[Contribution from the John Harrison Laboratory of Chemistry of the University of Pennsylvania]

THE ACTIVITY COEFFICIENT OF SODIUM HYDROXIDE IN AQUEOUS SOLUTION

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The activity coefficient of potassium hydroxide in moderately dilute and concentrated solutions has been determined by Chow[1] from measurements of the electromotive forces of cells of the type

$$Hg \mid HgO \mid KOH(m_1) \mid K_xHg \mid KOH(m_2) \mid HgO \mid Hg$$

and by Knobel[2] who measured the cells

$$H_2 \mid KOH(m_1) \mid K_xHg \mid KOH(m_2) \mid H_2$$

It seems probable that the results obtained by Knobel are more reliable than those of Chow, owing to the great ease with which the hydrogen electrode may be reproduced.

The present investigation is the beginning of a more extensive study of the activity coefficients of both sodium and potassium hydroxides in sodium and potassium chloride solutions, which includes an attempt to evaluate the independent ion activity coefficients of the ions present, and the ionic concentration product of water in solutions of salts of different valence types. Since no accurate data were available from which the activity coefficient of pure sodium hydroxide could be computed, it was first necessary to measure this quantity. Since many measurements were required in this and the subsequent investigations, it was a matter of considerable importance to simplify somewhat the method of measurement employed by Chow and by Knobel in order to extend the measurements with greater ease and rapidity to the solutions of the mixed electrolytes. In the present discussion, the apparatus, methods of preparation of materials and technique employed throughout will be described.

Experimental Technique

The technique of alkali amalgam cell measurements of solutions of electrolytes has been developed to a remarkable degree of reproducibility by MacInnes and Parker,[3] MacInnes and Beattie[4] and Knobel.[2] They employed in all cases dilute flowing amalgams and flowing solutions, took great precautions to remove all dissolved air from the solutions and exclude it from the apparatus. This exclusion of air is an essential precaution.

Preparation of Solutions.—Sodium hydroxide solutions free from

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[1] Chow, This Journal, **42,** 488 (1920).

[2] Knobel, *ibid.*, **45,** 70 (1923).

[3] MacInnes and Parker, *ibid.*, **37,** 1445 (1915).

[4] MacInnes and Beattie, *ibid.*, **42,** 1117 (1920).

carbon dioxide were made by first preparing a sodium amalgam by electrolyzing a concentrated sodium hydroxide solution. This amalgam was decomposed by water that had been previously boiled in a vacuum. The mercury was then drawn off through the bottom of the decomposition vessel and again employed for making the amalgam. The process was repeated until a strong solution of the hydroxide had been prepared. This solution was then drawn into a large bottle which contained carbon dioxide-free water and which was fitted with a side arm buret and soda lime tubes, and by this process was further diluted to about 0.8 *M* concentration. Its strength was determined by titration against standard hydrochloric acid. This standard solution was diluted to the desired strengths by drawing the required amounts into weighed quantities of water contained in evacuated vessels. A large quantity of approximately 0.01 *M* solution was made in this way and standardized by titration. For standardization of the dilute solutions both the methyl orange and phenolphthalein end-points were observed and the mean readings taken. In the absence of carbon dioxide there is a small difference between the color changes when 0.01 *M* solutions are titrated. The half-way point between these color changes should be the true equivalent point of titration. Solutions above 0.8 *M* concentration were made from sodium hydroxide solutions containing some carbonate. The latter was removed by the addition of a barium hydroxide solution drop by drop until precipitation ceased. All these standardized solutions contained dissolved air. Further precautions were therefore necessary to remove and then exclude the air.

Preparation of Amalgams.—Seventy cc. of a 0.1% sodium amalgam was first prepared by electrolysis of a concentrated sodium hydroxide solution. The amalgam was then permitted to flow into a 250cc. evacuated flask. This flask had a side arm attached to a high vacuum line. At the top was sealed a capillary tube and stopcock. After the amalgam had been completely dried and the vacuum had risen to 10^{-6} mm. the flask was sealed from the vacuum line, inverted and allowed to stand for five days or more until the impurities rose to the surface. This amalgam was then diluted by allowing it to flow through the capillary tube and stopcock into a highly evacuated liter flask containing 700 cc. of four times distilled mercury. This vessel was then sealed from the vacuum line and inverted. The amalgam prepared in this way was entirely free from surface scum. It could be drawn off from the flask through a stopcock into the amalgam dropper employed in the measurements.

