

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

## THE IONIC ACTIVITY COEFFICIENT PRODUCT AND DISSOCIATION OF WATER IN BARIUM CHLORIDE SOLUTIONS AT 25°

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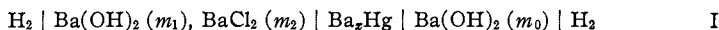
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The equilibrium constant,  $K$ , of the dissociation of water is given by

$$K = \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} m_H m_{OH} \quad (1)$$

where the “ $\gamma$ 's” and “ $m$ 's” are the activity coefficients and molal concentrations of the ions denoted by subscripts, and  $a_{H_2O}$  is the activity of the water. The quantities  $\gamma_H \gamma_{OH} / a_{H_2O}$  and, subsequently,  $m_H m_{OH}$  have been evaluated from suitable electromotive force measurements for the cases of aqueous cesium,<sup>2</sup> potassium, sodium<sup>3</sup> and lithium chloride<sup>4</sup> solutions and potassium and sodium bromide<sup>5</sup> solutions in earlier investigations. The present study is concerned with the evaluation of these important quantities in aqueous solutions of barium chloride by two methods which involve somewhat different cells and computations.

**The Determination of the Ionic Activity Coefficient and Dissociation of Water in Aqueous Barium Chloride Solutions by Method I.**—The electromotive forces at 25° of the cells



are given by the equation

$$E = 0.08873 \log \frac{\gamma_{(m_1+m_2)}}{\gamma_{m_0}} \frac{\sqrt[3]{m_1^2(m_1+m_2)}}{m_0} + 0.05915 \log \frac{p_{m_0}}{p_{m_1+m_2}} \quad (2)$$

$\gamma_{m_1+m_2}$  is the activity coefficient of barium hydroxide,  $\sqrt[3]{\gamma_{Ba} \gamma_{OH}^2}$  in the solution of barium chloride, and  $\gamma_{m_0}$  is the same quantity at a concentration  $m_0$  in the aqueous solution on the right of the cell which we have employed as reference and kept at a constant concentration of 0.05  $M$ .  $p_{m_0}$  and  $p_{m_1+m_2}$  are the vapor pressures of water in the reference solution and in the hydroxide-chloride solutions, respectively. From previous results,<sup>6</sup> we know that  $\gamma_{m_0}$  equals 0.527, and, consequently, from measurements of the above cells we may determine  $\gamma_{(m_1+m_2)}$  if we evaluate the term in equation (2) which contains the ratio of the vapor pressures.

The technique employed in these measurements has been described by

<sup>1</sup> This paper was constructed from material forming part of a dissertation presented to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1932.

<sup>2</sup> Harned and Schupp, *THIS JOURNAL*, **52**, 3892 (1930).

<sup>3</sup> Harned, *ibid.*, **47**, 930 (1925).

<sup>4</sup> Harned and Swindells, *ibid.*, **48**, 126 (1926).

<sup>5</sup> Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).

<sup>6</sup> Harned and Mason, *THIS JOURNAL*, **54**, 1439 (1932).

Harned and Mason. It is desirable to record the electromotive forces for cells containing barium hydroxide at the same concentration on both sides. Since the solutions were boiled *in vacuo*, it was necessary to apply a small correction in order to accomplish this result. A concentration of  $m_0$  and  $m_1$  equal to 0.05 was found to be convenient.

Table I contains the experimental results and the computed values of the vapor pressure ratios as well as the values of  $\gamma_{m_1 + m_2}$ . The second and third columns contain the observed electromotive forces and those read from a smooth curve drawn through them, respectively. The consistency of the results is thus seen to be good considering the difficulties of measurement of cells of this type. The fourth column contains the ratios of the vapor pressure of pure water to that of a barium chloride solution of concentration ( $m_2 + 0.05$ ) which we employed to compute  $\gamma$ . These were computed from the activity coefficients of barium chloride by the method described by Harned.<sup>7</sup> The activity coefficients employed in evaluating the constants of Harned's equation were obtained from the electromotive force measurements of Lucasse.<sup>8</sup> The equation

$$\log \gamma = -\beta m \alpha' + \alpha m \quad (3)$$

was found to give satisfactory agreement with the observed activity coefficients when  $\alpha$ ,  $\alpha'$  and  $\beta$  were taken to be 0.435, 0.381 and 0.835, respectively, and, consequently, the vapor pressure ratios may be obtained by the equation

$$\ln \frac{p_0}{p_m} = \frac{m}{55.5} \left[ \nu + \frac{2.303 \alpha \nu m}{2} - \frac{2.303 \nu \beta \alpha'}{\alpha' + 1} m \alpha' \right] \quad (4)$$

