[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Heat of Dilution of Aqueous Sodium Hydroxide Solutions at 25°

BY JULIAN M. STURTEVANT

The integral heats of dilution of hydrochloric acid have recently[1] been redetermined. In continuation of this work, similar data for sodium hydroxide are now reported.

Experimental Part

The calorimeter used in these measurements has been described elsewhere.[2] All due care was taken in the calibration of the apparatus.[1,2]

The stock solution of sodium hydroxide was made up from J. T. Baker analyzed material. A saturated solution of sodium hydroxide in distilled water was allowed to stand until the sodium carbonate had settled. An approximately 4 *m* solution was prepared from the decanted solution and distilled water, and was then treated with a slight excess of barium hydroxide. After the barium carbonate had settled, the solution was siphoned off and treated with the calculated quantity of sulfuric acid to remove the barium present. The barium sulfate was then allowed to settle, and the solution siphoned into a paraffined bottle, where it was stored under a slight pressure of tank nitrogen. All of the above operations were carried out under nitrogen.

The stock sodium hydroxide was analyzed at the start and completion of the measurements by weight titration (methyl red indicator) against freshly prepared hydrochloric acid which had been standardized by precipitation of silver chloride. The titrations were carried out in an atmosphere of nitrogen. The results of these analyses are:

Before measurements: 1 g. (vac.) NaOH soln. ≡ 0.0035836 mole HCl ± 0.02%

After measurements: 1 g. (vac.) NaOH soln. ≡ 0.0035825 mole HCl ± 0.04%

The percentage given in each case is the sum of the average deviations of four silver chloride determinations and four titrations. The solution was found to be 0.00015 *M* in chloride ion and 0.0005 *M* in barium ion, presumably present as barium hydroxide and barium carbonate. In the calculations it was deemed best to assign the total alkalinity of the solution to the sodium hydroxide, and accordingly the mean of the figures given above was used, the molality of the sodium hydroxide being taken as 4.1826.

Attempts were made to analyze the stock solution by neutralization with hydrochloric acid, evaporation to dryness, and weighing the sodium chloride formed. However the results ran uniformly about 0.2% higher than those obtained by titration, even though the sodium chloride samples were heated to about 400–450° for an hour. Allowance was made for the barium chloride present in the sodium chloride.

Considerable attention was given to preventing the contamination of the solutions with atmospheric carbon dioxide. The dilution cup of the calorimeter was filled from weight burets and sealed in a gas-tight box under a slight positive pressure of tank nitrogen. The diluting water in the calorimeter was distilled, boiled, and saturated with about 5 lb. pressure (above atmospheric) of nitrogen so that during short exposures to the air it would tend to lose nitrogen rather than to absorb air. The calorimeter was flushed out with nitrogen, and a slow stream of nitrogen was continued while the diluting water (or solution) was run in from a weight buret. This procedure caused greater evaporation of the water before the calorimeter could be closed, but in view of the fact that the filling operation was completed in less than thirty seconds, it seems unlikely that serious errors could have been introduced in this way.

It has been pointed out by Richards and Gucker[3] that in dilution experiments to high dilutions considerable heat of neutralization compared to the heat of dilution would be caused by the presence of even very small amounts of carbon dioxide in the diluting water. In accordance with the suggestion made by them, in all such cases in the present work very dilute sodium hydroxide was used as the diluent in place of water. The molal heat of a dilution of this type is given by the expression

$$\Delta H = \frac{\Delta q + n_2 \Delta H_{\text{dil}}}{n_1 + n_2} \qquad (1)$$

where Δq is the heat absorbed in the dilution, ΔH_{dil} is the heat of dilution per mole to the concentration of the diluent, and n_1 n_2 are the number of moles of sodium hydroxide in the initial solution and the diluent, respectively. Since the concentration of the diluent is beyond the range of the present measurements, the values of ΔH_{dil} were read from the extrapolated experimental curve. This procedure may introduce uncertainties beyond those of extrapolation according to the Debye–Hückel limiting law since Doehlemann and Lange[4] have shown that at very high dilutions relatively large heat effects enter due to disturbance of the water equilibrium. However, the lowest diluent concentrations are in the range where the water equilibrium effects are still not serious, and since the heat term due to the diluent is small (usually less than 1%, with a maximum of 4%), it is felt that errors from this source are negligible.

