THE THERMODYNAMICS OF THE
Ag, AgBr, MBr(m), Hg_2Br_2, Hg CELL

Thesis for the Degree of M. S.
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Thomas W. Dakin
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[redacted]

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Introduction and Literature

This research was undertaken to establish with more certainty the value of the normal electrode potential of the mercurous bromide electrode, and thereby calculate the free energy and heat of formation of mercurous bromide, and recalculate the activity coefficients of hydrobromic acid from measurements of the potential of the cell: H_2, HBr(m), Hg_2Br_2, Hg made at various m concentrations by Matthews[1] and Larson[2].

In view of the large amount of work done on the silver bromide electrode, and the recent papers by Keston[3], Harned, Keston, and Donelson[4] wherein the normal electrode potential of the AgBr electrode is determined very accurately, a measurement of the E^o of the Hg_2Br_2 electrode based only on the difference between the E^os of the AgBr and the Hg_2Br_2 electrodes should be subject to considerable accuracy. All the calculations of the E^o of the Hg_2Br_2 up to the present time have been based on the measurements of the activity coefficient of HBr by some other method, usually involving the AgBr electrode in an HBr solution (Livingston[5], Harned[6], Lewis and Storch[7]). Gerke[8], Larson[2], and Matthews[1], all based their calculations of E^o on the measurement of the activity coefficient of HBr determined by Harned[6] or Livingston[5]. Subsequent measurements of HBr activity coefficients by Harned, Keston, and Donelson, and those two papers by Harned[6] and Livingston[5] indicate a discrepency of around one per cent, giving, for example, .805, .802, .814 respectively for the activity coefficient of HBr at 0.100 molal concentration. In view of this,

some doubt can be thrown on the E^o values reported by Gerke[8], Larson[2], and Matthews[1].

Gerke and Geddes[8] report the value of the E^o of the mercurous bromide electrode as .1396v at 25.00°C. They furnish a value to the International Critical Tables of .1385 v at 25.00°C. Matthews[1] reports a value of .1396 v at 25.00°C using concentrations of HBr of around 1.0 molal. Larson, on the basis of Harned's[6] previously published activity coefficients, gave a value of .13927 v when the HBr concentration was .9864 molal and .13855 v when the HBr was about 0.1 molal in his cell, both at 25.00°C. A value calculated by Larson[2] from the best value of the cell: $Hg,Hg_2Br_2,HBr(.10015m),H_2(Pt)$ reported by Gerke and Geddes[8], and Harned's[6] activity coefficient was an E^o of .1391 v at 25.00°C.

The above values of the E^o of the mercurous bromide electrode have a divergence of a little more than a millivolt. They indicate that the true value probably lies between .1385 and .1396 v at 25.00°C.

As compared to the rather wide divergence of the above values for the E^o of the mercurous bromide electrode, let us look at the recently reported values for the E^o of the silver bromide electrode. Two types of silver bromide electrodes are now in use. One of them is the so called MacInnes type of electrode, wherein the AgBr is plated onto the electrode which is made the anode in a HBr solution. This is carried out at very low current densities. The base of the electrode is a Pt wire on which a coating of Ag has been formed either by plating or by the old

method of fusing a silver oxide paste at 450°C. The more recently devised fused type of silver bromide electrode, called the Keston[3] electrode, is made by fusing a paste of 10% $AgBrO_3$ and 90% Ag_2O for 7½ minutes at 650°C. Harned, Keston, and Donelson[4] checked these two types against one another and found practically no difference. The present paper also bears out that conclusion. Both types are reproducible to within a few hundredths of a millivolt.

Keston[3] reported a value for the E^o of the silver bromide electrode of .0711 v at 25.00°C, measuring the cell: Ag,AgBr, HBr(m),H_2(Pt), and extrapolating the results to infinite dilution. Owen and Foering[9], measuring the cell: Ag,AgBr, KBr(m), $NaBO_2(m_1)$,$HBO_2(m_2)$, H_2(Pt), extrapolated the results to infinite dilution and obtained an E^o for the AgBr electrode of .07128 v at 25.00°C. Jones and Baeckstrom[10] reported a value of .0712 v at 25.00°C, obtained from calculations from other data. Harned, Keston, and Donelson[4], measured the cell Ag,AgBr,HBr(m),H_2(Pt) and extrapolated the results to get the value of .07103 v at 25.00°C for the E^o of the AgBr electrode. In the most recent paper, Harned and Donelson[11] check Owen and Foering's results very closely after extrapolating the results on measurements of the cells: Ag,AgBr, LiBr(m),LiOH(0.01),H_2(Pt) and Ag,AgBr,LiBr(m),HBr(0.01),H_2(Pt), and report a value of .07131 v at 25.00°C for the E^o of the AgBr electrode.

The above brief survey is not at all complete in an historical sense, but it is indicative of the consistency of the E^o values reported by different authors using the latest technique developed. As Harned and Donelson[11] point out,

.07115 ±.00015 would include all of them. It is very likely that the true value of the E^o of the silver bromide electrode (for the reaction Ag Br^- AgBr e) is within the range -.07100 to .07130 v at 25.00°C. There is here a deviation of only .3 millivolt.

The cell measured in this paper is:

$Ag, AgBr, HBr(m), Hg_2Br_2, Hg$

The potential of this cell is independent of the concentration of the HBr, or of the type of electrolyte furnishing the bromide ions, whether HBr, KBr, or some other bromide salt, for it is a simple bromide ion exchange cell. The above statement is true of course only if the electrodes are prepared properly. The cell measures directly the difference between the normal electrode potentials of the silver bromide and the mercurous bromide electrodes. It is a cell similar to the cell measured by Randell and Young[12], Gerke[13], and Bronsted[14], using the corresponding chloride electrodes.

Because the three recent papers by Owen and Foering[9], Harned, Keston, and Donelson[4], and Harned and Donelson[11] all obtain their values of E^o directly by extrapolation to infinite dilution, and because they report the values for the E^o of the silver bromide electrode for various temperatures (at five degree intervals between 0° and 40°C), these E^os are each given equal weight and used as the basis for the calculation of the E^o of the mercurous bromide electrode in this paper. The E^os in these three papers are averaged together at each respective temperature, and the average values obtained are assumed to be the most likely values for the E^o

of the silver bromide electrode at the respective temperatures involved.

The free energy of formation of the bromide ion from liquid,gaseous, and aqueous bromine was determined in 1917 by Lewis and Storch[7], and more recently and probably more accurately by Jones and Baeckstrom[10]. The latter also determined the free energy of formation of silver bromide, measuring the cell: Pt-Ir,KBr(m) Br_2,KBr(m),AgBr,Ag. Randall and Spencer communicated to the International Critical Tables a value for the free energy of formation of AgBr of -22,910 cals at 25°C, based on data obtained from the paper of Lewis and Storch[7]. Randall and Spencer also communicated a value for the free energy of formation of Hg_2Br_2 to the International Critical Tables of-42,702 calories at 25°C, based on the E^o reported by Gerke and Geddes[8].

A large number of workers have reported values for the heat of formation of AgBr, many of which are too old to rely on: Bertholet[15](1875), Thomsen[16](1886), Klein[17](1901), and Jouniaux[18](1904). More recent work includes the value determined by Krahmer[19] from e.m.f. measurements of -24,193 cals. at 25°C, the value obtained by Webb[20] from calorimetric measurements of 23,810 calories at 25°C, and the value reported by Woitinek[21] from cell measurements of -23,815 calories at 25°C. Shibata and Taketa[22], gave a value of -23,430 calories at 25°C, based on cell measurements and on the heat of formation of aqueous HBr given by Bertholet and Thomsen, which fact throws some doubt on the accuracy of their value.

The data for the heat of formation of mercurous bromide is much more meager. Nernst[23], Thomsen[16], and Varet[24] before 1900 gave values from calorimetric measurements. The value in the International Critical Tables of -49,210 calories at 18°C is based on their data. Recently, Ishikawa and Ueda[25] published values for the heat and free energy of formation of mercurous bromide, based on cell measurements. They measured the temperature coefficients of the cells: H_2,HBr(.1012m),HgBr,Hg, and Pb(hetero amalgam),$PbBr_2$(satd. sol.),HgBr,Hg.

Preparation of Materials and Cells

Mercury:- The mercury which was used in making up the mercurous bromide electrodes was in the first step of purification, electrolyzed. It was made the anode in the bottom of a shallow dish, covered by an electrolyte of 3% nitric acid. The cathode, a Pt foil, was almost entirely surrounded by a glass cup to catch any metal which dropped off the cathode. A current source of 7½ volts was used, and the electrolysis was usually run for about eight hours, which was found to be sufficient time to remove all of the metallic impurities. If the mercury started with contained some sludge and solid contamination, it was first run several times through a capillary funnel into a column of two feet of nitric acid (3%), before it was electrolyzed. This in itself usually gave the mercury a mirror surface. After the electrolysis, the mercury was distilled twice in an all glass still, under a pressure of about 5mm. A small stream of air was led in through a capillary into the boiling mercury. The heater was an electric hot plate, on which was set a copper, asbestos covered, cylinder to surround the distilling flask. A stream of air from the air jet was directed on the condenser tube and cooled the condensing mercury nicely.

