2. The partial molal heat capacity of zinc sulfate in the standard state (infinite dilution in water) is $\bar{C}_p{}^\circ\ ZnSO_4 = -107$ calories per degree per mole.

3. The partial molal heat capacities, the relative partial molal and integral heat contents of zinc sulfate solutions have been computed at each concentration and the results compared with the theoretical formulas derived from the limiting forms of the Debye–Hückel theory using Wyman's determinations for the temperature dependence of the dielectric constant of water.

4. The contribution due to thermal expansion which has been neglected by previous investigators amounts to a correction of 16% at 25° in the theoretical limiting slope for the concentration dependence of the partial molal heat capacities.

5. The values for the integral heat of dilution of zinc sulfate are compared with the values for calcium sulfate as measured by Lange and Monheim for the same range of concentration. Aside from reasonable individual differences, which have been shown to persist to high dilution, the results are consistent with their valence type.

The Heat Capacity and Related Thermodynamic Properties of Aqueous Solutions. II. Lithium and Sodium Hydroxides at 25°

BY FRANK T. GUCKEP, JR., AND KARL H. SCHMINKE

Introduction

In order to widen the scope of our previous work, we have used the same methods to determine the specific heats of solutions of lithium and sodium hydroxides. The experiments were carried out in the Joule–Pfaundler *thermal balance*. In the *working calorimeter*, definite quantities, first of water and then of solution, were balanced against a fixed weight of water in the *tare* calorimeter. Using a multiple thermel, *temperature differences* were measured with a sensitivity of one or two hundred thousandths of a degree and specific heats were determined with an accuracy of about ±0.01%. The reader is referred to previous articles[1] for detailed descriptions of the apparatus and experimental technique.

Materials and Solutions

The hydroxides were prepared from the best available material, further purified in contact only with platinum, nickel or stainless steel.

(1) Gucker and Schminke, THIS JOURNAL, **54**, 1358 (1932); Gucker, *ibid.*, **50**, 1005 (1928); Richards and Gucker, *ibid.*, **47**, 1876 (1925).

The preparation of pure lithium hydroxide offered considerable difficulty. Finally it was accomplished in the following tedious but satisfactory way: C. P. lithium chloride was dissolved in absolute alcohol which was saturated with dry hydrogen chloride gas to precipitate out the sodium and potassium salts. The solution was filtered and the alcohol distilled off. The residue of lithium chloride was treated with a slight excess of pure concentrated sulfuric acid and evaporated in a platinum dish until fumes of sulfur trioxide ceased coming off.

C. P. barium hydroxide, recrystallized and drained centrifugally, was dissolved in hot distilled water. The solid lithium sulfate was added to this solution and, on metathesis, yielded a solution about 5 m in lithium hydroxide. This was decanted into a paraffin-lined bottle. The voluminous residue of barium sulfate was extracted several times with hot water, to increase the yield of hydroxide. The lithium hydroxide solution was then treated with pure sulfuric acid, a little at a time, until as much as possible of the excess barium ion was removed. The resulting solution contained a negligible quantity of barium and of sulfate ion, and gave equal turbidity when tested with equivalent amounts of either ion. It was found to contain about 0.04 mole per cent. of sodium and less than 0.02 mole per cent. of potassium, since it gave no precipitate with acetic acid and sodium cobaltinitrite solution. The first preparation (Expts. 1–8) contained 0.15 mole per cent. of chloride, which had escaped volatilization in the sulfuric acid treatment. In the second preparation (Expts. 9–15) the chloride ion was removed by treating the lithium sulfate with a small amount of silver sulfate. Any excess silver was removed when the barium hydroxide was added, and remained with the barium sulfate.

