These curves illustrate a point of considerable interest. In solutions between the limits of 0.01 and 0.05 *M*, the activity coefficients of both hydroxides are the same within the limits of accuracy of these experiments. Above this concentration, the activity coefficients of the sodium hydroxide lie below that of the potassium hydroxide. This is opposite to the behavior of the simple sodium and potassium salts. For example, sodium chloride and sulfate possess greater activity coefficients than the corresponding potassium salts.

The author wishes to express his appreciation for the valuable assistance of Dr. Walter W. Lucasse at times when the measurements were made.

Summary

1. Measurements of the cells, $H_2 \mid NaOH(m_2) \mid Na_xHg \mid NaOH(m_1) \mid H_2$, at 25° have been presented.

2. From these the activity coefficient of sodium hydroxide as well as the vapor pressures of the solutions have been computed.

3. The interesting fact is noted that the activity coefficient of potassium hydroxide is greater than that of sodium hydroxide at concentrations above 0.05 *M*.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

THE ACTIVITY COEFFICIENT OF SODIUM HYDROXIDE IN SODIUM CHLORIDE SOLUTIONS

BY HERBERT S. HARNED

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In the preceding article (Activity Coefficient of Sodium Hydroxide in Aqueous Solutions[1]) the technique was described whereby the activity coefficient of sodium hydroxide in aqueous solutions was determined by measurements of cells of the type,

$$H_2 \mid NaOH(m_2) \mid Na_xHg \mid NaOH(m_1) \mid H_2$$

In the present investigation, the activity coefficients of sodium hydroxide at 0.01 and 0.1 *M* concentrations in solutions of sodium chloride at various strengths have been determined by similar measurements of the cells,

$$H_2 \mid NaOH(m_1), NaCl(m) \mid Na_xHg \mid NaOH\ (m_1) \mid H_2$$

This is a continuation of similar studies carried out by Harned,[2] and by Harned and Brumbaugh[3] who measured the activity coefficients of hydrochloric acid in solutions of alkali metal and alkali-earth metal chlorides. The two principal objects of these investigations, besides the actual meas-

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[1] THIS JOURNAL, **47**, 676 (1925).

[2] Harned, *ibid.*, **38**, 1986 (1916); **42**, 1808 (1920).

[3] Harned and Brumbaugh, *ibid.*, **44**, 2730 (1922).

urements of these activity coefficients, are to approach, as nearly as is possible from electromotive-force measurements, the values for the individual ion-activity coefficients, and at the same time measure by direct thermodynamic methods the activity coefficient and ionic concentration of water in salt solutions of various types.

As shown in the preceding article, the electromotive forces of cells of the above type are related to the activities of the electrolyte by the equation

$$E + 0.02568\ ln \frac{a_{H_2O(s)}}{a_{H_2O(m_1)}} = 0.05915 \log \frac{a_{Na(s)}\ a_{OH(s)}}{a_{Na(m_1)}\ a_{OH(m_1)}}$$

$$= 0.05915 \log \frac{\gamma_{Na(s)}\ \gamma_{OH(s)}\ (m + m_1)}{\gamma_{Na(m_1)}\ \gamma_{OH(m_1)} m_1}$$

On introducing the vapor-pressure ratio for the water activity ratio, we obtain

$$E + 0.02568\ ln \frac{p_s}{p_1} = 0.05915 \log \frac{\gamma_{Na(s)}\ \gamma_{OH(s)}\ (m + m_1)}{\gamma_{Na(m_1)}\ \gamma_{OH(m_1)}\ m_1} \qquad (1)$$

where the subscript "*s*" refers to the solution. Thus from a knowledge of $\gamma_{Na(m_1)}\ \gamma_{OH(m_1)}$ in the pure hydroxide at a concentration m_1, $\gamma_{Na(s)}\ \gamma_{OH(s)}$ in the salt solution may be computed and, finally, the square root of this quantity or the activity coefficient. As in the determination in pure aqueous sodium hydroxide solutions, it is important to observe that in order to obtain this activity coefficient a knowledge of the activities of the water in the salt solutions and pure hydroxide solution is necessary.

The measurements were carried out in a manner identical with that described in the preceding article. The solution containing both the hydroxide and salt was pre-

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS

H_2 | NaOH(m_2), NaCl(m) | Na_xHg | NaOH(m_1) | H_2

m_2	m	m_1	E
	1. m_1 and m_2 approximately 0.1 M		
0.1029	0.2040	0.1024	0.02324
.1012	.5019	.1023	.03743
.1034	1.024	.1029	.05222
.1029	2.041	.1029	.06884
.1041	3.099	.1013	.08186
	2. m_1 and m_2 approximately 0.01 M		
.01041	0.0205	.01026	.02426
.01023	.0503	.01029	.03768
.01024	.05035	.01039	.03747
.01011	.1006	.01013	.05192
.01029	.1011	.01025	.05178
.01017	.2028	.01023	.06522
.01012	.5045	.01020	.08380
.01021	1.017	.01012	.09987
.01014	2.021	.01027	.11579
.01027	3.071	.01008	.12877

pared in the following manner. The desired quantity of salt was weighed out and introduced into the dried solution-vessel A, which was then evacuated. Sufficient hydroxide solution of a strength m_1 was next introduced to bring the salt concentration to the desired strength. This solution was then weighed, boiled in a vacuum and reweighed and its strength computed. One series of results was obtained with solutions containing sodium hydroxide at approximately 0.01 M concentration and another with hydroxide at approximately 0.1 M. The observed electromotive forces are given in Table I. The temperature was 25°. The first three columns contain the concentrations. The amalgam strength was approximately 0.01%.