By rearrangement of equation (2) we obtain

$$\log \gamma_{m_1 + m_2} = \frac{E}{0.08873} + \log \gamma_0 m_0 - \frac{1}{3} \log m_0^2 (m_0 + m_2) - \frac{2}{3} \log \frac{p_0}{p_{(m_0 + m_2)}} \quad (5)$$

by means of which the values of  $\gamma_{(m_1 + m_2)}$  given in the fifth and sixth columns of Table I were computed. We note at this juncture that the values of  $p_{m_0 + m_2}$  are those of pure aqueous barium chloride solutions at the concentration ( $m_0 + m_2$ ). These have been used in place of the vapor pressures of the solutions containing  $m_0$  barium hydroxide and  $m$  barium chloride. This procedure causes no large error since the last term on the right of equation (5) is small at low concentrations, and since at high concentrations there is present many times more barium chloride than hydroxide.

In Fig. 1, the values of the activity coefficient of barium hydroxide in barium chloride solutions as well as in pure aqueous solution have been

<sup>7</sup> See Taylor, "Treatise on Physical Chemistry," first ed., D. Van Nostrand Co., New York, 1924, Vol. II, pp. 751-753.

<sup>8</sup> Lucasse, THIS JOURNAL, 47, 743 (1925); Harned, *ibid.*, 48, 326 (1926); see table in Taylor, "Treatise on Physical Chemistry," second ed., D. Van Nostrand Co., New York, 1930, Vol. I, p. 772, Table IX.

TABLE I  
THE ACTIVITY COEFFICIENT OF BARIUM HYDROXIDE IN AQUEOUS SOLUTIONS OF BARIUM  
CHLORIDE AT 25° FROM MEASUREMENTS OF THE CELLS

$$\text{H}_2 \mid \text{Ba}(\text{OH})_2(0.05), \text{BaCl}_2(m_2) \mid \text{Ba}_2\text{Hg} \mid \text{Ba}(\text{OH})_2(0.05) \mid \text{H}_2$$

$m_2$	$E_{\text{exp.}}$	$E_{\text{curve}}$	$\frac{p_0}{p_{m_0+m_2}}$	$\gamma_{(m_1+m_2)}$ (obs.)	$\gamma_{(m_1+m_2)}$ (curve)
0.0	0.0000	0.0000	1.0015	(0.527)	(0.527)
.02096	.0014	.0014	1.0032	.488	.488
.03076	.0024	.0024	1.0036	.477	.476
.04881	.0034	.0033	1.0044	.458	.457
.05148	.0034	.0034	1.0046	.454	.454
.07219	.0041	.0042	1.0054	.434	.435
.09175	.0046	.0046	1.0063	.418	.418
.09427	.0046	.0047	1.0065	.416	.417
.1044	.0048	.0049	1.0068	.409	.410
.2012	.0063	.0064	1.0111	.360	.361
.2974	.0075	.0072	1.0155	.332	.330
.4025	.0081	.0080	1.0206	.308	.307
.4926	.0086	.0084	1.0253	.293	.291
.4979	.0081	.0084	1.0255	.288	.290
.5933	.0087	.0088	1.0308	.276	.277
.6981	.0091	.0091	1.0370	.265	.265
.7928	.0091	.0094	1.0512	.252	.254
.8686	.0098	.0096	1.0525	.249	.248
.9091	.0101	.0099	1.0531	.247	.246
1.0145	.0103	.0102	1.0549	.240	.239
1.2530	.0102	.0109	1.0779	.220	.224

plotted against the square root of the ionic strength. We note that the values of  $\gamma$  in the salt solutions are higher than in the pure aqueous solutions.