A rather convenient and simple method of closing off the top of the distilling flask, through which the capillary tube was lead was devised. It is detachable, does not involve any ground glass joints or glass seals to make it tight. It is made by sealing a smaller tube about five centimeters in length onto the neck of the distilling flask, extending it upward. The inside diameter of this tube should be about the same as the outside diameter of the tube which is to be drawn into the capillary. Thus the tube extending into the capillary will fit snugly inside the other tube for a length of about five centimeters. The top is made air tight by a rubber tube fitted as a sleeve over the outside tube and down onto the inside tube which goes through it. It is found from experience that this extension does not get warm during the distillation, and that the mercury never rises more than a tenth of the way up the narrow space between the inner and the outer tubes. Therefore it never gets to the rubber and effectively we have an all glass connection.

The mercury was kept under an atmosphere of nitrogen after it was distilled.

Hydrobromic Acid:- The source of the hydrobromic acid was Baker's Analyzed hydrobromic acid. Constant boiling HBr was prepared from this by distillation in an all pyrex still. It was distilled four times, the middle fraction being kept each time, and was water white when used. It was kept in the dark to prevent decomposition. Dilution of this constant boiling acid, which boiled at 123.6°C at 74.21 cm, made approximately the correct concentration of acid desired. Due to the nature of the cell, and the fact that analyses were made of the cell solutions, exact dilutions were not necessary.

Mercurous Bromide:- This was prepared from 0.1 molal hydrobromic acid made from the constant boiling acid mentioned in the above paragraph, and 0.1 molal mercurous nitrate, made by dissolving the proper quantity of Baker's

Analyzed mercurous nitrate in water (two cc of concentrated nitric acid per liter were added to the mercurous nitrate to aid in dissolving it). These two solutions were evacuated, while being warmed in hot water, to remove dissolved gases, especially oxygen. They were then placed under an atmosphere of nitrogen. Evacuation mentioned above caused the solution to boil, and this was continued for about one-half hour.

Equivalent quantities of the solutions were added together. The mercurous nitrate solution was placed in an amber bottle into which a stream of nitrogen was bubbling. A separatory funnel containing the hydrobromic acid was inserted through a rubber stopper. The separatory funnel was equipped with a tube allowing nitrogen to be bubbled into it. It was kept continually filled with nitrogen. The nitrogen escaping through the mercurous nitrate now bubbled up through the separatory funnel and the hydrobromic acid, when the stopcock was opened. The size of the nitrogen stream was regulated such that the pressure in the bottle just permitted the hydrobromic acid to drip into the mercurous nitrate from the separatory funnel. Thus, almost automatically, the precipitation was carried out, and stirred vigorously by the stream of nitrogen at the same time. After the precipitation was complete, the stream of nitrogen was ceased, and the precipitate allowed to settle. It was washed by decantation with evacuated water eight times, ,using 200 cc portions (200 cc of 0.1 m mercurous nitrate formed the precipitate). It was then washed five times with 150 cc portions of the hydrobromic acid which was to be used in the cell, and then placed under 250 cc of the same solution. Some mercury was added to this, and the bottle was shaken vigorously for several minutes by hand until the mercury was finely dispersed in the precipitate. This was allowed to stand for at least eighteen hours to equilibrate, before it was placed in the cell. All washing was done under an atmosphere of nitrogen, and the precipitate was kept in an amber bottle.

Silver Bromide Electrodes:- These were prepared by two different methods. Most of the electrodes were prepared by a method similar to the one described by Brown[26] for silver chloride electrodes. A Pt wire was sealed through the end of a 5 mm soft glass tube so that it extended about 2½ cm. It was plated with silver from a pure $KAg(CN)_2$ solution. Six of the electrodes were plated at once, while arranged circularly around the anode, which was surrounded by a porous cup. The total current for the six electrodes arranged in parallel was only two milliamps. Plating was continued for six hours. They were then washed over night, before coating with silver bromide. Before being plated the Pt wire was cleaned in boiling nitric acid. The plating solution contained 10 grams per liter of recrystallized $KAg(CN)_2$ and was prepared according to the directions of Brown[26] working with MacInnes.

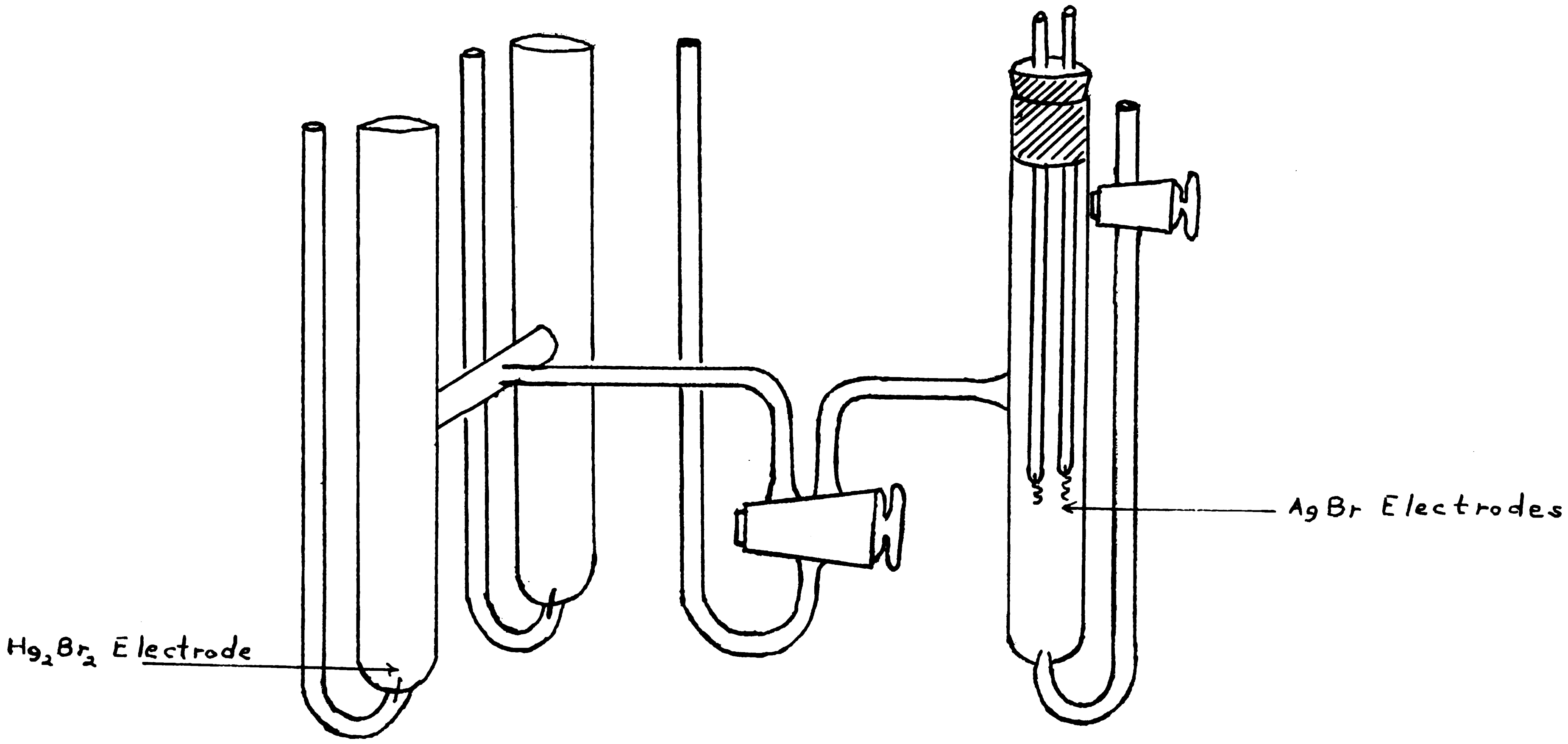
The silver bromide was put on by making the six electrodes anodes in a 0.1 m HBr solution, for one-half hour. The total current for the six electrodes arranged in parallel was again two milliamps. They were protected somewhat from the light during plating. After plating, they were evacuated in a solution of 0.1 m HBr to remove any adsorbed gases, and they were kept in an amber bottle in the same solution.

