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

dium chloride solutions was computed in the preceding paper.[1] The observed electromotive forces at 25° and at the concentrations designated are given in the fourth column of Table I. The fifth column contains these electromotive forces at salt concentrations calculated to round concentrations, namely 0.01 *M* and 0.1 *M* potassium hydroxide. This calculation was made by means of Equations 2 and 3 of the preceding paper.

The activity coefficients were then computed from the electromotive forces in Col. 5, Table I, by the equation

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

The activity coefficient of potassium chloride is given accurately in the concentration range from 0.01 to 3 *M* by the equation

$$\log \gamma = -0.292 m_{0.396} + 0.07\ m \qquad (2)$$

and the logarithm of the ratio of the vapor pressure of pure water to that of the solution by[2]

$$ln \frac{p_0}{p} = \frac{m}{55.5} [2 + 0.1621\ m - 0.3815\ m^{0.396}] \qquad (3)$$

From these calculations, the values of $0.02568\ ln \frac{p_s}{p_{0 \cdot 1}}$ and $0.02568\ ln \frac{p_s}{p_{0 \cdot 01}}$ were obtained at round concentrations and plotted. From this plot the values of $0.02568\ ln \frac{p_s}{p_1}$ given in the third column of Table II were obtained. The fifth column contains γ, computed by means of Equation 1.

TABLE II

ACTIVITY COEFFICIENT OF POTASSIUM HYDROXIDE IN POTASSIUM CHLORIDE SOLUTIONS

KOH = 0.1 *M*

m	E	$0.02568\ ln \frac{p_s}{p_1}$	$E + 0.02568\ ln \frac{p_s}{p_1}$	γ
0.0000	0.00000	0.000000	0.00000	0.789
.2022	.02290	− .000163	.02274	.706
.5060	.03802	− .000412	.03761	.666
1.009	.05213	− .000827	.05130	.643
2.005	.06958	− .001696	.06788	.645
3.025	.08260	− .002660	.07994	.669
		KOH = 0.01 *M*		
0.0000	.00000	.000000	.00000	.920
.02058	.02406	− .000016	.02404	.840
.0507	.03940	− .000041	.03936	.803
.1008	.05188	− .000083	.05180	.757
.2055	.06673	− .000165	.06657	.724
.509	.08503	− .000405	.08463	.663
1.085	.10217	− .000891	.10128	.631
2.033	.11856	− .001715	.11685	.626
3.035	.13176	− .002660	.12910	.651
3.015	.13143	− .002642	.12879	.649

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

[2] Harned, *ibid.*, **44**, 252 (1922).

Discussion

The values of γ, in Table II, are shown plotted against the concentrations, in Fig. 1. The plot of the activity coefficient of pure aqueous potassium hydroxide obtained from Knobel's results[3] are also included as well as the activity coefficient of sodium hydroxide at 0.01 *M* in sodium chloride solutions.[4] The potassium hydroxide plots exhibit pronounced minima. The plot of 0.01 *M* potassium hydroxide in the potassium chloride solutions lies somewhat higher than the similar sodium hydroxide plot, but the two are nearly identical in the dilute solutions. This behavior is particularly interesting since sodium chloride possesses a greater activity coefficient than potassium chloride, and it is usually the rule that the activity coefficient of an electrolyte is greater in the solution of an electrolyte which itself has the greater activity coefficient.[5] Thus, hydrochloric acid of a given strength has a greater activity coefficient in sodium chloride solutions than in potassium chloride solutions of the same concentrations. The phenomena with both the acid and hydroxide systems are to be explained by considering the water dissociation reaction, from which it is thermodynamically necessary that $K = \frac{a_{H}a_{OH}}{a_{H_2O}}$. Thus, if the hydrogen-ion activity of an acid is greater in a sodium than in a potassium chloride solution, we should expect the hydroxyl-ion activity to be less. This reciprocal relation is thus a fundamental factor in the behaviors of these systems and it seems probable that it lies behind the fact that the activity coefficient of sodium hydroxide is less than that of potassium hydroxide.

