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

THE ACTIVITY COEFFICIENT AND IONIC CONCENTRATION PRODUCT OF WATER IN SODIUM AND POTASSIUM CHLORIDE SOLUTIONS

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It is now possible from the combined data of the previous articles,[1] the data of Harned[2] and some more recently determined results to compute the activity coefficient and ionic concentration product of water in sodium and potassium chloride solutions.

General Method of Calculation

The electromotive forces of cells of the type,

$$\mathrm{Hg}\quad \mathrm{HgCl} \mid \mathrm{MCl}(m),\ \mathrm{HCl}(m_1) \mid \mathrm{H_2} \mid \mathrm{HCl}(m_1) \mid \mathrm{HgCl} \mid \mathrm{Hg}$$

which may be obtained from Harned's data are related to the activities of the hydrogen and chloride ions by the equation

$$E_1 = 0.05915 \log \frac{a_{\mathrm{H}(s)}\, a_{\mathrm{Cl}(s)}}{a_{\mathrm{H}(m_1)}\, a_{\mathrm{Cl}(m_1)}} = 0.05915 \log \frac{\gamma_{\mathrm{H}(s)}\, \gamma_{\mathrm{Cl}(s)}\, (m + m_1)m_1}{\gamma_{\mathrm{H}(m_1)}\, \gamma_{\mathrm{Cl}(m_1)}\, m_1^2} \qquad (1)$$

where the subscript (s) refers to the solution containing acid and salt and m_1 to the solution containing acid only. The electromotive forces of the cells, $\mathrm{H_2} \mid \mathrm{MCl}(m),\ \mathrm{MOH}(m_1) \mid \mathrm{M_xHg} \mid \mathrm{MOH}(m_1) \mid \mathrm{H_2}$, are related to the activities of the metal and hydroxyl ions by the equation

$$E_2 = 0.05915 \log \frac{a_{\mathrm{M}(s)}\, a_{\mathrm{OH}(s)}\, a_{\mathrm{H_2O}(m_1)}}{a_{\mathrm{M}(m_1)}\, a_{\mathrm{OH}(m_1)}\, a_{\mathrm{H_2O}(s)}} = 0.05915 \log \frac{\gamma_{\mathrm{M}(s)}\, \gamma_{\mathrm{OH}(s)}\, a_{\mathrm{H_2O}(m_1)}\, (m + m_1)m_1}{\gamma_{\mathrm{M}(m_1)}\, \gamma_{\mathrm{OH}(m_1)}\, a_{\mathrm{H_2O}(s)}\, m_1^2} \qquad (2)$$

where m_1 and m are the same as in the acid cell. If we add these two electromotive forces, and rearrange terms, we obtain

$$E_1 + E_2 = 0.05915 \log \frac{\gamma_{\mathrm{M}(s)}\, \gamma_{\mathrm{Cl}(s)}\, (m + m_1)^2}{\gamma_{\mathrm{M}(m_1)}\, \gamma_{\mathrm{Cl}(m_1)}\, m_1^2} + 0.05915 \log \frac{\gamma_{\mathrm{H}(s)}\, \gamma_{\mathrm{OH}(s)}\, a_{\mathrm{H_2O}(m_1)}}{\gamma_{\mathrm{H}(m_1)}\, \gamma_{\mathrm{OH}(m_1)}\, a_{\mathrm{H_2O}(s)}} \qquad (3)$$

Thus, if the first member on the right of Equation 3 be known, the ratio of $\frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}}{a_{\mathrm{H_2O}}}$, which we shall denote by $K_{\gamma(s)}$, in the salt solution to its value in the solution of a strength m_1 may be evaluated. Now, the electromotive forces of the cells

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{MCl}\ (m + m_1) \mid \mathrm{M_xHg} \mid \mathrm{MCl}(m_1) \mid \mathrm{AgCl} \mid \mathrm{Ag}$$

in the case of potassium and sodium chloride may be accurately calculated from the activity coefficients of these electrolytes by the equation

$$E_3 = 0.05915 \log \frac{\gamma_{\mathrm{M}(m+m_1)}\, \gamma_{\mathrm{Cl}(m+m_1)}\, (m + m_1)^2}{\gamma_{\mathrm{M}(m_1)}\, \gamma_{\mathrm{Cl}(m_1)}\, m_1^2} = 0.1183 \log \frac{\gamma_{\mathrm{MCl}(m+m_1)}\, (m + m_1)}{\gamma_{\mathrm{MCl}(m_1)}\, m_1} \qquad (4)$$

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[1] (a) Activity Coefficients of Sodium Hydroxide in Sodium Chloride Solutions. THIS JOURNAL, **47**, 684 (1925). (b) Activity Coefficient of Potassium Hydroxide in Potassium Chloride Solutions, *ibid.*, **47**, 689 (1925).