The other type of silver bromide electrode is the Keston fused type. They are prepared as directed by Keston[3]. Silver oxide and silver bromate are ground together in the weight rationof nine to one. Both compounds are prepared by precipitation from tenth normal solutions of recrystallized compounds. After they are ground together they are moistened with water and a paste made. Coils of Pt wire are sealed through the end of a 5 mm soft glass tubing. These are covered with the paste and heated for 7½ minutes in an electric furnace controlled with a thermocouple at 650°C. This type of electrode was used only in cells 25 and 26. They were evacuated and kept the same as the other type.

Potassium Bromide:- This salt was prepared by three times recrystallizing the Baker's analyzed product.

Water:- In the preparation of all solutions, water which had been redistilled from the ordinary distilled water was used. Distillation was carried out from a pyrex three liter flask using a block tin condenser. Permanganate was added to oxidize organic impurities. This water showed a specific conductivity of less than 2×10^{-6} reciprocal ohms.

Nitrogen:- Tank nitrogen was passed through two bottles each containing the ordinary oxygen absorbing alkaline pyrogallic acid to a depth of about five inches. It was then led through a bottle containing of electrolyte solution the same strength as was the solution through which it was eventually to be bubbled.



CELL VESSEL

The Cells Themselves:- The cell was of the design illustrated on page 12. Connection between the two half cells was made around the ungreased middle portion of the two way stopcock. Diffusion of one solution into the other was thus restrained. Some of the same solution which had been evacuated and placed over the precipitated mercurous bromide was retained under the nitrogen in an amber bottle and was used as the electrolyte in the silver bromide half of the cell. Thus the concentration of the HBr was usually exactly the same in both half cells.

In setting up the cell, tubes were extended to the bottoms of the mercurous bromide portions of the cell vessel and nitrogen was led into these tubes for about three or four minutes to wash the air out of the cell. During this time, the bottle containing the mercurous bromide mercury mixture, covered with HBr, was shaken vigorously. Some mercury was squirted into each of the portions of the cell vessel restricted for the mercurous bromide electrodes, forming a pool at the bottom of each, and then some of the mercurous bromide suspension was pipetted in until the level of the solution was near the top of the cell. All of the time nitrogen was bubbling up through the suspension keeping oxygen away. As the tubes were cautiously removed, stoppers were inserted.

The other side of the cell was filled in a similar way while nitrogen was bubbling from the jet indicated at the bottom of the silver bromide half of the cell vessel. The silver bromide electrodes, two of them, were necessarily exposed to the air for a brief moment while inserting them into the cell, but were allowed to remain in the stream of nitrogen bubbling up from the bottom to insure that no oxygen was present on them before the cell was closed and sealed. The stoppers were sealed with paraffin, and the cell was placed in the constant temperature bath. The process of filling the cell was carried out in some cases in the light of only a red lamp safe for bromide papers, in other cases , in the semidarkness of the laboratory after the shades had been pulled down. The manner of preparation in this respect is indicated with each cell. When the cell was dismantled, a sample of the electrolyte was removed from each side, and analyzed. The acid solutions were weighed and titrated with standard 0.1 N base, NaOH, using phenolphthalein as an indicator. The potassium bromide solutions were weighed and titrated with a standard 0.1 N silver nitrate solution, using the adsorption indicator, dichloflourescein.

Constant Temperature Baths:- In order to protect the cells from the daylight in the laboratory, the water in the baths was treated with some dyes which permitted only orange red light to enter the baths. The cells were almost completely submerged in this solution. The dyes which were found to be most suitable were a combination, about 50% each, of Acid Fuchsin and Amaranth. The Acid Fuchsin absorbs strongly in the green region, and the Amaranth in the blue violet region. To cool the 15° bath a stream of water from the cold water tap through some water jackets, proved to be satisfactory, if regulated from time to time. It proved to be much harder to regulate at a constant temperature over along period of time than either of the other baths, however. Beckman thermometers, calibrated against a Bureau of Standards thermometer, measured the temperature.

Potentiometer:- The potentiometer used in all the measurements was a Queen Potentiometer. The potentiometer permitted measurement to 1/100 of a millivolt with a fair degree of accuracy. The source of current for this was two Edison cells which maintained their voltage fairly constant over a long period of time. The standard was a Weston Standard cell #6506 calibrated by the Bureau of Standards and awarded certificate test # 71606 with a voltage at 25°C of 1.08618. A type R Leeds and Northrup high sensitive galvanometer # 78411, having an internal resistance of 500 ohms was used as a current detector.

The whole of the potentiometer set up was on an equipotential base, a copper sheet. The wires were carried with the exception of the ends, through conduit. The galvanometer rested on a lead sheet on a concrete block floating in sand, in order to guard against vibration. The standard cell was kept in a copper box suspended in the 25° constant temperature bath.

Humid weather always seemed to cause highly irregular results. On such days it was found necessary to suspend measurements. At first the leads from the potentiometer to the various baths were carried through conduit. This was found later to contribute to the irregularity of the measurements on humid days. Clip leads out in the air, gave much less irregular results on these days, although on dry days, no difference was observed.

Experimental Data

The cell diagram: Ag, AgBr, MBr(m), Hg_2Br_2, Hg applies to all of the cells measured in this paper, with the simple substitution of HBr or KBr as is the case for MBr, and of the proper concentration m as recorded for each particular cell. In order to obtain a balance with the potentiometer it was necessary to have the Ag electrode connected to the negative terminal of the potentiometer.

In recording the voltage of the following cells, the notation is used as follows: Hg'-Ag'' indicates that the potential measurement is between the first mercurous bromide electrode ~~and the second~~ and the second silver bromide electrode. The average values are corrected to round temperatures by the following equation: $E_{25.00} = E_t + .00031(t-25.00)$, where .00031 represents the approximate temperature coefficient of the cell. All potential readings are in volts.

Cell No. I (Made up in semidarkness)

Molality of HBr is .1022

Time, Hrs.	Temp.	Hg'-Ag'	Hg''-Ag'	Hg'-Ag''	Hg''-Ag''
20	24.80	.0676	.0682	.0679	.0679
71	24.80	.0679	.0679	.0679	.0679
74	24.80	.06790	.0679	.0679	.0679
88	24.80	.06792	.06785	.06784	.06782
111	24.80	.0681	.0680	.0681	.0680

Av..Value, E_{25} is .06797 v

Analysis of solution from the cell gave .1022 M for the Hg side and .1026 M for the Ag side.

E_{25}(corr.for concentration) is .06790 v

Cell No. 3 (Made up in red light, dim)

Molality of HBr is .1002

Time, Hrs.	Temp.	Hg'-Ag'	Hg''-Ag'	Hg'-Ag''	Hg''-Ag''
*13	24.86	.06602	.06605	.06760	.06763
		changed Ag' electrode			
*38	24.86	.06760	.06765	.06750	.06753
		changed Ag'' electrode			
*41	24.86	.06778	.06788	.06737	.06748
42	25.00	.06783	.06808	.06800	.06820
47	"	.06790	.06822	.06807	.06842
51	"	.06805	.06809	.06807	.06812
68	"	.06804	.06792	.06805	.06799
85	"	.06802	.06791	.06800	.06792
*132	"	.06823	.06768	.06745	.06781

* excluded from average

Ave. Value, E_{25} is .06804 v

No correction necessary for concentration.

Cell No. 4 (Cell madeup in dim red light)

Molality of HBr is .1002

Time. Hrs.	Temp.	Hg'-Ag'	Hg''-Ag'	Hg'-Ag''	Hg''-Ag''
16	24.86	.06765	.06763	.06780	.06777
38	"	.06768	.06768	.06802	.06801
85	"	.06766	.06781	.06798	.06808

Ave. value, E_{25} is .06781 v

No correction for concentration

Cell No. 5 (Made up in dim red light)

Molality of HBr is .1002

Time, Hrs.	Temp.	Hg'-Ag'	Hg''-Ag'	Hg'-Ag''	Hg''-Ag''
*14	24.85	.06763	.06754	.06764	.06754
18	15.30	.06502	.06511	.06493	.06505
21	15.25	.06515	.06494	.06507	.06515
24	24.84	.06693*	.06678*	.06790	.06778
		replaced Ag' electrode			
24½	24.84	.06790	.06777	.06785	.06770
36	24.84	.06810	.06802	.06797	.06789
38	24.86	.06811	.06802	.06797	.06790
41	35.33	.07147	.07121	.07132	.07102
*#60	34.67	.07105	.07041	.07076	.07023
*#62	24.85	.06808	.06762	.06760	.06748

\# Cell started to decline in e.m.f. here and became rather erratic.

* These values excluded from average.

Ave. Value, E_{15} is .06497 v

Ave. Value, E_{25} is .06797 v

Ave. Value, E_{35} is .07115 v

Analysis of the solution from the cell gave .1004 M for the Hg side and .0999M for the Ag side.