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[1] Sturtevant, THIS JOURNAL, **62**, 584 (1940).

[2] Sturtevant, *J. Phys. Chem.*, in press (1940).

[3] Richards and Gucker, THIS JOURNAL, **51**, 712 (1929).

[4] Doehlemann and Lange, *Z. physik. Chem.*, **170**, 391 (1934).

Experimental Results.—The observed heats of dilution are recorded in Table I. The first, second, and third columns of this table give the square root of the molalities of the initial, final and diluting solutions, respectively. In the fourth column are the heats of dilution, expressed in international joules per mole of sodium hydroxide, from the stock solution (4.1826 *m*) to the final concentration in the runs marked *a* or to the initial concentration in the runs marked *b*. Where necessary, the heat of dilution from the stock solution to some other concentration was obtained by graphical interpolation in the results of previous runs. Out of a total of 39 runs, 4 were omitted because of excessive deviation from the smooth curve drawn through the rest of the results. In the fifth and sixth columns of Table I are listed the deviations of the individual runs from the curve of Fig. 1, expressed in joules, and in microvolts, respectively. The average deviation, ± 0.04 microvolt, corresponds to 56 microdegrees, and is just about the reproducibility to be expected with the thermel-galvanometer system used.

TABLE I

INTEGRAL HEATS OF DILUTION OF SODIUM HYDROXIDE SOLUTIONS AT 25°

Square root of concentration (moles per 1000 g. $H_2O)^{1/2}$			Heat of dilution, ΔH, joules (int.) per mole	Deviation from curve in Fig. 1	
Initial	Final	Diluent		Joules	Microvolts
2.0451	0.1592	0.0402	205.9[a]	−13.3	−0.07
2.0451	.1998	.0336	249.8[a]	− 9.4	− .07
2.0451	.2486	.0598	325.7[a]	+ 5.7	+ .06
2.0451	.2746	0	343.0[a]	0	0
2.0451	.3546	0	397.9[a]	+ .3	+ .01
2.0451	.3795	0	405.5[a]	− 4.9	− .12
2.0451	.3925	0	416.3[a]	0	0
2.0451	.4424	0	435.1[a]	− 0.3	− .01
2.0451	.5205	0	453.8[a]	+ 2.0	+ .09
2.0451	.5697	0	451.5[a]	− 1.9	− .11
2.0451	.5852	0	453.1[a]	+ .7	+ .04
2.0451	.6199	0	446.1[a]	− 2.2	− .14
2.0451	.7906	0	393.6[a]	0	0
1.9377	.3937	0	− 77.1[b]	0	0
1.8179	.3671	0	−116.5[b]	0	0
1.6596	.3850	0	−114.7[b]	− .9	− .02
1.6472	.4152	0	−110.5[b]	+ .6	+ .02
1.5430	.4018	0	− 78.7[b]	0	0
1.3288	.3423	0	+ 35.1[b]	0	0
1.1243	.2977	0	183.2[b]	+ .9	− .01
1.1098	.2795	0	193.0[b]	− .3	+ .004
1.0288	.2979	0	253.5[b]	+ .9	− .01
0.9875	.2514	0	280.2[b]	− .9	+ .01
.8468	.2401	0	375.7[b]	−15.4	− .10
.8377	.2171	0	355.9[b]	−14.7	− .12
.7298	.1308	.0243	185.1[a]	+ 6.3	− .02
.7298	.1215	.0247	173.1[a]	+ 7.1	− .02
.6909	.1553	.0280	218.5[a]	+ 4.6	− .02
.6909	.1264	.0265	194.7[a]	+21.9	− .06
.6823	.1728	0	450.4[b]	+16.1	+ .08
.6372	.1238	.0246	178.9[a]	+ 9.9	− .02
.6372	.1114	.0202	158.7[a]	+ 8.4	− .02
.6372	.1034	.0213	107.7[a]	−30.4	+ .05
.5843	.1739	.0251	235.9[a]	− 2.2	+ .01
.5843	.1117	.0197	124.4[a]	−25.7	+ .05
			Mean	± 5.8	± .04

[a] Heat of dilution from 4.1826 *m* to final molality.
Heat of dilution from 4.1826 *m* to initial molality.