The sodium hydroxide was purified by recrystallization of the monohydrate from water solution. About 63 g. of water was added to every 100 g. of sodium hydroxide sticks. A slightly more concentrated solution solidifies completely at room temperature and a less concentrated one gives a low yield of crystals. When the mixture was heated to 60° the solid dissolved completely. The solution was stirred from time to time as it cooled to room temperature, so that it deposited crystals of the right size. These were then drained centrifugally for about ten minutes, to remove the viscous mother liquor as completely as possible. The only impurity which they then contained in appreciable quantities was carbonate, which is always picked up from the air. Fortunately, sodium carbonate is nearly insoluble in concentrated hydroxide and so it is removed quite easily. The crystals were dissolved in the minimum quantity of freshly-boiled distilled water and the resulting solution filtered by suction through a platinum sponge Gooch crucible into a paraffin-lined bottle containing water. The first preparation (Expts. 1–10) was found to contain 0.02 mole per cent. of carbonate, 0.06 mole per cent. of potassium and 0.002 mole per cent. of chloride. The second preparation (Expts. 11–20) was even more completely freed of carbonate. The sodium hydroxide was crystallized as before, then dissolved in the minimum quantity of water and treated with enough recrystallized barium hydroxide to remove all the carbonate. After suction filtration, the excess barium was removed as in the case of the lithium hydroxide. This second solution contained 0.07 mole per cent. of potassium.

All the solutions were made up with freshly-boiled distilled water and were stored in paraffin-lined bottles, whence they were siphoned out as needed through stainless steel or paraffin-lined glass tubes. In order to prevent contamination with carbon dioxide, the incoming air was bubbled through a gas-washing bottle containing some of the same solution.

The analytical methods were more than adequate for our purposes. The solutions were standardized by weight titration against standard hydrochloric acid solutions, using methyl red as indicator. In all but the very dilute solutions, pairs of analyses agreed within a few hundredths of a per cent. The hydrochloric acid solution used for

most of the comparisons was 0.61101 m, as determined by silver chloride residues at the beginning of the work, and 0.61094 m as determined by comparison with pure sodium carbonate at the end.   A 2.15 m hydrochloric acid solution, used for some of the most concentrated alkali solutions, was standardized by silver chloride residues and shown to be consistent with the less concentrated one.   The first sodium hydroxide solution was found to be 2.5510 m by titration against the first acid solution and 2.5515 m by titration against the second.

Experimental Results

Tables I and II summarize the experimental results.   All the experiments were carried out at an average temperature within a few hundredths of a degree of 25.00°, as determined by a standardized platinum resistance thermometer.   Since the temperature coefficient of the specific heat is small, no correction was required in any case and the exact temperature of each experiment is not tabulated.   Each series of experiments is numbered chronologically. m is the molality in moles per 1000.0 g. of water. All weights are reduced to the vacuum standard. Δg is the galvanometer deflection when the temperature of the calorimeters has been raised exactly one degree.

The *thermally equivalent* weight of water in each experiment is determined from the galvanometer deflection in the manner described in our former paper.[2]

Water standardizations made at frequent intervals showed a few individual variations slightly larger than before (amounting to $+0.03\%$ in one case and -0.03% in another).   Twelve of the experiments, however,

TABLE I

SUMMARY OF RESULTS FOR LITHIUM HYDROXIDE SOLUTIONS AT 25°

Expt.	m	Solution, g.	Δg, mm.	Equiv. wt. of water	Specific ht. s^a	Φ (obsd.)	Φ (calcd.)	$\sqrt{m}$
14	0.0404	250.904	+3.4	250.438	0.99814	−22	−18	0.201
15		250.963	+1.2	250.482	.99808	−24		
7	.0900	251.394	+0.7	250.495	.99642	−15.9	−16.2	.300
8		251.374	+1.9	250.468	.99640	−16.1		
5	.1600	252.040	+3.1	250.443	.99366	−15.8	−15.0	.400
6		252.085	+1.4	250.476	.99363	−16.1		
3	.3586	253.756	+0.3	250.502	.98719[1]	−12.11	−12.46	.599
4		253.776	−1.0	250.527	.98721	−12.05		
12	.6418	255.968	+2.0	250.465	.97850	−10.07	− 9.95	.801
13		256.008	+1.8	250.470	.97837	−10.27		
1	1.213	259.657	+3.4	250.437	.96454[2]	− 6.13	− 6.18	1.101
2		259.647	+3.9	250.426	.96454	− 6.13		
9	2.2728	265.020	−8.1	250.673	.94588[3]	− 1.17	− 1.09	1.508
10		265.870	−5.7	250.624	.94624	− 1.01		
11		265.870	−5.7	250.624	.94624	− 1.01		

^{a} These values were corrected for the known Cl^- and Na^+ in the solution, assuming linear change of s with mole per cent. at any one concentration of OH^-.   The corrections were: [1] $+0.1 \times 10^{-4}$; [2] $+0.6 \times 10^{-4}$; [3] $+0.1 \times 10^{-4}$.