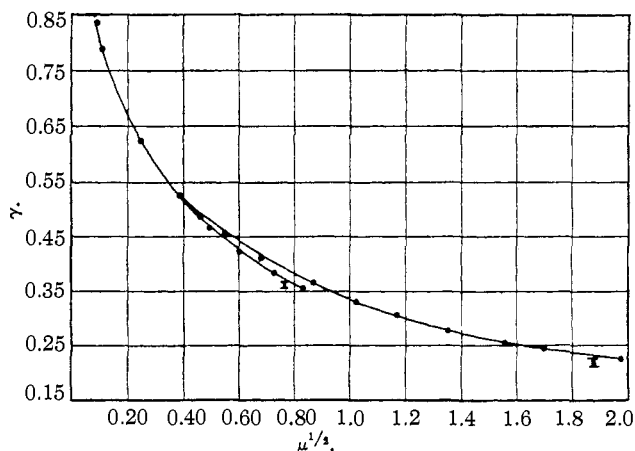


Fig. 1.—The activity coefficient of barium hydroxide in water and in aqueous barium chloride solutions: I, water; II, barium chloride solutions.

To obtain  $\gamma_H\gamma_{OH}/a_{H_2O}$  in the barium chloride solution by this method, it is necessary to know both the activity coefficient of hydrochloric acid at zero concentration, and the activity coefficient of barium hydroxide at zero concentration in a barium chloride solution of  $m$  molal concentration. Further, the activity coefficient of barium chloride in aqueous solution at a concentration  $m$ , and the activity of water in this solution are required. Thus, all the necessary quantities will be known in the same solution and from them  $\gamma_{Ba}\gamma_{OH}^2/a_{H_2O}^2$ ,  $\gamma_H\gamma_{Cl}$  and  $\gamma_{Ba}\gamma_{Cl}^2$  may be computed. From these quantities  $\gamma_H\gamma_{OH}/a_{H_2O}$  may be readily computed by the equation

$$K_\gamma = \frac{\gamma_H\gamma_{OH}}{a_{H_2O}} = \sqrt{\frac{\gamma_{Ba}\gamma_{OH}^2\gamma_H^2\gamma_{Cl}^2}{a_{H_2O}^2\gamma_{Ba}\gamma_{Cl}^2}} \quad (6)$$

The evaluation of  $\gamma_{Ba}\gamma_{OH}^2/a_{H_2O}^2$ , to be denoted  $\gamma''_{Ba(OH)_2}$  and  $\gamma_H\gamma_{Cl}$  in the pure barium chloride solutions was carried out by a graphical method which is illustrated by Figs. 2 and 3. The results are given in Table II.

TABLE II  
THE CALCULATION OF THE IONIC ACTIVITY COEFFICIENT PRODUCT OF WATER IN BARIUM CHLORIDE SOLUTIONS

$\mu$	$\gamma''_{Ba(OH)_2}$			$\gamma_{HCl}$			$\gamma_{BaCl_2}$	$K_\gamma$
	(1)	(2)	(3)	(4)	(5)	(6)		
0.01	0.809	...	0.809	0.902	0.902	0.891	0.795 <sup>a</sup>	0.815
.05	.652	...	.649	.829	.821	.818	.670	.638
.1	.570	...	.574	.796	.778	.776	.589	.577
.2	.489	0.498	.506	.766	.741	.739	.526	.515
.5	.390	.404	.411	.757	.704	.702	.454	.415
.7	.357	.373	.378	.771	.700	.699	.430	.403
1.0	...	.339	.343	.810	.700	.699	.411	.373
1.5	...	.299	.301	.903	.714	.713	.395	.338
2.0	...	.276	.279	1.019	.738	.737	.392	.327
2.5	...	.261	.264	1.151	.777	.776	.394	.331
3.0	...	.253	.256	1.320	.826	.825	.398	.351
3.5	...	.245	.248	1.520	.881	.879	.403 <sup>a</sup>	.373
4.0	...	.236	.238	1.762	.935	.934	.406 <sup>a</sup>	.392

(1)  $\gamma''_{Ba(OH)_2}$  in aqueous solution. (2)  $\gamma''_{Ba(OH)_2}$  (0.05) in barium chloride solutions. (3)  $\gamma''_{Ba(OH)_2}$  (0.00) in barium chloride solutions. (4)  $\gamma_{HCl}$  in aqueous solutions. (5)  $\gamma_{HCl}$  (0.01) in barium chloride solutions. (6)  $\gamma_{HCl}$  (0.00) in barium chloride solutions.