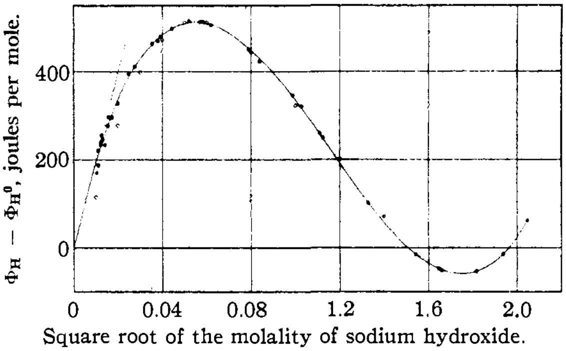

Fig. 1.—Relative apparent molal heat content of sodium hydroxide. The dotted line is the Debye–Hückel limiting law; ●, this research; ○, Rossini's values, modified as described in the text.

The dilution heats have been corrected to 25.00° using the following temperature coefficient, which is based on the data of Gucker and Schminke[5] for the apparent molal heat capacity of the solute

$$d(\Delta H)/dT = 73.2\ (m_1^{1/2} - m_2^{1/2}) \qquad (2)$$

where m_1, m_2 are the initial and final molalities, respectively. Since the heat capacity used to evaluate the energy change during the dilution was that of the products plus the calorimeter, the observed heat of dilution corresponds to the initial temperature of the experiment. The initial temperature deviated on the average about ±0.05° from 25°.

The heat capacity of the products plus the calorimeter was determined in only five of the runs. In these cases the observed values agreed to within ±0.05% with the values calculated from the measured heat capacity of the calorimeter and the data of Gucker and Schminke,[5] allowance being made for the varying amounts of nitrogen present in the calorimeter. In the other runs the calculated heat capacity was used.

Treatment of Results.—In treating the data of dilution experiments, it is customary to extrapolate the data to infinite dilution to obtain values for the relative apparent molal heat content of the solute. In the case of strong electrolytes the limiting slope of the extrapolation is usually made to correspond to the Debye–Hückel limiting law. However, the treatment given by Doehlemann and Lange[4] for the heat effects arising from displacement of the water equilibrium

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(5) Gucker and Schminke, THIS JOURNAL, **55**, 1013 (1933).

in very dilute solutions makes it evident that extrapolation according to the Debye–Hückel law is an arbitrary procedure,[6] especially in the case of acids and bases, for which substances the heat effects are particularly large. The present apparatus is far too insensitive to carry the dilutions to the point where these effects become noticeable, and it therefore seems justifiable, on the basis of convenience, to perform the usual Debye–Hückel extrapolation. In all practical applications one is interested in differences between apparent heat contents, so that the method of extrapolation to infinite dilution is of little significance.

The data of Table I were plotted on a large scale, and extrapolated to infinite dilution with the limiting slope 1997, calculated from the constants given by Harned and Ehlers.[7] The intercept obtained in this way, −52.4 joules per mole, is the negative of the apparent heat content of the stock solution, and the heats of dilution given in Table I are converted to apparent heat contents by adding to them 52.4.

In the second column of Table II are listed the values of the relative apparent molal heat content of the solute for round values of the square root of the molality. The values were read from a large-scale plot of the experimental data. Also given in Table II are values of the partial relative molal heat contents of the solute and solvent, calculated, respectively, by the formulas

$$\overline{L}_2 = \Phi_H - \Phi_H^0 + {}^1/_2 m^{1/2} \frac{d(\Phi_H - \Phi_H^0)}{dm^{1/2}} \qquad (3)$$

$$\overline{L}_1 = \frac{m}{55.506} (\Phi_H - \Phi_H^0 - \overline{L}_2) \qquad (4)$$

the values of $d(\Phi_H - \Phi_H^0)/dm^{1/2}$ being obtained by graphical differentiation.

