perchlorate is, however, troublesome because of its corrosive nature in contact with the skin.

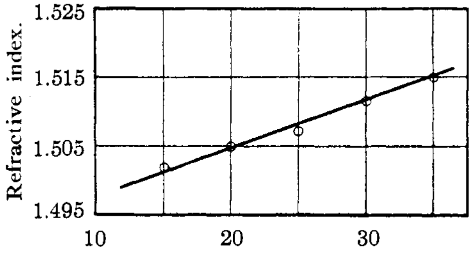

Fig. 2.—Refractive index of saturated silver perchlorate solutions at 15–35°.

The value of Hill for the transition temperature of silver perchlorate monohydrate to the anhydrous salt (43.1°) was checked in the usual manner and the authors find the value 43.0°.

TABLE II

THE SOLUBILITY AND SOLUTION DENSITY OF ANHYDROUS SILVER PERCHLORATE IN 60–73.6% PERCHLORIC ACID AT 25 AND 0°

| Temp., °C. | Acid concn., % | Solubility, g. $AgClO_4$ per 100 ml. sol. | Solubility, g. $AgClO_4$ per 100 g. of sol. | Density 25/4° | Density 0/4° |
|---|---|---|---|---|---|
| 25 | 73.60 | 5.252 | 3.011 | 1.7436 | .... |
| 25 | 68.02 | 10.332 | 6.080 | 1.6993 | .... |
| 25 | 64.08 | 20.080 | 11.765 | 1.7066 | .... |
| 25 | 60.00 | 38.449 | 21.611 | 1.7790 | .... |
| 0 | 73.60 | 3.754 | 2.136 | .... | 1.7575 |
| 0 | 68.08 | 7.104 | 4.151 | .... | 1.7107 |
| 0 | 64.31 | 13.478 | 7.931 | .... | 1.6987 |
| 0 | 60.16 | 30.500 | 17.41 | .... | 1.7520 |

**Perchloric Acid Solubility of Anhydrous Silver Perchlorate.**—The solubility determinations in strong perchloric acid and the density determinations of these solutions were carried out as previously described for the aqueous solutions. Anhydrous silver perchlorate was used as solute. The constant boiling perchloric acid (73.60% $HClO_4$) was prepared by the Smith and Koch method.[2] More dilute solutions of perchloric acid were made from this product by weight dilution. The data for the perchloric acid solubilities and solution densities are given in Table II.

## Summary

1. A redetermination of the solubility of silver perchlorate in the temperature range 0–35° has been made. The previously reported data by Hill[1] and the present data were found to be in substantial agreement.

2. The refractive index of saturated aqueous solutions of silver perchlorate over the temperature range 15–35° has been given.

3. The solubility of anhydrous silver perchlorate in strong perchloric acid (60–73.6%) at 0 and 25° has been determined. Solution densities are also given.

[2] Smith and Koch, *Ind. Eng. Chem., Anal. Ed.*, **3**, 52 (1931).

URBANA, ILLINOIS RECEIVED JUNE 14, 1937

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

# The Activity and Osmotic Coefficients of Some Hydroxide–Chloride Mixtures in Aqueous Solution

BY HERBERT S. HARNED AND MELVIN A. COOK

The cells

$$H_2 \mid MOH(m_1), MX(m_2) \mid M_xHg \mid MOH(m_0) \mid H_2 \qquad (1)$$

and

$$Ag\text{-}AgX \mid MOH(m_1), MX(m_2) \mid M_xHg \mid MX(m_0') \mid AgX\text{-}Ag \qquad (2)$$

in which X equals Cl, Br, are peculiarly adapted for the study of hydroxide-halide mixtures since by the first the activity coefficient of the hydroxide and by the second the activity coefficient of the halide may be evaluated in a given mixture. The first of these cells has been employed[1–4] for determining the activity coefficient of a hydroxide in a halide solution, but measurements of both cells have never been used before for the determination of the activity coefficients of both electrolytic components in the mixtures.