[2] Harned, *ibid.*, **42**, 1808 (1920).

Thus by subtracting E_3 from $E_1 + E_2$, the electromotive forces necessary for calculating the activity-coefficient ratio of water may be obtained. This subtraction involves the assumption that the activity coefficient of M^+ in an MCl solution at a concentration $(m + m_1)$ has the same value as in a solution of $MCl(m) + MOH(m_1)$, and that the activity coefficient of Cl^- in an MCl solution at a concentration $(m + m_1)$ has the same value as in a solution of $MCl(m) + HCl(m_1)$. This assumption is very probable in solutions in which m_1 is small and is subject to a direct test for the results obtained by employing solutions of different concentrations of m_1. For example, the results of the 0.01 and 0.1 *M* series should be superimposable at the same total concentrations. Fortunately, the necessary data are available to test this point.

It is important to note that this method leads to a measurement of the activity coefficient product of water and not the activity product, since the values of m_1 cancel out.

The Calculation

The electromotive forces of the cells containing 0.1 *M* acid and potassium and sodium chlorides were computed from the data of Harned;[2] those of the cells containing 0.01 *M* acid were computed from Harned and Brumbaugh's data;[3] while those of the 0.01 *M* acid containing sodium chloride were taken from an unpublished series of measurements. All these data are compiled in Table I.

Table I

Electromotive Forces of the Cells at 25°

$Hg \mid HgCl \mid MeCl(m), HCl(m_1) \mid H_2 \mid HCl(m_1) \mid HgCl \mid Hg$

KCl

$m_1 = 0.1$

$m + 0.1$	0.1000	0.2018	0.5086	1.0346	2.134	3.309
E	.00000	.02475	.04162	.05867	.08277	.10247

$m_1 = 0.01$

$m + 0.01$	0.01	0.06	0.11	0.31	0.51	1.01	2.01	3.01
E_1	.00000	.04125	.05465	.07723	.08930	0.10723	0.12915	0.14608

NaCl

$m_1 = 0.1$

$m + 0.1$	0.1000	0.1003	0.2014	0.3636	0.5061	0.6085	0.9183	1.023
E	.00000	.01600	.02519	.03655	.04311	.04756	.05854	0.06182
$m + 0.1$	1.243	1.871	2.078	2.094	2.711	3.202	3.726	
E	0.06779	0.08377	0.68819	0.08877	0.10202	0.11210	0.12189	

$m_1 = 0.01$[a]

$m + 0.01$	0.01	0.09	0.99	2.99
E	.00000	.05229	.10997	0.15572

[a] This series was obtained by Dr. Harry Seltz in this Laboratory.

The electromotive forces of the cells containing the hydroxide are taken from the fourth column of Table II of the second article of this

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[3] Harned and Brumbaugh, This Journal. **44**, 2729 (1922).

series (The Activity Coefficient of Sodium Hydroxide in Sodium Chloride Solutions, Ref. 1a) and the fifth column of Table I of the third article of the series (The Activity Coefficient of Potassium Hydroxide in Potassium Chloride Solutions, Ref. 1b).

The electromotive forces of the cells containing the pure salts were computed by Equation 4 from the activity coefficients. These latter were computed by the equations

$$\log \gamma = -0.292\, m^{0.396} + 0.07\, m \tag{5}$$

for potassium chloride and

$$\log \gamma = -0.286\, m^{0.407} + 0.1\, m \tag{6}$$

for sodium chloride. The electromotive forces of these cells are given in Table II.