E_{15} (corrected for conc.) is .06513 v

E_{25} " is .06813 v

E_{35} " is .07131 v

Cell No. 8 (Made up in semi darkness)
Molality of HBr is .1043

Time, Hrs.	Temp.	Hg'-Ag'	Hg''-Ag'	Hg'-Ag''	Hg''-Ag''
3	24.84	.06824	.06802	.06837	.06818
6	24.84	.06811	.06791	.06817	.06796
*21	24.86	.06792	.06784	.06795	.06788
		scrapped tapping key contacts			
21½	"	.06830	.06820	.06836	.06826
23	"	.06830	.06803	.06836	.06809
*43	"	.06762	.06776	.06766	.06770
46	35.36	.07124	.07100	.07130	.07107
48	35.33	.07138	.07111	.07144	.07115
74	24.84	.06812	.06802	.06817	.06804
#91	25.53	.06849	.06837	.06854	.06841
*115	24.90	.06778	.06760	.06782	.06764
*116	24.85	.06768	.06747	.06775	.06750
117	24.86	.06830	.06817	.06840	.06824

#These values corrected to 24.85 before averaging.

*These readings seem to be definitely out of line in a way that would definitely indicate that the measurement was in error due to dampness, and are excluded in the first average.

Ave. Value, E_{25} is .06824 v

Ave. Value (including * values), is .06807 v

Ave. Value, E_{35} is .07110 v

Analysis of the solution from the cell gave .1039M for the Hg side and .1045M for the silver side.

E_{25}(corrected for conc.) is .06802 v

E_{35}(corrected for conc.) is .07087 v

Cell No. 9 (Made up in semi darkness)

Molality of HBr is .1068

Time, Hrs.	Temp.	Hg'-Ag'	Hg''-Ag'	Hg'-Ag''	Hg''-Ag''
2½	24.89	.06800	.06802	.06809	.06811
4½	24.88	.06798	.06804	.06812	.06819
19	14.80	.06436	.06488	.06458	.06508
49	14.35	.06437	.06474	.06431	.06469
*53,	24.87	.06755	.06757	.06772	.06775

* Excluded from average (hysteresis evident)

Ave. value, E_{25} is .06811v

Ave. value, E_{15} is .06473v

Analysis gives .1065 M, Hg side, and .1068, Ag side.

Ave. value(corrected for conc.), E_{25} is .06803 v

Ave. value(corrected for conc.), E_{15} is .06465 v

Cell No. 15 (Made up in semi darkness)

Molality of HBr is .100

1½	24.86	.06810	.06812	.06807	.06810
6	24.90	.06813	.06817	.06811	.06815
24	24.86	.06829	.06832	.06825	.06828
47	24.84	.06817	.06811	.06820	.06814
50	24.86	.06760	.06772	.06796	.06806
*55	15.21	.06406	.06554	.06434	.06585
*58	"	.06471	.06553	.06481	.06571
*72	"	.06506	.06556	.06492	.06546

* N.B. These values are somewhat erratic but they are averaged together nevertheless.

Ave. value, E_{25} is .06814 v

Ave. value, E_{15} is .06507 v

Cell No. 16 (Made up in semidarkness)

Molality of KBr is .2052

Time, Hrs.	Temp.	Hg'-Ag'	Hg''-Ag'	Hg'-Ag''	Hg''-Ag''
17	24,86	.06807	.06807	.06817	.06818
23	24.87	.06799	.06798	.06809	.06808
41	15.66	.06420	.06426	.06410	.06412
71	15.17	.06435	.06422	.06423	.06417
*74	24.84	.06731	.06732	.06746	.06743

*Excluded from average (hysteresis evident)

Ave. Value, E_{25} is .06812 v

Ave. value, E_{15} is .06408 v

Cell No. 17 (Made up in semidarkness)

5	24.86	.06792	.06797	.06791	.06796
26	"			.06796	.06812
48	15.18	.06408	.06420	.06420	.06436
51	24.86	.06802	.06805	.06801	.06805
53	34.87	.07095	.07092	.07098	.07094
69	"	.07152	.07160	.07128	.07136
72	"	.07108	.07088	.07105	.07096

Ave. value, E_{25} is .06804 v

Ave. value, E_{15} is .06416 v

Ave. value, E_{35} is .07109 v

There is no correction for concentration for either of the above cells.

Cell No. 25 (Made up in semidarkness)

Molality of HBr is .0508

Time, Hrs.	Temp.	Hg'-Ag'	Hg''-Ag'	Hg'-Hg''	Hg''-Ag''
22½	34.76	.07108	.07098	.07108	.07098
24	34.75	.07128	.07120	.07125	.07115
24½	2 4.92	.06832	.06808	.06831	.06808
27	24.92	.06811	.06793	.06806	.06792
43	25.08	.06841	.06843	.06840	.06842
48	16.97	.06524	.06521	.06525	.06521
52	17.09	.06509	.06509	.06511	.06511
54	"	.06533	.06533	.06531	.06531
65	25.07	.06834	.06837	.06831	.06833
67	25.07	.06834	.06836	.06830	.06831
76	34.79	.07138	.07131	.07135	.07129
*89	25.07	.06765	.06779	.06755	.06772

*Excluded from average

Ave. value, E_{25} is .06826 v

Ave. value, E_{35} is .07126 v

Ave. value, E_{15} is .06459 v

Cell No. 26 (made up in semidarkness)

Molality of HBr is .0508

3½	25.08	.06792	.06800	.06792	.06801
7½	35.41	.07120	.07115	.07123	.07122
9	35.76	.07120	.07115	.07123	.07122
22	25.07	.06825	.06807	.06834	.06815
25	"	.06826	.06801	.06835	.06811
28	15.18	.06516	.06514	.06531	.06532
35	15.50	.06525	.06521	.06544	.06540

Cell No. 26 (continued)

Av. value, E_{25} is .06809 v

Av. value, E_{35} is .07102 v

Av. value, E_{15} is .06517 v

These last two cells, Nos. 25 and 26, were made up using the Keston type of fused AgBr electrodes. All other AgBr electrodes used in this research were of the plated type.

There is no correction for concentration for either of the above cells.

Cell No. 6 (Made up in dim red light)

Molality of HBr is .2014

Time, Hrs.	Temp.	Hg'-Ag'	Hg''-Ag'	Hg'-Ag''	Hg''-Ag''
14	24.83	.06797	.06775	.06785	.06791
16	24.84	.06777	.06779	.06796	.06797
19	16.10	.06461	.06457	.06488	.06485
22½	16.10	.06466	.06455	.06445	.06450
*36½	16.80	.06447	.06455	.06445	.06450
*44	24.85	.06746	.06758	.06748	.06759

*These values are excluded for the cell has obviously started to decline.

Ave. value, E_{25} is .06789 v

Ave. value, E_{15} is .06429 v

Analysis of the solutions for the above cell gives .2012M, Hg side, and .2015M. Ag side.

Ave. value, (corrected for conc) is E_{25}= .06783 v

Ave. value, (corrected for conc) is E_{15}= .06423 v

Cell No. 19 (made up in semi darkness)

Molality of HBr is .5120

Time, Hrs.	Temp.	Hg'-Ag'	Hg''-Ag'	Hg'-Ag''	Hg''-Ag''
3	24.89	.06770	.06814	.06758	.06803
6	24.87	.06783	.06774	.06762	.06751
27	24.88	.06768	.06774	.06762	.06751

Cell from this time on steadily declined in value.

Ave. value, E_{25} is .06777 v

Analysis of solutions after dismantling the cell, gave molality of .5120 for Ag side and .5046 for the Hg side. Correction of the above E for this, gives

E_{25}(corrected) = .06716 v

Cell No. 21 (made up in semi darkness) ; HBr .5082M

3½	24.90	.06676	.06675	.06675	.06675
24	24.90	.06692	.06698	.06676	.06683

Cell declined rapidly after these readings.

No correction was necessary for concentration.

Ave. value, E_{25} is .06681

Cell No. 22 (made up in semi darkness); HBr .5082M

19	25.05	.06671	.06670	.06665	.06677
27	25.14	.06700	.06695	.06675	.06681
*43	24.97	.06628	.06626	.06620	.06624
*93	24.88	.06467	.06473	.06480	.06483

* These readings are typical of all the cells having a molality of 0.5 HBr; they show the manner in which the e.m.f. declined as the cell stood. No correction was necessary for conc. in this cell.

Some discussion should be made of the divergent results obtained in the cells 19, 21, and 22. These cells gave an initial e.m.f. which was about one millivolt lower than the average of the other cells. These cells also showed a rapid decline in value. Due to the fact that the c cells declined so rapidly in value, it seems unreasonable to draw any conclusion from the fact that they were initially lower than the other cells of lower concentration. It seems likely that the result obtained is due to the AgBr electrodes which were of very small area. The AgBr plated on them would be relatively more soluble in the more concentrated HBr, and so much would dissolve off that they would be progressively and permanently affected. Livingston[5] came to the same conclusion.