The first step in the calculation of the activity coefficients is to correct the observed electromotive forces to exactly 0.1 M and 0.01 M hydroxide concentrations. This may be done without appreciable error by assuming that in a salt solution of a given strength the activity coefficient of the hydroxide does not vary between the hydroxide concentrations given in the table and these round concentrations. The total correction will then be given by

$$E = 0.1183 \log \frac{m_1}{0.1} - 0.05915 \log \frac{m_2\ (m + m_2)}{0.1\ (m + 0.1)} \qquad (2)$$

for the 0.1 M series and

$$E = 0.1183 \log \frac{m_1}{0.01} - 0.05915 \log \frac{m_2\ (m + m_2)}{0.01\ (m + 0.01)} \qquad (3)$$

for the 0.01 M series. In Table II are given these corrected electromotive forces; m is the salt concentration. The second column contains the positive correction given by the first numbers on the right of these equations, the third column the negative correction given by the second mem-

TABLE II

ELECTROMOTIVE FORCES OF THE CELLS, H_2 | $NaOH(m_2)$, $NaCl(m)$ | Na_xHg | $NaOH(m_1)$ | H_2, CORRECTED TO ROUND CONCENTRATIONS OF SODIUM HYDROXIDE

1 c	2 $(\text{Corr.})_1$	3 $(\text{Corr.})_2$	4 E
	$m_1 = m_2 = 0.1\ M$		
0.204	0.001183	−0.000888	0.02353
.5019	.001180	− .000305	.03830
1.024	.00142	− .000749	.05289
2.041	.00142	− .000929	.06931
3.099	.00066	− .001053	.08146
	$m_1 = m_2 = 0.01\ M$		
0.0205	.00130	− .001408	.02415
.0503	.00142	− .000680	.03842
.05035	.00194	− .000721	.03869
.1006	.00066	− .000296	.05228
.1011	.00128	− .000791	.05217
.2028	.00118	− .000426	.06597
.5045	.00101	− .000305	.08450
1.017	.00059	− .000532	.09993
2.021	.00136	− .000355	.11679
3.071	.00041	− .000680	.12850

bers and the fourth column the electromotive forces obtained by adding these corrections to the values in the fourth column of Table I.

In order to obtain the activity coefficient, it is first necessary to obtain $ln\ ps/p_1$ and then 0.02568 $ln\ ps/p_1$ and subtract this value from the electromotive forces. The activity coefficient of sodium chloride at 25° is given by the equation

$$\log \gamma = -0.286\ m^{0.407} + 0.1m \qquad (4)$$

with considerable accuracy within the concentration range under consideration, and $ln\ p_0/p$ by the equation

$$ln\ p_0/p\ \frac{m}{55.5}\ [2 + 0.2303\ m - 0.3811\ m^{0.407}] \qquad (5)$$

where p is the vapor pressure of the solution and p_0 the vapor pressure of pure water.[4] These calculations were made and from them $ln\ ps/p_{0.01}$ was calculated, and then 0.02468 $ln\ ps/p_{0.01}$ at round concentrations. These values were then plotted carefully, and from this plot the corrections for the electromotive forces at the desired total concentrations read off. It was assumed that the vapor pressures of the solutions containing both m sodium chloride and m_1 sodium hydroxide were the same as those of a sodium chloride solution of a strength $(m + m_1)$. This assumption in the present instance introduces no error as great as the error of the electromotive-force measurements. The results of this calculation and the final values for the activity coefficients are given in Table III. The elec-

TABLE III

THE ACTIVITY COEFFICIENT OF SODIUM HYDROXIDE IN SODIUM CHLORIDE SOLUTIONS

0.1 M NaOH

NaCl m	E	0.02568 $ln\ ps/p_1$	E + 0.02568 $ln\ ps/p_1$	γ
0.000	0.00000	0.000000	0.00000	0.775
.2040	.02353	− .000168	.02336	.700
.5019	.03830	− .000424	.03788	.660
1.024	.05289	− .000880	.05201	.636
2.041	.06931	− .001872	.06724	.620
3.099	.08146	− .003043	.07842	.6305
		0.01 M NaOH		
0.0000	.00000	.000000	.00000	.920
.0205	.02415	− .000016	.02413	.847
.0503	.03842	− .000040	.03838	.791
.05035	.03869	− .000040	.03863	.794
.1006	.05228	− .000084	.05220	.764
.1011	.05217	− .000084	.05209	.761
.2028	.06597	− .000169	.06580	.718
.5045	.08450	− .000423	.08408	.659
1.017	.09993	− .000845	.09909	.625
2.021	.11679	− .001832	.11496	.605
3.071	.12850	− .002980	.12552	.603

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[4] Harned, THIS JOURNAL, **44,** 252 (1922).

tromotive forces in the second column are taken from Col. 4 of Table II. The other column headings are self-explanatory. The values of γ were computed by Equation 1.

