

THE THERMODYNAMICS OF CONCENTRATED
AQUEOUS SOLUTIONS OF HYDROGEN BROMIDE

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by

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THE THERMODYNAMICS OF CONCENTRATED AQUEOUS
SOLUTIONS OF HYDROBROMIC ACID

A thesis submitted by Roy S. Yamasaki, and done under the direction of Associate Professor Wendell J. Biermann.

The accuracy and completeness of the thermodynamic characterization of hydrochloric acid by Akerlof and Teare with the silver-silver chloride electrode suggested that an analogous investigation of hydrobromic acid by an extension of the work of Hamed, Keston and Donelson with the silver-silver-bromide electrode would be practical. Electromotive forces of the cell $H_2; HBr(m); AgBr; Ag$ were measured over a range of concentration and temperature.

The slowness of establishment of equilibrium, ascribed to the solubility of $AgBr$ in HBr , limited the work to the region below 3.0 molal. In the region below 1.0 molal agreement was excellent with the earlier work of Hamed, Keston and Donelson.

Hamed, Keston and Donelson obtained the standard potentials by use of a conventional Hitchcock extrapolation. Re-extrapolation of their data using the "Debye-Hückel function" gives a substantially different set of results, and since the extrapolation is much more nearly a straight line, may be considered more reliable. Using the improved values of the standard potentials the activity coefficients and relative partial molal free energies of aqueous hydrobromic acid solutions were calculated up to 3.0 molal.

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Dr. W. J. Biermann for the helpful advice and sympathetic understanding during the course of this research, and to give thanks to Mr. T. H. Sutherland for the translation of some of the papers employed

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I. INTRODUCTION.

I. INTRODUCTION

Study of the behavior of concentrated electrolytic solutions has been somewhat neglected because of the lack of a suitable theoretic background with which to interpret results. Ever since the success of the Debye-Hückel theory (10), by predicting the mean activity coefficients of the electrolytes in dilute solutions in terms of interionic attraction, investigators endeavored to apply it with suitable modifications to more concentrated solutions. Hückel (26), attached a semi-empirical term to the Debye-Hückel equation and extended its range to three or more molal. More constants were added by Åkerlöf and Teare (1), to describe adequately the behavior of aqueous hydrochloric acid to 16 molal. Experimentally these were welcome strides, but much of the original theoretical effectiveness of the Debye-Hückel theory was lost.

It seems that the Theory is oversimplified for the concentrated solutions, and requires further considerations with respect to factors such as, interactions between the ions and between the solvent and the ions. Although some of these have been investigated (44, 45, 51, 52, 5, 49, 42), no complete analysis of these intricate problems has as yet been made.

Meanwhile to define the phenomena which require explanation, data collecting has been initiated. Thermodynamic properties of the electrolytes, particularly the presumably most simple 1-1 type began to be tabulated. Hydrogen chloride has been investigated in aqueous, nonaqueous, and in aqueous-nonaqueous solvent mixtures to the limit of solubility (23). However, hydrogen bromide has received less attention, and then only in an

aqueous medium.

The great chemical similarity between hydrogen chloride and hydrogen bromide suggests that the comparison of the thermodynamic properties of this pair would be interesting, since presumably we would be dealing with specific rather than structural differences. A reliable set of data for two chemically similar electrolytes does not yet exist. It has therefore been felt that further studies of aqueous hydrogen bromide would be valuable.

Bates and Kirschman (3), measured the vapor pressure of hydrobromic acid from 6 to 11 molal at 25°C. and determined the approximate free energy of formation of hydrogen bromide at various concentrations. With the cell, Pt, H₂ (1 atm.); HBr (m); AgBr (s); Ag, Livingston (33), found the mean activity of hydrogen bromide in 0.08 to 1.50 molal solutions at 25°C. Finally, Harned, Keston, and Donelson (22), employing the same technique, calculated the activity coefficient, the relative partial molal heat content, and the heat capacity of hydrogen bromide in 0.001 to 1 molal from 0 to 60°C.

Recently, the data for the concentrated regions of aqueous hydrochloric acid (1), from indirect potentiometric work, have been found to agree remarkably well with those obtained from a reliable but limited calorimetric method (4). Since then, the latter technique has also been applied to concentrated aqueous hydrobromic acid.

Thus, with the possible confirming data already present, and with the assurance of the feasibility of the more versatile electromotive force method, this research was undertaken to determine the thermodynamics of hydrogen bromide in water beyond 1 molal by potentiometry.

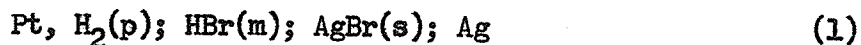
II. THEORETICAL AND EXPERIMENTAL CONSIDERATIONS

II. THEORETICAL AND EXPERIMENTAL CONSIDERATIONS

In order to utilize the electromotive force technique effectively, certain theoretical and experimental procedures must be followed.

A. Thermodynamic Calculations

The cell to be studied is given by



with a presumed reaction



so that e.m.f. at partial pressure p is

$$E_p = E^{\circ} - \frac{RT}{F} \ln \frac{a_{\text{H}} \not\rightarrow a_{\text{Br}^-}}{p^{\frac{1}{2}}} \quad (3)$$

and at one atmosphere is

$$\begin{aligned} E &= E^{\circ} - \frac{RT}{F} \ln \frac{a_{\text{H}} \not\rightarrow a_{\text{Br}^-}}{p} = E_p - \frac{RT}{2F} \ln p \\ &= E_p \not\rightarrow \frac{RT}{2F} \ln \frac{760}{P - p_{\text{HBr}}} \quad (4) \end{aligned}$$

where m is the concentration of hydrogen bromide in moles per 1000 grams of water, E° the standard molal electrode potential of the silver; silver bromide electrode, R the gas constant, T the absolute temperature, F the Faraday constant, a_{H} , a_{Br^-} the activity of the ions indicated, P the barometric pressure, and p_{HBr} the vapor pressure of hydrobromic acid.