<sup>a</sup> Extrapolated points.

In Fig. 2, the values of  $\log \gamma''$  are plotted against the concentration of barium hydroxide. The curve represents the activity coefficient of the hydroxide in aqueous solution and was obtained from the values in the second column of Table II and the points represented by the filled in circles are those taken from the third column. To extrapolate these latter results to zero hydroxide concentration, use was made of the law of the linear variation of the logarithm of the activity coefficient which states that at con-

stant total ionic strength  $\log \gamma$  varies linearly with the concentration of the substance whose activity coefficient is  $\gamma$ . Thus, by drawing straight lines from the curve through the point at the same total concentration of electrolyte, the extrapolation may be effected. Unfortunately, the saturated solution of barium hydroxide is at too low a concentration to accomplish this at all ionic strengths. Consequently, we have resorted to the expedient

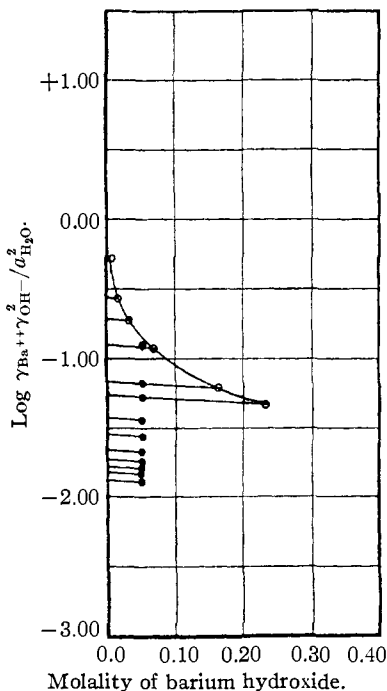
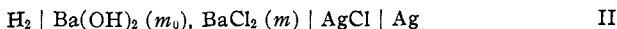


Fig. 2.—Plots of  $\log \gamma''$  against  $m_1$  at constant total ionic strength.

The last column contains  $K_\gamma$  computed from the results in the fourth, seventh and eighth columns by equation (6).

**The Evaluation of  $K_\gamma$  by the Second Method.**—The electromotive forces of the cells at 25°



are given by the equation

$$E = E_0 - 0.05915 \log \gamma_{\text{H}} \gamma_{\text{Cl}} m_{\text{H}} m_{\text{Cl}} \quad (7)$$

and the dissociation constant,  $K_w$ , of water is

$$K_w = \frac{\gamma_{\text{H}} \gamma_{\text{OH}} m_{\text{H}} m_{\text{OH}}}{a_{\text{H}_2\text{O}}} \quad (8)$$

<sup>9</sup> Randall and Young, *THIS JOURNAL*, 50, 989 (1928).

<sup>10</sup> Harned and Robinson, *ibid.*, 50, 3157 (1928).

<sup>11</sup> Lucasse, *ibid.*, 47, 743 (1925).

of drawing a system of parallel lines from the point to the ordinate, and reading from the curve the results given in the fourth column of the table. Figure 3 shows an exactly similar plot of the  $\log \gamma_{\text{HCl}}$  against the concentration of the acid. The curve is drawn through the points taken from the computations and data of Randall and Young<sup>9</sup> given in the fifth column of the table. The points near the ordinate through which the straight lines at constant ionic strength are drawn represent the activity coefficients of hydrochloric acid in barium chloride solutions determined by Harned and Robinson<sup>10</sup> and given in the sixth column. In this case, the parallel nature of such plots is very apparent. The extrapolated values of  $\gamma_{\text{HCl}}$  are given in the seventh column. The values of the activity coefficient of barium chloride in aqueous solution given in the eighth column were those computed from the amalgam cell measurements of Lucasse.<sup>11</sup>

