THE ACTIVITY OF HBr

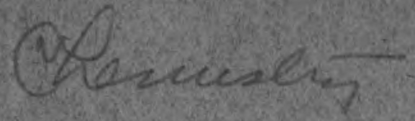
THESIS FOR THE DEGREE OF M. S.

William D. Larson

1931

Hydro - bromic acid

Chemistry, Organic



THE ACTIVITY OF HBr

A Thesis Submitted to the Faculty

of

MICHIGAN STATE COLLEGE

In Partial Fulfillment of the

Requirements for the Degree

of

Master of Science

Department of Chemistry

By

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I. INTRODUCTION AND LITERATURE

The cell H_2, HBr, Hg_2Br_2 + Hg was measured at concentration from 0.05 molal to 2.75 molal in order to determine the activity coefficients of hydrobromic acid in water, and to obtain more data on the electrode potential of the mercury, mercurous bromide electrode.

The only data available on the activity coefficients of hydrobromic acid are the following:

Lewis and Storch: (G. N. Lewis and Hyman Storch, J. Am. Chem. Soc., 39, 2544 (1917). They evaluated activity coefficients of hydrobromic acid from measurements of the cell, H_2, HBr, AgBr + Ag, at concentrations 0.01, 0.03, and 0.10 molal.

Bates and Kirschmann: (Bates and Kirschmann, J. Am. Chem. Soc., 41, 1991 (1919) obtained vapor pressure measurements on hydrobromic acid from 5.8 to 11.0 molal, and calculated the free energy at various concentrations.

Livingston: (R. S. Livingston, J. Am. Chem. Soc., 48, 45-53 (1926), evaluated activity coefficients by hydrobromic acid from 0.08 to 1.55 molal, using the cell, H_2, HBr, AgBr + Ag.

Harned: (H. S. Harned, J. Am. Chem. Soc., 51, 416, (1929) gave values of activity coefficients of hydrobromic acid from 0.01 to 3.0 molal.

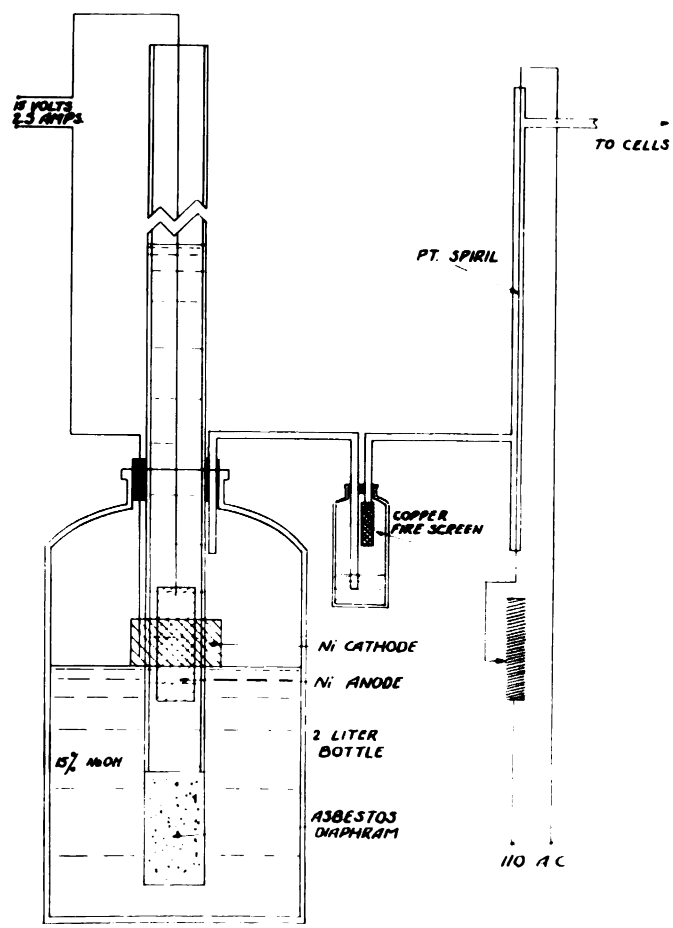
Matthews: (Julia L. Matthews, Ph.D. Thesis, M.S.C., (1930) discusses activity coefficients of hydrobromic acid.

II. PREPARATION OF SUBSTANCES

All substances used were prepared as described by Dr. Matthews (J. L. Matthews, Ph.D. Thesis, Michigan State College, 1930), with the exception of the hydrogen, which was generated electrolytically, and the treatment of mercurous bromide after precipitation.

The hydrogen generator used consisted of an ordinary five pound bottle of about two liters capacity, fitted with a rubber stopper carrying a four foot length of glass tubing 1½ inches in diameter, a small delivery tube, and the wire to the cathode. The cathode was of nickel gauze, and was on the outside of the large tube. The anode was also of nickel gauze, and inside the large tube. The end of the tube extended to about two inches from the bottom of the bottle, and was covered with two thicknesses of asbestos paper to prevent diffusion. The electrolyte was 15% NaOH.

Fifteen volts was sufficient pressure to operate the generator satisfactorily. The generator drew about 2.5 amperes on 15 volts. To obtain constant operation, three four-volt storage batteries were put in parallel with the line in such a manner that when the current in the line was shut off, the generator operated on current from the storage batteries, and when the line current was on, the batteries were charged.



HYDROGEN GENERATOR

The hydrogen as it came from the generator was passed through water, and then over a hot platinum spiral to remove any trace of oxygen.

The generator was run continuously for several months with no attention other than the occasional addition of small amounts of water, and the ordinary care that storage batteries would require.

The mercurous bromide was prepared by adding a liter of .02N potassium bromide to five hundred milliliters of mercurous nitrate which was about .05N, thus keeping Hg^+ in excess.

After precipitation, the mercurous bromide was allowed to settle; the supernatant liquid was drawn off by suction using a piece of glass tubing on which was a cotton filter. The precipitate was then washed eight times with one liter portions of evacuated water; the rinsings were drawn off as completely as possible each time by use of suction and cotton filter.

