It will be noted that the entropies of both the halogens and the interhalogen compounds in carbon tetrachloride solution do not differ greatly from each other; this is not the case for the gases.

Summary

The partial vapor pressures of iodine monochloride and chlorine above their carbon tetrachloride solutions have been measured and from the results, combined with those of other investigators, the free energy of formation of the monochloride in solution has been calculated.

Determinations of the heats of solution of iodine and bromine in carbon tetrachloride and the heats of formation of iodine monochloride, iodine monobromide and bromine monochloride in the same solvent have been made. These data were combined with the known free energy values to obtain the thermodynamic constants of the halogens and interhalogen compounds in their carbon tetrachloride solutions. The values are collected in Table IX, and in Table VIII are presented the corresponding data for the same substances in the gas phase.

It was found that the reaction between bromine and chlorine in carbon tetrachloride solution is appreciably slower than the corresponding reactions between iodine and chlorine and iodine and bromine.

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The Thermodynamics of Ionized Water in Potassium and Sodium Bromide Solutions

BY HERBERT S. HARNED AND WALTER J. HAMER

Recently considerable information regarding the behaviors of the ions of water in potassium and lithium chloride solutions from electromotive force measurements of cells without liquid junction has been obtained.[1] This study has now been extended to include similar data and calculations of related properties in potassium and sodium bromide solutions. To this end, measurements of the cells

$$H_2 \mid MOH(m_0), MBr\ (m) \mid AgBr \mid Ag, \quad \text{and} \qquad (A)$$
$$H_2 \mid HBr\ (m_0), MBr\ (m) \mid AgBr \mid Ag \qquad (B)$$

have been made throughout a temperature range of from 0 to 60°, where M represents potassium or sodium.

Much valuable information may be obtained from these data of which we have included (1) the ionization constant of water; (2) the normal potential, E_0, of the silver-silver bromide electrode; (3) the activity

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[1] (a) Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933); (b) Harned and Copson, *ibid.*, **55**, 2206 (1933).

coefficient of hydrobromic acid in potassium and sodium bromide solutions; (4) the ionic activity coefficient product of water in potassium and sodium bromide solutions; (5) the dissociation of water in potassium and sodium bromide solutions; (6) the partial molal heat content of hydrobromic acid in potassium and sodium bromide solutions; (7) the heat of ionization of water and the partial molal heat of ionization of water in potassium and sodium bromide solutions. All these quantities have been determined throughout the temperature range of 0 to 60°.

The only earlier investigation of a similar nature is that of Harned and James, who computed the ionic activity coefficient and dissociation of water at 25° in these solutions from measurements of three cells, of which two contained amalgam electrodes. These results were found to be good but far less extensive than the present series of measurements.[2]

Experimental Results

The apparatus employed was identical with that previously described by us. Vacuum technique and air-free solutions were employed. The same procedure was adopted in preparing the electrodes, except that in the case of the silver–silver bromide electrode the additional precaution of excluding light during their preparation was taken. The apparatus was painted black and the electrodes never turned dark. Freshly prepared electrodes were used in each cell. Constant boiling highest grade hydrobromic acid was twice distilled and diluted with conductivity water. This solution was analyzed gravimetrically. Potassium and sodium bromides were twice crystallized and dried at 110°. The salts were weighed and introduced into the solutions. Other details were carried out in the manner previously described by us.

Since the cell measurements were very extensive, we have expressed them by means of the linear equations

$$\left.\begin{aligned} E_A &= E_{25} + c(t - 25) + d(t - 25)^2 \\ E_B &= E_{25} + a(t - 25) + b(t - 25)^2 \end{aligned}\right\} \qquad (1)$$

and have recorded the constants E_{25}, a, b, c and d in Table I. Suffice it to say that four cells were measured at 5° temperature intervals throughout the temperature range of 0 to 60° and at each of the eleven salt concentrations recorded. This was done for each of the acid and hydroxide cells designated in the table. The actual over-all reproducibility of these cells was found to be ±0.08 mv. The mean deviation of the mean experimental values from those calculated by equation (1) was found to be ±0.03 mv.

The Ionization Constant of Water.—As a check upon the accuracy of both types of cells and the bromide electrode, we have determined the ionization constant of water, K, by the method previously described by us

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(2) Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).