TABLE II

ELECTROMOTIVE FORCES OF THE CELLS

Hg | HgCl | MCl(m + 0.01) | M_xHg | MCl(0.01) | HgCl | Hg

$m + m_1$	0.01	0.05	0.10	0.30	0.50	1.00	2.00	3.00
E_3(KCl)	.00000	.07782	.11052	.16110	.11842	.2156	0.2486	0.2698
E_3(NaCl)	.00000	.07847	.11124	.16255	.18640	.21975	.2569	.2814

Since most of these results were at odd concentrations, large-scale plots on accurate cross-section paper of log (m + m_1) against E were made. From these the values of E_1, E_2 and E_3 could be read with an error of not more than ± 0.15 mv. The only series of results which were not highly consistent were those of the cells containing 0.01 M acid and potassium chloride. In this case the values at 0.06 and 0.11 M ($m + m_1$) were 0.5 and 0.7 mv. off the smooth curve. In Table III are given E_1, E_2 and E_3 and $E_1 + E_2 - E_3$ at round concentrations which were read from these plots. This latter quantity is given by

$$E_1 + E_2 - E_3 = 0.05915 \log \frac{\dfrac{\gamma_H\, \gamma_{OH}}{a_{H_2O}}}{\dfrac{\gamma_{H(m_1)}\, \gamma_{OH(m_1)}}{a_{H_2O\,(m_1)}}} = 0.05915 \log \frac{K_{\gamma(s)}}{K_{\gamma(m_1)}},$$

The last column contains this ratio referred to the 0.01 and 0.1 M values, respectively.

The results in Table III show that the value of the ratio, $\dfrac{K_{\gamma(s)}}{K_{\gamma(0.01)}}$, first decreases, passes through a minimum, and then increases. Since $K_{\gamma(0.01)}$ is constant, $K_{\gamma(s)}$ must also pass through a minimum. Since a_{H_2O} does not differ much from unity in the dilute solutions, this behavior is similar to that of the activity-coefficient product of many strong electrolytes such as hydrochloric acid, sodium chloride and sodium hydroxide in solutions of other electrolytes. Further, it may be noted that this quantity, $K_{\gamma(s)}$, is less in the sodium chloride than in the potassium chloride solutions.

TABLE III

THE ACTIVITY-COEFFICIENT PRODUCT RATIO

I. 0.01 *M* ACID-HYDROXIDE SERIES A. KCl

$m + m_i$	E_1	E_2	E_3	$E_1 + E_2 - E_3$	$\frac{K_{\gamma(s)}}{K_{\gamma(0.01)}}$
0.01	0.0000	0.0000	0.0000	0.0000	1.000
.02	.0155	.0149	.0338	− .0034	.876
.03	.0245	.0236	.0532	− .0051	.820
.05	.0360	.0348	.0778	− .0070	.761
.1	.0517	.0498	.1105	− .0090	.704
.2	.0673	.0646	.1423	− .0104	.667
.3	.0764	.0732	.1611	− .0113	.644
.5	.0886	.0841	.1842	− .0115	.639
.75	.0987	.0933	.2026	− .0106	.662
1.	.1068	.0998	.2156	− .0090	.704
2.	.1290	.1178	.2486	− .0018	.932
3.	.1460	.1312	.2698	.0074	1.334

B. NaCl

$m + m_i$	E_1	E_2	E_3	$E_1 + E_2 - E_3$	$\frac{K_{\gamma(s)}}{K_{\gamma(0.01)}}$
0.01	0.0000	0.0000	0.0000	0.0000	1.000
.02	.0156	.0149	.0341	− .0036	.869
.03	.0247	.0236	.0537	− .0054	.810
.05	.0364	.0346	.0785	− .0075	.752
.10	.0521	.0495	.1112	− .0096	.688
.2	.0685	.0642	.1436	− .0109	.654
.3	.0782	.0728	.1626	− .0116	.637
.5	.0905	.0839	.1864	− .0120	.628
.75	.1012	.0928	.2057	− .0117	.634
1.	.1099	.0993	.2197	− .0105	.663
2.	.1360	.1164	.2569	− .0045	.839
3.	.1559	.1276	.2814	.0021	1.085