By eliminating  $m_H$  from these equations, rearranging terms, and substituting 0.2224 for the normal potential of hydrochloric acid,  $E_0$ ,<sup>12</sup> we obtain

$$\left[ E - 0.2224 + 0.05915 \log \frac{m}{m_0} \right] = -0.05915 \log K_w a_{H_2O} - 0.05915 \log \frac{\gamma_H \gamma_{Cl}}{\gamma_H \gamma_{OH}} \quad (9)$$

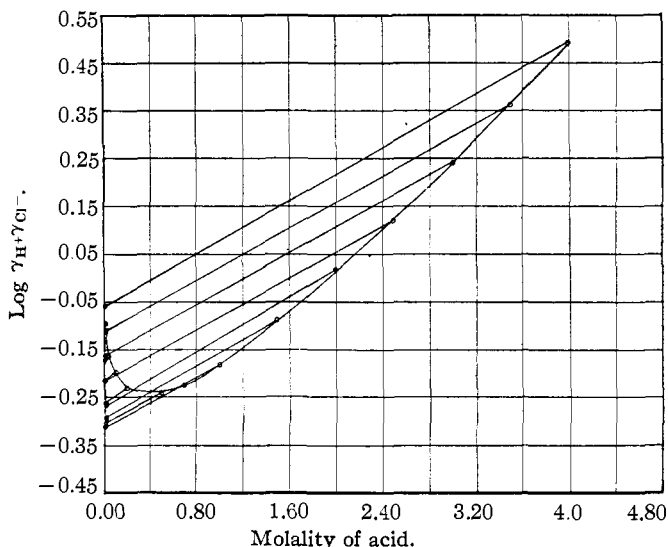


Fig. 3.—Plots of  $\log \gamma_H \gamma_{Cl}$  against the acid molality in barium chloride solutions of a constant total ionic strength.

The actual measurements of the cells are given in Table III. The number of cells at the concentrations designated in the first three columns which were measured is given in column four and the difference in millivolts in column five. Column six contains the mean values of the electromotive forces and column seven the value of the left side of equation (9).

In order to obtain results at convenient concentrations, the values of the left side of equation (9) were plotted against  $\mu$  as shown in Fig. 4. Since  $a_{H_2O}$ ,  $\gamma_H \gamma_{Cl}$  and  $\gamma_H \gamma_{OH}$  equal unity at zero ionic strength, the value of the ordinate at zero  $\mu$  equals  $-0.05915 \log K_w$ . Since the present results were not carried out at sufficiently low concentrations to obtain an accurate extrapolation, we have drawn the curve to 0.8280, corresponding to a value of  $K_w$  equal to  $1.005 \times 10^{-14}$ .<sup>13</sup>

The second column of Table IV contains the values of  $E - E_0 + 0.05915$

<sup>12</sup> Roberts, *THIS JOURNAL*, **52**, 3877 (1930); Harned and Schupp, Jr., *ibid.*, **52**, 3892 (1930); Harned and Ehlers, *ibid.*, **54**, 1350 (1932).

<sup>13</sup> This value, which was obtained by Lewis and Randall ["Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 434] is very close to the value recently obtained in this Laboratory and will be employed until the more recent results can be published.

TABLE III  
THE ELECTROMOTIVE FORCES OF THE CELLS  
 $\text{H}_2 \mid \text{Ba}(\text{OH})_2 (m_0), \text{BaCl}_2 (m) \mid \text{AgCl} \mid \text{Ag}, \text{at } 25^\circ$