Discussion

In Fig. 1 the activity coefficients of sodium hydroxide in the chloride solutions as well as those of the pure aqueous sodium hydroxide solutions have been plotted against the total salt concentrations. The plot of the 0.1 *M* hydroxide series passes through a minimum at about 2 *M* concentration. The plot of the 0.01 *M* series does not pass through a minimum below 2.5 *M* but probably does at or somewhat above this concentration. This behavior conforms with that of other strong uni-univalent electrolytes in solutions of salts.[5]

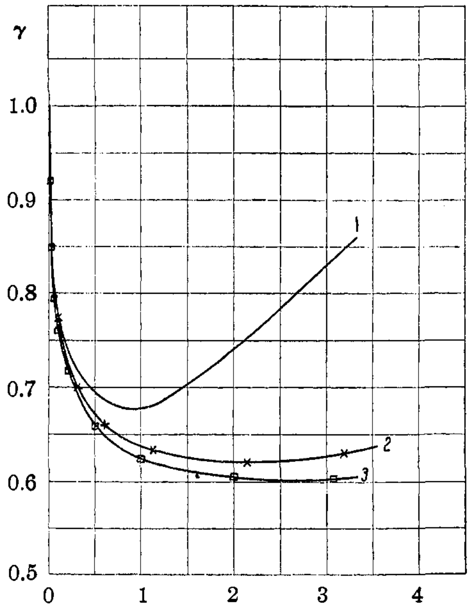

Fig. 1.—Activity coefficients of sodium hydroxide in sodium chloride solutions. 1, NaOH; 2, NaOH (0.1), NaCl; 3, NaOH (0.01), NaCl.

At a constant total molal concentration, the activity coefficient of the hydroxide decreases with decreasing hydroxide concentration in all cases where the experimental accuracy is sufficient to detect a difference. A test was made of the linear variation of the logarithm of the activity coefficient by plotting the values of log γ read from a smooth plot drawn through the points, against the hydroxide concentration of solutions of constant total molality. These plots are straight lines within the error of experiment in solutions as concentrated as 0.5 *M* total concentrations, above which there is an increasingly large deviation from the linear relationship. Consequently, although these results were obtained for another purpose, and but three were obtained at each total concentration, they indicate that in solutions of less than 0.5 *M* the logarithm of the activity coefficient of the hydroxide in sodium chloride solutions is a linear function of its concentration at constant total molality. That this conclusion is valid for other mixtures in not too concentrated solutions has been pointed out by Brönsted[6] and by Harned and Brumbaugh.

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[5] Ref. 3, p. 2729.

[6] Brönsted, This Journal, **44,** 938 (1922).

The author wishes to express his appreciation to Dr. Walter W. Lucasse who rendered valuable assistance in making these measurements.

Summary

1. Measurements of the cells,

$$H_2 \mid NaOH(m_1), NaCl(m) \mid Na_xHg \mid NaOH(m_1) \mid H_2$$

in which m_1 was at 0.1 and 0.01 *M* concentrations, respectively, and m was varied in concentration up to 3 *M* were made at 25°.

2. From these measurements, the activity coefficients of sodium hydroxide were computed.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

THE ACTIVITY COEFFICIENT OF POTASSIUM HYDROXIDE IN POTASSIUM CHLORIDE SOLUTIONS

BY HERBERT S. HARNED

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In the present investigation, the activity coefficient of potassium hydroxide at 0.01 and 0.1 *M* concentrations in potassium chloride solutions at a concentration m has been calculated from measurements of the cells

$$H_2 \mid KOH(m_1), KCl(m) \mid K_xHg \mid KOH(m_1) \mid H_2$$

in exactly the same way as the activity coefficient of sodium hydroxide in so-

TABLE I

ELECTROMOTIVE FORCES OF CELLS

$H_2 \mid KCl(m), KOH(m_2) \mid K_xHg \mid KOH(m_1) \mid H_2$

m_1 and m_2 approximately 0.1 *M*

m_2	m	m_1	E	E $m_1 = m_2 = 0.1$
0.1018	0.2022	0.1014	0.02282	0.02290
.1019	.5060	.1016	.03772	.03802
.1015	1.009	.1018	.05164	.05213
.1010	2.006	.1020	.06883	.06958
.1015	3.025	.1021	.08192	.08260

m_1 and m_2 approximately 0.01 *M*

m_2	m	m_1	E	E $m_1 = m_2 = 0.01$
.01017	.02058	.01010	.02414	.02406
.01011	.0507	.01021	.03867	.03940
.01005	.1008	.01015	.05132	.05188
.01010	.2055	.01012	.06640	.06673
.01015	.509	.01014	.08470	.08503
.01002	1.085	.01003	.10209	.10217
.01005	2.033	.01011	.11809	.11856
.01003	3.035	.01024	.13065	.13176
.01004	3.015	.01025	.13024	.13143