Estimate of Accuracy.—The experimental points fit the smoothed curve drawn through them with an average deviation of ±6 joules per mole. Since a large part of this average deviation is caused by the more inaccurate measurements at the lower concentrations, and since it is believed that no serious sources of systematic error have been overlooked, it would appear that a conservative estimate of the reliability of a heat of dilution between finite concentrations calculated from the smoothed apparent heat contents is the larger of the two quantities ±10 joules per mole or ± the number of joules per mole corresponding to 100 microdegrees. Differences between values of the relative heat contents are subject to somewhat larger errors since these quantities involve slopes read from a graph.

TABLE II

APPARENT AND PARTIAL RELATIVE MOLAL HEAT CONTENT OF SOLUTE AND PARTIAL RELATIVE MOLAL HEAT CONTENT OF SOLVENT IN AQUEOUS SODIUM HYDROXIDE SOLUTIONS AT 25°

Square root of molality of sodium hydroxide	Heat content, joules (int.) per mole		
	$\Phi_H - \Phi_H^0$	$\overline{L}_2$	$\overline{L}_1$
0.0000	0	0	0
.0500	97.6		
.1000	184.4	265.9	− 0.0147
.1500	258.9		
.2000	321.8	436.6	− .0827
.2500	374.0		
.3000	414.8	524.0	− .177
.3500	447.3		
.4000	472.3	556.6	− .243
.4500	490.1		
.5000	501.5	540.9	− .177
.5500	506.0		
.555	506.1 (max.)	506.1	0
.6000	503.5	468.9	+ .224
.6500	495.0		
.7000	481.3	369.9	.983
.7500	463.6		
.8000	441.9	252.5	2.18
.8500	416.7		
.9000	388.8	125.6	3.84
.9500	358.0		
1.0000	325.1	− 18.1	6.18
1.0500	289.9		
1.1000	253.1	−159.7	9.00
1.1500	215.5		
1.2000	178.2	−270.5	11.6
1.2500	141.7		
1.3000	106.9	−337.0	13.5
1.3500	73.9		
1.4000	43.6	−363.3	14.4
1.4500	16.2		
1.5000	− 7.9	−346.8	13.7
1.5500	−28.9		
1.6000	−46.3	−292.7	11.4
1.6500	−59.3		
1.7000	−67.5	−160.7	4.85
1.7500	−70.3 (min.)	− 70.3	0
1.8000	−66.8	+ 53.7	− 7.0
1.8500	−57.2		
1.9000	−41.4	322.3	−23.7
1.9500	−18.3		
2.0000	+13.7	(754.0)	(−53.3)
2.0451	52.4		

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(6) The author is indebted to Dr. A. L. Robinson of the University of Pittsburgh for calling to his attention the paper of Doehlemann and Lange.[4] In the previous paper[1] on the heat of dilution of hydrochloric acid the statement was made that some experimental results of Doehlemann and Lange ("Landolt-Börnstein Tabellen," 5th edition, Ergänzungsband III C, p. 2800) could not be reconciled with the requirements of the Debye–Hückel theory. This statement is probably incorrect, the apparently abnormal heat effects observed by Doehlemann and Lange presumably being due to the disturbance of the water equilibrium.

(7) Harned and Ehlers, THIS JOURNAL, 55, 2179 (1933).

TABLE III

COMPARISON OF HEATS OF DILUTION WITH PREVIOUS WORK AT 20°

Square root of molality		Heat of dilution, joules per mole				Deviation from this research,[c] °C.		
			$\Delta H_{25°}$					
Initial	Final	$\Delta H_{20°}$	Calcd. by (*a*)	Calcd. by (*b*)	This research	Calcd. by *a*	Calcd. by *b*	Ref.
1.4900	1.0536	461	301	288	291	+0.0025	−0.0008	*d*
1.4900	0.7451	767	494	471	469	.0032	+ .0002	*d*
1.4900	.5268	889	537	507	508	.0019	− .0001	*d*
1.4900	.3726	902	493	458	463	.0010	− .0002	*d*
1.4900	.2634	860	411	373	389	.0004	− .0002	*d*
1.4900	.1863	803	326	285	309	.0002	− .0002	*d*
1.4900	.1317	749	252	210	235	.0001	− .0001	*d*
1.4900	.0000	(682)	(137)	(98)	(+3)	....	....	*d*
1.4900	1.0536	466	306	293	291	+ .0038	+ .0005	*e*
1.4900	0.7451	768	495	472	469	.0034	.0004	*e*
1.4900	.5268	889	537	507	508	.0019	− .0001	*e*
1.4900	.3726	910	501	466	463	.0012	+ .0001	*e*
1.7624	1.4900	163	63	55	67	− .0019	− .0059	*f*
1.4900	1.4611	22.6	12.0	11.1	14.1	− .0010	− .0014	*f*