Apparatus and Experimental Procedure.—The concentration cell without liquid junction, $H_2 \mid NaOH(m_2) \mid Na_xHg \mid NaOH(m_1) \mid H_2$, where m_1 was approximately 0.01 *M* was employed. In the preliminary work, a cell was constructed which, similar to the cell of Knobel, allowed both the solution and amalgam to flow. This cell was found somewhat difficult to manipulate and required more time for assembling it than was desirable. The measurement was simplified considerably by working with stationary solutions and a flowing amalgam. Thus, by eliminating one of the processes described above, a considerable reduction in the time required for an observation was obtained and less risk was incurred of making a complete failure of an experiment. As will be shown, the accuracy of the experiment cannot be greatly reduced by this elimination. Every precaution was taken to eliminate air from the apparatus and remove dissolved air from the solutions. Our experience in this respect is in full accord with the work of MacInnes and his collaborators. Further, the capillary tube amalgam dropper as employed by Chow, MacInnes and Beattie, and Knobel was found to be quite satisfactory. The apparatus is pictured in Fig. 1.

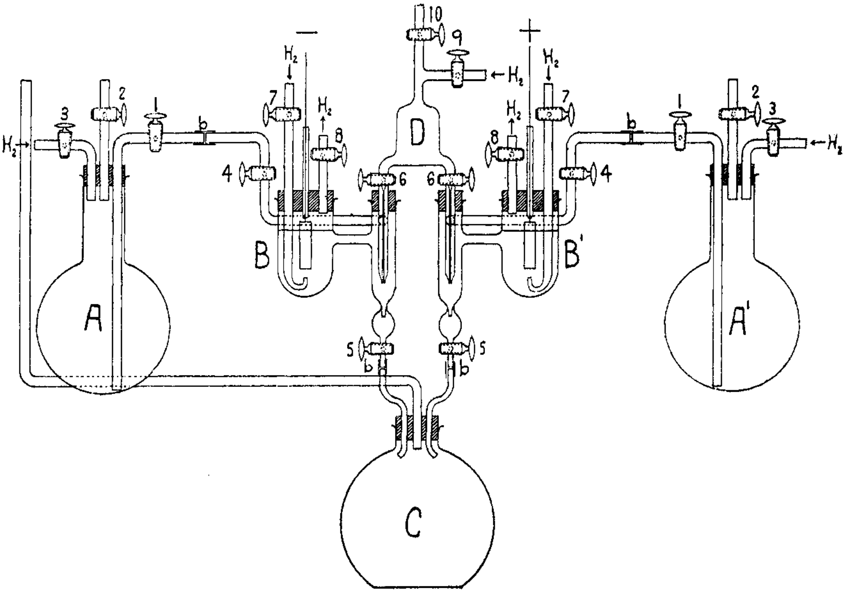

Fig. 1.—Apparatus.

A measurement was carried out in the following manner. Approximately the required amount of water was placed in the flask A, boiled in a vacuum and weighed. The amount of sodium hydroxide solution that, when added to this water, would give a solution of approximately the desired strength was run in through Stopcock 2 which was then closed. The solution was weighed, boiled in a vacuum and reweighed. The concentration of the solution was then computed. A′ was evacuated and a solution of 0.01 *N* sodium hydroxide was introduced, weighed, boiled in a vacuum, reweighed, and its concentration evaluated. In the meantime the amalgam dropper, D, was attached to the high vacuum line and the amalgam reservoir, after the capillaries and the stopcock bores had been filled with pure mercury. When the vacuum was attained, D was nearly filled with the amalgam, Stopcocks 9 and 10 were closed and then the dropper was removed from the vacuum apparatus. The cell vessels B and B′ were similar to those employed by MacInnes and Beattie.[4] The hydrogen electrodes were of sheet platinum about 2.5 cm. in length and 0.5 cm. in width and were coated with platinum black in the customary way. C is a reservoir for receiving the amalgam and rested on the bottom of the thermostat. The apparatus was assembled and joined by rubber tubes, bbbb. All of the stopcocks were closed except 4 4 and 5 5 and the system evacuated to 0.01 mm. by means of an oil pump. Stopcocks 3 3 were opened, 5 5 closed and 1 1 opened and the cell apparatus filled with the solutions. Then 1 1 and 4 4 were closed. Stopcocks 8 8 which were connected to a vessel containing hydrogen were opened, C was opened to the atmosphere and 5 5 were opened until the solution in the hydrogen electrode compartments of B and B′ were at suitable levels. Hydrogen was then introduced through 7 7 and the electrodes were allowed to attain equilibrium by standing for three to four hours. The measurement was then made in the following simple manner. Stopcocks 9 and 10 were opened and hydrogen passed over the amalgam. Stopcocks 6 6 were then opened completely and the amalgam which flowed into the bottoms of B and B′ removed as rapidly as it entered through the stopcocks 5 5. This flow was adjusted by hand and care was taken to keep the levels of the solutions in the hydrogen electrode compartments constant. The tube D which contained approximately 30 cc. of amalgam emptied in about ten minutes. During this time as many readings as possible were made on the potentiometer and the mean of these was taken as the electromotive force of the cell. When operated in this manner, it was found that 80–90% of the experiments took place without mishap and could be regarded as successful.