The washed precipitate was transferred to a 300 cc. Erlenmeyer flask. This washed and drained precipitate was then evacuated by using a one hole stopper and stopcock and aspirator. The nitrogen line was then attached to the inlet tube, and the stopcock slowly opened. The stopper was then removed and a stream of nitrogen was kept flowing into the open Erlenmeyer, while the bromide was rinsed several times with the desired concentration of hydrobromic acid. The mercurous bromide was then allowed to stand under the hydrobromic acid for at least thirtysix hours, with at least two more changes of hydrobromic acid.

Finally, the suspension of mercurous bromide in hydrobromic acid was transferred into a 250 cc. separatory funnel; some mercury was also added, and the mixture shaken for at least two and one-half hours, and the cells filled.

III. ANALYSES

In an attempt to explain some of the difficulties in getting e.m.f. checks on the system being studied, it was considered advisable to analyze the acid from each individual half-cell.

The concentration of the stock acid solution was determined gravimetrically by precipitation with silver nitrate. The acid which had been equilibrated with mercurous bromide and mercury was titrated with standard sodium hydroxide solution before being put into the cell, when the concentration was above 0.1 molal, and the concentration of the acid actually taken from the half-cells was determined gravimetrically as silver bromide. When the concentration was 0.1 molal or less, the concentration of the equilibrated acid was determined by titrating with standard mercurous nitrate solution, according to the method of L. von Zombory, (L. von Zombory, Z. Anorg. Allgem. Chem., 184, 237 (1929).

In this last titration, weighing burettes were used. About five milliliters of the acid were run into a fifty milliliter beaker, ten drops of bromphenol blue indicator prepared according to W. M. Clark (W. M. Clark, "The Determination of Hydrogen Ions", third edition, p. 91.) Then the hydrobromic acid was run in dropwise until the precipitate turned from violet to cream color. Then small amounts of mercurous nitrate and hydrobromic acid were added until the end point was reached accurately. At this point the precipitate appears partly cream colored and partly violet. No wash water may be added.

These analyses showed that, in general, the acid concentrations do change. The original concentration of acid, the average equilibrium concentration, and the change in concentration are given in Table I. All concentrations are expressed in mols per thousand grams of water throughout the thesis.

TABLE I

Molality of Original Acid	Molality of Equilibrated Acid (avg.)	Change in Molality
0.04757	0.0474	-0.0001
.1044	.104	- .0004
.2868	.290	+ .003
.5008	.503	+ .002
.8488	.858	+ .010
.9864	.998	+ .012
1.6935	1.725	+ .032
1.9998	2.038	+ .040
2.7351	2.780	+ .045

This change in concentration will affect the value of E^0 and the activity coefficient. Since the concentration in each cell was somewhat different from the mean, the value of E^0 was calculated for each cell, using the activity coefficients given by Harned (H.S. Harned, J. Am. Chem. Soc., 51, 416 (1929). From the average value of E^0 for any concentration, the value of the E of the cell at the nearest round concentration was calculated, and other calculations based on this value.

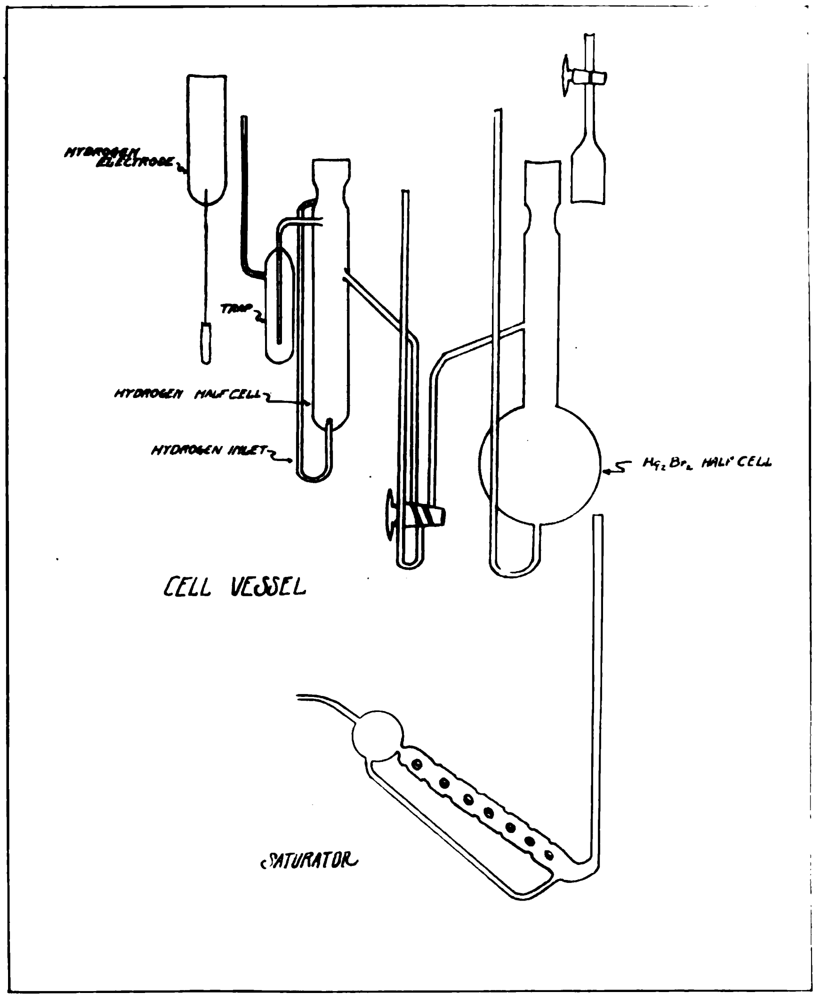
IV. THE CELL: SETTING UP AND MEASUREMENTS

The cell was designed to permit ease of filling, and to make it possible to fill without admitting oxygen.

The hydrogen electrode vessel was made of one inch pyrex tubing, with the hydrogen inlet tube sealed into the bottom. The tube connected to the twe-way stopcock was sealed to the side of the tube.

