After that time, all but 5 ml. of the solution was removed, and replaced by the 225 ml. of the original solution, the mixture shaken for twenty-four hours, the supernatant liquid removed and the process repeated once more. Knowing the volumes used and the bromide concentrations in the supernatant liquids, the amounts of bromide in the precipitate could be calculated. The results are given in Table IV.

TABLE IV

REPEATED ADDITION OF BROMIDE TO A YEAR OLD AgCl

Step	Period of shaking	$Br^- \times 10^4$ A	$Br^- \times 10^4$ B	Millimoles Br^- in precipitate A	Millimoles Br^- in precipitate B	K' A	K' B
1	24 hrs.	2.72	4.97	0.439	0.39	110	107
2	24 hrs.	3.58	6.46	.858	.74	175	164
3	24 hrs.	5.15	8.98	1.24	1.04	187	173
4	24 hrs.	6.42	10.92	1.60	1.29	205	185
5	24 hrs.	7.58	12.85	2.07	1.75	249	233
6	3 weeks	6.33	10.95	2.13	1.84	310	292
7	24 hrs.	10.37		2.39		212	
8	24 hrs.	11.03		2.64		247	

The values of K' obtained after each successive step of shaking for twenty-four hours increase gradually, showing that the kinetics of the reaction after each new addition of bromide are of the same order. The values obtained after three weeks of shaking are higher as the system tends to approach equilibrium.

Summary

The rapid formation of mixed crystals upon shaking of a solution containing chloride and bromide with well aged silver chloride cannot be attributed to a normal recrystallization of the solid by way of the solution. Experimentally, it has been shown that the rate of distribution increases with increasing ratio of bromide in solution to silver in the precipitate. When this ratio is very small the rate of distribution of bromide is determined by the speed of recrystallization of the silver chloride by way of the solution. The great initial speed of distribution found when the ratio of bromide to silver is larger is attributed to a direct attack upon the structure of the original particles. It is assumed that the bromide rapidly taken up in the surface layer by exchange causes a disrupture of the silver chloride lattice, exposing fresh surface to attack.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionic Activity Coefficient Product and Ionization of Water in Barium Chloride Solutions from 0 to 50°

BY HERBERT S. HARNED AND CHARLES G. GEARY[1]

Electromotive forces of the cells

$$H_2 \mid Ba(OH)_2\ (0.005).\ BaCl_2\ (m_2) \mid AgCl\text{–}Ag \qquad (A)$$

$$H_2 \mid HCl\ (0.01).\ BaCl_2\ (m_1) \mid AgCl\text{–}Ag \qquad (B)$$

have been obtained over the range 0 to 50°, and 0.03 to 3μ. Following the methods employed in this Laboratory,[2-6] we have computed: (1) the standard potential of the silver–silver chloride electrode from 0 to 50°; (2) the ionization constant of water from 0 to 50°; (3) the activity coefficient of hydrochloric acid in barium chloride solutions; (4) the ionic activity coefficient of water in barium chloride solutions; (5) the ionization of water in barium chloride solutions; (6) the relative partial molal heat content of hydrochloric acid in barium chloride solutions; (7) the heat of ionization of water in aqueous solution and barium chloride solutions.

Experimental Results

The cells were run in triplicate and in two series at 5° intervals, from 0 to 25°, and from 25 to 50°, so that at 25°, there were six checks of the electrodes used, and two on the composition of each solution. Reproducibility was in general better than ±0.05 mv., while the maximum deviation was about ±0.1 mv.

The measurements were corrected to one atmosphere of hydrogen by means of a special table prepared for this purpose. The vapor pressures of the solutions were determined (assuming the effects of 0.01 M hydrochloric acid and 0.005 M

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(1) This contribution contains material from a dissertation presented by Charles G. Geary 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 Hamer, THIS JOURNAL, **55**, 2194 (1933); *ibid.*, **55**, 4496 (1933).

(3) Harned and Copson, *ibid.*, **55**, 4496 (1933).

(4) Harned and Mannweiler, *ibid.*, **57**, 1873 (1935).

(5) Harned and Donelson, *ibid.*, **59**, 1280 (1937).