The electromotive force at one atmosphere can then be used to calculate the thermodynamic functions.

1. Observed Activity Coefficient Of Hydrogen Bromide In Water

Letting

$$k = \frac{2.3026 RT}{F}, \text{ and knowing that } a_{\text{H}^+} a_{\text{Br}^-} = a_{\pm}^2,$$

$$\text{and } a_{\pm} = \gamma_{\pm} m,$$

where a_{\pm} is the mean ionic activity of the hydrogen bromide, we see from equation (4) that the mean ionic molal activity coefficient γ_{\pm} is given by

$$\log \gamma_{\pm} = -\log m - \frac{(E - E^{\circ})}{2k} \quad (5)$$

2. Calculated Activity Coefficient Of Hydrogen Bromide In Water

To obtain the activity coefficients at even concentrations the equation given by Åkerlöf and Teare (1), namely:

$$\log \gamma_{\pm} = \frac{-u \sqrt{m} + Bm + Cm^2 + Dm^3 + Em^4}{1 - \sqrt{2m}}, \quad (6)$$

where u is a universal constant, B , C , D , and E are empirical constants, can then be employed.

3. Relative Partial Molal Free Energy Of Hydrogen Bromide In Water

This function is given by

$$\bar{F}_2 - \bar{F}_2^{\circ} = 2 RT \ln \gamma_{\pm} m \quad (7)$$

where \bar{F}_2 is the partial molal free energy of hydrogen bromide and \bar{F}_2° is the standard partial molal free energy of hydrogen bromide.

B. Silver; Silver Bromide Electrodes

So far, electrodes constructed in four different ways have been employed with aqueous hydrobromic acid and/or bromide solutions.

1. Literature

(a). Electrolytic-Thermal-Electrolytic Electrode

This electrode is made by successively, electroplating silver on a platinum helix, depositing on it porous, metallic silver by decomposing silver oxide paste by heat, and finally anodizing the electrode in aqueous bromide solution to form a silver bromide coating.

Harned and James (21), and Jones and Baekström (28), used this kind of electrode. The latter obtained electrodes that agreed within a few hundredths of a millivolt.

(b). Thermal-Electrolytic Electrode

This electrode is fashioned as above, with the silver plating being omitted.

Both Harned and Hamer (20), and Harned, Keston, and Donelson (22), employed this type, with the former obtaining a precision of ± 0.08 millivolt.

(c). Electrolytic-Electrolytic Electrode

This electrode is constructed as in (a) with the deposition of porous silver being left out.

Lewis and Storch (22), obtained an average deviation from the mean of less than 0.1 millivolt. Jahn (27), also employed this type of electrode.

(d). Thermal Electrode

This electrode is prepared by heating a 1:9 by weight paste mixture of silver bromate and of silver oxide, respectively on a platinum spiral at 650°C.

Keston (29), Harned, Keston, and Donelson (22), Harned and Donelson (18), and Owen and Foering (37), all utilized this type of electrode. The first two obtained reproducibilities of ± 0.05 and ± 0.1 millivolt, respectively. The last using cells containing borax and potassium bromide obtained agreement within 0.1 millivolt.

Keston (29), mentioned that he used this kind of electrode because of the speed and ease of preparation, relative insensitiveness to light (43), and much lower solubility in aqueous hydrobromic acid (48), decreasing possible junction potential. Owen and Foering (37), concluded that light, if diffuse, had no appreciable effect on the thermal electrode.

Harned, Keston, and Donelson (22), found agreement between the thermal and the thermal-electrolytic electrode of from 0.1 to 0.5 millivolt, while Harned and Donelson (18), got concordance within 0.04 millivolt.

Greater solubility of silver bromide in increasing concentration of hydrogen bromide in water (13), agreement between the thermal

and the thermal-electrolytic electrode, and the advantages found by Keston (29), prompted the employment of the former in this work.

2. Experimental

(a). Silver Oxide Preparation

A carbonate free, dilute solution of reagent sodium hydroxide was added to a hot solution of reagent silver nitrate. The brown precipitate was washed by decantation 21 times with fresh, distilled water, once in conductivity water, was filtered through sintered-glass crucibles and dried in a vacuum dessicator in the dark.

(b). Silver Bromate Preparation

Silver bromate was formed by adding slowly a cold, dilute solution of potassium bromate to that of silver nitrate, reagent grades being used. The white precipitate, washed six times by decantation with cold, fresh, distilled water, recrystallized from hot, fresh, distilled water, collected in a sintered-glass crucible, washed twice with cold, conductivity water, was finally dried in a dessicator in the dark.

Both oxide and bromate of silver were prepared in two batches at a six month interval from chemicals of different makers.

(c). Electrode Preparation

B. & S. gauge 24 platinum wire, wound into a helix 3 mm. in outside diameter and having 3 or 4 turns, was fused into soft-glass tubing.

Then silver bromate and silver oxide in the ratio of 1 to 9 by weight were ground and mixed thoroughly in an agate mortar, moistened with distilled water and allowed to cover the helix completely but relatively lightly, so that a white, porous coating resulted after heating for 8 minutes at 650°C.

C. Hydrogen Electrodes

1. Electrode Proper

(a). Literature

The primary requirements of the hydrogen electrode is that there must be a suitable surface on which molecular and ionic hydrogen dissolved in a liquid medium, may come into equilibrium. (15).

To accomplish this usually a noble metal such as platinum, gold, or palladium is plated with iridium, palladium, or platinum black and immersed in the hydrogen saturated solution. Smale (46), and Wilsmore (53), found that the choice of the noble metal, if inert, and the size within wide limits had no effect on its function. With respect to the coating, iridium black was recommended by Lewis, Brighton, and Sebastian (31), palladium black by Clark and Lubs (9), and platinum black by Andrews (2). The last found that palladium black was unreliable. Harned (17), and Prideaux (39, 40), preferred the light coating of the "black", while Ellis (12), and Blackadder (6), employed heavy plating. As mentioned by Hammett (16), current density in electroplating was of minor importance. The purity of the

commercial chloroplatinic acid was sufficient as evidenced by its wide use. Lastly, as demonstrated by Hills and Ives (24), the concentration of the dissolved hydrogen is the potential determinant, rather than the partial pressure in the gas phase. Thus, partial or total immersion of the electrode is of no consequence.