TABLE I

CONSTANTS OF EQUATION (1), $E_A = E_{25} + c(t - 25) + d(t - 25)^2$; $E_B = E_{25} + a(t - 25) + b(t - 25)^2$. VALID FROM 0 TO 60°

I. KBr

	Cell (A) H_2 | KOH (0.01), KBr (m) | AgBr | Ag			Cell (B) H_2 | HBr (0.01), KBr (m) | AgBr | Ag		
$\mu = m + 0.01$	E_{25}	$c \times 10^6$	$d \times 10^6$	E_{25}	$a \times 10^6$	$b \times 10^6$
0.01	.....	.....	.....	0.31355	291.91	−2.818
.02	0.89968	292.0	0.29	.29759	243.91	−2.818
.03	.88194	235.5	.275	.28844	218.09	−2.782
.04	.87161	202.0	.27	.28198	198.17	−2.765
.06	.85849	160.0	.26	.27281	166.27	−2.745
.11	.84096	99.0	.25	.25948	130.82	−2.636
.21	.82343	48.2	.036	.24509	89.45	−2.509
.51	.80019	− 25.2	− .036	.22460	32.82	−2.236
1.01	.78408	− 74.6	− .145	.20625	− 8.45	−2.090
1.51	.77461	−110.8	− .16	.19400	− 39.36	−1.872
2.01	.76743	−137.3	− .25	.18309	− 56.91	−1.781
3.01	.75686	−171.5	− .29	.16584	− 86.27	−1.654

II. NaBr

	Cell (A) H_2 | NaOH (0.01), NaBr (m) | AgBr | Ag			Cell (B) H_2 | HBr (0.01), NaBr (m) | AgBr | Ag		
$\mu = m + 0.01$	E_{25}	$c \times 10^6$	$d \times 10^6$	E_{25}	$a \times 10^6$	$b \times 10^6$
0.01	.....	.....	.....	0.31335	291.9	−2.818
.02	0.89947	289.0	0.26	.29737	243.9	−2.818
.03	.88160	233.0	.25	.28810	218.0	−2.800
.04	.87117	199.0	.22	.28172	198.2	−2.763
.06	.85793	151.0	.18	.27262	170.3	−2.745
.11	.83989	92.8	.16	.25895	128.7	−2.654
.21	.82160	44.55	.11	.24391	87.5	−2.509
.51	.79688	− 13.63	.073	.22190	38.8	−2.236
1.01	.77718	− 72.0	.00	.20133	0.0	−2.109
1.51	.76484	−104.4	− .073	.18591	− 18.2	−2.036
2.01	.75556	−136.7	− .13	.17327	− 33.4	−1.890
3.01	.74056	−177.0	− .29	.15117	− 44.8	−1.763

which does not involve a knowledge of the normal potential of the silver–silver bromide electrode, E_0. Equation (16) of our earlier communication is

$$E_B - E_A + \frac{RT}{NF}\ln\frac{m''_H m''_{Br} m'_{OH}}{m'_{Br}} - \frac{2RT}{NF}\left(\frac{5.908 \times 10^6}{D^{3/2}\, T^{3/2}}\right)\sqrt{\mu} = \frac{RT}{NF}\ln K - \beta\mu \qquad (2)$$

We plotted the left side of this equation against μ from the data of both the cells containing potassium bromide and sodium bromide, respectively. By extrapolation to zero μ, K was obtained and was found to agree within the estimated order of accuracy (±0.04 mv.) with the values obtained from the cells containing potassium and lithium chloride and contained in Table III of our earlier communication. This agreement leads us to have considerable confidence in the present results.

The Normal Electrode Potential of the Silver–Silver Bromide Electrode.—The electromotive forces of cells of type B, E_B, are given by the equation

$$E_B + \frac{RT}{NF}\ln m_H m_x = E_0 - \frac{RT}{NF}\ln \gamma_H \gamma_x \qquad (3)$$

