch, and D. C. Ginnings, *J. Research Natl. Bur. Standards* *10*, 179-183 (1933).

35. N. S. Osborne and C. H. Moyers, *J. Research Natl. Bur. Standards* *13*, 11-13 (1934).

36. C. W. Foulk and M. Hollingsworth, *J. Am. Chem. Soc.* *45*, 1223 (1923).

37. I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis", Revised ed., The MacMillan Co., New York, N. Y., 1948, p. 311.

38. *Ibid.*, p. 229.

39. R. G. Bates, *op. cit.*, p. 206.

40. D. G. Nicholson and C. E. Holley, Jr., "Inorganic Syntheses", Edited by W. C. Fernelius, Vol. II, 1st ed., McGraw-Hill Book Co., New York, N. Y., 1946, p. 4.

41. W. Zimmerman, III, *J. Am. Chem. Soc.* *74*, 852 (1952).

42. N. J. Anderson, *op. cit.*, p. 12.

43. R. J. Raridon, Ph.D. Thesis, Vanderbilt University, Nashville, Tenn. (1958), p. 93.

44. M. H. Lietzke, "An ORACLE Code for Least Squares", Oak Ridge National Laboratory Publication ORNL CF-59-2-20, February 4, 1959.

45. N. J. Anderson, *op. cit.*, p. 15.

46. "VDI-Wasserdampftafeln", Edited by E. Schmidt, 4th ed., Springer-Verlag, Berlin, 1956.

47. T. H. Gronwall, V. K. LaMer, and K. Sandved, *Physik. Z.* *29*, 358 (1928).

48. H. S. Harned and B. B. Owen, *op. cit.*, p. 166.

49. R. G. Bates, *op. cit.*, pp. 16-33 and 62-90.

50. E. A. Guggenheim, *J. Phys. Chem.* *34*, 1758 (1930).

51. R. G. Bates, *op. cit.*, p. 87.

52. W. R. Hainsworth, H. J. Rowley, and D. A. MacInnes, *J. Am. Chem. Soc.* *46*, 1437 (1924).

53. W. E. Deming and L. E Shupe, *Phys. Rev.* *40*, 848 (1932).

54. C. E. Holley, Jr., W. J. Worlton, and R. K. Zeigler, Los Alamos Scientific Laboratory Publication LA-2271, March 17, 1959, p. 20.

55. L. J. Gillespie, *Chem. Revs.* *18*, 361 (1936).

56. G. N. Lewis and M. Randall, "Thermodynamics", McGraw-Hill Book Co., New York, N. Y., 1923, p. 226.

57. E. P. Bartlett, *J. Am. Chem. Soc.* *49*, 65 (1927).

58. R. Wiebe and V. L. Gaddy, *J. Am. Chem. Soc.* *56*, 76 (1934).

59. A. Teadoravich and V. N. Ipatieff, *J. Gen. Chem. USSR* *4*, 395, (1934).

60. H. L. McGill, W. L. Sibbitt, H. K. Wiskind, and S. Suciu, Argonne National Laboratory Publication ANL-4603 (1951).

61. E. F. Stephan, N. S. Hatfield, R. S. Peoples, and H. A. H. Pray, Batelle Memorial Institute Publication BMI-1067, January 23, 1956.

62. J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes", 3rd ed., Reinhold Publishing Co., New York, N. Y., 1950, p. 238.

63. E. A. Guggenheim, "Mixtures", Clarendon Press, Oxford, 1952, p. 153.

64. J. H. Hildebrand and R. L. Scott, *op. cit.*, p. 233.

65. K. S. Pitzer, *J. Chem. Phys.* *7*, 583 (1939).

66. E. A. Guggenheim, *op. cit.*, p. 156.

67. J. A. Beattie and O. C. Bridgeman, *J. Am. Chem. Soc.* *49*, 1665 (1927).

68. W. H. Stockmayer, *J. Chem. Phys.* 9, 863 (1941).

69. F. G. Keyes, L. B. Smith, and H. T. Gerry, *Proc. Am. Acad. Arts Sci.* *70*, 319 (1936).

70. H. T. Gerry, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass. (1952) (referred to by W. H. Stockmayer, *op. cit.*, p. 865).

71. F. H. Getman and F. Daniels, "Outlines of Physical Chemistry", 7th ed., John Wiley and Sons, Inc., New York, N. Y., 1947, p. 22.