We have restricted this study to the investigation of sodium and potassium hydroxide-chloride mixtures in water at 25° at constant total molalities of 0.5 and 1 *M*. As shown by Harned and Harris, Jr.,[4] the hydroxide-chloride mixtures differ from other mixtures of strong uni-univalent electrolytes in that the logarithm of the activity coefficients of the hydroxide does not vary linearly with the hydroxide concentration at constant total molality. Our results will be shown to confirm this observation. Further, since the measurements of both cells lead to the

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[1] Harned, THIS JOURNAL, **47**, 684, 689 (1925).

[2] Harned and Swindells, *ibid.*, **48**, 126 (1926).

[3] Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).

[4] Harned and Harris, Jr., THIS JOURNAL, **50**, 2633 (1928).

determination of the thermodynamic properties of two of the three components of the system, and since the Gibbs–Duhem equation permits us to evaluate those of the third component, our knowledge of this subject is extended considerably by the more comprehensive method and treatment of the present study.

TABLE I

ELECTROMOTIVE FORCES AT 25° OF THE CELLS

$H_2$ | $MOH(m_1)$, $MCl(m_2)$ | $M_xHg$ | $MOH(m_0)$ | $H_2$: $E_1$
Ag–AgCl | $MOH(m_1)$, $MCl(m_2)$ | $M_xHg$ | $MCl(m_0')$ | AgCl–Ag: $E_2$

AND CONSTANTS OF EQUATIONS (5) AND (6)

| $m_1$ | $E_1$ | $E_2$ | $\frac{1}{2}\log\frac{p_0}{p}$ | $\gamma_1$ | $\gamma_2$ | $(\phi_{(x)} - \phi_{(0)})$ |
|---|---|---|---|---|---|---|
| M = K; $m_1 + m_2 = 1$; $m_0 = 0.04781$; $m_0' = 0.05754$; $\gamma_0 = 0.827$;[5] $\gamma_0' = 0.803$[6] | | | | | | |
| 1.0000 | 0.1524 | .... | 0.0073 | 0.756 | (0.639) | 0.123 |
| .9110 | .4186 | 0.0719 | .0072 | .736 | .639 | .099 |
| .8140 | .1444 | .0763 | .0071 | .718 | .631 | .075 |
| .7431 | .1409 | .0981 | .0070 | .701 | .625 | .060 |
| .6439 | .1365 | .1060 | .0069 | .691 | .620 | .042 |
| .5725 | .1321 | .1104 | .0068 | .673 | .615 | .032 |
| .4141 | .1230 | .1179 | .0067 | .663 | .609 | .014 |
| .3370 | .1171 | .1206 | .0066 | .655 | .607 | .008 |
| .2213 | .1056 | .1248 | .0066 | .646 | .604 | .002 |
| .1478 | .0947 | ... | .0065 | .640 | ... | .000 |
| .1068 | .0864 | .1284 | .0064 | .641 | .605 | −.0005 |
| .0854 | .0802 | ... | .0064 | .635 | ... | −.0005 |
| .0000 | .... | .1313 | .... | (.638) | .605 | .000 |
| M = Na; $m_1 + m_2 = 1$; $m_0 = 0.1349$; $m' = 0.0952$; $\gamma_0 = 0.742$;[7] $\gamma_0 = 0.780$[8,9] | | | | | | |
| 1.0000 | 0.0991 | .... | 0.0064 | 0.679 | (0.644) | 0.023 |
| .9174 | .0961 | 0.0469 | .0063 | .668 | .644 | .013 |
| .8706 | .0945 | .0585 | .0063 | .665 | .645 | .009 |
| .7230 | .0890 | .0782 | .0063 | .656 | .646 | −.003 |
| .6635 | .0860 | .0833 | .0063 | .655 | .648 | −.007 |
| .5702 | .0819 | .0898 | .0063 | .645 | .651 | −.010 |
| .4738 | .0771 | .0945 | .0063 | .644 | .645 | −.013 |
| .3471 | .0689 | .1001 | .0063 | .640 | .645 | −.013 |
| .2817 | .0633 | .1027 | .0063 | .638 | .647 | −.012 |
| .1854 | .0530 | .1064 | .0063 | .643 | .653 | −.010 |
| .1032 | .0378 | .1094 | .0063 | .642 | .660 | −.005 |
| .0000 | .... | .1120 | .... | (.638) | .658 | .000 |
| M = Na; $m_1 + m_2 = 0.5$ | | | | | | |
| 0.5000 | 0.0640 | .... | 0.0026 | 0.691 | (0.677) | 0.020 |
| .4670 | .0615 | 0.0079 | .0025 | .686 | .674 | .014 |
| .4317 | .0592 | .0269 | .0025 | .678 | .678 | .010 |
| .3956 | .0566 | .0378 | .0025 | .673 | .678 | .007 |
| .3840 | .0559 | .0402 | .0025 | .675 | .674 | .006 |
| .3099 | .0504 | .0532 | .0025 | .674 | .678 | .0025 |
| .2218 | .0415 | .0628 | .0024 | .669 | .676 | −.0005 |
| .2211 | .0412 | .... | .0024 | .668 | ... | −.0005 |
| .1223 | .0261 | .0709 | .0024 | .669 | .679 | −.0015 |
| .1124 | .0238 | .0718 | .0024 | .667 | .682 | −.001 |
| .0885 | .0176 | .0733 | .0024 | .667 | .682 | −.001 |
| .0000 | .... | .0784 | .... | (.666) | .683 | .000 |