Since during one of these experiments the solution was not allowed to flow, it is important to inquire as to whether there was sufficient amalgam decomposition to change the solution concentrations and thus influence the results. No such disturbing behavior was noticed in any of the experiments. This fact is well illustrated by the data in Table I. The column headings indicate the molal concentrations of the solutions of sodium hydroxide, under which are given the observed electromotive forces of the cells containing these solutions. They represent the readings taken at approximately one minute time intervals during which the amal-

TABLE I

OBSERVED ELECTROMOTIVE FORCES DURING THE EXPERIMENT WITH CELLS $H_2 \mid NaOH(m_2) \mid Na_xHg \mid NaOH(m_1) \mid H_2$

1. m_2, 0.00530; m_1, 0.01011. 2. m_2, 0.1047; m_1, 0.00998. 3. m_2, 3.1; m_1, 0.01012.

1.	E	−0.03140	−0.03154	−0.03152	−0.03148	−0.03141	−0.03144	−0.03154
							Mean	−0.03147
2.	E	.11177	.11158	.11146	.11163	.11151		
		.11165	.11156	.11160	.11151	.11158		
					Mean	.11158		
3.	E	.29268	.29266	.29245	.29255	.29265		
		.29263	.29273	.29260	.29255	.29248		
					Mean	.29260		

These typical results show definitely that the values of the electromotive forces fluctuate around a mean value and show no tendency to change uniformly in one direction. This would happen if a change in concentration of one or both of the solutions was taking place to an appreciable extent.

gam was flowing. Concentrations are given in moles per 1000 g. of water. All measurements were carried out at 25°. The amalgam strength was approximately 0.01%.

Experimental Results

The observed results are given in Table II. The first two columns contain the concentrations of the solutions in the two cell compartments, and the third column the observed electromotive forces. The temperature was 25°. The amalgam strength was always approximately 0.01%.

TABLE II

ELECTROMOTIVE FORCES OF THE CELLS: $H_2 \mid NaOH(m_2) \mid Na_xHg \mid NaOH(m_1) \mid H_2$

m	m	E	$\frac{\gamma_{0.1}}{\gamma_1}$	γ_1
0.00530	0.01011	−0.0315	0.968	0.951
.01	.01000	.0000	1.000	.920
.0202	.01001	.0338	1.045	.880
.0526	.01000	.0795	1.119	.822
.1047	.00998	.1116	1.195	.770
.1081	.00984	.1142	1.187	.775
.1934	.00997	.1416	1.226	.750
.3975	.00995	.1762	1.281	.718
.807	.01006	.2103	1.330	.692
1.020	.01016	.2221	1.309	.703
1.517	.01003	.2459	1.262	.729
2.024	.01014	.2630	1.194	.771
3.100	.01012	.2926	1.030	.893

Calculation of the Activity Coefficients

The electrode reactions of the cell, $Na_xHg \mid NaOH(m) \mid H_2(1\text{ atm.})$, are $Na(Na_xHg) = Na^+(m) + \ominus$, and $\frac{1}{2}H_2(1\text{ atm.}) + OH^-(m) = H_2O(m)$[5] $+ \ominus$, whence by subtracting, the cell reaction becomes,

$$Na(Na_xHg) + H_2O(m) = \tfrac{1}{2}H_2 + OH^-(m) + Na^+(m)$$

At two concentrations, the reactions will be,

$$Na(Na_xHg) + H_2O(m_1) = \tfrac{1}{2}H_2 + Na^+(m_1) + OH^-(m_1);\ E_1$$

and

$$Na(Na_xHg) + H_2O(m_2) = \tfrac{1}{2}H_2 + Na^+(m_2) + OH^-(m_2);\ E_2$$

whence, by subtraction, we obtain the reaction $Na^+(m_2) + OH^-(m_2) + H_2O(m_1) = Na^+(m_1) + OH^-(m_1) + H_2O(m_2)$ corresponding to the cell

$$H_2 \mid NaOH(m_2) \mid Na_xHg \mid NaOH(m_1) \mid H_2;\ E_1 - E_2 = E$$

From the fundamental relationship between electromotive force and activities of the ions and molecular species, we obtain

$$NEF = RT\ ln\ \frac{a_{Na(m_2)}\ a_{OH(m_2)}\ a_{H_2O(m_1)}}{a_{Na(m_1)}\ a_{OH(m_1)}\ a_{H_2O(m_2)}} \quad (1)$$

which becomes

$$E + 0.05915 \log \frac{a_{H_2O(m_2)}}{a_{H_2O(m_1)}} = 0.1183 \log \frac{\gamma_2 m_2}{\gamma_1 m_1} \quad (1)$$