(2) Gucker and Schminke, THIS JOURNAL, **54**, 1358 (1932).

TABLE II
SUMMARY OF RESULTS FOR SODIUM HYDROXIDE SOLUTIONS AT 25°

Expt.	m	Solution, g.	Δg, mm.	Equiv. wt. of water	Specific ht., s^a	Φ (obsd.)	Φ (calcd.)	$\sqrt{m}$
14	0.0396	251.067	+3.7	250.431	0.99747	−24	−23	0.199
15		251.210	−1.5	250.537	.99732	−28		
16		251.165	−1.6	250.539	.99751	−23		
20[b]		251.200	−1.8	250.545	.99739	−26		
9	.0910	251.905	−1.5	250.537	.99457	−19.9	−21.3	.302
10		251.857	+0.1	250.504	.99463	−19.2		
18	.1635	252.945	+1.8	250.468	.99021	−20.2	−19.5	.404
19		253.025	−1.6	250.541	.99018	−20.5		
7	.2394	253.961	+0.6	250.495	.98635	−17.6	−18.0	.489
8		254.005	−2.5	250.560	.98644	−17.2		
5	.4754	257.067	−1.1	250.529	.97457	−14.51	−14.52	.690
6		257.022	−1.4	250.535	.97476	−14.10		
3	.9999	263.069	−4.5	250.599	.95261[1]	− 9.28	− 9.10	1.000
4		262.960	+0.4	250.498	.95262	− 9.26		
11	1.8261	270.297	−0.2	250.510	.92683[2]	− 2.99	− 2.96	1.351
12		270.376	−3.2	250.574	.92679	− 3.02		
13		270.258	+0.2	250.503	.92693	− 2.93		
17		270.196	+6.1	250.381	.92669	− 3.07		
1	2.5513	258.945	−9.8	235.736	.91041[3]	+ 1.31	+ 1.34	1.597
2		275.150	−1.0	250.527	.91055	+ 1.37		

[a] These values were corrected for the known K^+ present in the solution, assuming linear change of s with mole per cent. at any one concentration of OH^-. The corrections were: [1] $+0.1 \times 10^{-4}$; [2] $+0.3 \times 10^{-4}$; [3] $+0.4 \times 10^{-4}$.

[b] The solution for Expt. 20 was made up determinate from the 0.1635 m solution and freshly boiled distilled water, in order to check independently the other experiments at the same concentration.

checked as well as before and showed that there was no permanent change from the calibration lines given on page 1363 of our previous article.[2] These were made the basis of our present calculations.

The specific heat, s, is obtained by dividing the equivalent weight of water by the weight of solution taken. The apparent molal heat capacity, Φ, is calculated as before from the equation

$$\Phi = \left[\frac{1000}{m} + M_2\right] s - \frac{1000}{m}$$

where M_2 is the molecular weight of the solute. The atomic weights used are those of the 1932 table. Since the specific heats are measured at 25°, the values of Φ are in calorie units corresponding to this temperature. The *calculated* values of Φ are obtained from linear equations for Φ against $\sqrt{m}$, derived from the experimental values by the method of least squares. Each value of Φ is given a weight proportional to m, since the error in Φ caused by a given percentage error in s is much larger in dilute than in concentrated solutions.[3]

(3) Ref. 2, p. 1366.