Recently, Hills and Ives (24), brought out a novel catalyst electrode and verified the reproducibility of the foil type of electrode to within 0.01 millivolt.

The consideration of the numerous reports on the hydrogen electrode indicates clearly that the platinum black on platinum foil electrode was the most satisfactory, and was thus adopted in this work.

(b). Experimental

Platinum foil 10 x 15 x 0.02 mm. was welded to a B. & S. gauge 24 platinum wire and sealed into a soft-glass tubing (8). After thorough cleaning with chromic acid and then with 50% aqua regia, it was electrolyzed as a cathode in 2% chloroplatinic acid solution for eight minutes at about 30 ma. cm^{-2} . The resulting electrode was washed repeatedly and stored in distilled water.

2. Hydrogen Gas

(a). Literature

To keep the liquid medium saturated with hydrogen gas, it is customary to bubble the gas continuously through it. However, any substance or substances present in the gas which will influence the

system must first be removed. Thus MacInnes and Cowperthwaite (35), found potential variations of the hydrogen electrodes from 5 to 50 millivolts using unpurified, commercial tank hydrogen. They remedied this by passing the gas over reduced copper oxide, heated at 650 to 700°C. to remove the last traces of oxygen. Loomis and Acree (34), employed palladinized asbestos kept at 120°C. for the same purpose. Other substances, such as carbon dioxide, which are reduced by the hydrogen electrode must also be eliminated.

(b). Experimental

Electrolytic tank hydrogen (99.7% H₂) was passed through Ascarite and magnesium perchlorate to remove carbon dioxide, and then over palladinized asbestos (50), heated to about 220°C., and finally through a trap. Most connections were of glass to glass, but where this was not practical thick rubber pressure tubing, previously treated with boiling sodium hydroxide solution to remove sulfur, was employed.

3. Pressure

Since the solubility of the hydrogen gas, and thus the potential of the hydrogen electrode vary with the pressure, it has become standard practice to calculate electromotive force at a hydrogen partial pressure of one atmosphere. For this purpose, the atmospheric pressure readings were taken with a mercurial barometer at the same level as the cell, and the hydrostatic pressure effect was calculated

according to Hills and Ives (24). The vapor pressures of the solutions were calculated from the preliminary activities of hydrogen bromide by means of the Gibbs-Duhem equation.

D. Hydrobromic Acid

1. Purification

Possible significant impurities found in commercial hydrobromic acid are HCl, HI, and Br₂. Previous workers (29, 22, 20), have resorted to distillation to purify the acid. However, Owen and Cooke (36), have found that purification was unnecessary, at least to prepare dilute solutions, and that oxygen and light had no effect. Nevertheless dealing with concentrated solutions distillation was used as a precautionary measure and dilution was accomplished with conductivity water. Thus, reagent 48% hydrobromic acid was distilled twice in an all-Pyrex still, constant-boiling fractions being collected.

Conductivity water with a specific conductance of 1.0×10^{-6} mho was obtained by distilling alkaline permanganate solution in a Pyrex still.

2. Deoxygenation

Since both electrodes are sensitive to oxygen (29), the hydrobromic acid solutions had to be deoxygenated. Two most widely used procedures are boiling and passing through an inert gas, such as nitrogen or hydrogen. Harned, Keston, and Donelson (22), boiled hydrobromic acid "in vacuo" and saturated it with hydrogen, while

Harned and Donelson (18), merely boiled it under vacuum. For this work, the required concentration of hydrobromic acid was boiled for three hours under reduced pressure. Then hydrogen was bubbled through for one to two hours to saturate the solution and to remove any oxygen still present.

3. Analysis.

Hydrogen bromide was analyzed gravimetrically as silver bromide (30), with an estimated accuracy of $\pm 0.03\%$. Weights used were calibrated against a similar set, which have been compared by the "Standards Division" of the Department of Trade and Commerce, Canada against their working standards set "C" 7 months previously. All the weighings were vacuum corrected and the International Atomic Weight Table of 1952 was employed.

E. Standard Electrode Potentials

Since the introduction of the Debye-Hückel theory (10), two main procedures have been adopted to carry out the extrapolation required in standard electrode potential determination. These are the methods of Hitchcock (25), which emphasizes the electromotive force measurements taken at medium concentrations and of Brown and MacInnes (7), which relies on determinations made in dilute regions. The former was led to his choice because as Randall and Young (41), pointed out, due to the solubility of the cell glass, the then existent data in the dilute area were probably erroneous. To accomplish this, he added an empirical term to the simplest Debye-Hückel equation and extended its validity to 0.1 molal, and performed the extrapolation with its aid.

Mathematically, substituting in equation (5) the appropriate numerical values for the constants at 25°C.

$$E \neq 0.11831 \log m - E^{\circ} = -0.11831 \log \gamma \neq$$

is obtained. (6)

(Constants employed in this work are those recommended by Dumond and Cohen (11). Ice point was taken as 273.16°K. and the dielectric constants of water were those of Wyman and Ingalls (55).) Taking the Hitchcock modification of the Debye-Hückel limiting equation as

$$\log \gamma \neq = -A\sqrt{m} \neq C_m \quad (7)$$

where A is a theoretical constant equal to 0.5092 for water at 25°C., and C is the previously mentioned empirical constant, and substituting for $\log \gamma \neq$ in equation (6) yields

$$E \neq 0.11831 \log m - 0.06024\sqrt{m} \neq = E^{\circ} - 0.11831 C_m. \quad (8)$$

The left-hand side of this expression should thus be a linear function of m and extrapolated to $m = 0$ should give E° , the standard electrode potential.