(6) Harned and Mason, *ibid.*, **54**, 3112 (1932).

barium hydroxide to be negligible) from the electromotive force measurements on barium chloride solutions, by the method of Harned,[7] using the data of Newton and Tippetts.[8] The calculated values were in good agreement with those measured directly by Newton and Tippetts[9] and with the activities over the entire range as calculated directly from the data of Tammann.[10]

The ratio p/p_0 was approximately constant throughout the temperature range, so that the vapor pressures of the solutions could be interpolated directly from a table of vapor pressures of water, by using the approximate relation $1/T_0 = 1/T + k$, or, less accurately, $t = t_0 + k'$ where t is the temperature of the solution, t_0 that temperature at which water will have the same vapor pressure, and k and k' are constant for each composition over the whole range from 0 to 50°.

The electromotive forces were corrected to round temperatures by plotting on a large scale against T. They were also corrected to suitable round concentrations by the usual methods.

TABLE I

ELECTROMOTIVE FORCES AT 25° OF CELLS (A)

CONSTANTS OF EQUATION (1)

μ	E'_{25}	$a' \times 10^6$	$b' \times 10^6$	$\Delta_{\text{max.}}$, mv.	$\Delta_{\text{av.}}$, mv.
0.03	1.04983	170	0.52	0.11	0.04
.05	1.02783	92	.51	.07	.04
.07	1.01597	50	.48	.07	.03
.1	1.00444	12	.40	.10	.04
.2	0.98339	− 64	.32	.09	.04
.5	.95620	−154	.0	.09	.04
.7	.94599	−186	.0	.07	.03
1	.93482	−216	.0	.08	.02
2	.91156	−284	.0	.16	.04
3	.89603	−330	− .4	.28	.05

ELECTROMOTIVE FORCES AT 25° OF CELLS (B)

CONSTANTS OF EQUATION (2)

μ	E''_{25}	$a'' \times 10^6$	$b'' \times 10^6$	$\Delta_{\text{max.}}$, mv.	$\Delta_{\text{av.}}$, mv.
0.01	0.46411	178	−3.20	0.10	0.02
.02	.45273	142	−3.15	.05	.02
.03	.44529	117	−3.12	.05	.02
.05	.43539	85	−3.12	.06	.01
.07	.42864	65	−3.01	.05	.02
.1	.42135	42	−2.96	.07	.02
.2	.40686	0	−2.70	.04	.01
.5	.38659	− 52	−2.33	.08	.02
.7	.37854	− 74	−2.30	.07	.02
1	.36936	− 97	−2.20	.07	.03
2	.34844	−142	−2.00	.05	.02
3	.33280	−174	−1.63	.07	.02

Since the original results were so numerous, they have been expressed by the equations

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

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

the constants of which are given in Table I. In the last two columns of the table are given the maximum and average absolute values, $\Delta_{\text{max.}}$ and $\Delta_{\text{av.}}$, of the deviations between the observed and calculated results. The ranges of validity of the equations are from 0 to 50°.

The Standard Potential of the Silver–Silver Chloride Electrode from Cells of Type B

The extrapolation of the measurements of the acid cells was made by a modification of the usual method. The equation for the electromotive forces of these cells, E_B, may be expressed

$$E_B = E_0 - k'T \log 0.01\ (2m_1 + 0.01) - 2kT \log \frac{\gamma_T}{\gamma_{25}} - 2k'T \log \gamma_{25} \qquad (3)$$

where k' equals $2.3026R/F$ or 0.00019841, and γ is the activity coefficient of hydrochloric acid in the barium chloride solution. Using an empirical equation suggested by the theory of Debye and Hückel, $\log \gamma_{25}$ may be expressed by

$$\log \gamma_{25} = -\frac{u\sqrt{\mu}}{1 + A\sqrt{\mu}} + B\mu \qquad (4)$$

in which the isothermal constants u, A, and B may be evaluated approximately as 0.5, 1.4 and 0.0533, respectively. Combining equations (3) and (4) and rearranging, we obtain

$$E_B + k'T \log \frac{0.01(2m_1 + 0.01)}{(0.01)^2} + 2k'T \left[\frac{-0.5\sqrt{\mu}}{1 + 1.4\sqrt{\mu}} + 0.0533\mu\right] = E_0 - k'T \log (0.01)^2 - 2k'T \log \frac{\gamma_T}{\gamma_{25}} \qquad (5)$$

Plotting the left side of this equation against μ, the intercept becomes $E_0 + 4\ k'T$.

This method worked most favorably at 25° where the plot for low concentrations was almost horizontal. At the lower temperatures, there was a slight curvature upward but the extrapolation could still be made with confidence. At the higher temperatures, the plot showed considerable curvature downward and the extrapolation was more uncertain. But here also the points showed a tendency to scatter so no attempt was made to refine the procedure. The values of E_0 obtained by this procedure differed from those obtained by Harned and Ehlers[11] from the cell containing

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(7) Harned, THIS JOURNAL, **44**, 252 (1922).