In Figs. 1 and 2 values of Φ for all the experiments are plotted against $\sqrt{m}$, together with the *calculated* best straight line through these points.
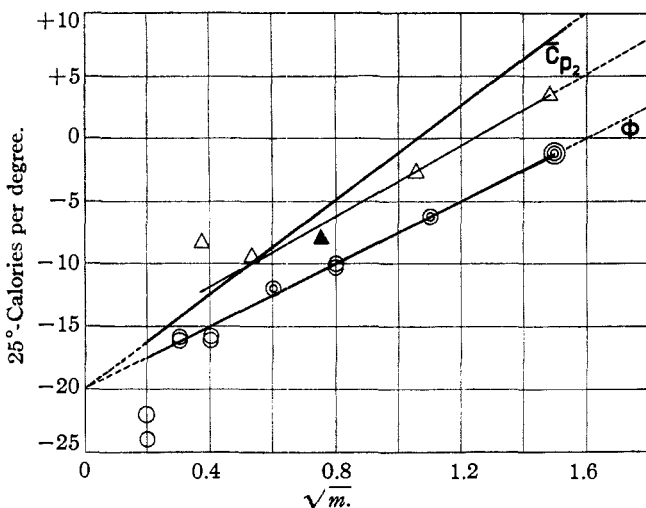

Fig. 1.—Lithium hydroxide: circles, Gucker and Schminke; triangles, Richards and Rowe.

It is evident that in both cases the straight lines represent the data within the experimental error from 0.04 m to over 2 m. There is no indication of an upward turn in the dilute end of the curve, at about 0.16 m, such as we
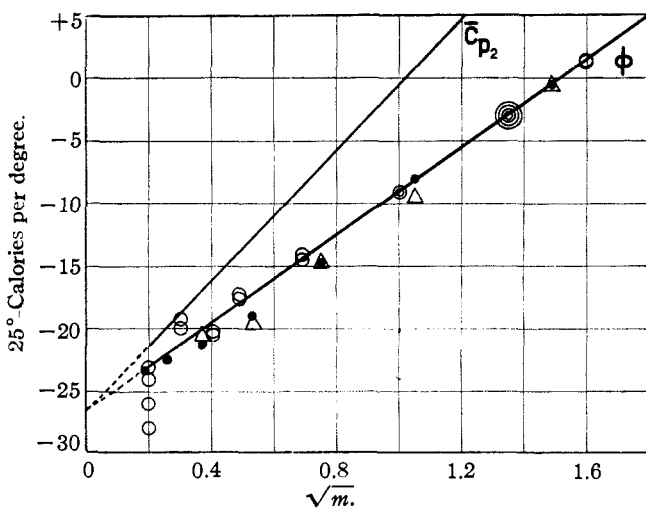

Fig. 2.—Sodium hydroxide: circles, Gucker and Schminke; dots, Richards and Gucker; triangles, Richards and Rowe, recalculated by Richards and Hall.

noted previously in the case of potassium hydroxide and hydrochloric acid, and the lines are continued to zero concentration.

The results for sodium hydroxide are in excellent agreement with the earlier work of Richards and Rowe (as recalculated by Richards and Hall)[4] and of Richards and Gucker.[5] These results (at 18°) are extrapolated to 25° by means of the temperature coefficient between 16 and 20° (dΦ/dt = 0.325) determined by Richards and Gucker for a single solution NaOH·-25H$_2$O ($\sqrt{m}$ = 1.49). Both sets of data were determined from the heat capacity of this same concentrated solution and the temperature coefficient of the heats of dilution of this solution to lower concentrations, using the well-known Person–Kirchhoff relation. The values of Φ are plotted in Fig. 2 and show a *maximum* deviation from our line which corresponds to only 0.07% difference in s (at $\sqrt{m}$ = 0.745) for the data of Richards and Gucker and 0.14% (at $\sqrt{m}$ = 1.05) for the earlier work of Richards and Rowe.

Our results for lithium hydroxide also agree reasonably well with those of Richards and Rowe[6] which, because of the less satisfactory purity of the material, they state "can hardly be considered as more than preliminary." The values for Φ calculated from their data were extrapolated from 18 to 25°, assuming that the temperature coefficient was the same as that of sodium hydroxide. A glance at Fig. 1 will show that all these values of Φ lie considerably above ours. The line which they define is included for comparison. Its *slope*, which depends only on the temperature coefficient of their heats of dilution, agrees very well with that of ours. The *position* of the line depends wholly on the specific heat of the LiOH·-100 H$_2$O ($\sqrt{m}$ = 0.745), which they measured directly and which is only 0.14% higher than that calculated from our results. The corresponding value of Θ, indicated by the black triangle, lies 2.6 calorie units above our line. If they had measured directly the *most concentrated* solution ($\sqrt{m}$ = 1.49) the same percentage difference in s would only have affected Φ by 0.7 calorie unit, and their whole line would have been in much better agreement with ours.