Numerical Constants of Equations (5) and (6)

| | $m_1+m_2$ | $-\log \gamma_{1(0)}$ | $\alpha_1$ | $\beta_1$ | $-\log \gamma_{2(0)}$ | $\alpha_2$ | $\beta_2$ |
|---|---|---|---|---|---|---|---|
| M = K | 1 | 0.1220 | 0.129 | −0.056 | 0.2185 | 0.007 | −0.034 |
| M = Na | 1 | .1690 | .055 | −.029 | .1818 | .029 | −.020 |
| M = Na | 0.5 | .1606 | .072 | −.080 | .1656 | .006 | .000 |

## Experimental Results

The electromotive forces are recorded in Table I.

## Thermodynamic Considerations

The activity coefficients of the hydroxides and chlorides in the mixtures may be computed from the cell equations

$$\frac{E_1}{0.1183} - \log\frac{(m_1+m_2)^{1/2}\, m_1^{1/2}}{m_0} + \log\gamma_0 = \frac{1}{2}\log\frac{p_0}{p} + \log\gamma_1 \tag{3}$$

$$\frac{E_2}{0.1183} - \log\frac{(m_1+m_2)^{1/2}\, m_2^{1/2}}{m_0'} + \log\gamma_0' = \log\gamma_2 \tag{4}$$

$\gamma_0$ and $\gamma_0'$ are the activity coefficients of the electrolyte in the reference solutions at the concentrations $m_0$ and $m_0'$, respectively. The values employed with references are given in Table I. $\gamma_1$ and $\gamma_2$ are the activity coefficients of the hydroxides and chlorides, respectively, in the mixtures. $m_1$ and $m_2$ are the molal concentrations of the hydroxides and chlorides, respectively. Both the potassium hydroxide–chloride and sodium hydroxide–chloride mixtures were investigated at a constant total molality of 1 *M*, and the sodium hydroxide–chloride mixture was also studied at 0.5 *M*. Values of $\gamma_1$ and $\gamma_2$ in each of the mixtures are recorded in Table I. In order to compute $\gamma_1$, it is necessary to evaluate the vapor pressure correction to the electromotive force on the right side of equation (3). $p_0$ is the vapor pressure of the reference solution and $p$ that of the solution under consideration. In the pure hydroxide or salt solution, these were determined by the usual graphical integration using the Gibbs–Duhem equation. The values in the mixtures were obtained by a method which will be developed in the subsequent discussion.