The platinum electrode was a piece of foil about one inch square, s aled into a ground glass stopper for the hydrogen electrode vessel.

The mercurous bromide electrode was a 25 cc. distilling flask, with the neck lengthened. The side arm of the flask was sealed to one arm of the two-way stopcock. Connection with the mercury was made possible by a tube sealed onto the bottom of the flask. The vessel was closed by a ground glass stopper made of a convenient size of tubing and a stopcock. The cell is shown in Fig. 2.


HYDROGEN ELECTRODE
TRAP
HYDROGEN HALF CELL
HYDROGEN INLET
Hg_2Br_2 HALF CELL
CELL VESSEL
SATURATOR

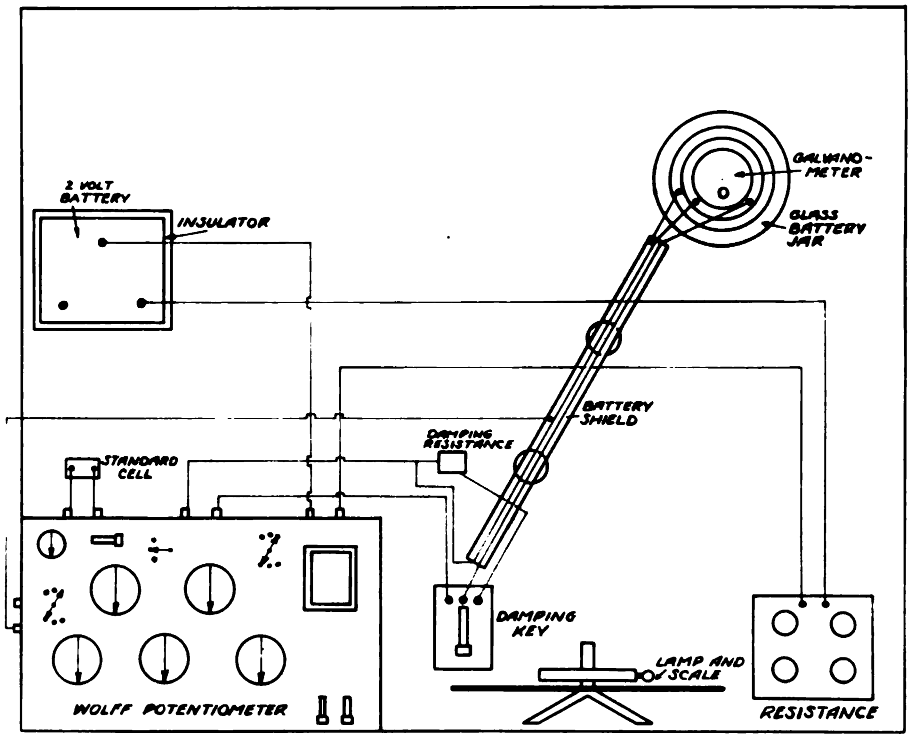
In filling the cell, the mercurous bromide electrode was first flushed with nitrogen. Then sufficient mercury was introduced to make a small button in the bottom of the flask. Nitrogen flowed through the vessel continually through the side arm, and out the top. Next the mercurous bromide paste was introduced from the separatory funnel, and sufficient acid run in to fill the flask and side-arm down to the two-way stopcock. The acid was drawn up into the stopper stopcock.

Next the saturator was flushed out with nitrogen, and filled with hydrobromic acid of the same concentration as used in the cell.

The hydrogen half cell was then filled with acid while nitrogen bubbled up through the hydrogen inlet. The platinum electrode (platinized by making it the cathode in a 1% chlorplatinic acid solution containing a trace of lead acetate) was put into place, and the cell placed in the thermostat, and hydrogen started.

Measurements could be begun about one hour after starting the hydrogen, but in general no reliable measurements could be made before twenty-four hours.

The potential measurements were made with Wolff five dial potentiometer (#7012) and a Leeds and Northrup type R series of galvanometer. The galvanometer and damping key were on a separate shield, insulated by glass from the shield on which the potentiometer rested.



SHIELDING SYSTEM

The working battery for the potentiometer stood on a heavy piece of insulating board. The galvanized iron tank of the oil bath was electrically connected to the potentiometer shield. The details of the shielding system are shown in the diagram (Fig. 3). The general scheme was according to White (W. P. White, J. Am. Chem. Soc., 36, 2011, 1914).

The temperatures at which the measurements were made were: 20.00°, 25.02°, and 35.58°C, as measured on B. of S. thermometer No. 49572. These temperatures were constant to within .01°C over long periods. The bath was the oil bath described by C. D. Tuttle (C. D. Tuttle, M.S. Thesis, M.S.C., 1931).

The standards of e.m.f. were two Bureau of Standards cells, Nos. 25887 and B.

The experimental data are presented in Table I. All concentrations are expressed in mols per 1000 grams of water.

TABLE II

0.04757 Molal Acid

Cell No.	Hours	E_{obs}	Baron press. obs.	Temp. obs.	Conc. Hyd. side	Conc. Hg_2Br_2 side	E corrected to 760mm	E corrected to .04757 m
67	23.2	0.30373	741.3	25.02	0.04758	0.04750	0.30436	0.30440
	47.5	.30367	737.8	25.02			.30435	.30439
	95.2	.30813	738.3	35.58			.30920	.30924
	120.0	.30810	738.3	35.58			.30917	.30921
	145.0	.30152	733.5	20.00			.30217	.30221
	153.2	.30139	729.5	20.00			.30211	.30215
	168.8	.30361	737.3	25.02			.30431	.30435
	175.5	.30366	738.7	25.02			.30433	.30437
68	23.2	.30357	723.7	25.02	.04756	.04746	.30420	.30428
	47.5	.30350	737.8	25.02			.30418	.30426
	95.2	.30796	738.3	35.58			.30903	.30911
	120.0	.30796	738.3	35.58			.30903	.30911
	145.0	.30126	733.5	20.00			.30191	.30199
	153.2	.30113	729.2	20.00			.30185	.30193
	168.8	.30345	737.3	25.02			.30415	.30423
	175.5	.30346	738.9	25.02			.30413	.30421
69	23.5	.30361	737.8	25.02	.04753	.04741	.30429	.30442
	49.2	.30346	728.8	25.02			.30433	.30446
	71.3	.30814	738.3	35.58			.30921	.30934
	83.9	.30815	738.3	35.58			.30922	.30935
	97.0	.30121	733.5	20.00			.30186	.30199
	103.9	.30120	729.2	20.00			.30192	.30205
	119.4	.30356	737.3	25.02			.30426	.30439
	131.3	.30358	738.2	25.02			.30425	.30438