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[5] (m) refers to water in a solution of m hydroxide concentration.

where a_{Na}, a_{OH}, etc., are the activities of the species denoted by subscripts and γ_2, γ_1 are the activity coefficients of the hydroxide in the two solutions. Thus, in order to obtain γ it is necessary to correct the electromotive forces for the activity ratio of the water in the two solutions. The activity of the water in a solution is measured by the ratio of its vapor pressure over the solution to the vapor pressure of pure water. Therefore, this latter equation becomes

$$E + 0.05915 \log \frac{p_2}{p_1} = 0.1183 \log \frac{\gamma_2 m_2}{\gamma_1 m_1} \qquad (1)$$

where p_1 and p_2 are the vapor pressures of water above the two solutions, respectively. Consequently, in order to calculate γ it is necessary to correct the observed electromotive forces by the amount calculable from the term involving the vapor pressures. Since no accurate vapor-pressure measurements were available, it was found necessary to compute them from these electromotive forces. Consequently the following method was employed. The approximate activity coefficients were first computed by neglecting the term in Equation 1 which contains the vapor pressures. Since this term is negative, these values are higher than the true activity coefficients. The activity coefficient of 0.01 M sodium hydroxide was taken to be 0.920, which was the same as that taken by Knobel for potassium hydroxide. These approximate activity coefficients, γ_1, and their ratios to the 0.01 M value, calculated from the electromotive forces in the third column, are given in Table II. In a previous communication,[6] it was shown that the activity coefficient of an electrolyte may be expressed as a function of the concentration, m, over a considerable concentration range and a constant temperature, by the equation

$$\log \gamma = -\beta m^{\alpha'} + \alpha m \qquad (2)$$

where β, α' and α are constants. Further, if this equation is employed, the vapor pressure of the solution may be calculated from the formula

$$ln \frac{p_0}{p} = \frac{m}{55.5}\left[2 + \frac{4.606\,\alpha}{2}\,m - \frac{4.606\,\beta'\alpha'}{\alpha'+1}\,m^{\alpha'}\right] \qquad (3)$$

In the present case, the activity coefficients in Table II can be calculated in the concentration range from 0.02 to 3 M if β, α' and α are assigned the values, 0.288, 0.387 and 0.13, respectively. These values were substituted in (3), the vapor pressure corrections made according to Equation (1) and the activity coefficients recalculated. These latter activity coefficients will be somewhat too low in the more concentrated solutions. Therefore, the constants β, α' and α were again evaluated from these corrected activity coefficients, the vapor pressures again calculated from this new series of constants, the electromotive forces again corrected and the activity coefficients recalculated. The final values of the constants

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

β, α' and α were 0.388, 0.287 and 0.122, respectively, whence

$$\log \gamma = -\ 0.288m^{0.387} + 0.122m \tag{4}$$

and

$$ln\,\frac{p_0}{p} = \frac{m}{55.5}\,[2 + 0.2810m - 0.3701m^{0.387}] \tag{5}$$

which equations are valid from 0.02 to 3 M. A similar calculation was made with Knobel's results on potassium hydroxide and β, α' and α were found to be 0.288, 0.387 and 0.169, respectively, whence

$$\log \gamma = -0.288m^{0.387} + 0.169m \tag{6}$$

and

$$ln\,\frac{p_0}{p} = \frac{m}{55.5}\,[2 + 0.3892m - 0.3701m^{0.387}] \tag{7}$$

valid from 0.02 to nearly 3 M. Table III contains the results of the final calculation when these values of the constants are employed. The first column contains the molal concentrations, the second the natural logarithm of the ratios of the vapor pressures of 0.0202 M to p_2, the vapor pressure of the more concentrated solution, and Col. 3 the correction in volts to be applied to the electromotive forces.