If we substitute for $\ln \gamma_H \gamma_x$ its value derivable from the limiting law of the theory of Debye and Hückel with an additional linear term, $\beta\mu$, and rearrange, we obtain

$$E_B + \frac{RT}{NF}\ln m_H m_x - \frac{8.324 \times 10^6\, RT}{D^{3/2}\, T^{3/2}\, NF}\sqrt{\mu} = E_0 - \frac{2RT}{NF}\beta\mu \qquad (3)$$

which is equation (6) given by Harned and Copson.[1b] If the left side of this equation is plotted against μ, its value at zero μ is E_0. A plot of this function is given in Fig. 1 of the paper by Harned and Copson for the case of the cell containing hydrochloric acid and lithium chloride. Their values of E_0 agreed to within ±0.04 mv. with those obtained by Harned and Ehlers,[3] who employed the cell containing hydrochloric acid and no salt. Since the activity coefficient of hydrochloric acid in lithium chloride solutions is very nearly the same as its value in pure water at concentrations from 0.01 to 0.1 M, this case is most favorable and close agreement is to

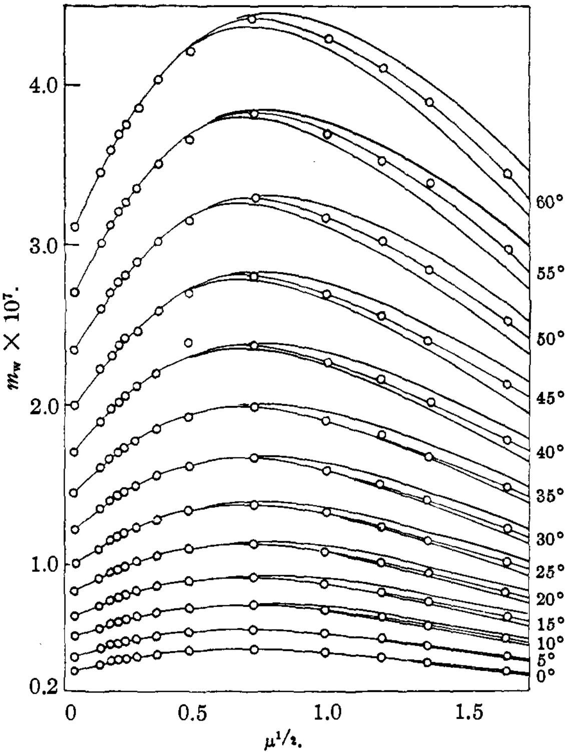

Fig. 1.—The dissociation of water in potassium chloride and bromide and sodium bromide solutions.

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(3) Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).

be expected. On the other hand, the activity coefficient of the hydrochloric acid in potassium chloride solutions becomes less than its value in pure aqueous solution in this region of concentration, particularly at the higher temperatures, a fact which is also true of hydrobromic acid in potassium bromide solutions and to a less degree of hydrobromic acid in sodium bromide solutions. Therefore, if we employ this method of extrapolation with the hydrochloric acid cells containing potassium chloride and draw the plot through the 0.01 *M* point, we can predict that the values of E_0 thus derived will be slightly lower than those obtained by Harned and Ehlers. This indeed was found to be the case. Very close agreement was found to occur at the lower temperatures but an increasing deviation occurs as the temperature increases, becoming 0.08 mv. at 25° and 0.14 mv. at 60°. Since this is the maximum deviation to be expected, we have confidence that the normal potential of the silver–silver bromide electrode may be evaluated to within 0.1 mv. by this method. This has been done for the cells containing both potassium and sodium bromide and the values obtained are given in the third and fourth columns of Table II. It should be noted that the values derived from the cells containing the potassium salt are about 0.05 mv. lower than those from the cells containing the sodium salt.

As a further interesting confirmation and also a test of the general consistency of the cells, we have resorted to a method of determining E_0 from the electromotive forces of the cells containing potassium hydroxide and bromide. The equation for cells of the type (A) is[4]

$$E_{\mathrm{A}} - E_0 + \frac{RT}{NF} \ln \frac{m_{\mathrm{Br}}}{m_{\mathrm{OH}}} = \frac{RT}{NF} \ln \frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}}{\gamma_{\mathrm{H}}\gamma_{\mathrm{Br}}\, a_{\mathrm{H_2O}}} - \frac{RT}{NF} \ln K \qquad (4)$$

At the lower concentrations, the activity coefficient ratio may be taken to be unity. Therefore, if we employ cells in which the ratio of m_{Br} to m_{OH} is unity, we obtain

$$E_{\mathrm{A}} + (RT/NF) \ln K = E_0 \qquad (5)$$

The electromotive forces of the cells containing 0.01 *M* hydroxide and bromide were used as well as the values of *K*, the ionization constant of water contained in Table III of our earlier communication. The values of E_0 thus derived are given in the second column of Table II. These were averaged with those obtained from the two acid cells and this average is given in the fifth column of the table. These average results were then subjected to the method of least squares whence the equation

$$E_0 = 0.07169 - 5.259 \times 10^{-4}(t - 25) - 3.022 \times 10^{-6}(t - 25)^2 \qquad (6)$$

was obtained. The deviations between the values computed by equation (6) and $E_{\mathrm{av.}}$ are given in the last column of the table.

