[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Ionized Water in Lithium Bromide Solutions

BY HERBERT S. HARNED AND JOHN G. DONELSON[1]

From measurements of cells of the types

$$H_2 \mid MOH\ (m_0),\ MX\ (m) \mid AgX - Ag \qquad (A)$$
$$H_2 \mid HX\ (m_0),\ MX\ (m) \mid AgX - Ag \qquad (B)$$

the ionic activity coefficient and the dissociation of water in potassium,[2] sodium,[3] and lithium chloride[4] solutions, and potassium and sodium bromide[5] solutions have been determined over wide ranges of variation of salt concentrations and temperature. Since measurements of this kind with lithium bromide solutions have only been obtained at 25°,[6] we have extended the measurements over a wide temperature range. The technique of cell measurement has been improved particularly due to the more recent methods of preparing the silver–silver bromide electrodes.

From the measurements, we have computed: (1) the standard potential of the silver–silver bromide electrode from 0 to 50°; (2) the ionization constant of water from 0 to 40°; (3) the activity coefficient of hydrobromic acid in lithium bromide solutions; (4) the ionic activity coefficient of water in lithium bromide solutions; (5) the ionization of water in lithium bromide solutions; (6) the relative partial molal heat content of hydrobromic acid in lithium bromide solutions; (7) the heat of ionization of water in pure aqueous solution and lithium bromide solutions.

Experimental Results

The solutions were prepared from the highest grade analyzed chemicals which were further purified by suitable methods. Hydrobromic acid, twice distilled in an all glass apparatus, was diluted to approximately 0.05 *M* and analyzed gravimetrically. The results of analysis indicated that the strength of the solution was known with an accuracy of ±0.03%. A saturated lithium hydroxide solution in which the carbonate is insoluble was filtered. After standing some time in the absence of carbon dioxide sufficient solution was siphoned into freshly boiled distilled water to form an approximately 0.20 *M* solution. Titration by weight burets against the standard hydrobromic acid indicated an error in solution strength which was not greater than ±0.04%. Twice recrystallized lithium bromide was dissolved in conductivity water to form 0.5 and 5.5 *M* stock solutions. Gravimetric analyses of these solutions indicated that their strengths were known with an accuracy greater than ±0.05%.

All cell solutions were made from these solutions and freshly distilled water by weighing. They were freed from dissolved air by boiling *in vacuo*, and the appropriate correction for water loss made. Hydrogen at a pressure slightly greater than atmospheric was introduced into the solution flasks. The concentrations of the electrolytes were known to within ±0.05%.

Preliminary to the actual measurements, a further study was made of silver–silver bromide electrodes prepared by heating mixtures of silver bromate and oxide to 650°, and by the customary electrolytic method.[7,8] Harned, Keston and Donelson showed that the electromotive force of the thermal type electrode agreed to within about ±0.2 mv. with that of the electrolytic type at temperatures from 0 to 50°. Since we were not altogether satisfied by this result, further direct comparison was made between the two electrodes immersed in solutions of 0.05 *M* hydrobromic acid, 0.05 and 0.5 *M* potassium bromide. Differences in electromotive forces greater than 0.04 mv. rarely were found although the cells were measured over periods of time of twenty hours and over considerable ranges of temperature. These results gave us confidence in both types but because of ease in preparation the thermal type was selected.

The electromotive forces of the cells (A) and (B) in which M = Li at each concentration were measured in triplicate over two temperature ranges, 0 to 30° and 30 to 60°. Results above 50° were discarded since inconsistencies appeared which we regarded as unsatisfactory. Since the lowest temperature reached was 0.15° a small correction to the electromotive force was made so as

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[1] This communication contains material from a Dissertation presented to the Graduate School of Yale University by John G. Donelson in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1937.

[2] Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933).

[3] Harned and Mannweiler, *ibid.*, **57**, 1873 (1935).

[4] Harned and Copson, *ibid.*, **55**, 2206 (1933).

[5] Harned and Hamer, *ibid.*, **55**, 4496 (1933).