The variation of the logarithm of the activity coefficients of the electrolytes at constant molality has been expressed as a function of their concentrations by the equations

$$-\log\gamma_1 = -\log\gamma_{1(0)} + \alpha_1 m_2 + \beta_1 m_2^2 \tag{5}$$

$$-\log\gamma_2 = -\log\gamma_{2(0)} + \alpha_2 m_1 + \beta_2 m_1^2 \tag{6}$$

$\gamma_1$ and $\gamma_2$ as before are the activity coefficients of the hydroxides and chlorides in the mixtures at concentrations $m_1$ and $m_2$, respectively. $\gamma_{1(0)}$ and $\gamma_{2(0)}$ are the activity coefficients of the hydroxides and chlorides in the pure aqueous solutions at the constant total molalities under consideration. $\alpha_1$, $\alpha_2$, $\beta_1$ and $\beta_2$ are the coefficients of the quadratic equations.

The vapor pressures and osmotic coefficients

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(5) Harned and Cook, THIS JOURNAL, **59**, 498 (1937).

(6) Harned and Cook, *ibid.*, **59**, 1290 (1937).

(7) Harned and Hecker, *ibid.*, **55**, 4838 (1933).

(8) Brown and MacInnes, *ibid.*, **57**, 1356 (1935).

(9) Harned and Nims, *ibid.*, **54**, 423 (1934).

may be computed by employing the Gibbs-Duhem equation in the form

$$2m_1\,\partial \log \gamma_1 + 2m_2\,\partial \log \gamma_2 = -55.51\,\partial \log a_w \quad (7)$$

where $a_w$ is the activity of the water. We let

$$m_1 = xm;\ m_2 = (1 - x)m \quad (8)$$

where $x$ has all values from 0 to 1. Differentiating (5), (6) and (8) and substituting in (7), and integrating from 0 to $x$

$$\alpha_2 x - \frac{1}{2}(\alpha_1 + \alpha_2)x^2 - m(\beta_1 - \beta_2)x^2 + \frac{2}{3}m(\beta_1 - \beta_2)x^3 = \frac{55.51}{2m^2}\log\frac{p_{(x)}}{p_{(0)}} \quad (9)$$

is obtained, upon substitution of the vapor pressure of water, $p$, for its activity. Since $d \log a_w = -(2m/55.51 \times 2.3303)\, d\phi$, the change in osmotic coefficient, $\phi$, with change in composition of mixture is given by

$$\phi_{(0)} - \phi_{(x)} = 2.303\, m \left[ (\alpha_2 x) - \frac{1}{2}(\alpha_1 + \alpha_2)x^2 - m(\beta_1 - \beta_2)x^2 + \frac{2}{3}m(\beta_1 - \beta_2)x^3 \right] \quad (10)$$

The vapor pressure term on the right of equation (3) given in the fourth column of Table I was determined by arithmetical approximation.