II. 0.1 *M* ACID-HYDROXIDE CELLS A. KCl

$m + m_i$	E_1	E_2	E_3	$E_1 + E_2 - E_3$	$\frac{K_{\gamma(s)}}{K_{\gamma(0.01)}}$
0.1	0.0000	0.0000	0.0000	0.0000	1.000
.2	.0152	.0142	.0308	− .0014	.945
.4	.0313	.0293	.0632	− .0026	.904
.6	.0412	.0383	.0820	− .0025	.907
.8	.0485	.0446	.0946	− .0015	.943
1.1	.0577	.0519	.1092	.0004	1.016
2.1	.0801	.0693	.1410	.0084	1.387
3.1	.0968	.0822	.1609	.0181	2.023

B. NaCl

$m + m_i$	E_1	E_2	E_3	$E_1 + E_2 - E_3$	$\frac{K_{\gamma(s)}}{K_{\gamma(0.01)}}$
0.1	0.0000	0.0000	0.0000	0.0000	1.000
.2	.0159	.0142	.0318	− .0017	.936
.4	.0327	.0293	.0644	− .0024	.911
.6	.0430	.0384	.0839	− .0025	.907
.8	.0509	.0446	.0973	− .0018	.932
1.1	.0607	.0522	.1133	− .0004	.984
2.1	.0863	.0685	.1488	.0060	1.263
3.1	.1082	.0804	.1761	.0125	1.627

We have still to determine $K_{\gamma(0.01)}$ in order to compute the absolute value of $K_{\gamma(s)}$ and of the activity coefficient of water, γ_s or $\sqrt{\gamma_H\gamma_{OH}}$. Since the behavior of this quantity is similar to that of other strong electrolytes in solutions of electrolytes, we shall make the assumption that at 0.01 *M* salt concentration it has approximately the same value as for other strong electrolytes. Since the value of this quantity is less in the sodium chloride than in the potassium chloride solutions, we shall assume that it is slightly less at 0.01 *M* concentration. These assumptions are tentative but may be expected to give results within about 1% of the correct value. Below 0.01 *M* we let

$$\log \gamma_{s(\mathrm{KCl})} = -0.40m^{\frac{1}{2}} \qquad (7)$$

and

$$\log \gamma_{s(\mathrm{NaCl})} = -0.41m^{\frac{1}{2}} \qquad (8)$$

so that $\gamma_{s(\mathrm{KCl})} = 0.912$, $\gamma_{s(\mathrm{NaCl})} = 0.910$, $K_{\gamma(\mathrm{KCl})} = 0.832$, and $K_{\gamma(\mathrm{NaCl})} = 0.828$ at 0.01 *M* concentration.

Table IV

$\frac{\gamma_H\gamma_{OH}}{a_{H_2O}}$ and $\sqrt{\gamma_H\gamma_{OH}}$ of Water in Potassium and Sodium Chloride Solutions

I 0.01 *M* Acid-hydroxide Cells A. KCl

1 $m + m_1$	2 $K_{\gamma(s)} = \frac{\gamma_H\gamma_{OH}}{a_{H_2O}}$	3 $0.02568\, ln \frac{p_{0.01}}{p_s}$	4 $E_4 = 0.1183 \log \frac{\gamma_s}{\gamma_{0.01}}$	5 $\gamma_s = \sqrt{\gamma_H\gamma_{OH}}$
0.01	0.832	0.00000	0.0000	0.912
.02	.729	.00001	− .0034	.854
.03	.682	.000016	− .0051	.826
.05	.633	.000035	− .0070	.796
.1	.586	.000077	− .0091	.764
.2	.555	.000155	− .01055	.743
.3	.536	.000237	− .0115	.729
.5	.532	.000405	− .0119	.723
.75	.551	.000604	− .0112	.7335
1.	.586	.000814	− .0098	.754
2.	.775	.001676	− .0034	.854
3.	1.110	.002621	.0048	1.001

B. NaCl

1 $m + m_1$	2 $K_{\gamma(s)} = \frac{\gamma_H\gamma_{OH}}{a_{H_2O}}$	3 $0.02568\, ln \frac{p_{0.01}}{p_s}$	4 $E_4 = 0.1183 \log \frac{\gamma_s}{\gamma_{0.01}}$	5 $\gamma_s = \sqrt{\gamma_H\gamma_{OH}}$
0.01	0.828	0.00000	0.0000	0.910
.02	.7195	.00001	− .0036	.8485
.03	.671	.000016	− .0054	.819
.05	.623	.000035	− .0075	.789
.1	.570	.000078	− .0097	.752
.2	.5415	.000157	− .01105	.7335
.3	.527	.000242	− .01185	.7225
.5	.520	.000414	− .0124	.715
.75	.525	.000626	− .0123	.716
1.	.549	.000847	− .01135	.729
2.	.695	.001801	− .0063	.805
3.	.898	.002900	− .0008	.895