[6] Vance, *ibid.*, **55**, 4518 (1933).

[7] Keston, *ibid.*, **57**, 1671 (1935).

[8] Harned, Keston and Donelson, *ibid.*, **58**, 989 (1936).

to obtain them at 0°. The actual cells contained lithium hydroxide or hydrobromic acid at concentrations slightly different from 0.01 *M*. Suitable corrections to the electromotive forces were made so that all results are those of cells containing these electrolytes at exactly 0.01 *M*.

Values of the electromotive forces at round concentrations of lithium bromide were obtained from suitable graphs. These plots also served for smoothing the results both with respect to salt concentration and temperature. Since the original results were obtained at fifteen concentrations and eleven temperatures, they have been expressed for the purpose of brevity by the equations

$$E_A = E'_{25} + a'(t - 25) + b'(t - 25)^2 \quad (1)$$
$$E_B = E''_{25} + a''(t - 25) + b''(t - 25)^2 \quad (2)$$

the constants of which are given in Table I. The deviations from the smoothed observed results are given in the last two columns of the table. $\Delta_{\text{max.}}$ represents the maximum deviation of any single calculated result from that observed, and $\Delta_{\text{ave.}}$ represents the sum of the magnitudes of the eleven deviations divided by eleven. The constants were evaluated by the method of least squares. Since the expected error in measurements of this kind is of the order of ±0.05 mv., it is clear that the electromotive forces calculated by these equations express adequately the observed results.

TABLE I

ELECTROMOTIVE FORCES AT 25° OF THE CELLS H_2 | LiOH (0.01), LiBr (*m*) | AgBr – Ag AND CONSTANTS OF EQUATION (1)

μ	E'_{25}	$a' \times 10^4$	$b' \times 10^6$	$\Delta_{\text{max.}}$, mv.	$\Delta_{\text{av.}}$, mv.
0.02	0.89884	3.23	0.73	0.04	0.02
.03	.88080	2.64	.67	.05	.02
.04	.87017	2.30	.59	.03	.02
.06	.85660	1.87	.47	.03	.02
.08	.84751	1.59	.36	.04	.02
.11	.83770	1.28	.28	.04	.02
.21	.81797	0.63	.13	.05	.02
.31	.80589	.22	.08	.09	.03
.41	.79693	– .06	.12	.10	.03
.61	.78348	– .49	.18	.09	.03
1.01	.76468	–1.07	.03	.05	.02
1.51	.74769	–1.55	–.18	.07	.03
2.01	.73375	–1.93	–.26	.10	.04
3.01	.71019	–2.51	–.40	.27	.10

ELECTROMOTIVE FORCES AT 25° OF THE CELLS H_2 | HBr (0.01), LiBr (*m*) | AgBr – Ag AND CONSTANTS OF EQUATION (2)

μ	E''_{25}	$a'' \times 10^4$	$b'' \times 10^6$	$\Delta_{\text{max.}}$, mv.	$\Delta_{\text{av.}}$, mv.
0.01	0.31290	3.24	–3.28	0.01	0.00
.02	.29661	2.75	–3.12	.03	.02
.03	.28723	2.46	–2.92	.03	.02
.04	.28067	2.27	–2.92	.05	.02
.06	.27147	1.99	–2.85	.05	.02
.08	.26489	1.79	–2.77	.06	.03
.11	.25760	1.59	–2.85	.04	.02
.21	.24221	1.18	–2.86	.03	.02
.31	.23240	0.92	–2.88	.04	.02
.41	.22498	.72	–2.91	.05	.02
.61	.21344	.40	–2.88	.04	.02
1.01	.19603	.02	–2.89	.18	.06
1.51	.17868	– .29	–3.06	.14	.04
2.01	.16302	– .60	–2.63	.18	.08
3.01	.13585	–1.19	–2.83	.08	.03