(8) Newton and Tippetts, *ibid.*, **56**, 1675 (1934).

(9) Newton and Tippetts, *ibid.*, **58**, 280 (1936).

(10) Tammann, *Ann. Physik*, **24**, 549 (1885).

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

hydrochloric acid only by the amounts: −0.07, −0.13, −0.09, −0.06, −0.03, +0.01, + 0.05, + 0.1, + 0.15, + 0.18, + 0.29 millivolts at 0, 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50°, respectively. This agreement is good since the present extrapolation involves an uncertainty due to the discontinuity in composition of the solutions. In the subsequent calculations, the values of Harned and Ehlers were employed.

The Ionization Constant of Water

Since the equation of cell (A) may be written,

$$E_A - E_0 + \frac{RT}{F}\ln\frac{2m_2}{0.01} = \frac{RT}{NF}\ln\frac{\gamma_H\gamma_{OH}}{a_{H_2O}} - \frac{RT}{NF}\ln\gamma_H\gamma_{Cl} - \frac{RT}{NF}\ln K \quad (6)$$

K may be determined by plotting the left side against the ionic strength.[2-5] The values obtained are contained in Table II. Along with these are given the independent determinations of K obtained by Harned and Hamer,[2] Harned and Mannweiler,[4] and Harned and Donelson[5] at the temperatures designated. The first result seems to be somewhat high at the lower temperatures as indicated by parentheses while our values of K from 0 to 10° inclusive are slightly low. At temperatures from 20 to 50° inclusive, the agreement is excellent with the exception of the result at 40° obtained from silver–silver bromide electrodes. In the next to last column, the mean of the results with exception of those in parentheses is given. These values differ only a little from the mean of all the results. This is indicated by the numbers in parentheses following these values which represent the change which occurs in the last two places upon averaging all the results. In the last column is given the total deviation of the values of K calculated to millivolts, which is a good method of showing the accuracy. At the three lower temperatures, the spread is such as to show that the results in parentheses are in error. If these be discarded, the maximum of the total deviation is about 0.1 mv. representing an error of ± 0.05 mv. or 0.2%.

TABLE II

THE IONIZATION CONSTANT OF WATER FROM 0 TO 50°

$K \times 10^4$

t	Ref. 2,3	Ref. 4	Ref. 5	This research	Mean	Mv.
0	(0.115)	0.1134	0.1132	(0.1125)	0.1133(35)	0.50
5	(.186)	.1850	.1842	(.1834)	.1846(48)	.33
10	(.293)	.2919	.2921	(.2890)	.2920(15)	.33
15	(.452)	.4505	.4504	.4500	.4503(07)	.11
20	.681	.6806	.6806	.6815	.6809	.03
25	1.008	1.007	1.007	1.009	1.008	.05
30	1.471	1.470	1.467	1.466	1.468	.09
35	2.088	2.091	2.088	2.090	2.089	.03
40	2.916	2.914	(2.891)	2.920	2.917(10)	.26
45	4.016	4.017	....	4.023	4.018	.04
50	5.476	5.482	....	5.465	5.474	.07

The Activity Coefficient of Hydrochloric Acid in Barium Chloride Solutions

Since the equation for the cell B is

$$\log\gamma = \frac{E_0 - E_B}{2k'T} + \frac{1}{2}\log(0.01)(2m_1 + 0.01) \quad (7)$$

the activity coefficient of hydrochloric acid at 0.01 M in barium chloride solutions may be obtained from the electromotive forces, E_B. The reference values of γ at 0.01 M derived from these results are 0.906, 0.906, 0.905, 0.905, 0.905, 0.905, 0.903, 0.903, 0.902, 0.901, and 0.900 at 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, and 50°, respectively. These agree with similar values of Harned and Ehlers[11] to within 0.001. For the sake of brevity, we have not included a table of these activity coefficients. They may be computed readily by equations (2) and (7) and the data in Table I.