TABLE IV (*Concluded*)

II 0.1 *M* ACID-HYDROXIDE CELLS A. KCl

$(m + m_1)$	$K_{\gamma(s)}$	$0.02568 \ ln \frac{p_{0.1}}{p_s}$	$0.1183 \log \frac{\gamma_s}{\gamma_{0.1}}$	γ_s
0.1	0.586	0.000000	0.0000	0.764
.2	.553	.000079	− .0015	.742
.4	.530	.000243	− .00285	.723
.6	.5315	.000407	− .0029	.722
.8	.553	.000571	− .0021	.7335
1.1	.595	.000821	− .0004	.758
2.1	.813	.001691	.0067	.871
3.1	1.182	.002636	.0155	1.022

B. NaCl

$(m + m_1)$	$K_{\gamma(s)}$	$0.02568 \ ln \frac{p_{0.1}}{p_s}$	$0.1183 \log \frac{\gamma_s}{\gamma_{0.1}}$	γ_s
0.1	0.570	0.000000	0.0000	0.752
.2	.5335	.000082	− .0018	.726
.4	.519	.000250	− .00265	.715
.6	.517	.000420	− .0029	.711
.8	.531	.000591	− .0024	.719
1.1	.561	.000859	− .00125	.738
2.1	.720	.001830	.0042	.817
3.1	.927	.002934	.0096	.980

These equations are justified because in dilute solutions the logarithm of the activity coefficient of uni-univalent electrolytes appears to be proportional to the square root of the concentration.[4]

Col. 2 of Table IV includes the values of $K_{\gamma(s)}$ calculated from the ratios in the sixth column of Table III. In order to obtain γ_s or $\sqrt{\gamma_H \gamma_{OH}}$ it is necessary to eliminate a_{H_2O}. This has been done by correcting the electromotive forces in the fifth column of Table III by the method employed in preceding articles of this series.[1] Therefore Col. 3 of Table IV contains the values of $0.02568 \ ln \frac{p_{m_1}}{p_s}$ at the concentrations designated which were read from the required plots. Col. 4 contains E_4 obtained by subtracting the values in Col. 3 from those in the fifth column of Table III, and Col. 5 the values of γ_s.

In Fig. 1, the values of γ_s and $K_{\gamma(s)}$ have been plotted against the total concentrations. The values computed from the 0.01 *M* acid and 0.01 *M* hydroxide cells and those computed from the 0.1 *M* acid and 0.1 *M* hydroxide cells are almost exactly superimposable. With four exceptions at the higher concentrations, the values of γ_s of the 0.01 and 0.1 *M* series lie within ± 0.3%, corresponding to an error of less than ± 0.15 mv. This is good confirmation of the accuracy of measurement and reversi-

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[4] Debye and Hückel's [*Physik. Z.*, **9**, 185 (1923)] limiting function is $\log \gamma = -0.495 \ m^{\frac{1}{2}}$. From the recent study of Randall and Vanselow [THIS JOURNAL, **46**, 2418 (1924)] it is shown that the value 0.495 in these equations gives a value of γ which is somewhat low at 0.01 *M*, and we have therefore chosen values nearer to 0.4.

bility of both the hydroxide-salt and acid-salt cells. Further, this agreement confirms the exactness of the method, and proves that the assumptions that the metal ion in the hydroxide-chloride solution has the same activity as in a solution of the same strength of chloride, and that the chloride ion in the acid-chloride cell has the same activity in the chloride solution of the same strength, are within the experimental error. These quantities may be regarded as determined by a thermodynamic method, and the difficulties usually encountered when liquid junctions are employed have been avoided.