The Standard Potential of the Silver–Silver Bromide Electrode from Measurements of Cell B.—The cells of type B are very well adapted for the determination of the standard potential of the silver–silver bromide electrode since the activity coefficient of hydrobromic acid in water is nearly the same as in lithium bromide solutions, and, consequently, no appreciable discontinuity is observed in passing from the salt solution to the acid solution. By combining the equation for the electromotive force of this cell with the limiting equation of Debye and Hückel, and rearranging terms, we obtain

$$E_B + \frac{RT}{F} \ln m''_H m''_{Br} - \frac{2R}{F} \frac{4.177 \times 10^6}{D^{3/2}\, T^{1/2}} \sqrt{\mu} = E_0 - \frac{RT}{F} \beta\mu \quad (3)^{9}$$

in which E_0 is the standard potential of the cell. The values of the physical constants employed are those given in the "International Critical Tables." The left side of this equation was computed and plotted against μ and its value, E_0, at $\mu = 0$ was obtained by graphical extrapolation. Wyman's values[10] of the dielectric constant *D*, computed by his equation

$$D = 78.54[1 - 0.00460(t - 25) + 0.0000088(t - 25)^2] \quad (4)$$

were used. The results obtained may be expressed to within ±0.05 by the empirical equation

$$E_0 = 0.07131 - 4.99 \times 10^{-4}(t - 25) - 3.45 \times 10^{-6}(t - 25)^2 \quad (5)$$

These values differ from those recently determined by Harned, Keston and Donelson[8] by amounts varying from 0.1 to 0.3 mv. Agreement to within about 0.05 mv. from 5 to 45° is obtained with the results of Owen and Foering.[11] Recent measurements have given closely agreeing results

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[9] Harned and Copson, THIS JOURNAL, **55**, 2206 (1933); equations (6) and (7).

[10] Wyman, *Phys. Rev.*, **35**, 623 (1930).

[11] Owen and Foering, THIS JOURNAL, **58**, 1575 (1936).

TABLE II

IONIZATION CONSTANT OF WATER FROM 0 TO 40°

	0	5	10	15	20	25	30	35	40
$K \times 10^{14}$	0.1132	0.1842	0.2921	0.4504	0.6806	1.007	1.467	2.088	2.891
%	+ .18	+ .43	− .07	+ .02	+ .06	0.0	+0.30	+0.14	+0.79

at 25°. Keston[7] and Harned, Keston and Donelson[8] obtained 0.0711 and 0.0710, respectively. Owen and Foering found 0.0713, which is the result we obtain. Jones and Baeckström[12] have recently obtained 0.0712. Since these results were obtained with different materials and electrodes, with different types of cells and by different investigators, this agreement is very satisfactory, particularly if we note that 0.07115 ± 0.00015 includes all these values.

The Ionization Constant of Water from 0 to 40°

The determination of the ionization constant of water from these results serves two purposes. It helps to establish the value of this quantity, particularly at temperatures below 10°, and by comparison with other determinations of the same quantity to confirm the accuracy of the results. The equation of the cells of Type A may be written

$$E_{\mathrm{A}} + \frac{RT}{F}\ln\frac{m_{\mathrm{Br}}}{m'_{\mathrm{OH}}} - E_0 = -\frac{RT}{F}\ln K - \frac{RT}{F}\ln \gamma_{\mathrm{H}}\gamma_{\mathrm{Br}} + \frac{RT}{F}\ln\frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}}{a_{\mathrm{H_2O}}} \quad (6)$$

Since the standard potential, E_0, has been evaluated, the left side of this equation is known. This quantity was plotted against μ and extrapolated to zero μ, at which point it equals $-(RT/F)\ln K$. From these values K was computed at temperatures from 0 to 50° at 5° intervals. The results obtained from 0 to 40° were found to agree very closely with those obtained by Harned and Mannweiler[3] from 0 to 35°, and also with Harned and Hamer[2] in this range of temperature with the exception of the result at 0 and 5°. Above 40°, the agreement was not so good, a fact which gives us less confidence in the results at 45 and 50°. In Table II our values of K are given with the per cent. deviation from Harned and Mannweiler's values from which it is apparent that the agreement is excellent from 0 to 35°.

