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

THE ACTIVITY COEFFICIENTS OF SODIUM AND POTASSIUM HYDROXIDES IN THEIR CORRESPONDING CHLORIDE SOLUTIONS AT HIGH CONSTANT TOTAL MOLALITY

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The logarithm of the activity coefficient of hydrochloric acid in solutions of an alkali halide at constant total molality has been found to vary linearly with the acid concentration. Thus, if γ is the activity coefficient, and m the molal concentration of the acid

$$\log \gamma = \alpha m + \log \gamma_0 \quad (1)$$

γ_0 is the activity coefficient of the acid at zero acid concentration in the salt solution of a given total molality and α is a constant.

In an extraordinarily careful study, Güntelberg[1] has shown that at 0.1 M total concentration this law is valid for the activity coefficient of the acid in lithium, sodium, potassium and cesium chloride solutions to within 0.04%. Harned[2] has shown that at 1 M and 3 M total molalities the above expression is valid to within ±0.2% for sodium and potassium chloride–hydrochloric acid mixtures. Results more recently obtained indicate that this law is valid for hydrochloric acid–sodium chloride mixtures at 6 M total molality.

The object of this investigation was to find whether equation (1) is also valid for the activity coefficients of all univalent alkaline hydroxides in their corresponding chloride solutions.

The thermodynamic properties of the alkali metal hydroxides differ from those of the corresponding chlorides. For example, sodium chloride has a higher activity coefficient than potassium chloride but the opposite is true of the corresponding hydroxides. As previously pointed out,[3] the hydroxides occupy a somewhat anomalous position in comparison with other strong electrolytes. If, therefore, deviations from the law expressed by Equation 1 are to be found, it is to be expected that they will be observed in the cases of the hydroxide–salt mixtures and will be more pronounced for sodium hydroxide–chloride than for potassium hydroxide–chloride mixtures. These latter mixtures have already been investigated at constant hydroxide–varying salt concentrations. From the few results obtained at constant total molality, indications were obtained that there was but little if any departure from the linear relation-

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[1] Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

[2] Harned, THIS JOURNAL, **48**, 326 (1926).

[3] (a) Harned, *ibid.*, **47**, 676 (1925); (b) *Z. physik. Chem.*, **117**, 1 (1925); (c) Harned and Swindells, THIS JOURNAL, **48**, 126 (1926).

ship. Since these previous studies did not constitute an exhaustive test, the electromotive forces of cells of the type

$$H_2 \mid MOH(m_1),\ MCl(m_2) \mid M_xHg \mid MOH(m_0) \mid H_2 \qquad (2)$$

in which $(m_1 + m_2)$ was kept constant, were measured.

Experimental Results

The experimental technique as well as the methods of preparation of the amalgams, solutions and electrodes was with minor alterations the same as that developed by Knobel,[4] Harned[5] and Åkerlöf,[6] and will require no further discussion. The electromotive forces are given in Table I. All measurements were made at 25°.

TABLE I

THE ELECTROMOTIVE FORCES OF THE CELLS $H_2 \mid MOH(m_1), MCl(m_2) \mid M_xHg \mid MOH(m_0) \mid H_2$ AND THE ACTIVITY COEFFICIENTS OF THE HYDROXIDES IN THE SALT SOLUTIONS

m_1	m_2	E	E, (mean)	γ	$\gamma_{\text{calcd.}}$	Δ
(a) MOH = KOH; MCl = KCl; M = K; $m_1 + m_2 = 3.5$; $m_0 = 0.1080$						
3.5	0	0.20412, 0.20423	0.2042	1.273	1.273	0.00
3	0.5	.19511, 0.19487	.1950	1.151	1.171	.88
2.5	1	.18597, 0.18627	.1861	1.061	1.076	.72
2	1.5	.17654, 0.17618	.1764	0.981	0.990	.58
1.5	2	.1648, 0.1639	.1644	.896	.910	.80
1	2.5	.14970, 0.14976	.1497	.826	.837	.68
0.5	3	.1280, 0.1284	.1282	.770	.770	.00
(b) MOH = NaOH; MCl = NaCl; M = Na; $m_1 + m_2 = 5$; $m_0 = 0.1080$						
0.5	4.5	0.1397, 0.1384, 0.1374	0.1385	0.766	0.766	0.00
1	4	.1587, 0.1584	.15855	.800	.801	.06
1.5	3.5	.1703, 0.1697	.1700	.817	.838	1.30
2	3	.17953, 0.17944	.1795	851	.876	1.49
2.5	2.5	.18757, 0.18754	.1876	.889	.916	1.54
3	2	.19425	.19425	.926	.957	1.69
3.5	1.5	.20028	.2003	.964	1.001	1.94
4	1	.2070, 0.2072	.2071	1.029	1.047	0.89
4.5	0.5	.21372	.2137	1.104	(1.094)	(−0.46)
5	.0	.21851, 0.21821	.2184	1.144	1.144	.00
(c) MOH = NaOH; MCl-NaCl; M = Na; $m_1 + m_2 = 3$; $m_0 = 0.1060$						
0.5	2.5	0.11901, 0.11915	0.1191	0.666	0.667	0.08
1	2	.13853, 0.13831	.1384	.687	.692	.37
1.5	1.5	.15037, 0.15032	.1503	.707	.718	.79
1	2	.15975, 0.15954	.15965	.7335	.745	.76
2.5	0.5	.16728, 0.16751	.1674	.763	.773	.67
3	.0	.17433, 0.17434	.1743	.802	.802	.00