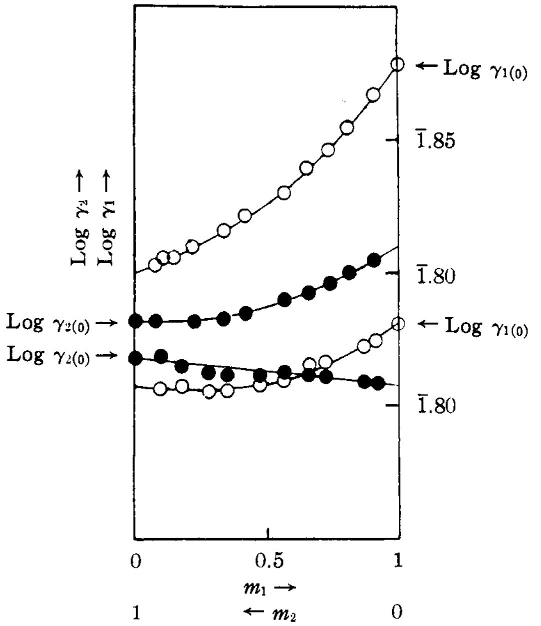

Fig. 1.—Plots of log $\gamma_1$ and $\gamma_2$ *versus* $m_2$ and $m_1$ at a total molality of 1 $M$. Two curves at top represent KOH–KCl mixtures; two curves at bottom NaOH–NaCl mixtures. Diameter of circles equals 0.5 mv.

The vapor pressure, $p$, of the solution containing one electrolyte must be corrected for the change produced upon adding the second electrolyte. This change was computed in the following manner. A preliminary value of log $\gamma_1$ was obtained by equation (3) by taking $p$ equal the vapor pressure of the pure hydroxide solution. These values were employed in equation (5) to give preliminary values of $\alpha_1$ and $\beta_1$, and then $p_{(x)}$ was computed by equation (9). From these the vapor pressure term on the right of equation (3) was computed, and corrected values of log $\gamma_1$ were then computed. By repetition of this process until all equations were satisfied, final values of the vapor pressure term, $\gamma_1$, $\alpha_1$ and $\beta_1$ were obtained. From these $\phi_{(x)} - \phi_{(0)}$ was determined by equation (10). Values of this quantity are given in the last column of the table. We note that $\phi_{(0)}$ is the osmotic coefficient of pure chloride, $\phi_{(x)}$ that of the mixture, and $\phi_{(x=1)}$ that of pure hydroxide. Values of log $\gamma_{1(0)}$, log $\gamma_{2(0)}$, $\alpha_1$, $\beta_1$, $\alpha_2$ and $\beta_2$ required for these calculations are given at the bottom of the table.

## General Characteristics of the Mixtures

The characteristics of the results at a total molality of unity are illustrated in Fig. 1. The two curves at the upper part of the figure represent the behavior of the potassium hydroxide–chloride mixtures while the two curves at the bottom of the figure represent the sodium hydroxide–chloride mixtures, both at 1 $M$. At the top (circles) the logarithm of the activity coefficient of potassium hydroxide in the chloride solutions is plotted against its concentrations. The curve below this (dots) represents the logarithm of the activity coefficient of the chloride in the hydroxide solution. log $\gamma_{1(0)}$, the activity coefficient of the hydroxide, and log $\gamma_{2(0)}$, that of the chloride, both in pure water are indicated. Similarly, the two lower curves represent the behavior of the sodium hydroxide–chloride system. The circles are the values of the logarithm of the activity coefficient of sodium hydroxide in the chloride solution, and the dots represent the activity coefficient of the sodium chloride in the same mixtures. In all cases the solid curves are those calculated by equations (5) and (6) employing the values of the parameters at the bottom of Table I. The characteristics of these results may be summarized briefly:

**I. Potassium Hydroxide-Potassium Chloride Mixtures.**—(1) Neither log $\gamma_1$ or log $\gamma_2$ varies linearly with the concentration of a component of the mixtures, a fact previously noted by Harned