[a] Calculated using $\Phi_C - \Phi_C^0 = 73.2\, m^{1/2}$; Gucker and Schminke, THIS JOURNAL, **55**, 1013 (1933). [b] Calculated using $\Phi_C - \Phi_C^0 = 79.4\, m^{1/2}$; Rossini, *Bur. Standards J. Research*, **6**, 791 (1931). [c] Calculated neglecting the heat capacity of the calorimetric system. [d] Richards and Gucker, THIS JOURNAL, **51**, 712 (1929). [e] Richards and Rowe, *ibid.*, **43**, 779 (1921), recalculated by Richards and Hall, reference *f*. [f] Richards and Hall, *ibid.*, **51**, 731 (1929).

Comparison with Previous Work.—The only earlier work with which direct comparison can be made is that of Richards and his co-workers, which was done at 20°. This comparison is shown in Table III. Inspection of the relatively large differences between the figures in the fourth and fifth columns of this table, which represent dilution heats calculated from 20 to 25° with two different temperature coefficients, makes it evident that the apparent discrepancies between the earlier work and the present results cannot be regarded as very serious.

In Fig. 1, the open circles represent values of the apparent heat content deduced by Rossini[8] from the data of Richards and co-workers. These values have been calculated from 18 to 25° with the value of the apparent molal heat capacities given by Rossini, and have then been brought into coincidence with the curve representing the present results at 0.36 *m* by subtracting 115 joules per mole from each value given by Rossini. Bringing the two sets of values into coincidence at a point where each set should be quite reliable eliminates the effects of differences in extrapolation to infinite dilution. As in the case of the comparison made in Table III, the doubt in the temperature coefficient precludes any very significant comparison between these two sets of values.

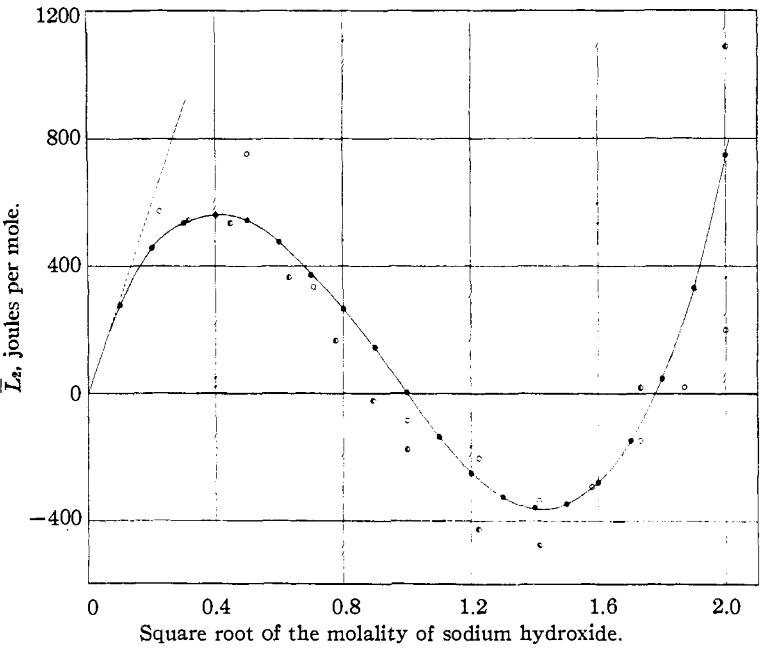

Fig. 2.—Relative partial molal heat content of sodium hydroxide. The dotted line is the Debye–Hückel limiting law; ●, this research; ◐, Åkerlöf and Kegeles; ○, Harned and Hecker.

Two determinations[9] of the relative partial molal heat contents of sodium hydroxide have been made by means of the electromotive force method. These data are compared with the

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[8] Rossini, *Bur. Standards J. Research*, **6**, 791 (1931).