$m_0$	$m$	$\mu$	No. of cells	$\Delta(\text{mv.})$	$E$	$\left[ E - E_0 + 0.05915 \log \frac{m}{m_0} \right]$
0.05058	0.01067	0.1838	2	0.01	1.0883	0.8259
.05043	.02027	.2121	2	.15	1.0715	.8257
.05088	.02023	.2133	2	.05	1.0719	.8258
.05052	.02125	.2153	2	.5	1.0702	.8256
.05019	.03148	.2450	2	.06	1.0602	.8258
.05149	.03156	.2491	2	.07	1.0607	.8257
.05092	.04988	.3024	2	.03	1.0483	.8254
.05014	.07174	.3656	2	.03	1.0381	.8249
.05027	.09620	.4394	2	.06	1.0302	.8245
.05088	.1028	.4610	2	.04	1.0287	.8244
.04912	.1912	.7210	2	.06	1.0095	.8220
.05073	.2053	.7681	2	.06	1.0090	.8225
.05049	.3012	1.0551	2	.00	0.9972	.8207
.05040	.4071	1.3725	2	.01	.9875	.8188
.05020	.5120	1.6569	2	.01	.9808	.8176
.05105	.6115	1.9877	2	.01	.9741	.8155
.05026	.6863	2.2097	2	.04	.9696	.8144
.05007	.7855	2.5067	2	.01	.9647	.8130
.05096	.8145	2.5964	2	.07	.9638	.8126
.05017	.9017	2.8556	2	.06	.9593	.8111
.05030	.9124	2.8881	2	.06	.9587	.8107
.05081	1.0079	3.1761	2	.03	.9554	.8097
.05092	1.2444	3.8808	2	.15	.9460	.8072
.04920	1.3171	4.1041	1	..	.9455	.8067

TABLE IV  
CALCULATION OF  $K_\gamma$  FROM THE DATA IN TABLE III, AND VALUES OF  $m_w$ ,  $\gamma_{\text{H}}\gamma_{\text{OH}}$ ,  
AND  $\sqrt{\gamma_{\text{H}}\gamma_{\text{OH}}}$  COMPUTED AT ROUND CONCENTRATION

$\mu$	$\left[ E - E_0 + 0.05915 \log \frac{m}{m_0} \right] (1)$	$K_\gamma$		$m_w \times 10^7$		$\gamma_{\text{H}}\gamma_{\text{OH}}$		$\gamma$	
		(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
0.01	0.8279	0.815	0.792	1.11	1.13	0.815	0.793	0.903	0.890
.05	.8276	.638	.660	1.26	1.23	.637	.659	.798	.813
.1	.8272	.577	.582	1.32	1.31	.576	.581	.759	.762
.2	.8264	.515	.514	1.40	1.40	.513	.512	.716	.717
.5	.8242	.415	.426	1.56	1.54	.412	.423	.642	.651
.7	.8229	.403	.401	1.58	1.58	.398	.397	.630	.630
1.0	.8210	.373	.373	1.64	1.64	.367	.368	.606	.607
1.5	.8180	.338	.345	1.72	1.71	.330	.337	.575	.581
2.0	.8154	.327	.335	1.75	1.73	.316	.325	.562	.570
2.5	.8129	.331	.335	1.74	1.73	.317	.321	.563	.566
3.0	.8104	.351	.343	1.69	1.71	.333	.325	.577	.570
3.5	.8085	.373	.361	1.64	1.67	.349	.339	.591	.582
4.0	.8069	.392	.384	1.60	1.62	.362	.355	.602	.596

(1) Method I. (2) Method II.

$\log (m/m_0)$  read from the plot of Fig. 4.  $K_\gamma$  may now be readily calculated as can be seen by rearranging (9) as follows

$$\log K_\gamma = \log \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} = \frac{E - E_0 + 0.05915 \log (m/m_0)}{0.05915} + \log K + \log \gamma_H \gamma_{Cl} \quad (9a)$$

$\gamma_H \gamma_{Cl}$  is the activity coefficient product of hydrochloric acid in the barium chloride solutions or the square of  $\gamma_{HCl}$  given in the seventh column of Table II. The values of  $K_\gamma$  thus obtained are given in the fourth column

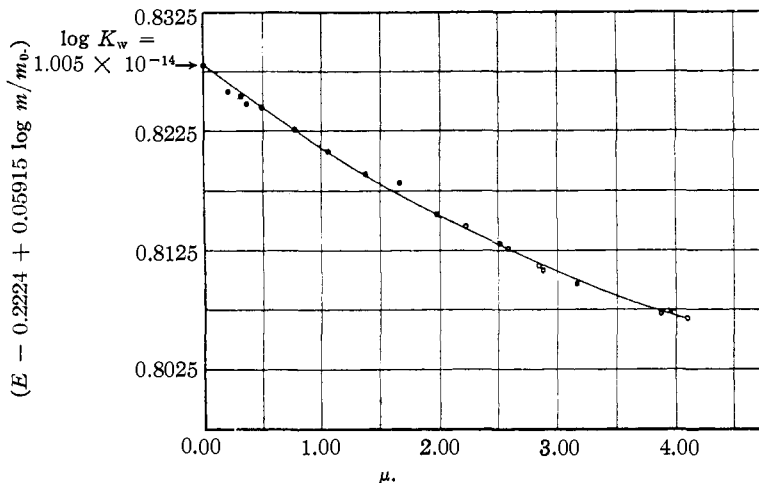


Fig. 4.—Plot of the values of the left side of equation (9) against ionic strength.