Since then Harned and Ehlers (19), Harned, Keston, and Donelson (22), Harned and Hamer (20), and others have employed this method for E° determinations because of the relative unreliability of the silver; silver chloride and the silver; silver bromide electrodes in very dilute solutions.

On the other hand, the second method utilized the full Debye-Hückel expression for the extrapolation.

Taking the Debye-Hückel equation as

$$\log \gamma_{\pm} = \frac{-A \sqrt{m}}{1 + a^{\circ} B \sqrt{m}} \quad (9)$$

where A and B are theoretical constants, and a° is a constant usually interpreted as the mean distance of the closest approach of the ions, and substituting in equation (6) at 25°C. gives

$$E - E^{\circ} - (E - 0.11831 \log m - E^{\circ}) a^{\circ} B \sqrt{m} = 0 \quad (10)$$

Hence, plotting the left-hand side against $(E - 0.11831 \log m - E^{\circ}) \sqrt{m}$, should result in a straight line giving E° at $m = 0$, noting that successive approximations must be carried out with the preliminary E° values.

Brown and MacInnes compared the two methods with the concentration cell involving sodium chloride at 25°C. (7). They mentioned that with the Hitchcock method the line showed "a distinct curvature throughout its whole length, making an accurate extrapolation impossible." Furthermore, they found that the "full" equation gave activity coefficients in excellent agreement with those observed up to 0.04 or 0.05 molal.

Since then, Hills and Ives (24), in their accurate work at 25°C. also compared the two methods in the case of the hydrogen-calomel cell, and reached the same conclusion as Brown and MacInnes. They

determined $E^{\circ}\text{Hg}; \text{Hg}_2\text{Cl}_2 (s)$ within ± 0.01 millivolt by the second procedure. They also found that the ion-exchange effect between Pyrex and 0.005 N, or even 0.001 N aqueous hydrochloric acid was slight. With aqueous hydrobromic acid, Keston (29), found that both Pyrex and quartz cells at 25°C . containing even 0.0004 molal of the acid gave concordant results, indicating inappreciable solvation of glass for at least 5 or 6 hours.

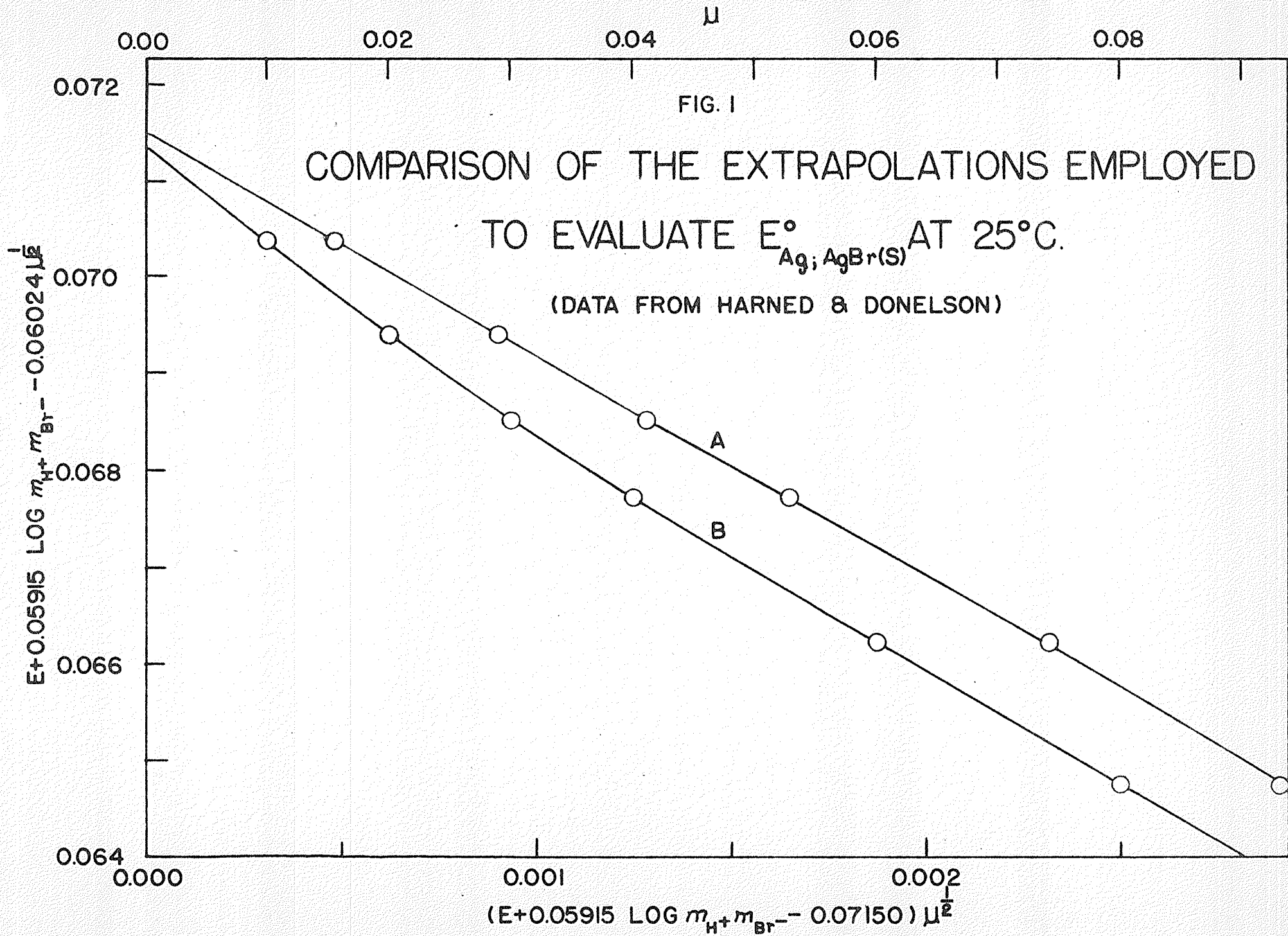
With respect to the concentration range of the acid from which extrapolation is to be made, Hills and Ives (24), have pointed out that linearity in the extrapolating function was obtained from about 0.02 molal of the hydrochloric acid. This was also the case with Harned and Ehlers' data (19). Therefore, for a similar system at least, it seems that the data in very dilute solutions where electrodes may behave unreliably are not required. If this is the case the second procedure should be favored.