Although this is not so good a method of determining E_0 as that which employs the cells containing the acid alone, the results thus obtained give

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(4) Equation (4). Harned and Hamer, Ref. 1.

values of the activity coefficient from the electromotive forces at 0.01 *M* hydrobromic acid which are quite reasonable and agree closely with similar values obtained for hydrochloric acid throughout the entire temperature range. It should be borne in mind that these are the normal potentials of a silver–silver bromide electrode prepared by heating silver oxide paste and subsequent electrolysis. These values may differ by a few tenths of a millivolt from those obtained with electrodes prepared by some other method. The present results are very consistent and give very reasonable values of the thermodynamic properties.

TABLE II

THE NORMAL POTENTIAL OF THE SILVER–SILVER BROMIDE ELECTRODE

t, °C.	E_0 (KOH-KBr)	E_0 (HBr-KBr)	E_0 (HBr-NaBr)	E_0 (Mean)	$E_{0\text{calcd.}} - E_0$ (mv.)
0	0.08288	0.08299	0.08301	0.08296	−0.01
5	.08091	.08095	.08100	.08095	+ .05
10	.07884	.07883	.07889	.07885	+ .06
15	.07663	.07660	.07665	.07662	+ .03
20	.07422	.07417	.07422	.07420	+ .03
25	.07172	.07165	.07170	.07169	.00
30	.06905	.06895	.06899	.06900	− .01
35	.06613	.06603	.06607	.06608	+ .05
40	.06311	.06299	.06305	.06305	+ .07
45	.05999	.05986	.05992	.05992	+ .04
50	.05675	.05655	.05660	.05663	+ .02
55	.05328	.05309	.05316	.05318	+ .01
60	.04975	.04955	.04961	.04964	− .06

The Activity Coefficient of Hydrobromic Acid in Potassium and Sodium Bromide Solutions.—From these values of E_0 and by means of the equation for cells of type (B), namely

$$E_B = E_0 - \frac{RT}{NF} \ln m_H m_{Br}\, \gamma_H \gamma_{Br} \qquad (7)$$

the activity coefficient of hydrobromic acid in sodium and potassium bromide solutions was computed. The accuracy is estimated to be ±1 in the third decimal place of activity coefficient. For reasons of brevity and because at the present juncture we wish to emphasize certain novel features calculable from these data, we shall not incorporate the results of these calculations in the present communication.

The Ionic Activity Coefficient and Dissociation of Water in Potassium and Sodium Bromide Solutions.—From the differences in electromotive force, $E_A - E_B$, of the hydroxide–salt and acid–salt cells, the ionic activity coefficient of water in the bromide solutions may be computed by a rearranged form of an equation from our earlier communication, namely[5]

$$\ln \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} = (E_A - E_B)\frac{NF}{RT} - \ln \frac{m''_H m''_{Br} m_{OH}}{m'_{Br}} + \ln K \qquad (8)$$

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[5] Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933); Equation (14).

K is the ionization constant of water, m''_{H} and m''_{Br} are the molalities of the hydrogen and bromide ions in the acid cells (B), and m'_{OH} and m'_{Br} those of the hydroxide and bromide ions in the hydroxide cells (A). The values K employed are given in Table III of our previous investigation.