0.04757 Molal Acid (Continued)

Cell No.	Hours	E_{obs}	Barom press. obs.	Temp. obs.	Conc. Hyd. side	Conc. Hg_2Br_2 side	E corrected to 760mm	E corrected to .04757m
70	23.5	0.30374	737.8	25.02	0.04734	0.04748	0.30442	0.30450
	49.2	.30356	728.8	25.02			.30443	.30451
	71.3	.30820	738.3	35.58			.30927	.30935
	83.9	.30824	738.3	35.58			.30931	.30939
	97.0	.30140	733.5	20.00			.30205	.30213
	103.9	.30134	729.2	20.00			.30206	.30214
	119.4	.30365	737.3	25.02			.30435	.30443
	131.3	.30365	738.2	25.02			.30432	.30440

0.1044 Molal Acid

Cell No.	Hours	E obs	Barom press. obs.	Temp. obs.	Conc. Hyd. side	Conc. $HgBr_2$ side	E corrected to 760mm	E corrected to 0.1044m
39	48.1	0.26557	739.0	25.02	0.1040	0.1045	0.26624	0.26616
	73.1	.26551	737.0	25.02			.26621	.26613
	97.0	.26559	740.1	25.02			.26624	.26616
	120.5	.26565	743.7	25.02			.26623	.26615
	144.3	.26564	744.0	25.02			.26622	.26614
							Av = .26623	.26615
40	23.3	.26568	733.3	25.02	.1044	.1037	.26645	.26629
	48.1	.26579	739.0	25.02			.26646	.26630
	71.5	.26574	737.4	25.02			.26644	.26628
	97.0	.26581	740.1	25.02			.26646	.26630
	120.5	.26590	743.7	25.02			.26649	.26633
	144.3	.26590	744.0	25.02			.26648	.26635
							Av = .26645	.26629
41	52.0	.26566	741.6	25.02	.1042	.1041	.26629	.26618
	77.7	.26560	730.9	25.02			.26626	.26615
	95.8	.26557	739.2	25.02			.26624	.26613
	121.8	.26561	743.0	25.02			.26621	.26610
	149.3	.26555	740.1	25.02			.26620	.26609
							Av = .26625	.26614
42	50.7	.26554	741.6	25.02	.1043	.1036	.26616	.26592
	72.8	.26555	741.3	25.02			.26618	.26594
	95.8	.26546	738.1	25.02			.26614	.26590
	119.5	.26553	742.7	25.02			.26613	.26589
	168.7	.26542	739.4	25.02			.26608	.26584
							Av = .26614	.26590

0.1044 Molal Acid (Continued)

Cell No.	Hours	E_{obs}	Barom press. obs.	Temp. obs.	Conc. Hyd. side	Conc. Hg_2Br_2 side	E corrected to 760 mm	E corrected to 0.1044m
43	14.5	0.26569	741.4	25.02	0.1036	0.1043	0.26631	0.26607
	37.0	.26567	739.9	25.02			.26632	.26608
	60.5	.26559	738.1	25.02			.26627	.26603
	108.5	.26564	743.0	25.02			.26624	.26600
	156.5	.26541	729.8	25.02			.26624	.26600
							Av = .26624	.26600
44	14.5	.26547	741.4	25.02	.1038	.1039	.26610	.26581
	37.0	.26548	739.6	25.02			.26614	.26585
	60.5	.26550	738.8	25.02			.26617	.26588
	108.5	.26558	743.1	25.02			.26617	.26588
	156.5	.26529	730.9	25.02			.26609	.26580
							Av = .26613	.26587

0.1040 Molal Acid

Cell No.	Hours	E obs.	Barom press. obs.	Temp. obs.	Conc. Hyd side	Conc. Hg_2Br_2 side	E corrected to 760mm	E corrected to 0.1040m
63	26.1	0.26556	738.5	25.02	0.1039	0.1035	0.26624	0.26615
	32.5	.26555	737.9	25.02			.26624	.26615
	44.5	.26883	737.8	35.58			.26992	.26983
	56.6	.26886	738.0	35.58			.26998	.26989
	73.2	.26398	734.3	20.00			.26463	.26454
	91.9	.26394	734.1	20.00			.26459	.26450
	97.6	.26550	738.8	25.02			.26617	.26608
	99.7	.26552	739.2	25.02			.26619	.26610
64	26.1	.26563	738.8	25.02	.1040	.1036	.26630	.26620
	32.5	.26563	737.9	26.02			.26632	.26622
	44.5	.26895	737.8	35.58			.27004	.26994
	56.6	.26900	738.0	35.58			.27010	.27000
	73.2	.26409	734.3	20.00			.26464	.26454
	91.9	.26410	734.1	20.00			.26675	.26665
	99.7	.26562	739.2	25.02			.26629	.26619