The values at 0 and 5° are probably more exact than 0.115 and 0.186 obtained by Harned and Hamer.[2] Since an error of 0.1% in this quantity corresponds to an error of 0.05 mv. in the extrapolated function, we consider the agreement highly satisfactory.

The Activity Coefficient of Hydrobromic Acid

Since the equation for cell B may be written

$$2\ln\gamma_{\mathrm{HBr}} = -(F/RT)(E_{\mathrm{B}} - E_0) - \ln m''_{\mathrm{H}}m''_{\mathrm{Br}} \quad (7)$$

and E_0 is known, γ_{HBr} in 0.01 M hydrobromic acid, or in 0.01 M hydrobromic acid–lithium bromide mixtures may be computed from the results in Table II. The values of this quantity of 0.01 M hydrobromic acid solutions derived from the present results are 0.911, 0.910, 0.910, 0.909, 0.908, 0.907, 0.905, 0.904, 0.902 at 0, 5, 10, 15, 20, 25, 30, 35, and 40°, respectively. These agree to within ±0.001 with the values reported by Harned, Keston and Donelson and are probably correct to within this limit. In former computations, because of a less thorough knowledge of silver–silver bromide electrodes, somewhat lower values of this quantity were employed[3,5,6] in certain calculations. Future revision of the results should take this into account. For reasons of brevity, no table of activity coefficients of hydrobromic acid in lithium bromide solutions has been appended. This quantity readily may be computed by means of equations (2) and (7) and the data in Table I.

The Ionic Activity Coefficient Product of Water in Lithium Bromide Solutions

Values of the ionic activity coefficient product $\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}/a_{\mathrm{H_2O}}$ may be calculated by combining equations (6) and (7) to give

$$\ln\frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}}{a_{\mathrm{H_2O}}} = \frac{F}{RT}(E_{\mathrm{A}} - E_{\mathrm{B}}) - \ln\frac{m''_{\mathrm{H}}m''_{\mathrm{Br}}m'_{\mathrm{OH}}}{m'_{\mathrm{Br}}} + \ln K_{\mathrm{w}} \quad (8)$$

As an alternate method we may employ equation (6) in the form

$$\ln\frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}}{a_{\mathrm{H_2O}}} = \frac{F}{RT}(E_{\mathrm{A}} - E_0) + 2\ln\gamma_{\mathrm{HBr}} + \ln\frac{m'_{\mathrm{Br}}}{m'_{\mathrm{OH}}} + \ln K \quad (9)$$

As a test of consistency of method and a check on the calculation both equations (8) and (9) were employed to evaluate the ionic activity coefficient product with the result that excellent agreement between the two sets of results was obtained. Table III contains values of this quantity at some of the temperatures.

The result at 25° is in good agreement with that obtained by Vance[6] if the latter is corrected for

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[12] Jones and Baeckström, THIS JOURNAL, 56, 1524 (1934).

TABLE III

THE IONIC ACTIVITY COEFFICIENT PRODUCT OF WATER IN LITHIUM BROMIDE SOLUTIONS

	$\gamma_H\gamma_{OH}/a_{H_2O}$					
μ	0°	10°	20°	25°	30°	40°
0.02	0.778	0.777	0.771	0.769	0.770	0.767
.03	.736	.738	.733	.731	.733	.729
.04	.707	.709	.704	.702	.704	.698
.06	.659	.663	.660	.658	.659	.653
.08	.624	.630	.628	.627	.628	.622
.11	.590	.594	.592	.590	.591	.584
.21	.525	.528	.524	.522	.522	.513
.31	.492	.494	.489	.486	.484	.476
.41	.469	.469	.464	.461	.460	.451
.61	.442	.441	.435	.432	.430	.421
1.01	.426	.424	.416	.412	.409	.398
1.51	.442	.436	.425	.419	.415	.400
2.01	.473	.469	.455	.449	.443	.424
3.01	.553	.544	.527	.517	.509	.486