We have not incorporated these values but have computed from them the dissociation of water m_{w} or $\sqrt{m_{\mathrm{H}}m_{\mathrm{OH}}}$ in the bromide solutions by means of the equation

$$m_{\mathrm{w}} = \sqrt{Ka_{\mathrm{H_2O}}/\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}} \tag{9}$$

Plots of these values are given in Fig. 1. At a given temperature, the top curve shows the effect of sodium bromide, the middle curve that of potassium bromide and the lower curve that of potassium chloride. The order of these effects at 25° verifies the earlier work of Harned and James.[6]

The Relative Partial Molal Heat Contents of the Halide Acids in Uni-univalent Halide Solutions.—In order to compute the partial molal heat content of the acid relative to its value in the 0.01 M solution of hydrobromic acid, use was made of equation (1) in which E_{B} is expressed as a function of the temperature. By employing the Gibbs–Helmholtz equation in the manner described by Harned and Hamer,[1a] $\overline{H} - \overline{H}_{0.01}$ of hydrobromic acid in potassium and sodium bromide solutions was computed. The values thus determined at the five degree temperature intervals have been expressed by the linear equation

$$\overline{H} - \overline{H}_{0.01} = (\overline{H} - \overline{H}_{0.01})_0 + \alpha t + \beta t^2 \tag{10}$$

in which $(\overline{H} - \overline{H}_{0.01})_0$, α and β are constants, and t is the temperature in degrees centigrade. Values of these constants are given in Table III.

TABLE III

THE RELATIVE PARTIAL MOLAL HEAT CONTENT OF HYDROBROMIC ACID IN POTASSIUM AND SODIUM BROMIDE SOLUTIONS $(\overline{H} - \overline{H}_{0.01})$

	I. KBr			II. NaBr		
μ	$(\overline{H} - \overline{H}_{0.01})_0$	α	$\beta \times 10^3$	$(\overline{H} - \overline{H}_{0.01})_0$	α	$\beta \times 10^3$
0.01	0	0	0	0	0	0
.02	38	0	0	42	0	0
.03	59	0.50	0.6	73	0.30	0.5
.04	66	0.70	0.8	71	.65	.70
.06	52	1.00	1	82	.83	.95
.11	79	2.41	2	83	2.21	1.9
.21	84	4.02	5	99	3.92	4.5
.51	78	7.46	12	181	7.38	11.5
1.01	170	9.47	15	347	9.07	14.0
1.51	167	12.10	21	553	10.08	17.0
2.01	268	13.31	23	691	12.09	18.0
3.01	422	14.92	25	1083	13.32	24.0

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[6] Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926); see also, Harned, *Trans. Am. Electrochem. Soc.*, **51**, 571 (1927); Taylor, "Treatise on Physical Chemistry," 2d edition, 1931, Vol. I, p. 808, D. Van Nostrand Co., New York.

These results as well as those of hydrochloric acid in potassium chloride and lithium chloride solutions recently determined by us and by Harned and Copson are the only reasonably accurate ones of this kind yet determined. Earlier attempts were made by Harned, who determined $(\overline{H} - \overline{H}_{0.1})$ of hydrochloric acid in potassium, sodium and lithium chloride solutions at 25°, and by Harned and Brumbaugh, who determined the same quantity in the alkaline earth chloride solutions. Although these results are of the right magnitude and the effects of the different salts are in the correct sequence, they are far less consistent than the more recently determined values. This is due in part to the reasons that they obtained results at only three temperatures, that the method of computation used by them was less accurate and that they employed calomel electrodes. The more recent results of Harned and Murphy are better but measurements were not made at a sufficient number of temperatures to render the determination of the temperature coefficients with equal precision. The vacuum technique recently employed has also greatly improved the consistency of the measurements.[7]

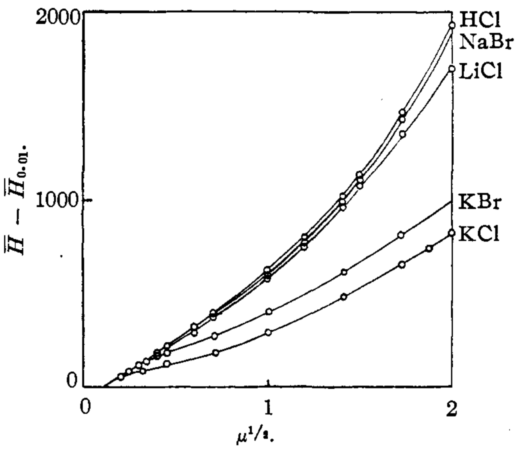

Fig. 2.—The relative partial molal heat content of hydrochloric and hydrobromic acid in their corresponding halide solutions.