0.2868 Molal Acid

Cell No.	Hours	E obs.	Barom press. obs.	Temp. obs.	Conc. Hyd. side	Conc. Hg_2Br_2 side	E corrected to 760mm	E corrected to 0.2868m
45	23.5	0.21470	731.4	25.02	0.2883	0.2901	0.21550	0.21592
	74.0	.21484	738.4	25.02			.21552	.21594
	121.0	.21486	741.4	25.02			.21549	.21591
	147.5	.21474	734.3	25.02			.21549	.21591
							Av = .21550	.21592
46	23.5	.21466	731.4	25.02	.2875	.2911	.21546	.21590
	74.0	.21461	729.8	25.02			.21544	.21588
	121.0	.21481	741.4	25.02			.21544	.21588
	147.5	.21466	734.3	25.02			.21543	.21587
							Av = .21544	.21588
47	24.0	.21476	738.4	25.02	.2870	.2895	.21544	.21583
	71.5	.21475	738.4	25.02			.21543	.21582
	98.0	.21466	734.3	25.02			.21542	.21581
	148.5	.21470	736.0	25.02			.21542	.21581
							Av = .21543	.21582
48	30.5	.21488	738.4	25.02	.2870	.2916	.21556	.21600
	71.5	.21495	740.7	25.02			.21559	.21603
	120.2	.21483	734.3	25.02			.21558	.21602
	150.0	.21487	736.0	25.02			.21559	.21603
							Av = .21558	.21602
49	47.3	.21484	739.3	25.02	.2869	.2900	.21548	.21577
	95.7	.21479	736.0	25.02			.21551	.21580
	143.3	.21493	745.5	25.02			.21552	.21581
	189.3	.21491	743.2	25.02			.21550	.21579
							Av = .21551	.21580

0.2868 Molal Acid (Continued)

Cell No.	Hours	E obs.	Barom press. obs.	Temp. obs.	Conc. Hyd. side	Conc. Hg_2Br_2 side	E corrected to 760mm	E corrected to 0.2868m
50	47.3	0.21456	728.0	25.02	0.2871	0.2903	0.21542	0.21575
	95.7	.21490	743.1	25.02			.21550	.21583
	143.3	.21490	743.6	25.02			.21550	.21583
	189.3	.21493	743.2	25.02			.21552	.21585
							Av = .21552	.21585
65	26.3	.21503	738.8	25.02	.2870	.2895	.21570	.21584
	32.5	.21502	737.9	25.02			.21571	.21585
	44.5	.21708	737.8	35.58			.21817	.21831
	56.2	.21707	738.0	35.58			.21819	.21833
	73.7	.21398	734.3	20.00			.21463	.21477
	92.3	.21463	734.1	20.02			.21463	.21477
	97.4	.21497	738.8	25.02			.21564	.21578
66	26.3	.21500	738.8	25.02	.2868	.2898	.21567	.21580
	32.5	.21503	737.9	25.02			.21572	.21585
	44.5	.21710	738.4	35.58			.21816	.21832
	56.2	.21709	738.2	35.58			.21821	.21835
	73.7	.21394	734.3	20.00			.21459	.21483
	92.3	.21397	734.1	20.02			.21462	.21486
	97.4	.21500	739.3	25.02			.21567	.21581

0.5008 Molal Acid

Cell No.	Hours	E obs.	Barom press. obs.	Temp. obs.	Conc. Hyd. side	Conc. Hg_2Br_2 side	E corrected to 760mm	E corrected to 0.2808m
19	23.0	0.18580	741.1	25.02	0.5026	0.5032	0.18644	0.18666
	43.3	.18572	736.8	25.02			.18645	.18665
	96.5	.18572	736.9	25.02			.18643	.18665
	119.1	.18561	731.2	25.02			.18642	.18664
	142.7	.18561	731.0	25.02			.18643	.18665
							Av = .18643	.18665
20	23.0	.18575	743.1	25.02	.5003	.5032	.18634	.18643
	43.3	.18664	737.0	25.02			.18634	.18643
	96.5	.18564	736.9	25.02			.18634	.18643
	119.1	.18553	730.8	25.02			.18634	.18643
	142.7	.18556	733.0	25.02			.18633	.18642
							Av = .18634	.18643
21	17.9	.18569	731.2	25.02	.5019	.5009	.18650	.18631
	24.6	.18569	731.2	25.02			.18650	.18631
	48.2	.18569	731.2	25.02			.18650	.18631
	71.2	.18566	729.6	25.02			.18650	.18631
	77.0	.18568	730.6	25.02			.18650	.18631
	166.6	.18580	751.6	25.02			(.18625)	(.18606)
							Av = .18650	.18631
22	18.5	.18572	739.5	25.02	.5022	.5020	.18638	.18651
	51.1	.18573	740.2	25.02			.18638	.18651
	70.2	.18570	739.6	25.02			.18636	.18649
	95.8	.18594	751.6	25.02			.18639	.18652
	119.2	.18595	751.6	25.02			.18638	.18651
	145.2	.18573	741.6	25.02			.18636	.18649
							Av = .18638	.18651

0.5008 Molal Acid (Continued)

Cell No.	Hours	E obs.	Barom press. obs.	Temp. obs.	Conc. Hyd. side	Conc. Hg_2Br_2 side	E corrected to 760mm	E corrected to 0.5008m
23	24.3	0.18580	740.8	25.02	0.5016	0.5024	0.18644	0.18657
	51.1	.18574	737.1	25.02			.18644	.18657
	70.2	.18599	750.7	25.02			.18645	.18658
	96.7	.18602	751.6	25.02			.18646	.18659
	119.5	.18603	751.6	25.02			.18644	.18657
	145.2	.18591	745.5	25.02			.18646	.18659
							Av = .18644	.18657

