

tures would lead to equations for the specific heat which do not exhibit maxima and do not have positive second differences.<sup>22</sup>

(22) On first consideration it might be thought that a sufficiently good fit might be made with two constants. For the red lead monoxide similar weighting yields

$$h_{t-25} = 0.051895(t - 25) + 1.1143 \times 10^{-5}(t - 25)^2 \quad (11)$$

$$C_p = 10.100 + 4.9743 \times 10^{-3}T \quad (12)$$

Two of the deviations of Eq. 11 are within the probable errors and the sum of the squares of the deviations is about twice as large as that derived from the cubic equation. For the yellow lead monoxide all the deviations from an equation similar to Eq. 11 are larger than the probable errors and the sum of the squares of the deviation is seven times as large as that from the cubic equation.

### Summary

1. The construction of an aneroid calorimeter of the type used by Jaeger and co-workers has been described.

2. The heat contents of yellow and red lead monoxides have been measured between 25° and 400 to 650° and 400 to 550°, respectively.

3. Equations expressing the heat capacities of the yellow and red lead monoxides have been derived.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

## Conductances of Aqueous Solutions of the Hydroxides of Lithium, Sodium and Potassium at 25°

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Previous work done in this Laboratory on the conductance of acids and salts led to the belief that the application of this same conductance method to the hydroxides of lithium, sodium, and potassium would give information as to whether these bases behaved as typical strong electrolytes or whether they exhibited evidence of incomplete ionization.

The conductances were measured using the same apparatus and technique described in previous publications.<sup>3,4,5</sup> The values of Jones and Bradshaw<sup>6</sup> for the specific conductivities of potassium chloride solutions were used to determine the cell constants.

The hydroxide solutions were prepared by dilution of saturated solutions. In the case of the saturated solution of potassium hydroxide, a small amount of saturated barium hydroxide solution was added to precipitate the carbonate completely. This was unnecessary in the cases of the saturated solutions of the other two hydroxides. Preliminary tests showed that the conductances of lithium hydroxide solutions were the same whether the saturated solutions from which they were prepared had been treated with barium hydroxide or not. The saturated solutions were

prepared in all cases from the highest grade hydroxides. The standardization of the bases was accomplished indirectly as follows: the stock solution was titrated, using phenolphthalein indicator, against benzoic acid and also against potassium acid phthalate, both certified by the Bureau of Standards. A hydrochloric acid solution was then titrated against the stock solution, using phenolphthalein indicator, thus establishing the titer of the acid solution. The accepted titer of the stock solution of base was obtained by titration against this acid solution using sodium alizarine sulfonate indicator; this value thus included both the base and the carbonate content of the solution. It differed from the direct standardization (using phenolphthalein indicator) by about 0.1% for the 0.2 demal stock solution, while for the more concentrated solution the difference was negligible. The titrations were performed with weight burets and were completed with a solution one-tenth the concentration of the main solution; the reproducibility was about one part in ten thousand. Care was exercised to exclude carbon dioxide at all times. All stock solutions were prepared from water having a measured specific conductance less than  $10^{-6}$  reciprocal ohms.

$\Lambda_0'$  was plotted against  $C$ , as shown in Fig. 1, in an attempt to express the measured equivalent conductances in the dilute region by means of Shedlovsky's extension of Onsager's equation.<sup>7,8,9</sup>

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(3) Saxton and Langer, *THIS JOURNAL*, **55**, 3638 (1933).

(4) Saxton and Meier, *ibid.*, **56**, 1918 (1934).

(5) Saxton and Darken, *ibid.*, **62**, 846 (1940).

(6) Jones and Bradshaw, *ibid.*, **55**, 1780 (1933).

(7) Onsager, *Physik. Z.*, **27**, 388 (1926), **28**, 277 (1927).

(8) Onsager, *Trans. Faraday Soc.*, **23**, 341 (1927).

(9) Shedlovsky, *THIS JOURNAL*, **54**, 1405 (1932).