To check the validity of the arguments, Harned and Donelson's data (18), regarded as the most reliable for hydrogen bromide, was extrapolated by both methods at six different temperatures. Figure 1 illustrates the results obtained at 25°C . Ionic strength μ is employed since both hydrogen and lithium bromides having similar activities in dilute solutions were involved. Curve B with the abscissa scale on the top is a result of the first method and shows a distinct curvature before the extrapolation was attempted. Harned and Donelson employed this

procedure. On the other hand, employing the second method, curve A gave a strictly linear plot along the last three points. E° obtained with a line along the four points was only 0.02 millivolt lower, although beyond the validity of the full Debye-Hückel equation. Similar results were obtained at five other temperatures with the extrapolations reproducible to within ± 0.01 millivolt, which is considerably better than ± 0.05 millivolt attained by Harned and Ehlers (19), by the first procedure. The corrected data are given in Table I and were employed where required in all subsequent calculations.

F. Cell

Erber (13), has shown that silver bromide becomes increasingly soluble in rising concentrations of aqueous hydrobromic acid, more so than silver chloride in hydrochloric acid (14). In addition, Åkerlöf and Teare (1), have found that the silver ion was then able to plate out on the hydrogen electrode, causing it to behave very erratically. Therefore, a long path between the electrodes with a stopcock below the silver; silver bromide electrode compartment opened momentarily during the readings, was provided. Further, to prevent the complete solution of the silver bromide, the "bromide" compartment was made small.



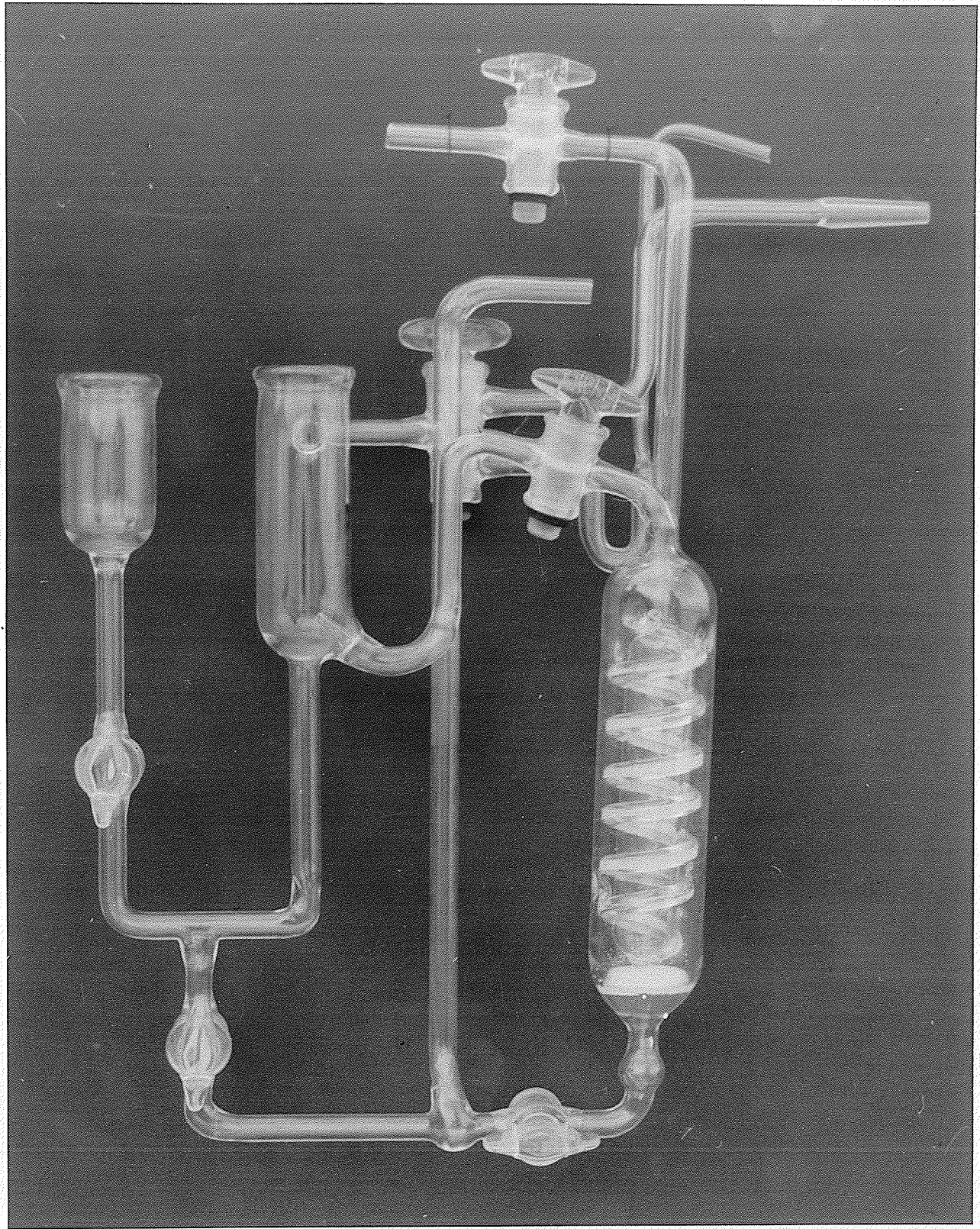
It is necessary to equilibrate the incoming hydrogen gas with the solution being studied, before admitting it to the cell main, to prevent a concentration change of the acid around the hydrogen electrodes. A bubble tube with a coarse sintered-glass base was employed. Since both electrodes are oxygen sensitive, the cell had to be filled with the acid in complete absence of oxygen. For this, the design and the method of Hamer and Acree (15), were followed. Finally, to minimize the contamination of the acid, Pyrex was used in the construction of the cell. Thus, the final cell became a hybrid of those of Åkerlöf and Teare (1), and Hamer and Acree (15), with additional modifications. It is illustrated in Plate 1 with the silver; silver bromide electrode compartment at the left, that of the hydrogen in the center, and the bubble tube at the right. Rubber stoppers were found to be visibly unaffected by immersion in 48% hydrobromic acid for a week. Therefore, they were employed to hold the electrodes.