One other thing was noted in regard to these cells. When the cells were dismantled, the Hg_2Br_2 of the Hg_2Br_2 electrodes appeared decidedly darker. No such effect was observed with the weaker concentrations of HBr. Apparently in the case of these cells the dye in the constant temperature baths was not sufficient protection from the light.

For the reasons stated above, these cells are not included in the final calculations.

The following two cells are included to show the type of results obtained using the Hg_2Br_2 precipitated from .02M $HgNO_3$ and .05M KBr in air according to the method of Matthews and Larson. The Hg_2Br_2 after being washed eight times with water as indicated in their theses, was washed five times with the HBr which was to be used in the cell. From the time of contact with the acid, it was kept continually under N_2 in amber bottles. Original precipitation was carried out in an amber bottle, and exposure to light was slight if at all. It was allowed to stand under the HBr which was going into the cell, along with some Hg, and shaken occasionally from time to time, for about eighteen hours (equilibration time).

Cell No. 13 (Made up in semi darkness)

Molality of HBr is .100

The e.m.f. started at a low value around .063 v and gradually rose over two days' time until the readings below begin.

Time.Hrs.	Temp.	Hg'-Ag'	Hg''-Ag'	Hg'-Ag''	Hg''-Ag''
48	24.80	.06739	.06785	.06740	.06786
53	24.86	.06725	.06773	.06736	.06783
147	24.90	.06664	.06722	.06672	.06735

Cell No. 14 (Same solution as above except that it had stood 5 days with the Hg_2Br_2. Values started around .064 v and gradually rose in two days' time to indicated values.)

48	24.90	.06744	.06792	.06770	.06821
53	"	.06660	.06725	.06729	.06770
70	"	.06666	.06740	.06690	.06766
		shook for a minute			
79	"	.06798	.06829	.06834	.06864
81	24.87	.06817	.06873	.06838	.06894
139	24.86	.		.06784	.06832

These results indicate that if sufficient time is allowed and if sufficient shaking is given the suspension of Hg_2Br_2 in HBr, in order to allow it to come to equilibrium, about the same results will be obtained as with the method used in the preparation of the rest of the cells in this research. The results show here with the Matthews' method of preparation indicate that much more time and care would be necessary in order toobtain consistent results, for the results are very erratic in these two cells. The advantage of the author's method over Matthews' in saving of time (the cells come to equilibrium much more rapidly) warrants its use.

Table I

Summary of all e.m.f.s for the Cell
$Ag, AgBr, MBr(m), Hg_2Br_2, Hg$
(corrected averages)

Cell No.	Molal conc.	E_{15}	E_{25}	E_{35}
1	.1022HBr		.06790 v	
3	.1002 "		.06804 v	
4	. "		.06781	
5	"	.06513	.06813	.07121
6	.2014HBr	(.06423)	.06783	
8	.1043HBr	.	.06802	.07109
9	.1068HBr	.06465	.06803	
15	.100 HBr	.06507	.06814	.07109
25	.0508HBr	.06459	.06826	.07126
26	.0508HBr	.06517	.06809	.07102
16	.2052KBr	(.06408)	.06812	
17	"	(.06416)	.06783	.07109
	Average (All cells)	.06492 v	.06805 v	.07111 v

This condensed data shows that there is no apparent t trend of the e.m.f. of the cell with concentration, except in the case of the already discussed and eliminated data obtained with the 0.5M HBr cells. The values are quite consistent and do not vary more than .24 millivolts in the maximum from the average, and the average deviation is much less. The values obtained with the Keston fused AgBr electrode (cells 25 and 26) agree perfectly with the others.

The temperature coefficient of this cell is constant within experimental error, and is equal to:

$$dE/dT = .000310 \text{ volts}/^{\circ}C$$

between 15 and 35°C.

Because the voltage of this cell is almost a straight line function of the temperature (see graph I), it is perfectly proper to interolate values. The table below gives the average values of the cell at five degree intervals between 15 and 25°C.

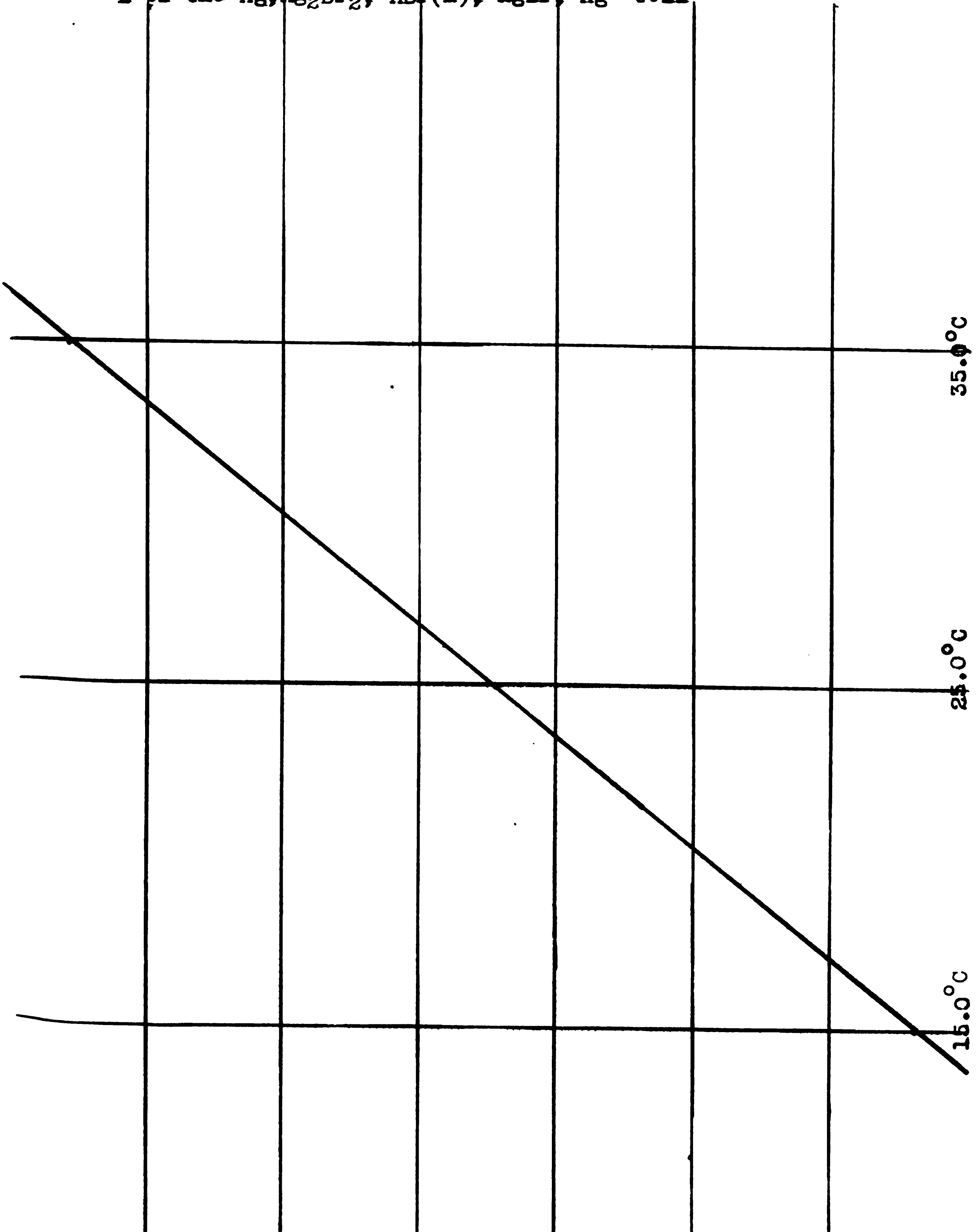
Table II

Temperature	E_{cell}
15.00°C	.06492 v
20.00°C	.06649
25.00	.06804
30.00	.06959
35.00	.07111

The E of this cell is represented by the following equation between 15 and 35°C.

$$E = .06804(1 + (t - 25.).000310)$$

E of the Hg, Hg_2Br_2, HBr(m), AgBr, Ag Cell



The values reported for the E^o of the silver bromide electrode by Harned, Keston and Donelson[4], Owen and Foering[9], Harned and Donelson[11] are tabulated below and averaged. The average values are assumed to be the most probable values of the E^o of the AgBr electrode at the respective temperatures.