TABLE II

VALUES OF OSMOTIC COEFFICIENTS AND THEIR DIFFERENCES

| | $(m_1 + m_2)$ | Ref. | $\phi_{25}$ | $(\phi_{(x=1)} - \phi_{(0)})_{25}$ | $(\phi_{(x=1)} - \phi_0)_{25}$ Eq. 10 | $\phi_0$ E. m. f. | $\phi_0$ F. p. | $(\phi_{(x=1)} - \phi_{(0)})_0$ E. m. f. | $(\phi_{(x=1)} - \phi_{(0)})_0$ F. p. |
|---|---|---|---|---|---|---|---|---|---|
| NaOH | 0.5 | (7) | 0.938 | ... | ... | 0.933 | ... | ... | ... |
| NaCl | .5 | (8) (9) | .923 | 0.015 | 0.020 | .918 | 0.913 | 0.015 | 0.020 |
| KOH | 1 | (5) | 1.006 | ... | ... | 1.009 | ... | ... | ... |
| KCl | 1 | (6) | 0.898 | .108 | .123 | 0.885 | .882 | .124 | .127 |
| NaOH | 1 | (7) | .956 | ... | ... | .941 | ... | ... | ... |
| NaCl | 1 | (8) (9) | .936 | .020 | .023 | .923 | .916 | .018 | .025 |

and Harris, Jr., for the variation of log $\gamma_1$ at higher total molalities. (2) The results may be expressed by quadratic equations (5) and (6). (3) Since a quadratic is necessary to express the variation of log $\gamma_1$ and log $\gamma_2$, the osmotic coefficient varies according to equation (10), a cubic. (4) log $\gamma_1$ in a pure potassium chloride solution does not equal log $\gamma_2$ in the pure hydroxide solution. These extrapolated values are given in parentheses in Table I.

**II. Sodium Hydroxide–Sodium Chloride Mixtures.**—(1) At 1 *M* total concentration log $\gamma_1$ and log $\gamma_2$ vary according to a quadratic equation but at 0.5 *M* log $\gamma_2$ may be expressed by a linear equation. (2) This leads according to equation (10) to a cubic variation of the osmotic coefficient, $\phi$. (3) log $\gamma_1$ in the pure salt solution does not equal log $\gamma_2$ in the pure aqueous hydroxide solution. (4) The sodium chloride-hydroxide mixtures possess a further peculiarity. The curves slope in opposite directions, a behavior not previously observed with uni-univalent electrolyte mixtures.

## Osmotic Coefficients

The value of $(\phi_{(x=1)} - \phi_0)$ is the difference between the osmotic coefficient of the pure hydroxide and pure chloride. This quantity may be calculated at 25° from the activity coefficients of the pure salt and hydroxide solutions by means of the equation, $\phi = 1 + 2.3026/m \int_0^m m \, \partial \log \gamma$. We have evaluated this quantity by graphical integration of values of $\gamma$ recently determined from electromotive force measurements and have collected the results in Table II. The third column indicates the source of data employed. The fifth column contains the differences between the osmotic coefficients of the hydroxides and chlorides determined in this manner, and the sixth column contains this computed from the present data by equation (10).

The agreement between the values of $(\phi_{(x=1)} - \phi_{(0)})$ obtained by the two methods is satisfactory since it involves the errors of four independent series of measurements. A further check has been made with the data obtained by Scatchard and Prentiss[10] from freezing point measurements. Their values of $\phi$, given at the freezing point of the solution, were altered slightly so as to be comparable with the values obtained from electromotive forces at 0°. The differences between the values of $\phi$ at 0° determined by freezing point and electromotive forces are caused principally by difficulties encountered in the extrapolations involved. In the last two columns of the table are given the differences between the osmotic coefficients of the hydroxides and their corresponding halides as determined by the two methods. These differences compare favorably with those obtained at 25° by equation (10).

## Summary

1. By measuring suitable cells, the activity coefficient of the hydroxide and the activity coefficient of the chloride in a mixture of chloride and hydroxide at 0.5 and 1 *M* total concentrations have been determined. This is the first time this has been accomplished. The procedure makes possible a thorough study of the thermodynamics of such mixtures.

2. It is found that the logarithm of the activity coefficients varies with their concentrations according to a quadratic function. This behavior is different than that yet observed for other uni-univalent electrolyte mixtures.

NEW HAVEN, CONN. RECEIVED JUNE 26, 1937

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[10] Scatchard and Prentiss, THIS JOURNAL, **55**, 4355 (1933).