the new reference value, 0.907, of the activity coefficient of hydrobromic acid at 0.01 *M*. (Vance employed 0.904.) This correction adds 0.007 to log $\gamma_H\gamma_{OH}/a_{H_2O}$ at each concentration. A similar correction should be made for the potassium, sodium and lithium bromide results in Table III of the contribution of Harned and Mannweiler.[3] It is difficult to estimate the over-all error of these values of $\gamma_H\gamma_{OH}/a_{H_2O}$ since they involve the errors of both series of cells. In solutions of 0.02 to 1.01 μ, they are probably correct to within ±0.001, and at higher concentrations the accuracy is somewhat less than that but of the order of ±0.002.

The Heat of Ionization of Water.—The electromotive force of the combined cells A and B is given according to equation (8) by

$$E_B - E_A = -\frac{RT}{F}\ln\frac{\gamma_H\gamma_{OH}}{a_{H_2O}} - \frac{RT}{F}\ln\frac{m''_H m''_{Br} m'_{OH}}{m'_{Br}} + \frac{RT}{F}\ln K_w \quad (10)$$

If this value of the electromotive force be substituted in the Gibbs–Helmholtz equation, we obtain the expression

$$\Delta H = RT^2\frac{d\ln K}{dT} - RT^2\frac{d\ln(\gamma_H\gamma_{OH}/a_{H_2O})}{dT} \quad (11)$$

for the total heat of ionization. The first term on the right is the heat of ionization, ΔH_i, while the second term on the right is the relative partial molal heat content of the species designated in the lithium bromide solution.

By combining equations (1) and (2), we obtain

$$E = E_{25} + a(t-25) + b(t-25)^2 \quad (12)$$

where $E = E_B - E_A$, $E_{25} = E''_{25} - E'_{25}$, $a = a'' - a'$, and $b = b'' - b'$. Upon substitution in the Gibbs–Helmholtz equation, the equation for the computation of ΔH

$$\Delta H = -FE_{25} + aFT + F(2bT - a)(t-25) - bF(t-25)^2 \quad (13)$$

is readily obtained. These values of ΔH at each temperature were plotted against $\mu^{1/2}$ and the points were found to lie within ±50 cal. from a straight line drawn through them. Since an experimental error of this amount is to be expected, the results were treated by the method of least squares using the equation for the straight line, namely

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

In Table IV, the values of ΔH_i and ω are given at the temperatures designated.

TABLE IV

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

t	ΔH_i	ω
0	14,440	289
5	14,360	222
10	14,160	262
15	13,940	305
20	13,720	350
25	13,480	397
30	13,230	447
35	12,990	496
40	12,730	546

With the exception of the result at 0°, these values of ΔH_i check within 30 cal. the results obtained by Harned and Hamer[5] using the same method with cells containing hydrochloric acid, potassium chloride and hydroxide.

The Relative Partial Molal Heat Content of Hydrobromic Acid in Lithium Bromide Solutions.—From the electromotive forces of the cells of type B, $\overline{H} - \overline{H}_{0.01}$, the partial molal heat content of hydrobromic acid at 0.01 *M* in lithium bromide

TABLE V

CONSTANTS OF EQUATION (15)

μ	$(\overline{H} - \overline{H}_{0.01})_0$	α	β
0.01	0	0	0
.02	−27.06	2.52	0.0046
.03	−52.92	4.16	.0076
.04	−52.01	4.91	.0090
.06	−45.51	5.42	.0099
.08	−31.25	5.42	.0099
.11	0.62	5.42	.0099
.21	58.70	5.42	.0099
.31	119.96	5.42	.0099
.41	153.59	5.42	.0099
.61	227.25	5.42	.0099
1.01	340.04	5.42	.0099
1.51	520.21	5.42	.0099
2.01	709.53	5.42	.0099
3.01	1143.73	5.42	.0099

solutions has been calculated relative to its value in 0.01 *M* hydrobromic acid solution. These results have been expressed in a brief form by recording in Table V the constants of the equation

$$\overline{H} - \overline{H}_{0.01} = (\overline{H} - \overline{H}_{0.01})_0 + \alpha t + \beta t^2 \qquad (15)$$

$(\overline{H} - \overline{H}_{0.01})_0$, α and β are functions of E''_{25}, a'' and b'' of equation (2).