Table III

Temp.	$E^o_{AgBr,Ag}$			
	Harned, Keston & Donelson	Owen & Foering	Harned & Donelson	Average of all 3
15.00°C	.07561	.07599	.07596	.07586
20.00	.07340	.07372	.07371	.07361
25.00	.07103	.07128	.07131	.07121
30.00	.06845	.06871	.06873	.06863
35.00	.06575	.06600	.06598	.06591

This E^o corresponds to the reaction:

$$AgBr + \ominus \longrightarrow Ag + Br^-$$

The E°of the Mercurous Bromide Electrode

This cell digram will apply to any of the cells measured directly in this paper, with the simple substitution of KBr for HBr in several cases and the various concentrations of each individual cell for c.

The polarity as marked are the terminals of the potentiometer to which the respective electrodes of the cell were connected when a balance was obtained.

$$Ag,\ AgBr,\ HBr(c),\ Hg_2Br_2,\ Hg$$

Half cell reactions:

$$Ag + Br^-(c) \longrightarrow AgBr + \textcircled{e}$$

$$\tfrac{1}{2}Hg_2Br_2 + \textcircled{e} \longrightarrow Hg + Br^-(c)$$

Total cell reaction:

$$Ag + \tfrac{1}{2}Hg_2Br_2 \longrightarrow AgBr + Hg$$

$$E_{cell} = E^{o}_{Ag,AgBr} + E^{o}_{Hg_2Br_2,Hg}$$ (where the E_{cell} is taken as positive)

then $$E^{o}_{Hg_2Br_2,Hg} = E_{cell} - E^{o}_{Ag,AgBr}$$

The last of these equations is used to calculate the E° for the mercurous bromide electrode, using the appropriate values of the E of the cell taken from the table II and the values of the E° for the AgBr electrode from table III.

Table IV.

Temperature	$E^{o}_{Hg_2Br_2,Hg}$ (for the reaction: $\tfrac{1}{2}Hg_2Br_2 + \textcircled{e} \rightarrow Hg + Br^-$
15.00°C	.14078 v
20.00	.14010 v
25.00	.13925 v
30.00	.13822 v
35.00	.13702 v

Temperature Coefficient of the E^o of the Hg_2Br_2 Electrode

The average temperature coefficients between 15.00 and 20.00°C, 20.00 and 25.00°C, and so on were calculated with the formula below, and were assumed to be the temperature coefficients at 17.50, 22.50°C, and so on respectively. They are tabulated below.

$$(dE^o/dT) = (E^o_{20} - E^o_{15})/5$$

Temperature	dE^o/dT
17.50°C	-.000136 volts/°C
22.50	-.000170
27.50	-.000206
32.50	-.000240

These values wer plotted in graph III and found to lie very nearly on a straight line. Values at round temperatures were taken from this graph for the temperature coefficient and tabulated below. Their accuracy is as great as the calculated values given.

Table V

Temperature	dE^o/dT
15.00°C	-.000119 volts/°C
20.00	-.000154
25.00	-.000189
30.00	-.000223
35.00	-.000258

Free Energy and Heat of Reaction

In calculating the free energy and heat of reaction, the following formulas are used, well known equations in chemical thermodynamics:

$$-\Delta F^{\circ} = NFE^{\circ}\text{ joules} = \frac{NFE^{\circ}}{4.186}\text{ calories}$$

When N is two faradays, NF/4.186   46106.

$$\Delta H^{\circ} = \frac{NF}{4.186}\left(T\left(\frac{dE^{\circ}}{dT}\right) + E^{\circ}\right)$$

For the reaction:

$$2Ag + Hg_2Br_2 \rightarrow 2AgBr + 2Hg$$

which is the reaction in the cell Ag, AgBr, HBr(m), Hg_2Br_2,Hg when two faradays of plus current are passed to the right. This is the cell measured directly in this paper. The temperature coefficient of this cell is

$$dE/dT = .000310\text{ volts}/^{\circ}C$$

and it is constant throughout the temperature rang e involved.

Table VI

Temperature	$-\Delta F$
15.00°C	2993 calories
20.00	3066
25.00	3137
30.00	3209
35.00	3279

The heat of reaction, ΔH, is constant throughout this temperature range and is:

$$\Delta H = 1152\text{ calories}$$

The constancy of this heat of reaction with temperature indicates that the sum of the specific heats of the products is equal to the sum of the specific heats of the reactants.

Jones and Baeckstrom[10] give for the free energy of formation of silver bromide from liquid bromine and solid silver:

$$Ag + \frac{1}{2}Br_2 \longrightarrow AgBr \quad ; \quad -\Delta F = 22{,}935 \text{ calories } (25^\circ C)$$

We have already calculated the free energy for the following reaction:

$$2Ag + Hg_2Br_2 \longrightarrow 2AgBr + 2Hg \quad ; \quad -\Delta F = 3137 \text{ calories } (25^\circ C)$$

Thus by doubling the first reaction and adding it to the reverse of the second reaction, we get:

$$2Hg + Br_2 \longrightarrow Hg_2Br_2 \quad ; \quad -\Delta F = 42{,}733 \text{ calories } (25^\circ C)$$

This value compares favorably with the value obtained by Ishikawa and Ueda[25] of 42,700 calories, obtained by a different cell measurement.

For the heat of formation of silver bromide from its elements at 25°C there is given by Krahmer(1920)[19], Webb(1925)[20], and Woitinek(1932)[21] -24,193, -23,810, and -23,815 calories respectively. The probable value is about -23,813 calories.

$$Ag + \frac{1}{2}Br_2 \rightarrow AgBr \quad ; \quad \Delta H = -23{,}813 \text{ calories } (25^\circ C)$$

The value for the heat of the following reaction is given on the previous page:

$$2Ag + Hg_2Br_2 \rightarrow 2Hg + 2AgBr \quad ; \quad \Delta H = 1152 \text{ cal. } (25^\circ C)$$

Thus by doubling the first reaction and adding it to the reverse of the second reaction we get:

$$2Hg + Br_2 \rightarrow Hg_2Br_2 \quad ; \Delta H = -48{,}778 \text{ calories}(25^{\circ}C)$$

Therefore the heat of formation of mercurous bromide (Hg_2Br_2) from liquid bromine and solid silver at 25°C is

$$\Delta H = - 48{,}778 \text{ calories/ mole}$$

This compares favorably with the result obtained by Ishikawa and Ueda[25] of -48,940 calories.

The Entropy of Formation of Mercurous Bromide

According to the relationship,

$$\Delta F = H - T\Delta S$$

using the values for the free energy and heat of reaction calculated in the previous section, we get:

$$-42{,}733 = -48{,}788 - 298\Delta S$$

and then

$$\Delta S = -20.4 \text{ calories/mole/degree Abs.}$$

For the reaction:

$$2e + Hg_2Br_2 \longrightarrow 2Hg + 2Br^-$$

which is the reaction in the half cell; $-HBr(m), Hg_2Br_2, Hg$ when two faradays of positive electricity arepassed to the right. The values of the temperature coefficients for this cell are taken from the table V, and the appropriate values for the E^o are taken from the table IV. The decrease in free energy and the heat of reaction is calculated at five different temperatures and tabulated below.

Table VII

Temperature	$-\Delta F^o$
15.00°C	6491 calories
20.00	6460
25.00	6420
30.00	6373
35.00	6317

Table VIII

Temperature	$+\Delta H^o$
15.00°C	-8071 calories
20.00	-8540
25.00	-9017
30.00	-9488
35.00	-9981

These values were plotted in a graph and found to lie very nearly on a straight line, indicating a relationship like this: $H_t^o = H^o_{25}(1+k(t-25))$

This was calculated and found to be:

$$H_t^o = -9017(1 + 95.4(t - 25))$$

which will hold with an accuracy of about 0.1% between

15 and 25°C.

Specific Heat of Mercurous Bromide

It is noted in the section dealing with heat of reaction that the heat of this reaction is constant with temperature.

$$Ag + \frac{1}{2}Hg_2Br_2 \longrightarrow Hg + AgBr$$

Thus according to Kirchoff's law, the sum of the specific heats of the reactants is equal to the sum of the specific heats of the products. Since the International Critical Tables list the following specific heat data for Ag, Hg, and AgBr, and none for Hg_2Br_2, Kirchoff's law gives a means of calculating the specific heat of mercurous bromide.