0.8488 Molal Acid

Cell No.	Hours	E obs.	Barom press. mm.	Temp. obs.	Conc. Hyd. side	Conc. HC_2Br_2 side	E corrected to 760 mm	E corrected to 0.8488m
24	24.5	0.15513	736.9	25.02	0.8444	0.8565	0.15584	0.15588
	49.2	.15502	729.2	25.02			.15587	.15591
	71.5	.15515	734.7	25.02			.15590	.15594
	97.3	.15530	745.2	25.02			.15586	.15590
	121.1	.15539	749.2	25.02			.15589	.15593
	141.2	.15523	740.5	25.02			.15588	.15592
							Av = .15588	.15592
25	24.5	.15510	736.9	25.02	.8503	.8412	.15581	.15567
	49.2	.15493	729.2	25.02			.15578	.15564
	71.5	.15507	734.7	25.02			.15582	.15568
	97.3	.15523	745.2	25.02			.15580	.15566
	121.1	.15533	749.2	25.02			.15582	.15568
	141.2	.15514	737.2	25.02			.15585	.15571
							Av = .15580	.15566
26	49.2	.15505	729.2	25.02	.8507	.8567	.15590	.15600
	71.5	.15517	734.7	25.02			.15592	.15602
	97.3	.15531	745.2	25.02			.15589	.15599
	121.1	.15540	749.2	25.02			.15588	.15598
	216.2	.15512	738.2	25.02			.15591	.15591
							Av = .15589	.15599
27	25.5	.15474	727.8	25.02	.8500	.8623	.15561	.15605
	47.8	.15469	725.9	25.02			.15559	.15603
	73.3	.15497	739.8	25.02			.15563	.15607
	97.4	.15500	741.5	25.02			.15563	.15607
	126.0	.15504	743.0	25.02			.15564	.15608
							Av = .15562	.15606

0.8488 Molal Acid (Continued)

Cell No.	Hours	E obs.V	Bar. press. obs. mm.	Temp. obs.	Conc. Hyd. side	Conc. Hg_2Br_2 side	E corrected to 760 mm.	E corrected to 0.8488m
28	9.0	0.15497	742.6	25.02	0.8503	0.8625	0.15559	0.15605
	25.5	.15472	726.7	25.02			.15561	.15607
	50.7	.15479	728.2	25.02			.15565	.15611
	75.0	.15497	740.2	25.02			.15562	.15608
							Av = .15562	.15608
29	23.0	.15543	744.6	25.02	.8504	.8537	.15599	.15608
	48.2	.15538	740.5	25.02			.15603	.15623
	71.6	.15543	741.6	25.02			.15605	.15625
	95.9	.15529	735.0	25.02			.15602	.15622
	118.5	.15545	743.3	25.02			.15604	.15624
	144.5	.15541	741.7	25.02			.15603	.15623
	178.9	.15530	736.8	25.02			.15600	.15620
							Av = .15602	.15622
30	26.6	.15554	742.8	25.02	.8509	.8555	.15614	.15641
	71.6	.15551	741.6	25.02			.15614	.15641
	95.9	.15539	735.0	25.02			.15613	.15640
	144.4	.15545	740.6	25.02			.15609	.15636
	188.9	.15511	723.2	25.02			.15608	.15635
							Av = .15610	.15637
31	48.0	.15523	739.6	25.02	.8502	.8563	.15589	.15616
	72.1	.15505	729.8	25.02			.15589	.15616
	120.2	.15528	741.5	25.02			.15591	.15618
	169.1	.15515	736.0	25.02			.15588	.15615
	204.0	.15532	744.4	25.02			.15590	.15617
							Av = .15590	.15617

0.9864 Molal Acid

Cell No.	Hours	E obs.V	Bar. press. obs. mm.	Temp. obs.	Conc. Hyd. side	Conc. Hg_2Br_2 side	E corrected to 760 mm.	E corrected to 1.00 m.
77	23.5	0.14578	728.1	25.02	0.9880	1.0002	0.14664	0.14642
	52.2	.14579	728.6	25.02			.14665	.14643
	70.2	.14490	730.5	35.58			.14612	.14590
	79.0	.14487	730.1	35.58			.14610	.14588
	95.8	.14605	733.3	20.00			.14670	.14648
	102.7	.14605	733.0	20.00			.14671	.14649
	118.5	.14575	736.3	25.02			.14647	.14625
	124.0	.14578	736.5	25.02			.14649	.14627
78	23.5	.14574	728.1	25.02	.9872	.9974	.14660	.14626
	52.2	.14574	728.6	25.02			.14660	.14626
	70.2	.14485	730.5	35.58			.14607	.14573
	79.0	.14481	730.1	35.58			.14605	.14571
	95.8	.14602	733.3	20.00			.14664	.14630
	102.7	.14600	733.0	20.00			.14667	.14633
	118.5	.14570	736.3	25.02			.14642	.14608
	124.0	.14571	736.5	2502			.14642	.14608

1.6935 Molal Acid

Cell No.	Hours	E obs.	Barom press. obs.	Temp. obs.	Conc. Hyd. side	Conc. Hg_2Br_2 side	E corrected to 760 mm.	E corrected to 1.6935 m
32	22.3	0.10823	744.6	25.02	1.6923	1.7241	0.10890	0.10950
	48.0	.10799	735.2	25.02			.10888	.10942
	73.6	.10822	742.1	25.02			.10892	.10952
	97.1	.10804	733.3	25.02			.10891	.10951
	119.1	.10824	742.5	25.02			.10893	.10952
						Av =	.10890	.10950
33	22.3	.10817	744.6	25.02	1.7084	1.7237	.10874	.10966
	48.0	.10801	735.2	25.02			.10875	.10967
	73.6	.10812	742.1	25.02			.10874	.10966
	97.1	.10797	733.2	25.02			.10874	.10966
	140.1	.10805	738.5	25.02			.10873	.10965
	217.0	.10815	743.4	25.02			.10874	.10966
						Av =	.10874	.10966
34	23.0	.10826	743.4	25.02	1.7219	1.7206	.10886	.11009
	48.7	.10807	735.4	25.02			.10881	.11004
	97.1	.10824	743.5	25.02			.10884	.11007
	144.0	.10811	737.1	25.02			.10882	.11005
	168.8	.10822	743.4	25.02			.10881	.11004
						Av =	.10883	.11005
35	48.5	.10779	737.1	25.02	1,6920	1.7307	.10848	.10924
	71.7	.10797	745.0	25.02			.10854	.10930
	102.5	.10781	736.7	25.02			.10851	.10927
	144.3	.10773	733.7	25.02			.10848	.10924
	195.0	.10780	736.5	25.02			.10852	.10928
						Av =	.10851	.10927