In Fig. 2 we have plotted $(\overline{H} - \overline{H}_{0.01})$ of hydrochloric acid,[8] $(\overline{H} - \overline{H}_{0.01})$ of hydrochloric acid in potassium and lithium chloride solutions, and of hydrobromic acid in potassium and sodium bromide solutions at 25°. Although all the experimental points are not shown, the consistency of the results is encouraging. To illustrate, the curve for hydrochloric acid is of the same general form and agrees closely in the more dilute solutions with that of hydrochloric acid in lithium chloride solutions. Further, the formal agreement of these curves with that of hydrobromic acid in sodium bromide solutions should be noted. In fact, the whole system of graphs is consistent. As far as we are able to judge, the results are correct to within ±30 calories, which corresponds to an error in the temperature coefficient of electromotive force of ±0.004 mv. Very similar results are found at all temperatures which have been investigated.

(7) Harned, THIS JOURNAL, **42**, 1808 (1920); Harned and Brumbaugh, *ibid.*, **44**, 2729 (1922); Harned and Murphy, *ibid.*, **53**, 8 (1931).

(8) Harned and Ehlers, **55**, 2179 (1933).

The Total Heat of Ionization of Water in Halide Solutions.—The electromotive force, $E_B - E_A$, of the double cell

$$H_2 \mid MOH\ (0.01),\ MX\ (m) \mid AgX \mid Ag \mid AgX \mid MX\ (m),\ HX\ (0.01) \mid H_2$$

where M represents potassium or sodium and X represents chloride or bromide, is given by equation (8) in the form

$$(E_B - E_A) = -\frac{RT}{F}\ln\frac{\gamma_H\gamma_{OH}}{a_{H_2O}} - \frac{RT}{F}\ln\frac{m''_H m''_X m'_{OH}}{m'_X} + \frac{RT}{F}\ln K \qquad (11)$$

The cell reaction is simply that of the dissociation of water into ions. If this value of $(E_B - E_A)$ be substituted in the Gibbs–Helmholtz equation, we obtain

$$\Delta H = RT^2\frac{\mathrm{d}\ln \mathrm{K}}{\mathrm{d}T} - RT^2\left(\mathrm{d}\ln\frac{\gamma_H\gamma_{OH}}{a_{H_2O}}\Big/\mathrm{d}T\right) \qquad (12)$$

The first term on the right equals the heat content of ionization at zero salt concentration, ΔH_i, while the second term on the right is the partial molal heat content of the hydrogen and hydroxyl ions, $\Delta\overline{H}$, in the salt solution of a given strength. Thus, ΔH is the total heat content of ionization.

ΔH was computed from the electromotive forces by employing equations (1) and the Gibbs–Helmholtz equation. The equation thus derived is

$$\Delta H = -F(E_B - E_A)_{25} - FT(\mathrm{A}) + F[(\mathrm{A}) - 2T(\mathrm{B})](t - 25) + F(\mathrm{B})(t - 25)^2 \qquad (13)$$

where $(E_B - E_A)_{25}$ are the differences in electromotive forces at 25°, t is °C., (A) equals $(c - a)$, and (B) equals $(d - b)$. The values of ΔH thus obtained at the different salt molalities were then plotted as illustrated in Fig. 3. As far as may be determined from these results the plots are straight lines. Judging from other results of a similar nature, we do not regard this as strictly true but merely as a first approximation. The deviations of the points from the lines were within ±50 cal. with very few exceptions and considerably less than this for the majority of the results. The results were then least squared at constant temperatures using the equation for a straight line, namely

$$\Delta H = \Delta H_i + \omega\mu^{1/2} \qquad (14)$$

The constants of this equation are given in Table IV. These computations were made with three independent series of data which give us the total heat of ionization of water in potassium chloride and bromide solutions and in sodium bromide solutions. Consequently, each heat of ionization, ΔH_i, was determined independently. The average values of the three determinations are given in the table. The results are quite good since this determination involves the combined errors of both the acid and hydroxide cells. By the method of least squares, the equation for ΔH_i

$$\Delta H_i = 20{,}182 + 0.026117T - 0.078067T^2 + 0.0000079127T^3 \qquad (15)$$

was obtained. Deviations of the observed results from those computed by this equation are shown in the last column of the table.

Previously, we evaluated K directly and calculated ΔH_i from K. The values of ΔH_i obtained by the present method and given by equation (14) are in all probability of greater accuracy through the entire range of temperature than the former ones computed by the indirect method.