72. J. M. Smith and D. L. Katz, Oak Ridge National Laboratory Publication ORNL-1069, September 24, 1951.

73. I. R. Krichevsky and J. S. Kasarnovsky, *J. Am. Chem. Soc. 57*, 2168 (1935).

74. J. H. Jonte and D. S. Martin, Jr., *J. Am. Chem. Soc. 74*, 2052 (1952).

75. F. T. Gucker, Jr., and K. H. Schminke, *J. Am. Chem. Soc.* 54, 1358 (1932).

76. F. D. Rossini, *J. Research Natl. Bur. Standards 9*, 679 (1932).

77. A. K. Covington and J. E. Prue, *J. Chem. Soc.*, 3696 (1955).

78. M. H. Lietzke, "Tables of the Activity Coefficient of a 1-1 Electrolyte and its Derivatives Calculated Using a Modified Debye-Hückel Equation", Oak Ridge National Laboratory Publication ORNL-2628, November 28, 1958.

79. Private Communication from M. H. Lietzke, 1956.

80. F. A. Posey, *J. Electrochem. Soc.*, to be published.

81. N. J. Anderson, Ph.D. Thesis, University of Chicago, Chicago, Ill. (1945), p. 16.

82. M. H. Lietzke and R. W. Stoughton, *J. Phys. Chem.*, to be published.

83. R. M. Fuoss, Paper Presented before the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959.

84. H. S. Harned and B. B. Owen, *op. cit.*, p. 467.

85. Private Communication from R. W. Stoughton, 1956.

APPENDIXES

APPENDIX I

CONSTANTS USED IN THE CALCULATIONS

A. Fundamental Constants (Chemical Scale)[20]

Ice-point Temperature	T	$273.1500 \pm 0.0002\ ^{\circ}K.$
Gas Constant	R	$8.31470 \pm 0.00034 \times 10^{7}$ erg. mole.$^{-1}$ deg.$^{-1}$
Joule Equivalent	J_{15}	4.1854 ± 0.0004 abs. J. cal.$^{-1}$
Faraday	F	$96{,}495.7 \pm 1.1$ coulombs (g. mole)$^{-1}$.
Standard Atmosphere (defined)		1,013,250 dynes cm.$^{-2}$
Electronic Charge	e	$4.80286 \pm 0.00009 \times 10^{-10}$ abs. esu.
Velocity of Light	c	$299{,}793 \pm 0.3$ km. sec.$^{-1}$
Boltzmann Constant	k	$1.38044 \pm 0.00007 \times 10^{-16}$ erg. deg.$^{-1}$
Avogadro Number	N	$6.02322 \pm 0.00016 \times 10^{23}$ (g. mole)$^{-1}$.
Standard Volume (perfect gas)	V_o	$22{,}414.6 \pm 0.9$ cm.^{3} atm. mole^{-1}.
Acceleration of Gravity	g	32.174 ft. sec.$^{-2}$

B. Derived Constant

Debye-Hückel Limiting Slope x $(DT)^{3/2}$

$$So = \sqrt{\frac{2\ N\ e^{6}}{1000\ k^{3}}} = 4.20222 \times 10^{6}.$$

C. Measured Constants

Dielectric Constant of Water[22]

$$D = 5321/T + 233.76 - 0.9297\ T + 0.001417\ T^2 - 8.292 \times 10^{-7}\ T^3.$$

Density of Water[23]

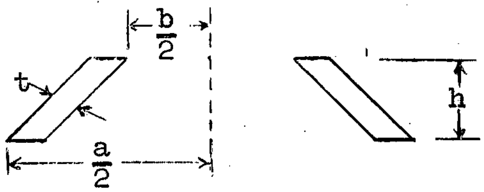
$$\rho_0 = 1.00157 - 1.56096 \times 10^{-4} t - 2.69491 \times 10^{-6} t^2.$$

APPENDIX II

DESIGN OF BELLEVILLE SPRING WASHER[26]

It was desired to have a washer which would yield to the upward thrust of the expanding Teflon liner-gasket but which would maintain a pressure-tight seal during both the upward thrust upon heating up and the contraction upon cooling down. A Belleville spring washer was found to have the required properties. Inconel X, heat treated 16 hr. at 1350°F. followed by air cooling, was found to be a suitable material.

Let the washer be represented as shown in cross section:



then

$$P = \frac{E}{(1 - \sigma^2) m (\frac{a}{2})^2} \left[(h - \delta)(h - \frac{\delta}{2}) t + t^3 \right] \qquad (1)$$

where

P = pressure desired,

δ = deflection necessary to give pressure desired,

E = modulus of elasticity = 29×10^6 psi at 500°F.,

σ = Poisson Ratio = 0.3,

m = function of a and b (= 0.55 for a = 3 in. and b = 1.875 in.).