The fourth column contains the observed electromotive forces of the cells refered to 0.0202 M (E —0.0338). This was first corrected in such a way that each concentration would be compared to an exactly 0.01

TABLE III

ACTIVITY COEFFICIENT RATIOS AND ACTIVITY COEFFICIENTS

SODIUM HYDROXIDE

1 M	2 $ln\,\frac{p_{0.0202}}{p_m}$	3 $0.02568\ ln\,\frac{p_m}{p_{0.0202}}$	4 E	5 E (Ref. to 0.01)	6 E (Final)	7 $\frac{\gamma_{0.0202}}{\gamma_m}$	8 γ
0.0202	0.00000	0.000000	0.0000	0.0000	0.0000	1.000	0.880
.0526	.00109	− .000028	.0457	.0457	.0457	1.070	.822
.1047	.00283	− .000073	.0778	.0777	.0776	1.145	.768
.1081	.00294	− .000075	.0804	.0796	.0795	1.139	.773
.1934	.00577	− .000148	.1078	.1077	.10755	1.179	.748
.3975	.01256	− .000322	.1424	.1426	.1423	1.233	.714
.807	.02671	− .000686	.1765	.1768	.1761	1.297	.678
1.020	.03446	− .000884	.1883	.1891	.1882	1.295	.680
1.517	.0535	− .001373	.2121	.2122	.2108	1.241	.709
2.024	.0752	− .001929	.2292	.2299	.2280	1.185	.743
3.1	.1276	− .003276	.2588	.2594	.2561	1.050	.838

POTASSIUM HYDROXIDE

	$ln\,\frac{p_{0.03}}{p_m}$	$0.02568\ ln\,\frac{p_m}{p_{0.03}}$					
0.0300	.00000	.000000	.0000	....	.0000	1.000	.857
.05	.00068	− .000017	.0241	....	.0241	1.043	.822
.10	.00236	− .000061	.0577	....	.0576	1.086	.789
.30	.00915	− .000235	.1113	....	.1111	1.150	.746
1.0	.03534	− .000907	.1750	....	.1741	1.128	.760
3.0	.1376	− .00353	.2511	....	.2476	0.807	1.062

molal solution (Col. 5). Col. 6 contains the electromotive forces corrected for the vapor pressure and which in turn are given by

$$E = 0.1183 \log \frac{\gamma_2 m_2}{\gamma_1 m_1} \qquad (8)$$

Col. 7 contains the activity coefficient ratios and Col. 8 the activity coefficients, calculated from the electromotive forces in Col. 6. The values of γ at 0.0053 and 0.01 are the same as in Table II.

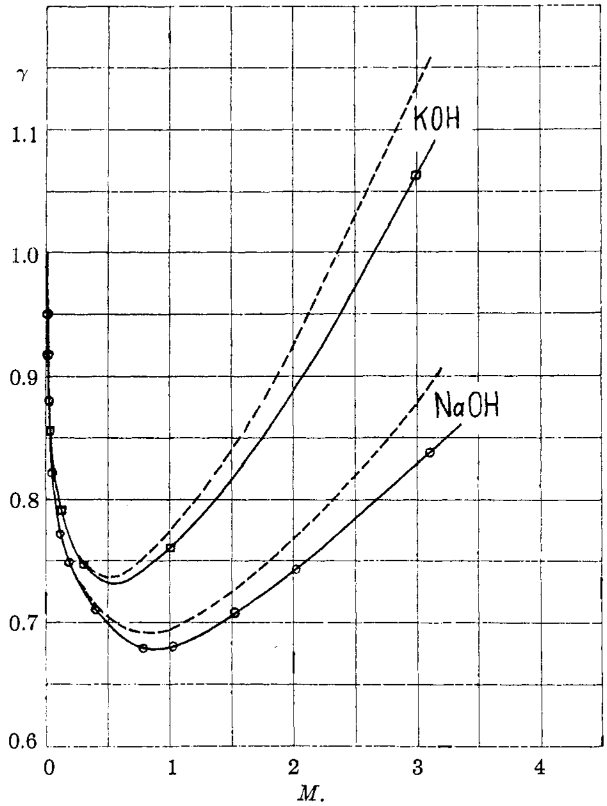

Fig. 2.—Activity coefficients of sodium and potassium hydroxides.

Discussion

In Fig. 2 are plotted the activity coefficients of potassium and sodium hydroxides taken from Col. 8, Table III, against the molal concentrations. The activity coefficients computed from the original electromotive forces without allowing for the activity of the water are also plotted (dotted lines). The extent of this correction is very small in the dilute solutions but amounts to 2% at M and 7% at 3 M concentrations.

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, $H_2 | NaOH(m_2) | Na_xHg | NaOH(m_1) | H_2$, 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

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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).