The range of validity of equation (15) is from 0 to 40°. In the intermediate range of temperatures, 5 to 35° inclusive, the accuracy is of the order of ±30 cal.

Summary

1. Measurements of the cells

$$H_2 \mid LiOH\ (0.01),\ LiBr\ (m) \mid AgBr - Ag$$
$$H_2 \mid HBr\ (0.01),\ LiBr\ (m) \mid AgBr - Ag$$

have been made at 5° intervals from 0 to 50° inclusive.

2. From these results, the ionization constant of water, the standard electromotive force of the silver–silver bromide electrode, the activity coefficient, the relative partial molal heat content of hydrobromic acid in lithium bromide solutions, the ionic activity coefficient product and heat of ionization of water in lithium bromide solutions have been computed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization of Acetic Acid in Aqueous Sodium Chloride Solutions from 0 to 40°

BY HERBERT S. HARNED AND F. C. HICKEY, O.P.[1]

Harned and Robinson[2] and Harned and Owen[3] have shown that the ionization constant and the actual ionization of an acid in a salt solution may be determined from electromotive force measurements of unbuffered cells without liquid junctions of the type

$$H_2 \mid HAc\ (M),\ MCl\ (m) \mid AgCl - Ag - AgCl \mid HCl\ (0.01) \mid H_2 \qquad (1)$$

Harned and Owen[3] developed the thermodynamic theory of these cells, the details of the computation, and applied the method to measurements at 25° of acetic acid in sodium chloride solutions, and of formic acid in potassium and sodium chloride solutions. Likewise, Harned and Murphy[4] investigated the ionization of acetic acid in sodium and potassium chloride solutions at 15, 25 and 35°.

Although these cells are the best for the determination of the ionization of the acid in salt solutions, they are not so suitable for the determination of ionization constants as the buffered type

$$H_2 \mid HAc\ (M),\ MAc\ (m),\ MCl\ (m) \mid AgCl - Ag \qquad (2)$$

From electromotive forces of the latter type, Harned and Ehlers[5,6] obtained accurate values of the ionization constant of acetic acid at temperatures from 0 to 60°. Since these values were at our disposal, we decided to make a more thorough and accurate investigation of aqueous acetic acid solutions containing sodium chloride. To this end, measurements of unbuffered cells were made with an improved technique from 0 to 40°, inclusive, at 5° intervals. The concentration of acetic acid was varied from 0.1 to 0.5 *M* and the salt concentration from 0.05 to 3 *M*. From these results, the ionization and activity coefficient of the acid in the salt solutions were determined, and the temperature variation of ionization at all salt concentrations investigated. Further, the heat of ionization of acetic acid and its variation as a function of salt concentration has been computed for the first time.

Experimental Results

Since the experimental procedure was essentially the same as that previously used by others,[5] a brief summary is sufficient. (1) A vacuum technique was employed which served to free all cell solutions from dissolved gases. The previous work with unbuffered cells was carried out with solutions containing some dissolved air. (2) All chemicals were purified carefully. (3) The acetic acid content of the solutions was known with an accuracy of ±0.1%. The sodium chloride content was known with considerably greater accuracy. (4) The hydrogen electrodes were of platinum foil type. The silver–silver

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[1] This contribution contains material from a dissertation presented by Frederick C. Hickey to the Graduate School of Yale University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1937.

[2] Harned and Robinson, THIS JOURNAL, **50**, 3157 (1928).

[3] Harned and Owen, *ibid.*, **52**, 5079 (1930).

[4] Harned and Murphy, *ibid.*, **53**, 8 (1931).

[5] Harned and Ehlers, *ibid.*, **54**, 1350 (1932).

[6] Harned and Ehlers, *ibid.*, **55**, 652 (1933).