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[4] Knobel, THIS JOURNAL, **45,** 70 (1923).

[5] Harned, *ibid.*, **47,** 676 (1925).

[6] Åkerlöf, *ibid.*, **48,** 1160 (1926).

Calculation of the Activity Coefficients

The activity coefficients of the hydroxides in the salt solutions were calculated according to the equation

$$E = 0.05915 \log \frac{\gamma_{M(s)}\gamma_{OH(s)}\, a_{H_2O(m_0)}\, (m_1 + m_2)\, m_1}{\gamma_{M(m_0)}\gamma_{OH(m_0)}\, a_{H_2O(s)}\, m_0^2} \qquad (3)$$

where the subscripts (s) and (m_0) refer to the salt solutions and to the reference solutions, respectively. In all of the subsequent discussion, we let

$$\gamma = \sqrt{\frac{\gamma_{M(s)}\gamma_{OH(s)}}{a_{H_2O(s)}}} \text{ and } \gamma_0 = \sqrt{\frac{\gamma_{M(m_0)}\gamma_{OH(m_0)}}{a_{H_2O(m_0)}}}$$

and Equation 3 becomes

$$E = 0.1183 \log \frac{\gamma\sqrt{(m_1 + m_2)m_1}}{\gamma_0\, m_0} \qquad (4)$$

The values employed for γ_0 were taken from the data of Harned and Åkerlöf.[7] Thus, for potassium hydroxide, $\gamma_{0.108}$ was taken to be 0.776, and in the case of sodium hydroxide, $\gamma_{0.106}$ and $\gamma_{0.108}$, were taken to equal 0.758 and 0.757, respectively. The final values computed in this manner are given in Table I.

Discussion of the Results

Figure 1 contains the plot of log γ_{KOH} against m_{KOH} in the solutions of 3.5 total molality. The upper plot is a straight line drawn through the points at 0.5 M and 3.5 M potassium hydroxide concentrations, and the lower curve is drawn through all the points. A slight curvature is noticeable although it should be remarked that if we had drawn the straight line through the 0.5 M and 3 M points, all points except that at 3.5 M hydroxide would have fallen on it with an error of about ±0.2 mv. In this case, however, the 3.5 M point would have been over a millivolt off the curve. We regard the results, therefore, as indicating a very small curvature. On the other hand, a pronounced curvature is observable in the case of sodium hydroxide–sodium

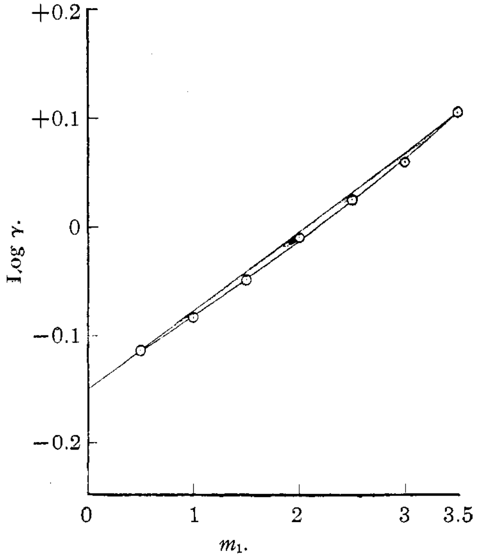

Fig. 1.—Log γ–m_1 of potassium hydroxide–chloride mixtures.