In operation, after the rubber stoppers (each holding either three silver; silver bromide or two hydrogen electrodes) were posited, the vacuum line was connected to the central, vertical tubing, the hydrogen supply to the tubing with the stopcock on the top, and the acid source to the ground-glass stopper on the right. Then the dry cell was tested for vacuum-tightness and was smeared with silicone grease to minimize possible electrical leakage from the

water-filled thermostat (24). Next, oxygen was flushed out by successive evacuation and passage of hydrogen into the cell. This having been carried out four times, with the final evacuation the acid was allowed to fill the cell completely for washing, and after twenty minutes was pumped out. The cell was again filled with the solution and was returned to atmospheric pressure by the passage of hydrogen through the bubbler. Then the hydrogen flow was adjusted to about one bubble a second (24), letting it escape through the U-shaped trap. Finally, the cell was immersed into the bath and hydrogen flow initiated after allowing twenty minutes for thermal equilibration. It was allowed to attain equilibrium overnight or longer, and was kept in very diffuse light throughout the run. Potential readings constant for about an hour were taken as the equilibrium value and were thought to be sufficient, since measurements could be taken down to the microvolt region. E.m.f.s. were measured at 20, 25, and 30°C., and again at 20°C. to test the saturator and the "aging" (47), of the silver; silver bromide electrodes.

G. Thermostat

Since both Hamer and Acree (15), and Hills and Ives (24), have found that water-filled bath was unobjectionable for this type of work, distilled water was employed as a thermostating medium. It was kept at the required temperature, with a temperature variation within $\pm 0.005^\circ\text{C}$. with a variable, copper-plated steel, mercury thermo-



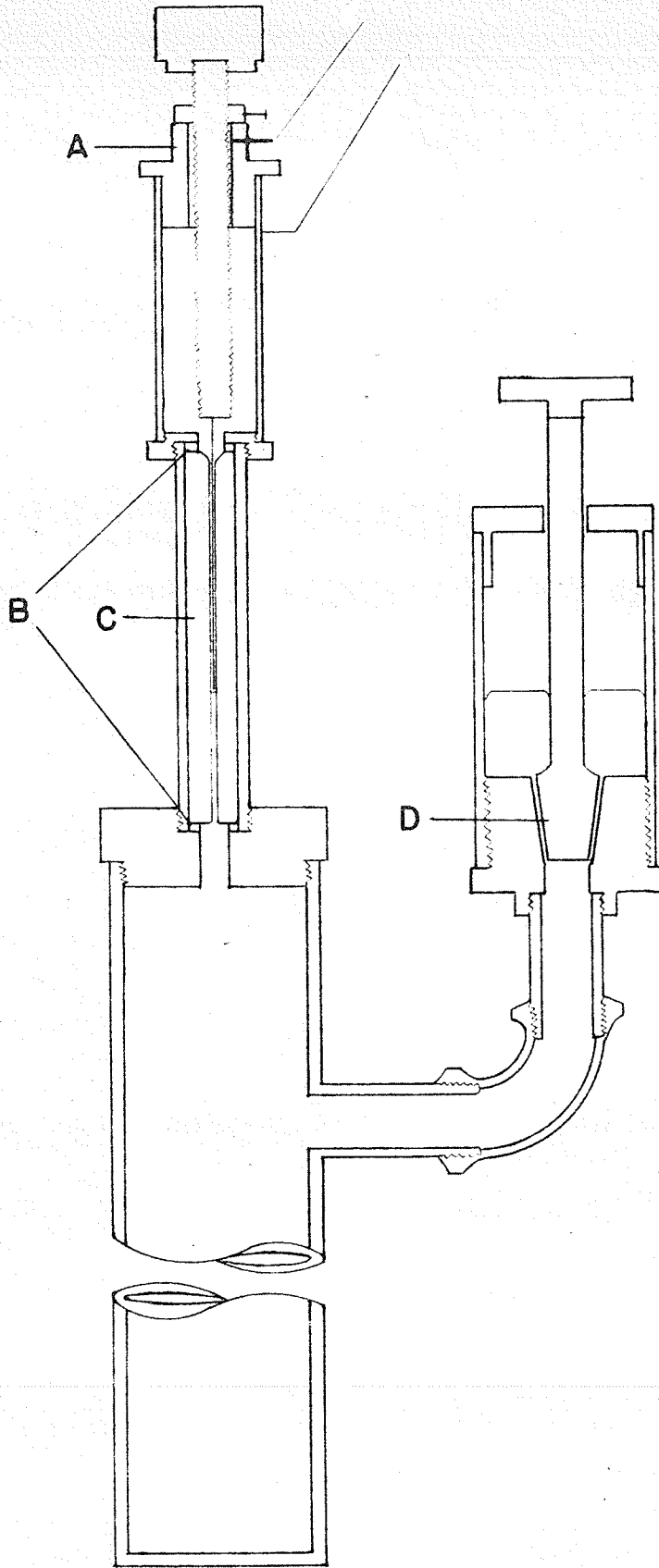
THE CELL
PLATE I

regulator as shown in Figure 2, actual size except for the bore of the capillary. The design was similar to those of Hamer and Acree (15), with one exception, steel being employed instead of glass. The advantages were its relatively quick response and ruggedness. In the diagram, A denotes fibre, B the Teflon gaskets, C a glass capillary 0.05 cm. in diameter, and finally D a ground-steel joint. The "body" is 27 cm. long. In use, when the required temperature was reached the floating joint was locked and the steel needle adjusted accordingly.