1.6935 Molal Acid (Continued)

Cell No.	Hours	E obs.	Barom press. obs.	Temp. obs.	Conc. Hyd. side	Conc. Hg_2Br_2 side	E corrected to 760 mm.	E corrected to 1.6935 m
36	48.5	0.10780	737.1	25.02	1.6931	1.7210	0.10849	0.10928
	71.7	.10803	745.0	25.02			.10880	.10959
	126.5	.10786	734.8	25.02			.10859	.10938
	168.8	.10808	746.3	25.02			.10862	.10941
	196.0	.10790	736.5	25.02			.10862	.10941
							Av = .10858	.10937
37	23.7	.10811	743.5	25.02	1.6927	1.7239	.10870	.10930
	53.5	.10787	736.5	25.02			.10869	.10929
	97.1	.10787	731.5	25.02			.10867	.10927
	144.7	.10800	738.1	25.02			.10869	.10929
	167.2	.10796	737.0	25.02			.10865	.10925
							Av = .10867	.10927
38	23.7	.10811	743.5	25.02	1.6931	1.7242	.10870	.10931
	53.5	.10798	736.5	25.02			.10868	.10929
	97.1	.10786	731.5	25.02			.10866	.10927
	144.7	.10799	738.1	25.02			.10868	.10929
	167.2	.10801	740.1	25.02			.10867	.10928
							Av = .10867	.10928

1.9998 Molal Acid

Cell No.	Hours	E obs.V	Barom press. obs.	Temp. obs.	Conc. Hyd. side	Conc. $HgBr_2$ side	E corrected to 760 mm.	E corrected C = 2.000
75	24.0	0.09845	734.3	25.02	2.0048	2.0372	0.09920	0.09974
	75.7	.09827	728.6	25.02			.09913	.09967
	93.8	.09650	730.5	35.58			.09772	.09876
	102.5	.09651	730.1	35.58			.09774	.09828
	119.2	.09925	733.3	20.00			.09990	.10044
	150.3	.09924	733.0	20.00			.09992	.10046
	166.0	.09844	736.3	25.02			.09916	.09970
	171.5	.09848	735.8	25.02			.09920	.09974
76	24.0	.09836	733.0	25.02	2.0029	2.0305	.09913	.09974
	75.7	.09825	728.6	25.02			.09911	.09972
	93.8	.09648	730.5	35.58			.09770	.09831
	102.5	.09650	730.1	35.58			.09773	.09834
	119.2	.09928	733.3	20.00			.09993	.10054
	150.3	.09928	733.0	20.00			.09994	.10055
	166.0	.09840	736.3	25.02			.09912	.09973
	171.5	.09839	735.8	25.02			.09911	.09972

2.7351 Molal Acid

Cell No.	Hours	E obs.	Barom press. obs.	Temp. obs.	Conc. Hyd. side	Conc. Hg_2Br_2 side	E corrected to 760 mm.	E corrected to 2.7351 m
71	21.2	0.05693	742.9	25.02	2.7407	2.7786	0.05756	0.05776
	72.7	.05699	743.6	25.02			.05758	.05778
	93.3	.05411	743.4	35.58			.05488	.05508
	100.9	.05412	743.3	35.58			.05489	.05509
	120.0	.05833	734.7	20.00			.05876	.05896
	140.9	.05830	733.0	20.00			.05876	.05896
	148.2	.05684	729.5	25.02			.05748	.05768
	153.1	.05682	728.0	25.02			.05748	.05768
72	21.2	.05708	742.9	25.02	2.7391	2.7707	.05769	.05788
	72.7	.05709	743.6	25.02			.05769	.05788
	93.3	.05425	743.4	35.58			.05502	.05521
	100.9	.05426	743.3	35.58			.05503	.05522
	120.0	.05845	734.7	20.00			.05889	.05808
	140.9	.05842	733.0	20.00			.05889	.05808
	148.2	.05695	729.5	25.02			.05759	.05778
	153.1	.05695	728.0	25.02			.05761	.05780
73	18.0	.05692	738.4	25.02	2.7410	2.7804	.05771	.05788
	44.8	.05713	743.6	25.02			.05772	.05789
	65.4	.05405	743.4	35.58			.05502	.05519
	74.2	.05396	738.2	35.58			.05502	.05519
	92.0	.05822	734.7	20.00			.05885	.05902
	112.8	.05816	731.6	20.00			.05883	.05902
	120.2	.05677	729.5	25.02			.05762	.05779
	139.2	.05686	734.0	25.02			.05761	.05778

2.7351 Molal Acid (Continued)

Cell No.	Hours	E obs.	Barom press. obs.	Temp. obs.	Conc. Hyd. side	Conc. Hg_2Br_2 side	E corrected to 760 mm.	E Corrected to 2.7351m
74	18.0	0.05675	733.4	25.02	2.7381	2.7765	0.05754	0.05770
	44.8	.05698	743.6	25.02			.05757	.05773
	65.4	.05392	743.4	35.58			.05489	.05505
	74.2	.05383	738.2	25.58			.05492	.05508
	92.0	.05811	734.7	20.00			.05874	.05890
	112.8	.05806	731.6	20.00			.05875	.05891
	120.2	.05668	729.5	25.02			.05752	.05768
	130.2	.05675	734.0	25.02			.05752	.05768

V. THE VALUE OF THE ELECTRODE POTENTIAL.

Dr. Matthews reports a value of electrode potential of -0.13965 volt, using Harned's published activity coefficients. She measured cells near a concentration of 1.0 molal. The corresponding value obtained in this work, using an acid concentration -0.9864 molal and Harned's published activity coefficient is -0.13927.

At approximately 0.1 molal, we found the value of E^0 to be -0.13855 volts using Harned's coefficients. Dr. Matthews reports six cells at 0.09785 molal averaging 0.2715 volts. The value of E^0 calculated from these results is -0.1408 volts. This may be compared with the result of Gerke (R. H. Gerke, J. Phys. Chem. 31, 886-9 (1927)). At a concentration of 0.10015 molal he found the best value of E was 0.2685 volts. From this, we find E^0 = -0.1391 volts using Harned's coefficient.