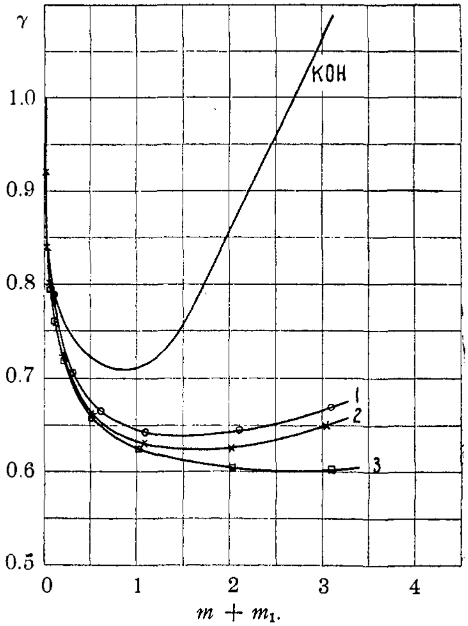

Fig. 1.—Activity coefficient of potassium hydroxide in potassium chloride solutions. 1, KOH (0.1), KCl; 2, KOH(0.01), KCl; 3, NaOH (0.01), NaCl.

The author wishes to express his appreciation for the valuable assistance rendered by Dr. Walter W. Lucasse.

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

[4] Ref. 1, Table III.

[5] Lewis and Randall, THIS JOURNAL, **43**, 1112 (1921); "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p. 367.

Summary

1. Measurements of the cells, $H_2 \mid KOH(m_1), KCl(m) \mid KOH(m_1) \mid H_2$ containing potassium hydroxide at 0.01 and 0.1 *M* concentrations, have been presented.

2. The activity coefficients of the hydroxide in the mixtures have been calculated.

3. The activity coefficient of potassium hydroxide in a potassium chloride solution is greater than that of sodium hydroxide in a sodium chloride solution when the hydroxides and salts are at the same strength.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NEW JERSEY COLLEGE FOR WOMEN]

THE PREPARATION AND PROPERTIES OF SOME PROTECTED SILVER SOLS

BY IRA D. GARARD AND GRACE E. DUCKERS

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In 1839[1] Wöhler obtained a brown, soluble mass by the reduction of dry silver citrate or silver mellitate with hydrogen at 100°. This was the first recorded preparation of colloidal silver. Since then many experimenters have prepared the metal in the colloidal state by some modification of one of the two general methods: (a) the reduction of a silver compound in solution,[2] or (b) the dispersion of the massive metal by an electric arc,[3] by ultra-violet light,[4] or by simply boiling the metal in water.[5,6] The reduction method has been most widely employed and reducing agents in great variety have been recommended by different authors.

That metallic sols were stabilized by the addition of certain organic substances had been known for many years, but no considerable investigation of the phenomenon was made until that of von Meyer and Lottermoser[7] in 1897. Since then this protective effect has been investigated from several angles by Zsigmondy,[8] Groh,[9] Rideal,[10] Iredale,[11] and Friend and Vallance.[12]

Many concentrated, protected silver sols have been made, but they are

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[1] Wöhler, *Pogg. Ann.*, (2) **46**, 629 (1839).

[2] Lea, *Am. J. Sci.*, (III) **37**, 476; **38**, 47, 129, 237 (1889).

[3] Bredig, *Z. Elektrochem.*, **4**, 51 (1898).

[4] Svedberg, *Ber.*, **42**, 4375 (1910).

[5] Traube-Mengarini, *Z. Chem. Ind. Kolloide*, **10**, 113 (1912).

[6] Nordenson, *Kolloidchem. Beihefte*, **7**, 91 (1915).

[7] Von Meyer and Lottermoser, *J. prakt. Chem.*, (2) **56**, 241 (1897).

[8] Zsigmondy, *Z. anal. Chem.*, **40**, 697 (1902).

[9] Groh, *Z. physik. Chem.*, **88**, 414 (1914).

[10] Rideal, THIS JOURNAL, **42**, 749 (1920).

[11] Iredale, *J. Chem. Soc.*, **119**, 109 (1921); **121**, 1536 (1922).

[12] Friend and Vallance, *ibid.*, **121**, 466 (1922).