[9] Harned and Hecker, THIS JOURNAL, **55**, 4838 (1933); Åkerlöf and Kegeles, *ibid.*, **62**, 620 (1940).

present data in Fig. 2, in which the black circles represent the values of $\overline{L}_2$ given in Table II. With the possible exception of a few of the points, the deviations found are within the estimated accuracy of the e. m. f. method. The value obtained in the present work at 4 m is subject to greater doubt than those at lower concentrations, since this point is near the end of the concentration range studied and the slope is therefore more poorly defined.

Gucker and Pickard[10] have pointed out recently that experiments in which a relatively large volume of air is contained in the dilution cup over a concentrated solution may be subject to significant errors arising from distillation of water from the diluent into this air space after mixing has taken place. This correction and the correction for the condensation of water vapor from the air over the diluent have been applied throughout, the necessary vapor pressure data being taken from the work of Åkerlöf and Kegeles.[9] Unfortunately, the work of Gucker and Pickard was noted at too late a date to allow correction of the curves in Figs. 1 and 2, though all the data given in the tables are corrected. The dilution heats were lowered on the average approximately 3 joules per mole by these corrections, so that most of the changes are practically invisible on the small scale of Figs. 1 and 2.

Corrections of this type have no significant effect in the case of the data on the heats of dilution of aqueous glycine solutions previously published,[11] but cause changes somewhat larger than the estimated uncertainty in some of the data on hydrochloric acid.[1] It is hoped that a recalculation of the latter data will be published in the near future.

Summary

The heat of dilution of aqueous solutions of sodium hydroxide has been determined at 25° up to a concentration of 4 m. From these data have been calculated the apparent and partial relative molal heat content of the solute, and the partial relative molal heat content of the solvent.

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[10] Gucker and Pickard, THIS JOURNAL, **62**, 1464 (1940).

[11] Sturtevant, *ibid.*, **62**, 1879 (1940).

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

The Thermodynamics of the Silver Bromide–Mercurous Bromide Cell[1]

BY THOMAS W. DAKIN[2] AND D. T. EWING

A measurement of the simple cell

$$Hg/Hg_2Br_2,\ MBr\ (aq.\ soln.),\ AgBr/Ag \qquad (1)$$

where MBr is either hydrogen bromide or potassium bromide and its concentration immaterial, leads directly to the difference between the standard electrode potentials of the silver bromide and the mercurous bromide electrodes and the difference between the free energies of formation of silver bromide and mercurous bromide. A measurement of the temperature coefficient of this cell leads to the difference between the heats and entropies of formation of silver bromide and mercurous bromide. Using the comparatively accurate values of these constants for silver bromide which are in the literature, the corresponding constants for mercurous bromide may be calculated. The present investigation was carried out to redetermine by measurement of the above cell at three temperatures the standard electrode potential of the mercurous bromide electrode and the thermodynamic functions of the formation of mercurous bromide.

The values found in the literature[3] for the standard electrode potential of the mercurous bromide electrode at 25° vary over a range from 0.1385 v. to 0.1400 v. and for the most part are based on somewhat deviating values for the activity coefficients of hydrobromic acid solutions. Larson[4] measured a cell similar to the one reported in the present paper, using potassium bromide solutions exclusively, and at the temperatures 20, 25 and 30°. He obtained a value for the standard electrode

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[1] This paper was presented at an Ohio–Michigan regional meeting of the A. C. S. in October, 1939.

[2] The material of this paper has been abstracted from a thesis submitted to the faculty of the Graduate School of Michigan State College by T. W. Dakin in September, 1938, in partial fulfillment of the requirements for the M. S. degree. The present address of the junior author is Harvard University.

[3] Gerke and Geddes, *J. Phys. Chem.*, **31**, 886 (1927); Matthews, Ph.D. Thesis, Michigan State College (1930); Larson, M. S. Thesis, Michigan State College (1931); Gerke, "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1930, Vol. VI, p. 332; Ishikawa and Ueda, *J. Chem. Soc. Japan*, **51**, 59 (1930).

[4] Larson, THIS JOURNAL, **62**, 764 (1940).