The Ionization and Ionic Activity Coefficient of Water in Barium Chloride Solutions

The ionic activity coefficient product of water, $\gamma_H\gamma_{OH}/a_{H_2O}$, was calculated by means of equation (6). The value of K determined by us, not the mean value as given in Table II, was employed. This procedure was adopted to render the present calculations more self-consistent. The values of the activity coefficient of hydrochloric acid at 0.01 M in the salt solution were corrected slightly so that the values used in the calculation referred to zero concentration of the acid. Rather than construct a table of these results, we have resorted to a briefer method of expression. The thermodynamic equation for the ionization of water is

$$K = \frac{\gamma_H\gamma_{OH}}{a_{H_2O}}m_H m_{OH} = \frac{\gamma_H\gamma_{OH}}{a_{H_2O}}m_w^2 \quad (8)$$

TABLE III

THE IONIZATION OF WATER IN BARIUM CHLORIDE SOLUTIONS

Constants of Equation (9)

μ	$A' \times 10^5$	$B' \times 10^5$	$C' \times 10^5$
0.03	81929	76.91	0.353
.05	81724	75.73	.372
.07	81587	75.11	.336
.1	81420	74.16	.316
.2	81042	71.84	.288
.5	80509	68.38	.228
.7	80322	67.56	.220
1	80142	67.00	.216
2	79939	64.82	.168
3	79960	63.11	.096

Knowing $\gamma_H\gamma_{OH}/a_{H_2O}$ and K, m_w was calculated, and it was found that this quantity may be expressed within the experimental accuracy by the equation

$$-0.00039684\, T \log m_w = A' + B'(t - 25) + C'(t - 25)^2 \quad (9)$$

The values of A', B' and C' are given in Table III.

The Relative Partial Molal Heat Content of 0.01 *M* Hydrochloric Acid in Barium Chloride Solutions

From the values of the electromotive forces of cells of type (B), $\overline{H}-\overline{H}_{0.01}$, the partial molal heat content of 0.01 *M* hydrochloric acid in barium chloride solutions relative to its value in 0.01 *M* hydrochloric acid solution has been calculated. The results, valid from 0 to 40°, have been expressed by the equation

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

the constants of which are given in Table IV. $(\overline{H} - \overline{H}_{0.01})_0$. α and β are functions of E''_{25}, α'' and β'' of equation (2).

TABLE IV

CONSTANTS OF EQUATION (10)

μ	$(\overline{H} - \overline{H}_{0.01})_0$	α	$\beta \times 10^3$
0.02	−18	0.76	1.4
.03	−35	1.39	2.5
.05	−53	2.39	4.4
.07	−69	3.15	5.8
.1	−85	4.18	7.6
.2	−95	6.30	11.5
.5	−98	10.33	18.9
.7	−92	11.97	21.9
1	−67	13.85	25.4
2	71	17.25	31.6
3	69	18.77	34.4

The Heat of Ionization of Water in Barium Chloride Solutions

The total heat of ionization of water may be obtained from the equation

$$\Delta H = RT^2 \frac{d \ln m_w^2}{dT} \quad (11)$$

which upon combination with equation (9) and differentiation becomes

$$\Delta H = F[(A' - 298.1B' + (298.1)^2C') - C'T^2] = (\Delta H)_0 - C''T^2 \quad (12)$$

Values of $(\Delta H)_0$ and C'' at the designated concentrations are given in Table V.

TABLE V

THE TOTAL HEAT OF IONIZATION OF WATER

Constants of Equation: $\Delta H = (\Delta H)_0 - C''T^2$

μ	$(\Delta H)_0$	$C'' \times 10^4$
0.03	20839	814
.05	21262	858
.07	20535	775
.10	20152	729
.20	19651	664
0.5	18536	526
0.7	18385	507
1	18301	498
2	17402	387
3	16067	221

To evaluate the heat of ionization at zero salt concentration, an extrapolation was made using the limiting law of the Debye and Hückel theory for the relative partial molal heat content. The results were in close agreement with those derived from similar cells containing potassium,[2] sodium chlorides[4] and lithium bromide[5] except at 0°. To illustrate, we obtained 14,230, 13,950, 13,730, 13,490, 13,180, 12,940 and 12,680, at 10, 15, 20, 25, 30, 35 and 40°, respectively. Harned and Donelson[5] obtained 14,160, 13,940, 13,720, 13,480, 13,230, 12,980, and 12,730 at these temperatures. The agreement is good considering all the difficulties in obtaining heat data from free energy measurements, and the fact that the above two determinations require the measurements of four cells.

Summary

1. The electromotive forces of the cells

H_2 | $Ba(OH)_2$ (0.005). $BaCl_2$ (m) | AgCl–Ag
H_2 | HCl (0.01). $BaCl_2$ (m) | AgCl–Ag

have been measured at 5° intervals from 0 to 50°.

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

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