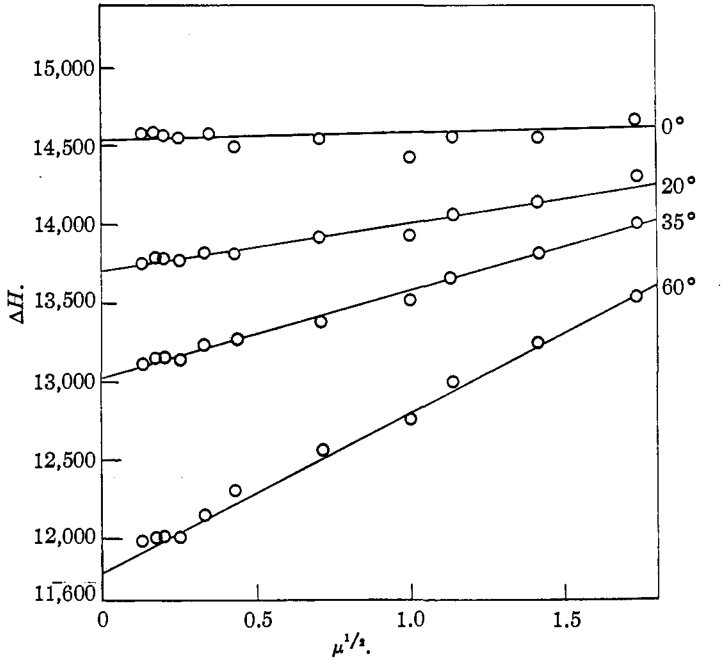

Fig. 3.—The total heat content of ionization of water in potassium bromide solutions.

From 0 to 30°, however, the agreement between the values obtained by both methods is excellent and the deviation is less than 0.3%. At 35, 40,

TABLE IV

CONSTANTS OF EQUATION (14) AND HEAT OF IONIZATION OF WATER IN CALORIES

	(1) KCl		(2) KBr		(3) NaBr			
t, °C.	ΔH_i	ω	ΔH_i	ω	ΔH_i	ω	ΔH_i(av.)	Δ^a
0	14,567	85.9	14,531	4.8	14,472	162.3	14,523	+5
5	14,365	143.3	14,326	71.8	14,283	217.8	14,325	−3
10	14,139	215.7	14,121	143.6	14,079	283.5	14,113	0
15	13,921	279.8	13,906	226.3	13,871	350.4	13,899	+1
20	13,699	345.3	13,693	303.7	13,660	471.1	13,684	−2
25	13,488	401.2	13,472	386.2	13,445	486.3	13,468	−5
30	13,235	485.5	13,242	472.9	13,226	556.9	13,234	+7
35	12,997	553.1	13,023	551.5	13,016	619.8	13,012	0
40	12,768	622.8	12,794	635.1	12,778	700.2	12,780	+2
45	12,526	694.9	12,569	715.0	12,548	744.7	12,538	+8
50	12,279	772.2	12,334	800.8	12,316	848.0	12,310	−2
55	12,030	843.2	12,084	896.3	12,079	927.6	12,064	+3
60	11,777	916.1	11,849	969.0	11,849	995.4	11,825	−4

[a] $\Delta = \Delta H_{i\,(\text{Eq. 15})} - \Delta H_{i\,(\text{av.})}$.

45, 50, 55, and 60° the deviations are 0.3, 0.4, 0.5, 0.6, 0.8, and 1%, respectively. The new values at these temperatures are in all cases lower than the previously determined ones. We may sum up by saying that our best values for ΔH_i are given by equation (14), and our best values for K are the observed ones in Table III of our former contribution.

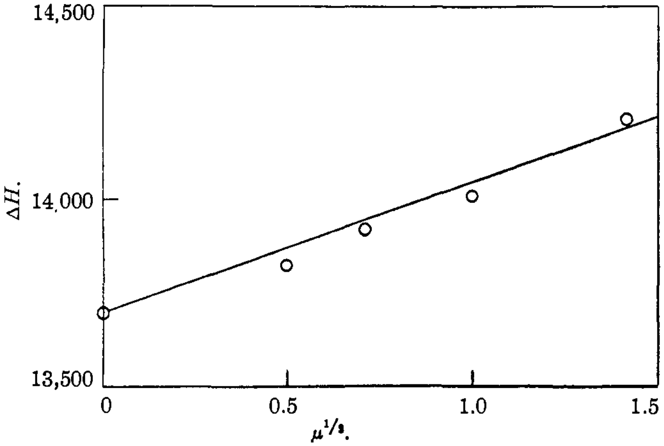

Fig. 4.—The total heat content of ionization of water in potassium chloride solutions from electromotive forces and calorimetric data.