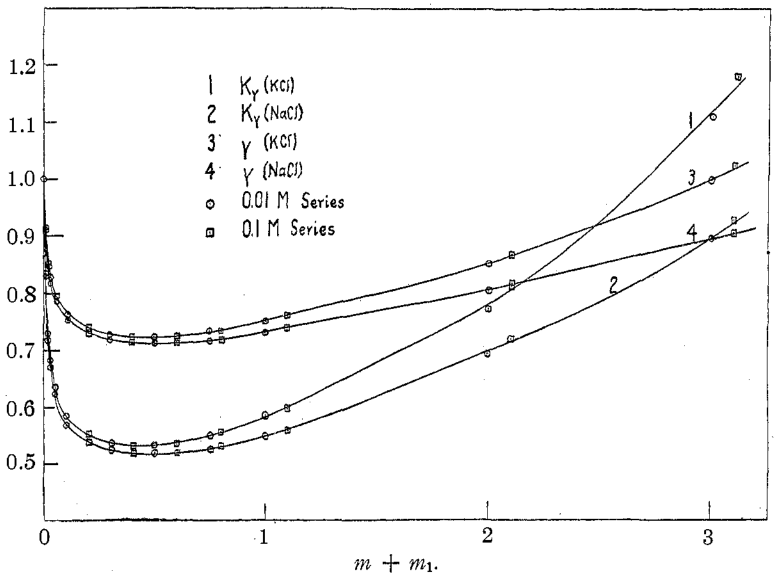

Fig. 1.—The activity coefficient product and activity coefficient of water in sodium and potassium chloride solutions.

The Ionic Concentration Product of Water

It is a simple matter now to compute the concentrations of the hydrogen and hydroxyl ions in these salt solutions. For according to the equation representing the dissociation of water, it is a thermodynamic necessity that

$$K_w = \frac{a_{\mathrm{H}}a_{\mathrm{OH}}}{a_{\mathrm{H_2O}}} = \frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}m_w^2}{a_{\mathrm{H_2O}}}$$

whence

$$m_{\mathrm{H}} = m_{\mathrm{OH}} = m_w = \sqrt{\frac{K_w \times a_{\mathrm{H_2O}}}{\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}}} = \sqrt{\frac{K_w}{K_{\gamma(s)}}} \qquad (9)$$

Thus, from the values of $K_{\gamma(s)}$ in Col. 2, Table IV and the ionic product K_w, we may compute m_w. For K_w at 25°, we shall employ the value 1.005×10^{-14} which may be computed from the standard molal electrode potentials given by Lewis and Randall.[5] The values of m_w in both the potassium and sodium chloride solutions are given in Table V. These results depend on the absolute value of K_w which may be somewhat in error, owing to the fact that its calculation involves the estimation of two liquid junctions and somewhat erroneous values for the activity coefficients of hydrochloric acid, and potassium hydroxide.[6] For this calculation, the values of $K_{\gamma(s)}$ were read from their plot at round salt concentrations.

TABLE V

THE HYDROGEN- AND HYDROXYL-ION CONCENTRATIONS IN AQUEOUS SODIUM AND POTASSIUM CHLORIDE SOLUTIONS

1. m	0.0	0.005	0.01	0.02	0.03	0.05	0.1	0.2	0.3	0.5	0.75	1	2	3
2. $m_w \times 10^7$, KCl	1.0025	1.071 (1.081)	1.099 (1.116)	1.174	1.214	1.260	1.309	1.347	1.368	1.376	1.353	1.313	1.134	0.944
3. NaCl	1.0025	1.072 (1.082)	1.102 (1.119)	1.182	1.224	1.270	1.324	1.363	1.381	1.393	1.382	1.353	1.199	1.056

In Fig. 2 the values of $m_w \times 10^7$ in both the sodium and potassium chloride solutions are plotted against the square root of the salt concentration. As a result, we find that the dissociation of water is first very rapidly increased by the addition of the salt, reaches a maximum by further addition and then decreases in the concentrated solutions. Further, the addition of sodium chloride increases the dissociation to a somewhat greater extent than potassium chloride. The conclusion that such an increase in dissociation must occur is in accord with that already reached by Brönsted[7] who showed that the rapid decrease in activity coefficients of the ions in dilute solutions with increasing concentrations must lead to an increase in dissociation of a weak electrolyte in solutions of strong electrolytes. For the same reason, the dissociation of a weak acid such as acetic will be increased by the addition of neutral salts, a conclusion made by Arrhenius[8] from a study of the effect of neutral salts on the velocity of inversion of cane sugar catalyzed by acetic acid. As Brönsted points out, this increase in dissociation of water is greater than would be expected from an increase in the dielectric constant of the medium. The results of these direct measurements serve to confirm the conclusions of Arrhenius and Brönsted in the dilute solutions. The present investigation is a considerable extension of this point of view. The measurements have been extended to concentrated solu-

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[5] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p. 434.