The temperature of the bath was set with type 8160 "calorimetric" platinum resistance thermometer constructed and calibrated by the Leeds and Northrup Company, and checked to within 0.01°C . by comparison with M5A platinum resistance thermometer, calibrated by the Physics Division of the National Research Council of Canada. A Mueller bridge made by the Rubicon Company, was thermostated at 28°C . and was calibrated in terms of a standard resistor certified by the Rubicon Company.

H. Electromotive Force

A Rubicon Type B High Precision Potentiometer calibrated internally was employed. In conjunction with this, a Leeds and Northrup Type E galvanometer with a 0.5 microvolt per scale division sensitivity was used. An Eppley standard cell of the unsaturated type, calibrated by the Eppley Laboratory Inc., and checked against another was employed. All equipment where necessary, was mounted

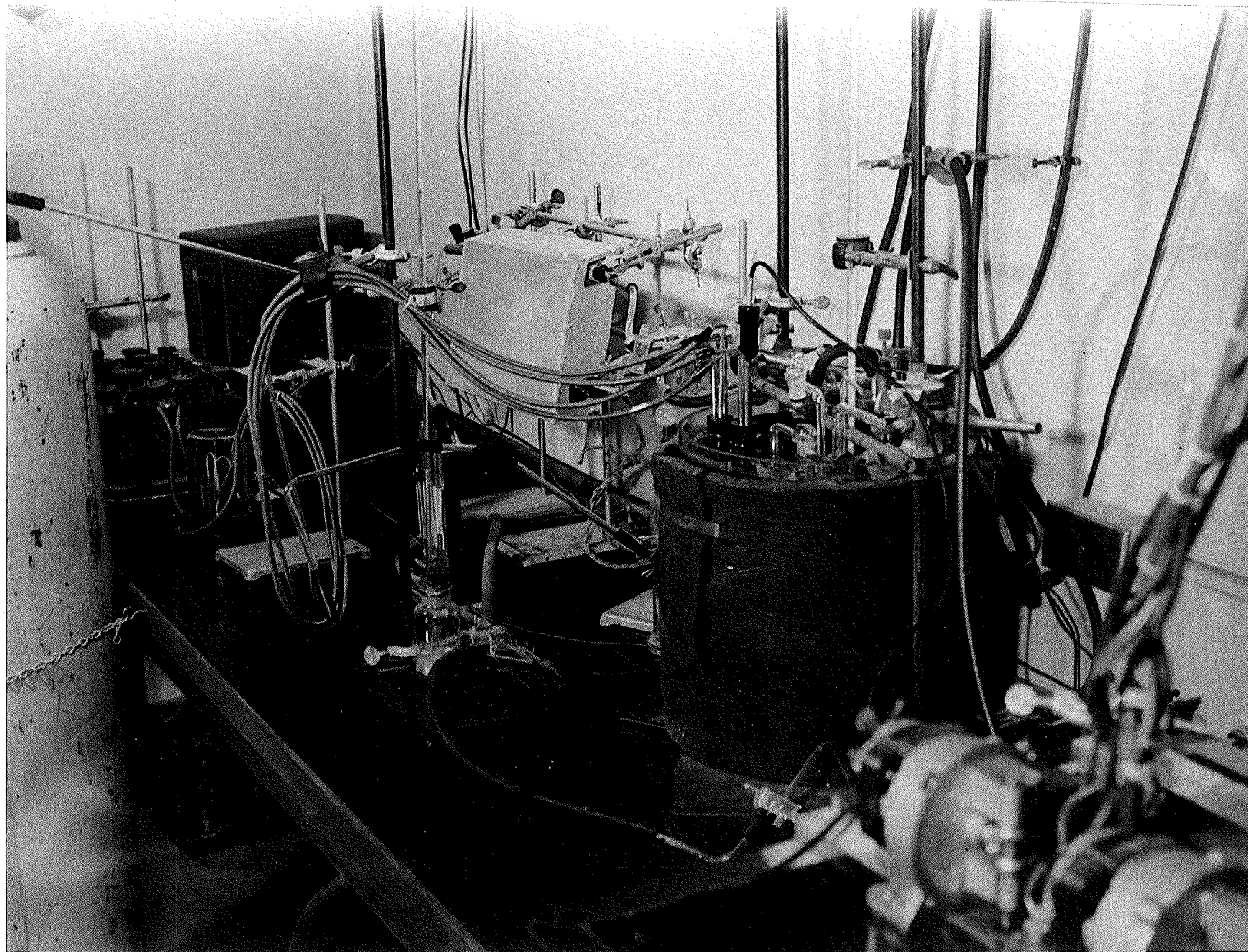


VARIABLE THERMOREGULATOR

FIG. 2

on an "equipotential surface" of aluminum foil (54). Connections between the electrodes and the potentiometer were made by means of shielded, well insulated, high voltage cables and mercury switches.

The entire setup is illustrated in Plate 2.



GENERAL SETUP — PLATE 2

III. EXPERIMENTAL RESULTS AND THEIR TREATMENT

III. EXPERIMENTAL RESULTS AND THEIR TREATMENT

It was generally found that the hydrogen electrodes gave more concordant readings when completely, rather than partially immersed in the solution. Possible seepage of oxygen through a short length of pressure-rubber tubing could not be detected by the hydrogen electrodes. Usual reproducibility of the hydrogen electrodes was within 0.04 millivolt.