In Fig. 4, we have drawn our plot of the total heat of ionization of water, ΔH, in potassium chloride solutions at 20° against $\mu^{1/2}$. Fortunately, the same quantity was determined directly by calorimetric measurements of the heat of neutralization of hydrochloric acid and potassium hydroxide by Richards and Rowe.[9] Their results are shown by the circles. At 0.25, 0.5, 1 and 2 μ, the agreement is within 53, 38, 30 and −24 cal., respectively. Their extrapolated value would be approximately 40 cal. lower than ours if they had employed a straight line function for the purposes of extrapolation. We consider this agreement which is within 0.3% as excellent confirmation of the method which we have employed to evaluate these quantities.[10]

As previously mentioned the partial molal heat contents, $\Delta\overline{H}$, of the hydrogen and hydroxide ions in potassium and sodium bromide and potassium chloride solutions may be computed by the equation

$$\Delta\overline{H} = \omega\sqrt{\mu}$$

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[9] Richards and Rowe, THIS JOURNAL, **44**, 684 (1922).

[10] Rossini [*Bur. Standards J. Research*, **6**, 847 (1931)] has recently given an equation for ΔH_i. Although the value computed by this equation agrees with ours at 15°, discrepancies occur at other temperatures. We believe that a considerable part of this lack of agreement is due to uncertainties in the values of $\overline{C}p_0$ of NaCl, HCl, and NaOH which were combined to compute ΔCp of the dissociation of water. Thus, Rossini computes 57.9 cal. for ΔCp at 18° while we find approximately 44 cal. The more recent values of $\overline{C}p_0$ of HCl and NaOH at 25° obtained by Gucker and Schminke [THIS JOURNAL, **54**, 1358 (1932); **55**, 1013 (1933)] give a value for ΔCp at 25°, 6 cal. lower than that of Rossini if we employ the value of $\overline{C}p_0$ of NaCl given by Rossini. It seems improbable that our values of ΔH_i can be in error to the above extent since we have obtained excellent agreement with calorimetric data at 20° at which temperature accurate heats of neutralization have been measured.

from the values of ω given in Table IV with an estimated accuracy in the middle range of temperatures of about ±30 cal. At the higher and lower temperatures the accuracy is not so good as this but is probably approximately ±50 cal. The evidence derived from these results indicates approximately that $\Delta\overline{H}$ varies linearly with $\mu^{1/2}$.

Summary

1. Measurements of the cells

$$H_2 \mid MOH\ (0.01),\ MBr\ (m) \mid AgBr \mid Ag$$
$$H_2 \mid HBr\ (0.01),\ MBr\ (m) \mid AgBr \mid Ag$$

in aqueous solution from 0 to 60° have been made. M is potassium or sodium.

2. The dissociation constant of water was computed from these results and the values obtained agreed with those previously obtained by us from cells containing hydrochloric acid and potassium chloride.

3. From these cells the values of the normal potential of the silver–silver bromide electrode, E_0, has been computed from 0 to 60° at 5° intervals. These are given by $E_0 = 0.07169 - 5.259 \times 10^{-4}(t - 25) - 3.022 \times 10^{-6}(t - 25)^2$ with an accuracy estimated to be ±0.1 mv.

4. Methods are indicated for computing the activity coefficient of hydrobromic acid and the ionic activity coefficient product of water in potassium and sodium bromide solutions.

5. The partial molal heat content of the acid in potassium and sodium bromide solutions from 0 to 60° has been computed and compared with that of hydrochloric acid in chloride solutions.

6. The total heat content of the dissociation of water as well as the relative partial molal heat content of the hydrogen and hydroxide ions in potassium chloride and bromide solutions and sodium bromide solutions from 0 to 60°, have been computed. Good agreement is found with calorimetric data from heats of neutralization at 20°.

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