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[7] Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

chloride mixtures at a total concentration of 3, and a very pronounced deviation from the straight line is apparent at a total molality of 5. This is shown by the graphs in Fig. 2. It should be noted that we have plotted $\sqrt{\gamma_M \gamma_{OH}/a_{H_2O}}$, not $\sqrt{\gamma_M \gamma_{OH}}$, owing to our lack of knowledge of the activity of water in these mixtures. The small change in a_{H_2O} in passing from the pure hydroxide to the pure salt solution would be expected to be approximately linear, and in any case would not be responsible for the pronounced curvatures. The points at 0.01 *M* and 0.1 *M* sodium hydroxide concentrations at a total concentration of three were obtained from the data of Harned.[3b]

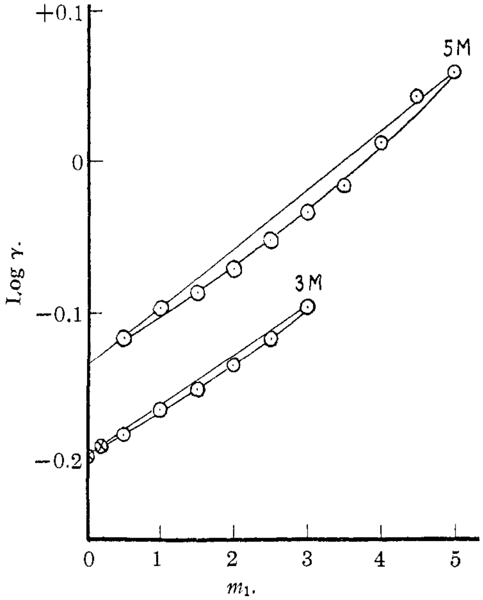

Fig. 2.—Log γ–m_1 plots of sodium hydroxide–chloride mixtures.

The extent of the deviations from the straight lines shown in the figures is made apparent by the last two columns in Table I. The calculated values of γ were obtained from the equations for the straight lines, namely

$$\begin{array}{lll} \text{(a)} & \text{KOH–KCl } (3.5\ M);\ \log y = 0.0728m - 0.150 & \\ \text{(b)} & \text{NaOH–NaCl } (5\ M);\ \log \gamma = 0.0387m - 0.135 & \text{(1a)} \\ \text{(c)} & \text{NaOH–NaCl } (3\ M);\ \log \gamma = 0.0320m - 0.192 & \end{array}$$

The differences between the calculated and observed values have been computed by the equation

$$\Delta = 118.3 \log \frac{\gamma_{\text{calcd.}}}{\gamma_{\text{obs.}}} \qquad (5)$$

and are, therefore, in millivolts.

These results leave little doubt that in the case of these solutions at these high concentrations there is a definite departure from the linear relationship. The maximum deviation is 0.88 mv. in the potassium hydroxide series. This corresponds to a 1.76% difference between the observed and calculated activity coefficients. The same maximum difference is obtained in the case of the sodium hydroxide–chloride mixtures at 3 *M* total molality. The 5 *M* total sodium hydroxide–chloride series indicates a maximum difference of 1.95 mv., which corresponds to a 3.9% difference between the calculated and observed activity coefficients.

Summary

1. Measurements at 25° of the cells

$$H_2 \mid KOH(m_1), KCl(m_2) \mid K_xHg \mid KOH(m_3) \mid H_2$$

in which $(m_1 + m_2)$ was kept at a constant molality of 3.5 have been made.

2. Similar measurements of the cells

$$H_2 \mid NaOH(m_1), NaCl(m_2) \mid Na_xHg \mid NaOH(m_3) \mid H_2$$

at total molalities of 3 and 5 have been presented.

3. From these data the activity coefficients of the hydroxides in the chloride solutions have been computed.

4. The linear relationship given by Equation 1 does not hold for the activity coefficients of the hydroxides in these mixtures. The differences between the observed and calculated activity coefficients were not very large. The maximum difference which occurred with the 5 *M* sodium hydroxide–chloride mixtures was 3.9%.

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THE CATALYTIC OXIDATION OF CARBON MONOXIDE. IV. THE PORE VOLUME OF THE CATALYSTS MANGANESE DIOXIDE, COPPER OXIDE AND MIXTURES OF THESE OXIDES

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In this paper are presented the results of experiments, completed in 1922, on the pore volume and related physical properties of the catalysts investigated and reported on in the first papers of this series.[1] Results of tests upon the catalytic efficiency of related series of catalysts, in which the composition varied between MnO_x (where x is less than 2) and CuO, showed that all the mixtures were more catalytically active than either of the pure components, whether the mixing was effected by thorough kneading of the moist hydrated oxides with subsequent drying,[1a] or by stirring together finely ground portions of the previously dried or ignited components.[1c] These results point to the conclusion that the component oxides retain their characteristic properties in the mixtures and that the "mixture effect" is due to a speeding up of the electronic rearrangement postulated in the mechanism for the catalytic reaction.[2]

As in the previous papers, the members of the three series reported on here (Almquist's Series 1, 2 and 3) will be referred to by the numbers from 1 to 6, in the order of decreasing manganese dioxide content. The compo-

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[1] (a) Almquist and Bray, THIS JOURNAL, **45**, 2305 (1923); (b) Hoskins and Bray, *ibid.*, **48**, 1454 (1926); (c) Bray and Doss, *ibid.*, **48**, 2060 (1926).

[2] Ref. 1 b, pp. 1470–1473.