From the equation for the apparent molal heat capacity as a function of the square root of the concentration, it is a simple matter to obtain the partial molal heat capacity of the solute ($\overline{C}_{p_2}$) and the relative partial molal heat capacity of the solvent ($\overline{C}_{p_1} - \overline{C}_{p_1}^{\circ}$) by the method of Randall and Rossini.[7] The requisite equations are

$$\overline{C}_{p_2} = \Phi + \frac{1}{2}m^{1/2} (d\Phi/dm^{1/2}) \qquad \text{and}$$

$$\overline{C}_{p_1} - \overline{C}_{p_1}^{\circ} = -\frac{m}{55.507} \left(\frac{1}{2}m^{1/2} \cdot \frac{d\Phi}{dm^{1/2}} \right)$$

(4) Richards and Hall, THIS JOURNAL, **51**, 734 (1929).

(5) Richards and Gucker, *ibid.*, **51**, 722 (1929).

(6) Richards and Rowe, *ibid.*, **43**, 781 (1921).

(7) Randall and Rossini, *ibid.*, **51**, 323 (1929), and Rossini, *Bur. Standards J. Research,* **4**, 316, (1930).

Since these quantities are very useful in numerous thermodynamic calculations, we have included them here. The equations which summarize our results for the two solutions are thus found to be

LiOH	NaOH
$\Phi = -19.98 + 12.53\ m^{1/2}$	$\Phi = -26.59 + 17.49\ m^{1/2}$
$\overline{C}_{p_2} = -19.98 + 18.80\ m^{1/2}$	$\overline{C}_{p_2} = -26.59 + 26.24\ m^{1/2}$
$\overline{C}_{p_1} - \overline{C}_{p_1}^{\circ} = -0.1129\ m^{3/2}$	$\overline{C}_{p_1} - \overline{C}_{p_1}^{\circ} = -0.1579\ m^{3/2}$

Summary

We have used the adiabatic twin calorimeter method to determine the specific heats of aqueous solutions of lithium and sodium hydroxides at 25° from 0.04 m to over 2 m. From these data we have calculated the apparent molal heat capacity of the solutes. When plotted against $\sqrt{m}$ they both give straight lines over the whole range of concentration. Equations are included for the apparent and partial molal heat capacities of the solute and the relative partial molal heat capacity of the solvent. From these it is possible to calculate the heat capacity of these solutions with great precision at any concentration in the range studied.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. III. The Dissociation Constant

BY RAYMOND M. FUOSS AND CHARLES A. KRAUS

I. Introduction

Experimental data for weak electrolytes in water and for most electrolytes in solvents of lower dielectric constant indicate the existence of an equilibrium of the type

$$A^+ + B' \rightleftharpoons AB \tag{1}$$

In the preceding paper of this series,[1] we have shown that it is possible to describe conductance data (up to moderate concentrations) exactly by means of the mass action equation, provided the influence of interionic forces, in the usual sense of the term, on the thermodynamic properties and mobilities of the ions be taken into account.[2]

(1) Fuoss and Kraus, THIS JOURNAL, **55**, 476 (1933).

(2) It should be pointed out that all terms in activity and migration velocity of higher order than $c^{1/2}$ in concentration are necessarily included in our dissociation constants derived from conductance data. Since the method of calculation is applied only to low (ion) concentrations, we believe that our K describes primarily the effect which we are naming mass action, *i. e.*, the formation of electrically neutral structures from ions. It is evident, both on experimental and theoretical [Kramers, *Proc. Amsterdam*, **30**, 145 (1927)] grounds that some *specific* interaction between ions of opposite charges must be considered in addition to the interionic effect described by Debye's time–average potential. The specific interaction is most simply treated by means of arguments based on Equation (1).