The International Critical Tables list the following data:

Material	Specific heat at 20°C
Ag	25.2 joules/gm atom/deg
Hg	27.9 "
AgBr	55.3 joules/gm mole/deg

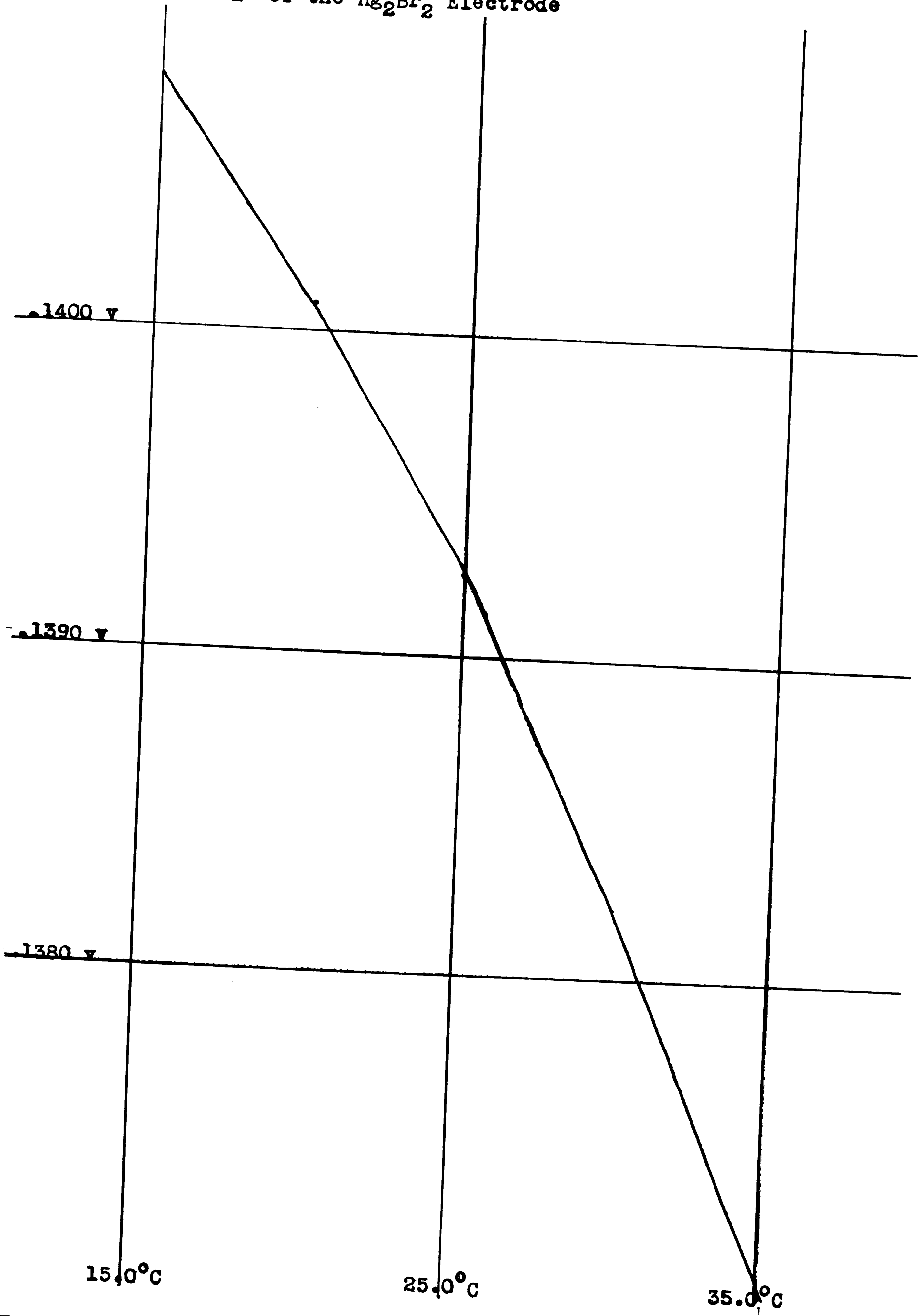
The following relationship must hold:

$$C_p(Ag) + C_p(\frac{1}{2}Hg_2Br_2) = C_p(Hg) + C_p(AgBr)$$

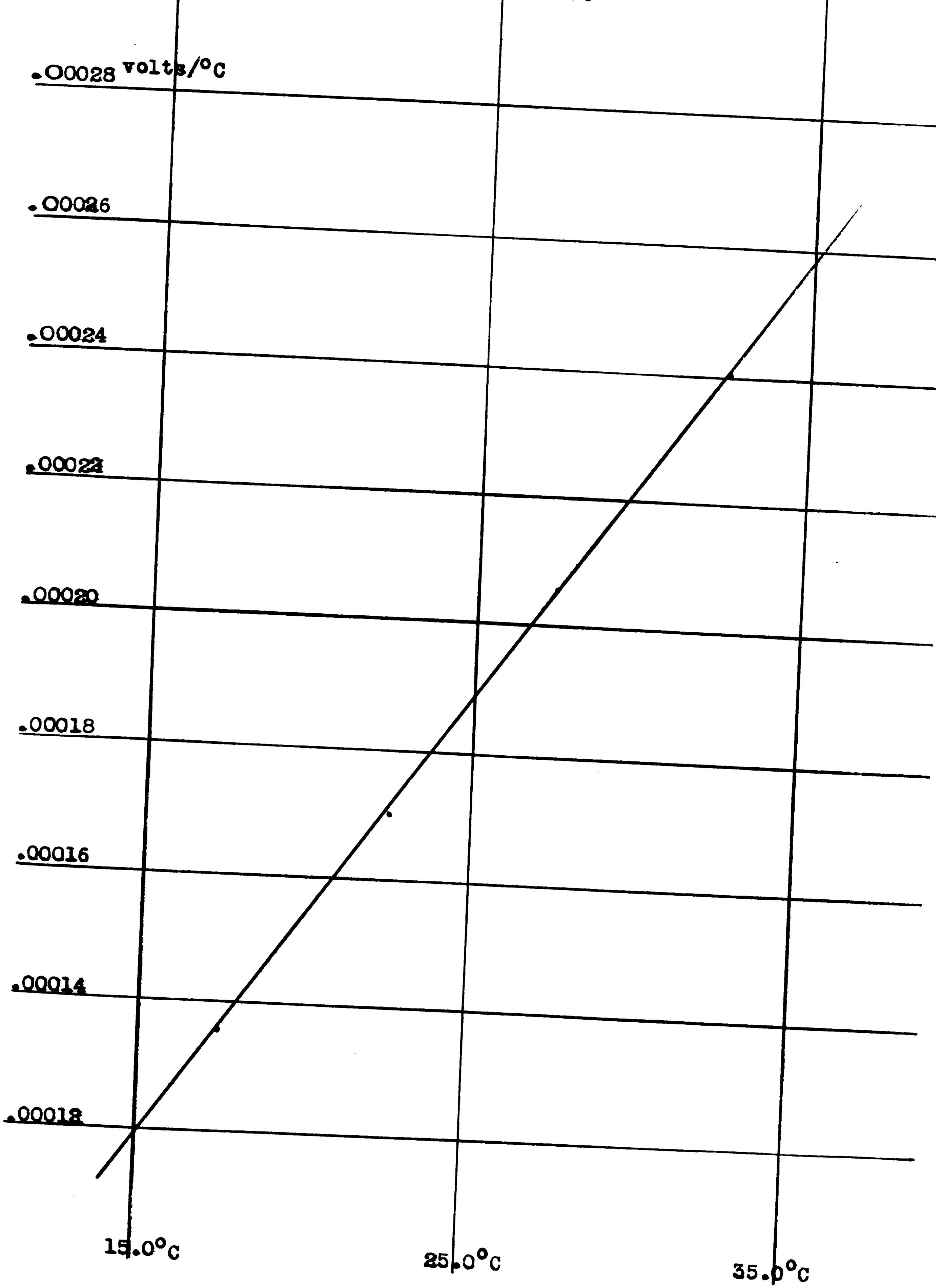
$$25.2 + \text{"} = 27.9 + 55.3$$

or $C_p(\frac{1}{2}Hg_2Br_2) = 58$ at 20°C joules/gm mole/deg.