The silver; silver bromide electrodes generally agreed within 0.06 to 0.07 millivolt and never turned dark, although as a test, used electrodes were exposed to light for over a month. No systematic potential differences of the silver; silver bromide electrodes prepared from the two batches of chemicals were found.

Thus, the overall agreement of the electrodes was about 0.1 millivolt.

As mentioned by Livingston (33), at and above one molal, equilibrium was not usually established overnight. The potential drifted, the rate being greater at higher concentrations but falling off in approaching the equilibrium value. The direction of the drifts was such that the readings always increased although the polarity changed at about three molal. Meanwhile, the like electrodes showed good to fair agreement, the difference either remaining constant or showing a slight drift. In one run at four molal the potential kept rising for, at least, three days. In attempts to remedy this situation the experimental technique was varied and improved where possible but to no avail. In all probability the silver; silver bromide electrode is unusable in solutions of this ionic strength. Pearce and Hart (38), working on hydriodic acid with silver; silver iodide electrode also experienced a similar phenomenon.

Therefore equilibrium potential readings above three molal could not be obtained. Thus, it was thought that the comparison of the thermodynamic properties of hydrogen chloride and hydrogen bromide with the meager data was out of place and was not made.

A. Corrected Potential

The average values of the electromotive forces of four possible silver; silver bromide and the hydrogen electrode combinations, (Two of the three silver; silver bromide electrodes which gave better agreement were employed.) corrected to one atmosphere by means of equation (4) and of Hills and Ives' "supersaturation factor", are given in Table II.

B. Logarithm Of The Observed Activity Coefficient

With the aid of equation (5) the logarithms of the activity coefficients were calculated and are given in Table III.

C. Calculated Activity Coefficient

To obtain the activity coefficients at even concentrations equation (6) was employed, since the familiar Hückel equation was inadequate.

Practically, at each temperature, four simultaneous equations were set up at 0.4871, 0.9703, 2.009, and 2.977 molal to obtain the numerical values of the constants given in Table IV. Then, to check the consistency of the data and the faithfulness of the equation, the observed and the calculated logarithms of the activity coefficients

were compared as shown in Table III. Finally, the activity coefficients were calculated at even concentrations and were compared against the recalculated values of Harned, Keston, and Donelson (22), as given in Table V.

D. Relative Partial Molal Free Energy

Next, using equation (7) the relative partial molal free energies of hydrogen bromide at various concentrations were calculated and are given in Table VI.

TABLE I

Standard Molal Electrode Potentials In Abs. Volt
(Data from Harned and Donelson (18))

Temperature in °C.					
15	20	25	30	40	50
0.07611	0.07390	0.07150	0.06891	0.06323	0.05682

TABLE II

Average Potentials In Abs. Volt Of The Cell

Pt, H₂(1 atm.); HBr(m); AgBr(s); Ag

Concentration in molal	Temperature in °C.		
	20	25	30
0.4871	0.12150	0.12016	0.11868
0.9703	0.08176	0.07983	0.07778
2.009	0.02939	0.02676	0.02399
2.017	0.02884	0.02621	0.02343
2.932	-0.00658	-0.00959	-0.01272
2.977	-0.00828	-0.01123	-0.01430

TABLE III

Comparison Of The Observed And The Calculated Logarithms
Of The Activity Coefficients Of Hydrogen Bromide In Water

Concentration in molal	Temperature in °C.					
	20		25		30	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0.4871	-0.0968		-0.0989		-0.1013	
0.9703	-0.0545		-0.0573		-0.0606	
2.009	0.0796		0.0752		0.0705	
2.017	0.0826	0.0808	0.0781	0.0763	0.0735	0.0717
2.932	0.2247	0.2258	0.2182	0.2187	0.2114	0.2115
2.977	0.2327		0.2255		0.2181	

TABLE IV

Constants Of Equations (5) And (6)

Temp. in °C.	2k	u	B	C	D	E
20	0.11632	0.5046	0.17973	-0.039099	0.020012	-0.002936
25	0.11831	0.5092	0.17888	-0.039281	0.020110	-0.002979
30	0.12029	0.5140	0.17730	-0.039238	0.020395	-0.003084

TABLE V

Comparison Of The Activity Coefficients
Of Hydrogen Bromide In Water

Concentration in molal	Temperature in °C.					
	20		25		30	
	This work	H. K. & D.	This work	H. K. & D.	This work	H. K. & D.
0.5	0.802	0.800	0.798	0.796	0.793	0.791
1.0	0.888	0.885	0.883	0.878	0.876	0.871
2.0	1.198		1.185		1.173	
3.0	1.724		1.695		1.666	

TABLE VI

Relative Partial Molal Free Energies Of
Hydrogen Bromide In Water In Def. Calories

Concentration in molal	Temperature in °C.		
	20	25	30
0.5	-1065	-1089	-1114
1.0	-138	-148	-160
2.0	1018	1023	1027
3.0	1914	1927	1938

IV. SUMMARY

IV. SUMMARY

- A. The data of Harned and Donelson (18), were recalculated and extrapolated by the method of Brown and MacInnes (7), to obtain the improved standard molal electrode potentials of the silver; silver bromide electrode at 15, 20, 25, 30, 40, and 50°C.
- B. The potential measurements of the cell
Pt; H₂(p); HBr(m); AgBr(s); Ag
at 20, 25, and 30°C. from 0.5 to 3 molal have been made.
- C. The corrected electromotive force data were employed to calculate the logarithms of the activity coefficients of hydrogen bromide in water. Then, with the aid of the equation
- $$\log \gamma_{\pm} = \frac{-u \sqrt{m}}{1 \pm \sqrt{2m}} \pm Bm \pm Cm^2 \pm Dm^3 \pm Em^4$$
- activity coefficients of hydrogen bromide at round concentrations were computed and were compared against the recalculated values of Harned, Keston, and Donelson (22).
- D. From the logarithms of the activity coefficients the relative partial molal free energies of hydrogen bromide in water were calculated.

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