of Table IV. In the third column the values of  $K_\gamma$  obtained by the first method are given for purposes of comparison. Both series of values are

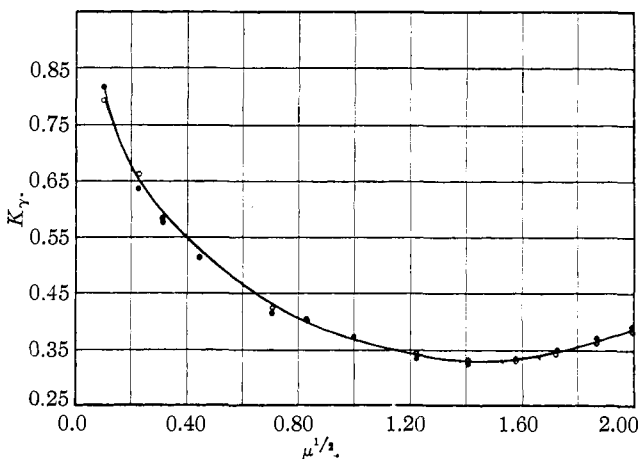


Fig. 5.—Plot of the ionic activity coefficient product, of water,  $K_\gamma$ , in barium chloride solutions: ●, method I; ○, method II.

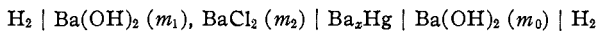
plotted against  $\mu^{1/2}$  in Fig. 5. The agreement is excellent when we consider the difficulties involved in measuring cells containing barium amalgam.



The fifth and sixth columns of Table IV contain the values of  $m_w = m_H = m_{OH}$  computed by equation (8). The next two columns contain the values of  $\gamma_H \gamma_{OH}$  computed by multiplying  $K_\gamma$  by  $a_{H_2O}$ , and the last two columns  $\gamma$  or  $\sqrt{\gamma_H \gamma_{OH}}$ . The values of  $\gamma$  obtained by the two methods rarely differ by more than 1% or  $\pm 0.5\%$  from their mean.

### Summary

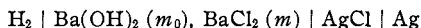
1. Measurements of the electromotive forces of the cells



have been made, and the activity coefficient of barium hydroxide in aqueous barium chloride solutions has been computed.

2. From these and other suitable results previously determined, the ionic activity coefficient of water in barium chloride solutions has been computed.

3. The cells



have been measured and the ionic activity coefficient of water has been computed from the results, and compared with the values obtained from the amalgam cells.

4. The dissociation of water in barium chloride solutions increases, passes through a maximum and then decreases with increasing ionic strength, a behavior similar to that observed in solutions of the alkaline halides. The maximum dissociation occurs at  $1.5\mu$ .

NEW HAVEN, CONNECTICUT

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[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY, CHEMICAL LABORATORY OF THE BAVARIAN ACADEMY OF SCIENCES, MUNICH, GERMANY, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH, PITTSBURGH, PENNSYLVANIA]

## INTEGRAL HEATS OF DILUTION AND RELATIVE PARTIAL MOLAL HEAT CONTENTS OF AQUEOUS SODIUM BROMIDE AND POTASSIUM BROMIDE SOLUTIONS AT TWENTY-FIVE DEGREES\*

BY H. HAMMERSCHMID AND A. L. ROBINSON

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### Introduction

The measurement of heats of dilution of strong electrolytes at concentrations low enough to permit an unambiguous extrapolation of the results to infinite dilution makes possible a combination of such measurements with data obtained at higher concentrations to calculate the relative partial molal heat contents of the components of the solutions. These are the partial molal heat contents referred to the molal heat contents of

\* Communication Number 37 on Thermochemical Investigations by E. Lange and co-workers.