E° of the Hg_2Br_2 Electrode

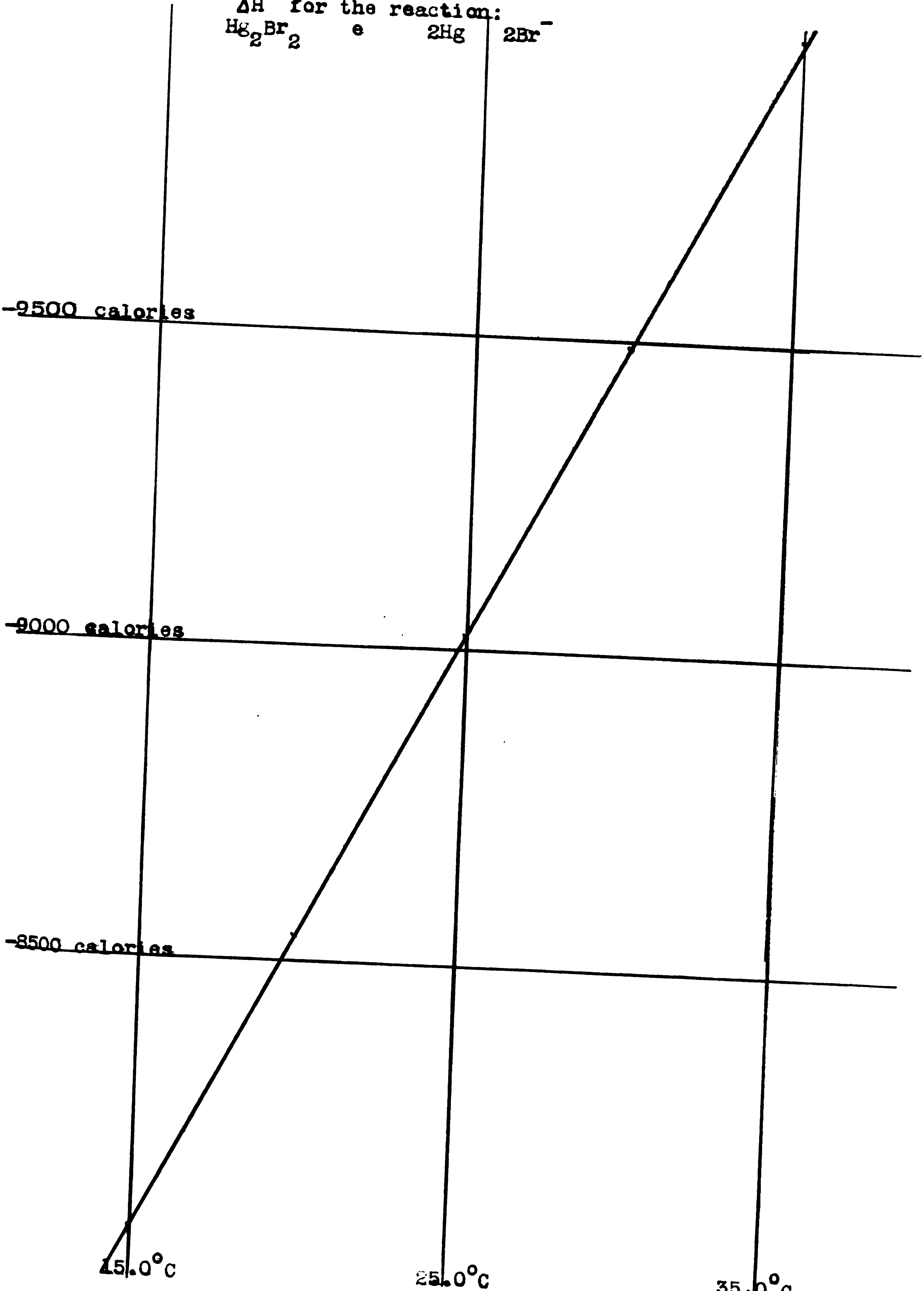


Temperature coefficient, dE^{o}/dT, of the E^{o} of the Mercurous Bromide Electrode



ΔH° for the reaction:

$Hg_2Br_2 \quad e \quad 2Hg \quad 2Br^-$



William D. Larson[2] measured the cell:

$(Pt)H_2$, $HBr(m)$, Hg_2Br_2, Hg

Cell reaction: $\frac{1}{2}Hg_2Br_2 + \frac{1}{2}H_2 \rightarrow Hg + Br^- + H^+$

$$E = E^o - RT/nF \cdot \log_e m_{Br^-} m_H \gamma_{Br^-} \gamma_{H^+}$$

The average values for the voltage of the cells he measured are taken from Table V, p 33, of his thesis. They are tabulated below.

Table IX

Molality HBr	E_{20}	E_{25}	E_{35}
.050	.29940 v	.30172 v	.30638 v
.100	.26643	.26813	.27157
.300	.21243	.21357	.21585
.500	.18568	.18650	.18814
.850		.15604	
1.00	.14643	.14625	.14590
1.70		.10819	
2.00	.10038	.09971	.09837
2.75	.05906	.05784	.05539

From the above data, using the E^o for the Hg_2Br_2 electrode determined in this paper, the activity coefficients of the HBr were calculated. A modification of the equation at the top of the page is used.

$$\log_e \gamma = -\log_e m_{HBr} - \frac{(E - E^o)}{2RT/F}$$

where γ is the mean activity coefficient of the HBr and E^{o} corresponds to the reaction for the cell at the top of the page. These activity coefficients are tabulated in table X below.

Table X

Molality HBr	$\gamma_{20^{c}}$	$\gamma_{25^{o}}$	$\gamma_{35^{o}}$
.05	.853	.846	.823
.10	.819	.813	.793
.30	.796	.784	.755
.50	.811	.797	.763
.85	.	.848	
1.00	.882	.873	.846
1.70		1.056	
2.00	1.098	1.080	1.036
2.75	1.810	1.774	1.692

Summary

The cell: $Ag, AgBr, MBr(m), Hg_2Br_2, Hg$ has been measured at three different concentrations with HBr as MBr, and at one concentration with KBr as MBr. Two different types of silver bromide electrodes have been used. The e.m.f. of this cell shows no apparent trend with type of electrolyte (KBr or HBr), concentration, or type of AgBr electrode. The cell was also measured at three different temperatures, 15°, 25°, and 35°C, and its temperature coefficient calculated.

From the above data, the free energy and heat of reaction of the reduction of mercurous bromide by silver:

$$2Ag + Hg_2Br_2 \longrightarrow 2AgBr + 2Hg$$

was calculated, at five degree intervals from 15 to 35°C.

Making use of the previously, by other authors, accurately determined E^0 of the AgBr electrode, the E^0 of the Hg_2Br_2 electrode is calculated at five degree intervals from 15 to 35°C, also the free energy and heat of the following reaction:

$$2\textcircled{e} \quad Hg_2Br_2 \longrightarrow 2Hg + 2Br^-(a=1)$$

Also making use of the accurately determined data obtained recently by other authors for the free energy and heat of formation of silver bromide from its elements, the free energy, heat and entropy of formation of mercurous bromide from its elements is calculated.

Using Kirchoff's law and the International Critical Table values for the specific heat of Ag, Hg, and AgBr, the specific heat of Hg_2Br_2 is calculated at 20°C

Activity coefficients of HBr are recalculated from the data of W. D. Larson using the above newly determined E^0 of the mercurous bromide electrode.

References

1. Matthews, J. L., PhD Thesis, Michigan State College (1930).

2. Larson, W. D., M.S. Thesis, Michigan State College (1931).

3. Keston, A. S., J. Am. Chem. Soc., 57, 1671 (1935).

4. Harned, H. S., Keston, A. S., and Donelson, J.G., J. Am. Chem. Soc., 58, 989 (1936).

5. Livingston, R. S., J. Am. Chem. Soc., 48, 45 (1926).

6. Harned, H. S., J. Am. Chem. Soc., 51, 416 (1929).

7. Lewis, G. N., and Storch, H., J. Am. Chem. Soc., 39, 2544 (1917).

8. Gerke, R. H., and Geddes, J. R., J. Phys. Chem., 31, 886 (1927).

9. Owen, B. B., and Foering, L., J. Am. Chem. Soc., 58, 1575 (1936).

10. Jones, G., and Baeckstrom, J. Am. Chem. Soc., 56, 1524 (1934).

11. Harned, H. S., and Donelson, J. G., J. Am. Chem. Soc., 59, 1280 (1937).

12. Randall, M., and Young, L. E., J. Am. Chem. Soc., 50, 989 (1928).

13. Gerke, R. H., J. Am. Chem. Soc., 44, 1684 (1922).

14. Bronsted, J. N., Z. Physik. Chem., 50, 481 (1904).

15. Berthollet, M., Ann. Chem. Phys., 4, 160(1875).

16. Thomsen, J., "Thermochemische Untersuchung", 1882-1886, 4Vols.

17. Klein, A., Z. Physik. Chem., 36, 361 (1901).

18. Jouniaux, A., J. Chim. Phys., 1, 609 (1904).

19. Krahmer, C.,Z. Electrochem., 26, 97 (1920).

20. Webb, T. J., J. Phys. Chem., 29, 827 (1925).

21. Woitinek, H., Z Electrochem., 38,, 359 (1932)

22. Shibata, F. L. and Taketa, T., J. Sci. Hiroshimo Univ., Ser. A, 2, 243 (1932).

23. Nernst, W., Z.Physik.Chem., 2, 23 (1888).

24. Varet, R., Ann. Chem. Phys., 8, 79 (1876).

25. Ishikawa, F., and Ueda, Y., Sci. Repts. Tohoku Imp. Univ., 1st Ser., 22, 249 (1933).

26. Brown, A. S., J. Am. Chem. Soc., 56, 646 (1934).

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The thermodynamics of the Ag, AgBr, MBr(m), Hg_2Br_2, Hg cell.