[6] Randall and Vanselow, THIS JOURNAL, **46**, 2418 (**1924**).

[7] Brönsted, *J. Chem. Soc.*, **119**, 574 (1924).

[8] Arrhenius, *Z. physik. chem.*, **31**, 197 (1899).

tions, a maximum dissociation has been shown to exist, and further it is shown that sodium chloride produces a greater dissociation than potassium chloride when at the same concentration.[9]

Since the values given in Table V were obtained by a complicated calculation which necessitated certain assumptions, and which employed a number of series of results, the assumptions employed and the sources of uncertainty will be summarized. In computing the activity coefficient of water relative to 0.01 M solution, only two extra-thermodynamical assumptions were made, which were that the activity of chloride ion in the hydrochloric acid-chloride solutions of a given total concentration was the same as in the pure chloride solution of this concentration, and that the same was true of the sodium and potassium ions in the hydroxide-chloride solutions relative to the pure sodium and potassium chlorides. These assumptions are shown to be valid since the curves obtained from the 0.01 M and 0.1 M series superimpose and, therefore, the values of $\gamma_{(s)}$ relative to 0.01 M are as accurate as the experimental results. An uncertainty as to the exactness of the measurements of amalgam cells

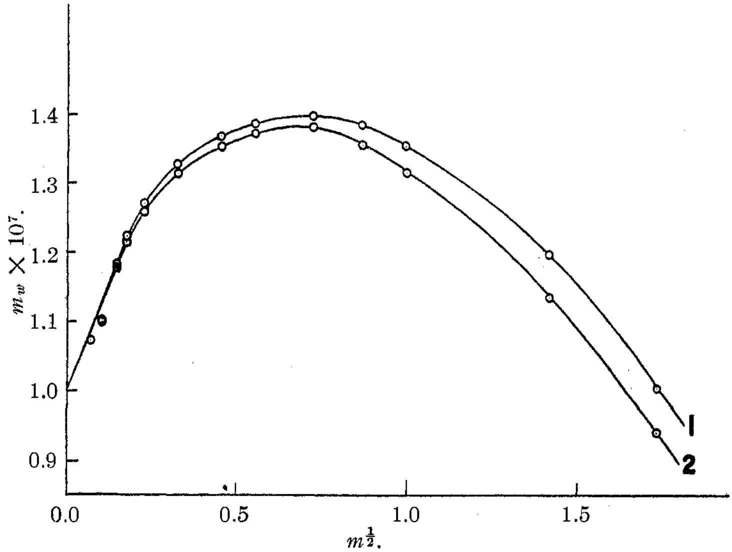

Fig. 2.—Hydroxyl- and hydrogen-ion concentrations in aqueous NaCl and KCl solutions. 1, NaCl; 2, KCl.

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[9] Since this calculation was made, we find that Schreiner [*Z. anorg. Chem.*, **135**, 333 (1924)] has arrived at a similar conclusion regarding the dissociation of water in KCl solutions. By employing Bjerrum's theory of ionic hydration, he calculates a maximum dissociation at 0.5 M KCl, and predicts that above 2.1 M the dissociation becomes less than that of pure water. This conclusion agrees strikingly with the results in Table V. Schreiner calculates a maximum increase in dissociation of 60% over that of water while we find an increase of 38%.