A range of linearity is indicated in the cases of potassium hydroxide and sodium hydroxide wherein the equivalent conductances may be represented by the equations

NaOH:  $\Lambda = 248.85 - 116.38C^{1/2} + 103C(1 - 0.2274C^{1/2})$   
 KOH:  $\Lambda = 272.0 - 121.64C^{1/2} + 141C(1 - 0.2274C^{1/2})$

The scatter of the points below 0.02 demal amounts to  $\approx 0.1-0.2\%$ , which is a considerably larger error than occurred in the measurements on salts and acids. Although this scatter tends to obscure irregularities in the curves, the curve for lithium hydroxide is notably different from the other two. The points in the most dilute region lie somewhat above the best straight line drawn through the more concentrated points, whereas for the other two bases the experimental error is in the opposite direction. Also, the slope is only about one-fifth the value of the coefficient of  $C^{1/2}$  in the Onsager equation; Shedlovsky<sup>9</sup> has pointed out that the slope of the  $\Lambda_0'$  vs.  $C$  plot for a strong electrolyte is numerically nearly equal to this value. The  $\Lambda_0$  value for lithium hydroxide obtained by extrapolation of this straight line is not in agreement with that predicted for it from

TABLE I  
 COMPARISON OF LIMITING EQUIVALENT CONDUCTANCES OF CHLORIDES AND HYDROXIDES

	Cl	OH	OH-Cl
Li	115.03	237.2 (236.4)	122.2 (121.4)
Na	126.46	248.85	122.4
K	149.86	272.0	122.1

TABLE II

Series	$m$	$c$	$\Delta$
	LiOH		
		0.001	233.4
		.0025	231.3
		.005	229.0
		.01	225.6
		.02	221.1
		.03	217.9
		.04	215.3
A	0.05645	.05638	211.7
A	.07103	.07097	209.1
B	.14017	.14032	199.8
B	.17618	.17655	196.3
B	.23022	.23105	191.9
B	.38740	.39054	182.1
B	.46292	.46764	178.3
B	.58130	.58903	173.1
C	.58130	.58903	173.2
C	.74191	.75511	168.2
C	1.01326	1.0386	157.9
C	1.3673	1.4145	147.5
C	2.0977	2.2089	129.0
C	2.7353	2.9251	114.6
C	4.5047	5.0092	79.7

	NaOH		
A	0.06509	0.06508	225.7
B	.06851	.06851	224.9
A	.09129	.09139	222.4
B	.09419	.09431	221.7
A	.11267	.11290	220.2
B	.11415	.11439	219.6
B	.14347	.14396	217.0
A	.15116	.15173	216.7
B	.17043	.17121	214.8
A	.20639	.20767	212.6
B	.20676	.20805	212.2
C	.20707	.20835	212.8
A	.24789	.24988	210.0
A	.28732	.29013	207.7
C	.29025	.29312	207.7
C	.36855	.37349	203.5
C	.44099	.44827	200.0
C	.55447	.56650	195.0
C	.77126	.79540	186.2
C	1.1103	1.1617	173.8
C	1.3919	1.4737	164.1
C	2.0492	2.2273	142.9
D	2.0492	2.2273	142.9
D	2.6369	2.9322	125.0
D	3.6129	4.7122	86.63
D	8.0572	10.849	23.67
D	12.554	19.128	6.477

	KOH		
C	0.06080	0.06081	249.8
D	.06127	.06129	249.7
B	.06338	.06340	249.5
C	.07914	.07923	247.6
B	.08541	.08553	246.9
D	.10138	.10160	245.4
B	.11985	.12022	243.8
B	.15064	.15133	241.5
E	.27833	.28152	234.6
E	.37583	.38175	230.5
E	.50549	.5167	225.6
E	.6794	.7003	219.7
E	1.0204	1.0697	209.0
E	1.2959	1.3758	201.0
E	1.7740	1.9266	187.33
E	2.2782	2.5338	173.14
F	2.2782	2.5338	173.11
F	3.4544	4.0591	140.92
F	4.6172	5.726	110.94
F	5.9823	7.897	79.00
F	7.5030	10.611	49.35

the  $\Lambda_0$ 's of sodium hydroxide, potassium hydroxide, lithium chloride, sodium chloride and potassium chloride by application of the principle of the independence of ionic mobilities at infinite dilution. In Table I the  $\Lambda_0$  obtained by linear extrapolation of  $\Lambda_0'$  vs.  $C$ , and the value for OH-Cl resulting from this  $\Lambda_0$ , are given parenthetically.

On the assumption that lithium hydroxide is

incompletely dissociated,  $\Lambda$  for  $(\text{Li}^+ + \text{OH}^-)$  was calculated from the data of Shedlovsky<sup>10</sup> on lithium chloride and potassium chloride (corrected for the difference between the Parker and Parker<sup>11</sup> and Jones and Bradshaw<sup>6</sup> values for the absolute conductance of potassium chloride solutions) and the above equation for the conductance of potassium hydroxide. This equation was obtained

$$\text{Li}^+ + \text{OH}^-; \Lambda_e = 237.2 - 113.73C^{1/2} + 135.2C(1 - 0.2274C^{1/2})$$

and from it sets of apparent values of  $\Lambda_0'$  were calculated assuming various values of the ionization constant. It was found that  $K = 1.2$  reproduces the experimental values of  $\Lambda$  well within the experimental error, which can be seen from Fig. 1, where the curve thus calculated passes through the lithium hydroxide points. As the assumption that lithium hydroxide is not completely ionized accounts for the very small slope and the minimum observed in the plot of  $\Lambda_0'$  vs.  $C$ , and furthermore brings the limiting conductance into concordance with the other limiting conductances as shown in Table I, the argument seems fairly strong that lithium hydroxide is a weak electrolyte with an ionization constant in the neighborhood of unity.