Rearranging equation (1) for $t = \delta$

$$t = (P(1 - \sigma^2)\, m(\tfrac{a}{2})^2 / \sqrt{2}\, E)^{1/4} \qquad (2)$$

$= 0.068$ in. for $P = 1000$ psi.

Now

$$h = t\sqrt{2} = 0.096 \text{ in.} \qquad (3)$$

Therefore a washer 3 in. O.D. and 1.875 in. I.D. (as required to fit the autoclave head) having a thickness 0.068 in. and a height 0.096 in. would serve up to 1000 psi.

The deflection necessary to withstand steam pressure at any temperature was calculated from:

$$\delta = \frac{P\,(1 - \sigma^2)(m)(\frac{a}{2})^2}{E} \quad \frac{1}{(h - \delta)(h - \frac{\delta}{2})\,t + t^3} \qquad (4)$$

and the following table used in assembling the autoclave:

Highest Temperature Expected During Run (°C)	Highest Pressure Including Safety Factor (psig)	Deflection δ (in.)
200	250	0.009
250	600	0.025
275	1000	0.096

Deflections were measured during the tightening of the cap bolts with a special micrometer depth gauge.

APPENDIX III

FORMULA AND VALUES FOR CORRECTING STEAM PRESSURE FOR THE PRESENCE OF HYDROGEN[85]

Let P_1 = vapor pressure of H_2O at T in the absence of H_2,

P_2 = vapor pressure of H_2O at T in the presence of H_2,

P_H = partial pressure of H_2 at T,

$\bar{v}$ = molar volume of water = $\frac{18.0}{\rho}$,

ρ = density of water,

R = gas constant,

F = free energy.

Then, from the change in free energy with pressure at constant temperature:

$$\left(\frac{\partial F}{\partial P}\right)_T = \bar{v} \tag{1}$$

Integrating:

$$F_1 - F_2 = \int_1^2 \bar{v}dp = \bar{v}(P_H + P_2 - P_1) \tag{2}$$

Also:

$$F_1 - F_2 = RT \ln \frac{P_2}{P_1} \tag{3}$$

Therefore:

$$\ln \frac{P_2}{P_1} = \frac{\bar{v}}{RT}(P_H + P_2 - P_1) = \frac{18.0}{\rho RT}(P_H + P_2 - P_1). \tag{4}$$

Since P_2/P_1 is close to unity we may expand the logarithm as follows:

$$P_2 = P_1\left[1 + \frac{18.0}{\rho RT}(P_H + P_2 - P_1)\right] \tag{5}$$

and since $P_1 \sim P_2$:

$$P_2 = P_1\left[1 + \frac{0.219}{\rho T} P_H\right] \tag{6}$$

$$= P_1 + \frac{0.219 P_1}{\rho T} P_H . \tag{7}$$

TABLE OF VALUES

Temp. °C	Vapor Pressure of Water $\underline{P}_1$ (psia)	Correction Term per atm. H_2 $\frac{0.219\ P_1}{\rho_0\ T}$ (psi)
125	33.66	0.02
150	69.04	0.04
175	129.45	0.07
200	225.45	0.12
225	369.90	0.20
250	576.58	0.30
275	862.80	0.46

Corrected Water Vapor Pressure = Uncorrected $\underline{P}$ + (corr'n term x $\underline{P}_{H_2}$)

where $\underline{P}_{H_2}$ = hydrogen pressure in atmospheres.

VITA

Richard Stiles Greeley was born in Framingham, Massachusetts on [redacted] He graduated from Framingham High School in June 1945 and entered Harvard College in September of that year. He joined the U. S. Naval Reserve Officers Training Crops in September 1947 and remained at Harvard until Commencement in June 1949, at which he received a B.S. degree with a major in chemistry. He continued his studies under the naval program at Northwestern University and obtained the M.S. degree with a major in chemistry and was commissioned Ensign, U. S. Naval Reserve in June 1951. At Northwestern he was awarded an S. C. Johnson and Sons, Company research fellowship. He was called to active duty immediately upon being commissioned and served three years aboard the USS Van Valkenburgh (DD 656) as Engineering Officer. Following his release from active duty he joined the staff of the Oak Ridge National Laboratory where he is now employed in the Reactor Experimental Engineering Division. In September 1954 he entered the Graduate School of the University of Tennessee and took up studies toward the doctorate degree in chemistry at the University Extension in the Oak Ridge Institute of Nuclear Studies. In June 1956 he began the experimental part of the doctoral program under the auspices of the Chemistry Division at the Oak Ridge National Laboratory.

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