of the kind employed in regions below about 0.03 *M* exists. This was emphasized by Lewis and Randall[10] and, according to their conclusions, the activity coefficients in the dilute solutions as measured by this method fall too rapidly with increasing electrolyte concentration. From these considerations, these results are most valid in the salt concentration range of from 0.02 or 0.03 *M* to the high concentrations. The next step involved the assumption that the square root of the activity coefficient products of the hydrogen and hydroxyl ions in the dilute solutions is given by Equations 7 and 8 which involve the square root concentration law for the variation of log $\gamma_{(s)}$. The value calculated for this quantity in the presence of sodium and potassium chlorides at 0.01 *M* is 0.91 which agrees approximately (to about 1%) with the values obtained for other strong electrolytes at this total concentration. This assumption is tentative, and perhaps this value of 0.91 for $\gamma_{(s)}$ is somewhat high. In plotting the values in Table V, the curve in Fig. 2 was drawn slightly above the first two points and is a straight line through the origin to the third or 0.02 *M* point. By this procedure the observed results above 0.02 *M* are brought into accord with the square root law. The values in brackets at 0.005 and 0.01 *M* in Table V were read from this curve. Finally, an error in K_w influences the entire series of results in Table V. Possible sources of error in the value employed have been mentioned above.

Summary

1. From measurements of three different kinds of concentration cells without liquid junctions, the values of the activity coefficients of water in sodium and potassium chloride solutions have been computed.

2. Values of the activity coefficient product, $\frac{\gamma_H\gamma_{OH}}{a_{H_2O}}$ have also been obtained.

3. From these results and the value for the ionic product of water the concentrations of the hydrogen and hydroxyl ions in the salt solutions have been computed.

4. The uncertainties regarding both the relative and the absolute values have been discussed.

5. The dissociation of water is first increased very rapidly by the salt addition. This result is in accord with the conclusions already drawn by Arrhenius and Brönsted, that the dissociation of a weak electrolyte is increased by the addition of a neutral salt.

6. The present investigation considerably extends this point of view, and it is shown that the dissociation of water first increases, then passes through a maximum, and finally decreases with increasing salt addition.

7. It is probable that the same is true for any weak electrolyte which

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[10] Lewis and Randall, THIS JOURNAL, **43**, 1112 (1921).

produces an ion or ions possessing high activity coefficients (such as, for example, the hydrogen ion).

8. At a given molal salt concentration, sodium chloride produces a greater dissociation of water than does potassium chloride.

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THE EFFECT OF SMALL ALTERNATING CURRENTS ON SOME POLARIZED ELECTRODES

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During the course of certain investigations[1] on the overvoltage of an electrode polarized by intermittent current, it was found that the potential of the electrode fell rapidly as soon as the polarizing current was switched off, but soon reached its normal value when the current was thrown on again. When the electrode was connected with the potentiometer system for the whole of a cycle, the potential recorded was the average of the varying potential of the electrode. This fact has an important bearing upon the measurement of electrode potentials under the influence of superimposed alternating and direct currents. Almost all of the workers[2] in this field have measured the potentials by the direct method, and have thus really measured the average of a varying potential rather than a definite value corresponding to an equilibrium condition. The only exception appears to be W. B. Jones,[3] who has shown that by superimposing alternating current upon direct current the potential of a lead cathode varies continuously throughout the whole of a cycle, and under some conditions even its sign may alter. It should also be pointed out that even though the actual sign of the electrode potential may not be reversed, yet since the direction of the current becomes reversed when the amount of alternating current exceeds the value of the direct current, the potential due to the resistance of the metal-gas-electrolyte system at the surface of the electrode will now act in the opposite direction, and thus cause an appreciable decrease in the average potential as measured by the direct method. All of the potentials recorded in the literature, except those of Jones, for the influence of alternating current on an electrode polarized by direct current are thus of uncertain value, and hence it seemed natural to question the belief that overvoltage may be reduced by the superposition of alter-

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[1] Glasstone, *J. Chem. Soc.*, **123**, 2926 (1923).

[2] (a) Ruer, *Z. physik. Chem.*, **44**, 81 (1903). (b) Von Wartenberg and Archibald, *Z. Elektrochem.*, **17**, 812 (1911). (c) Reitlinger, *ibid.*, **20**, 261 (1914). (d) Ghosh, THIS JOURNAL, **37**, 733 (1915). (e) Grube and Dulk, *Z. Elektrochem.*, **24**, 237 (1918). (f) Goodwin and Knobel, *Trans. Am. Electrochem. Soc.*, **37**, 617 (1920).

[3] Jones, *ibid.*, **41**, 151 (1922).