The plot of  $\Lambda_0'$  vs.  $C$  for sodium hydroxide also has a slope slightly less than the theoretical coefficient for  $C^{1/2}$ . However, the extrapolated value for  $\Lambda_0$  is not lower than that calculated from the  $\Lambda_0$ 's of potassium hydroxide, potassium chloride and sodium chloride as it would be if this base were weak; it is slightly higher, and probably within the experimental error. Also no suggestion of a minimum is observed in the plot. If the same method be followed here as in the case of lithium hydroxide, it is found that an ionization constant of 5.0 gives the best fit of the curve of  $\Lambda_0'$  against  $C$  up to a concentration of 0.06 demal, but predicts a slight curvature (but no minimum) in the curve which the experimental points do not indicate. The straight line represented in Fig. 1 seems to be a better fit; therefore the data presented here offer no conclusive evidence that sodium hydroxide is not completely ionized.<sup>12</sup>

The experimental work for sodium hydroxide and potassium hydroxide is represented up to 0.06

(10) Shedlovsky, *THIS JOURNAL*, **54**, 1411 (1932).

(11) Parker and Parker, *ibid.*, **46**, 312 (1924).

(12) Even if sodium hydroxide is incompletely ionized and has the ionization constant 5.0, then the degree of ionization of a 0.1 demal solution is about 99%.

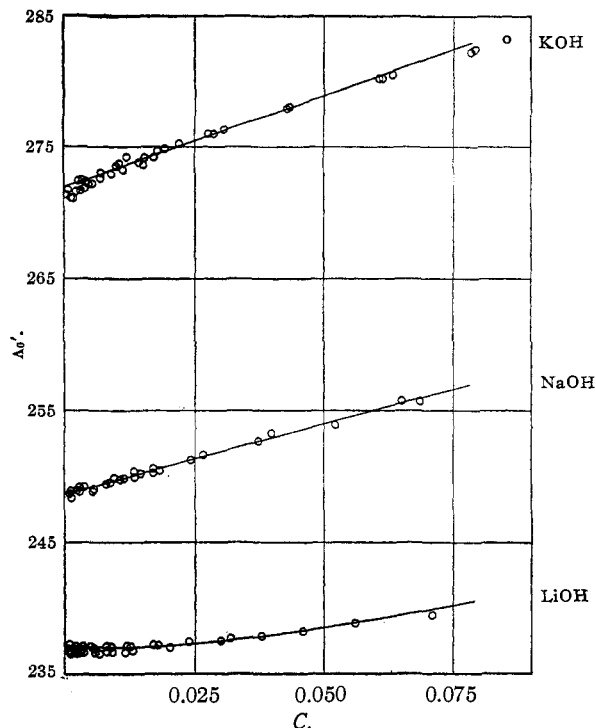


Fig. 1.

demal by the equations given previously; above this concentration the data are given in Table II. The experimental data for lithium hydroxide above 0.05 demal are also given in Table II; the data below 0.05 demal are from a smoothed plot. On account of uncertainties in the density,  $m$ , the number of moles per 1000 g. of solution is included in this table. The following equations were used to express the densities

$$\begin{aligned} \text{LiOH: } d &= 0.9970 + 0.02996C - 0.003003C^{3/2} \\ \text{NaOH: } d &= 0.9970 + 0.04699C - 0.004448C^{3/2} \\ \text{KOH: } d &= 0.9970 + 0.05120C - 0.00365C^{3/2} \end{aligned}$$

The data used in determining the constants were taken from the "International Critical Tables," except in the case of potassium hydroxide.<sup>13,14</sup>

### Summary

The conductances of aqueous solutions of lithium, sodium, and potassium hydroxides have been measured at 25° and the limiting equivalent conductances have been determined therefrom. Sodium and potassium hydroxides behave at low concentrations as typical strong electrolytes; lithium hydroxide appears to show measurable deviation from complete ionization.

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(13) Hitchcock and McIlhenny, *Ind. Eng. Chem.*, **27**, 461 (1935).

(14) Harned and Cook, *THIS JOURNAL*, **59**, 496 (1937).