It is, therefore, evident that the activity coefficients may be calculated on several bases. We might take either of the values of E^0 reported by Dr. Matthews or the value -0.1385 volts reported by R. H. Gerke in the International Critical Tables. Also, we might assume the activity coefficient of either Harned or Livingston at some concentration at which measurements were made, and calculate a corresponding value of the activity coefficients.

VI. THE VALUES OF THE ACTIVITY COEFFICIENTS OF HYDROBROMIC ACID IN AQUEOUS SOLUTION.

The activity coefficients in the following table were calculated by use of the familiar formula

$$\log_{10} \gamma = \frac{E^{o} - E - .11826 \log m}{.11826}$$

Column 2, Table III gives the values if we assume the value of Harned at 0.1 molal, and calculate a value of E^o from our measurements at 0.1 molal. Column 3 gives the values if we assume the value of E^o (-0.1385 volts) given by Gerke in the I.C.T. Column 4 gives the values assuming Dr. Matthews' value of E^o when she used Harned's activity coefficient, and column 5 gives the values assuming Dr. Matthews' values and Livingston's activity coefficient.

TABLE III

m	E° = 0.13855	E° = -0.1385	E° = -0.13965	E° = -0.13906	Harned	Livingston	ICl
0.05	0.834	0.834	0.852	0.842	0.831	0.830	0.860
0.10	(.802)	.802	.819	.810	.802	.814	.814
0.30	.773	.773	.790	.781	.774	.786	.788
0.50	.784	.784	.803	.792	.788	.792	.762
0.85	.839	.839	.855	.846	.847		
1.00	.861	.861	.879	.869	.873	.864	.823
1.70	1.040	1.040	1.034	1.051	1.078		
2.00	1.075	1.075	1.088	1.080	1.169		
2.75	1.750	1.750	1.788	1.787	1.846		

VII. THE DECREASE IN FREE ENERGY AND IN HEAT CONTENT ATTENDING THE CELL REACTION

The reversible reaction occurring in the cell studied is

$$H_2(1\ \text{atm.}) + Hg_2Br_2(\text{solid}) = 2\ Hg(\text{liquid}) + 2\ HBr(\text{at } m)$$

when two faradays of electricity are passed.

The decrease in free energy in calories may be calculated from the familiar formula:

$$-\Delta F = \frac{E\ N\ F}{4.185} \quad \text{calories}$$

which becomes, on passage of two faradays:

$$-\Delta F = 46106\ E \ \text{calories}$$

The decrease in heat content may be calculated by the Gibbs-Helmholtz equation:

$$E + \frac{\Delta H}{NF} = T\frac{dE}{dT}$$

which when simplified becomes:

$$\Delta H = 46106\ (T\frac{dE}{dT} - E)$$

As an example of the method used, consider the data in Table IV, for the concentration 0.05 sw.

$$T = 298^{o} \text{ and } \frac{dE}{dT} = +\ 0.000153\ \frac{\text{volts}}{\text{degrees}}$$

Therefore

$$T\frac{dE}{dT} = .04557. \quad E = 0.30173 \text{ volts}$$

Substituting these values in the simplified equation, we obtain

$$\Delta H = 46106\ (.04557 - 0.30173) = -7523 \text{ cals.}$$

The decrease in free energy, the temperature coefficient, and the decrease in heat content at each concentration are given in Table IV. Also, the decrease in heat content calculated from the heat of formation of mercurous bromide, the heat of formation of hydrogen bromide, and the heats of dilution of hydrogen bromide (all values from the I.C.T) are given.

TABLE IV

Conc.	E volts	$-\Delta F$ Cal.	$\frac{dE}{dT}$ Volts/deg.	E.M.F. ΔH Cal.	Heat Data ΔH Cal.
0.05	0.30173	13912	+0.000465	-7523	-7982
.10	.26814	12363	+ .000343	-7350	-7934
.30	.21357	9847	.000228	-6714	-7732
.50	.18650	8599	+ .000164	-6346	-7789
.85	.15604	7194			
1.00	.14625	6743	- .000035	-7224	-7316
1.70	.10919	5034			
2.00	.09971	4597	- .000134	-6438	-7344
2.75	.05784	2667	- .000245	-3366	-6928

DISCUSSION

In Table V are given a summary of the data obtained in this investigation, together with the values of the activity coefficient calculated from the experimental data.

These coefficients were calculated on the basis E^0 = -0.13855 volts, which value is obtained when one assumes Harned's activity coefficient at the concentration 0.10 molal. By inspection, one may see that the values are always somewhat lower than Harned's except at the highest concentration, namely 2.75 molal. The high concentration of HBr may have had some effect on the glass, the mercury, or may have dissolved an excessive amount of mercurous bromide. The low value for the E^0 in this case suggests that some such effect must be at work.

TABLE V

Conc.	$E^0_{25.02}$	E_{20}	$E_{35.00}$	$E_{25.02}$	on basis E^0= .13855 γ	Harned γ
0.050	0.13836	0.29940	0.30638	0.30173	0.834	0.831
.100	.13855	.26643	.27157	.26814	(.802)	(.802)
.300	.13858	.21243	.21585	.21357	.773	.774
.500	.13866	.18568	.18814	.18650	.784	.788
.850	.13916	-	-	.15604	.839	.847
1.00	.13927	.14643	.14590	.14625	.861	.873
1.70	.14030	-	-	.10919	1.040	1.078
2.00	.14333	.10038	.09857	.09971	1.075	1.169
2.75	.13217	.05906	.05539	.05784	1.750	1.546

SUMMARY

The electromotive force of the cell

$$H_2(g), HBr(c), Hg_2Br_2(s) + Hg(l)$$

has been studied at nine concentrations and at three temperatures.

From these data the activity coefficients of hydrobromic acid, the decrease in free energy, the temperature coefficients, and the decrease in heat content have been calculated.