[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

FURTHER STUDIES ON THE THERMOCHEMICAL BEHAVIOR OF SODIUM HYDROXIDE SOLUTIONS[1]

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Scope of Work

This paper contains an account of the investigation of the thermal behavior of sodium hydroxide solutions with a study of the heats of dilution of solutions more concentrated than $NaOH \cdot 25H_2O$. From these results the specific heats of the more concentrated solutions have been calculated. Further data were obtained to confirm the short extrapolation necessary to correct the heat of dilution of $NaOH \cdot 25.31H_2O$ and $NaOH \cdot 50.38H_2O$ to integral values.[2] Also the maximum of the curve for heats of dilution with decreasing concentration was determined at 20°.

In the latter part of this paper are collected the thermal data, dealing with sodium hydroxide solutions, which have been found in this Laboratory during the past twenty years. These data have been recalculated, whenever necessary, using the more accurate values for specific heats which have been published recently.[3]

Apparatus and Methods of Procedure

Since approximate results were desired as quickly as possible, an attempt was made to use a simple calorimeter consisting of a 500-cc. Dewar flask with glass stirrer, Beckmann thermometer, glass pipet (for delivering water) and cover. The pipet, bent into a compact U-shape (after the idea of Sugden),[4] was immersed in the hydroxide solution in the vacuum flask in order to keep all parts of the system at the same temperature. After measurement of the fore drift, the water in the pipet was blown by an aspirator bulb into the solution and the temperature change noted.

By this method it was evident that at about a dilution of $NaOH \cdot 17.5H_2O$ there was no measurable heat change upon the addition of small amounts of water. However, too much irregularity existed in this method to yield trustworthy results. Unless the solution inside the Dewar flask was at the same temperature as that of the room, there was always an important temperature drift. The large amount of glass permitted a large and uncertain heat interchange between the room and the solution. Thermal equilibrium within the Dewar was established very slowly. Added to these difficulties was the large and almost indeterminable heat capacity of the Dewar flask.

Accordingly, the Dewar flask calorimeter was abandoned and a simple adiabatic one, very similar to that used by Richards and Rowe,[5] was found to be more satisfactory in every respect.

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[1] On account of the death of Professor Richards on April 2, 1928, the work here described was completed and the manuscript was prepared by the junior author.

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

[3] (a) Richards and Gucker, *ibid.*, **47,** 1876 (1925); (b) Richards and Hall, *ibid.*, **51,** 707 (1929).

[4] *Cf.* Perman and Lovett, *Trans. Faraday Soc.*, **22,** 10 (1926).

[5] Richards and Rowe, THIS JOURNAL, **42,** 1621 (1920).

The mercury thermometers (made especially for thermochemical work at 16 to 20°) were carefully standardized by comparison with a calibrated platinum resistance thermometer. Since the apparatus was not perfect, it was necessary to apply a small temperature correction for the drift which was measured both before and after each dilution experiment.

The solutions used in all these dilutions were made from recrystallized "C. P." sodium hydroxide. They contained a few tenths of 1% of carbonate, which would decrease the heat evolved on dilution, but the effect was beyond the accuracy of the method as performed with mercury thermometers. It was found, as would be expected, that a trace of carbonate although present in small varying amounts did not change the value of the temperature coefficients.

The following table summarizes the heats of dilution (corrected to exactly 16 and 20°) and their temperature coefficients, expressed in calories, for the range of concentrations studied.

TABLE I

HEATS OF DILUTION (IN CALORIES)

Original soln.	Product of dilution	ΔH at 20°	ΔH at 16°	ΔC_p
$NaOH \cdot 10.0H_2O$	$NaOH \cdot 17.5H_2O$	−93	−60	− 8.2
$NaOH \cdot 10.0H_2O$	$NaOH \cdot 17.87H_2O$	−92	−59	− 8.2
$NaOH \cdot 17.87H_2O$	$NaOH \cdot 25.00H_2O$	+39	+60	− 5.3
$NaOH \cdot 10.0H_2O$	$NaOH \cdot 25.00H_2O$	−51	+ 4	−13.8
$NaOH \cdot 25.00H_2O$	$NaOH \cdot 26.00H_2O$	+ 5.4	+ 7	....

The value found for the change from $NaOH \cdot 25H_2O$ to $NaOH \cdot 26H_2O$ agrees with the value found by interpolation of the curve for heats of dilution which was used in the publication of this series by Richards and Gucker.[2] This corroboration is important because at a greater concentration than $NaOH \cdot 25H_2O$ the curve suddenly changes its course. Thomsen stated[6] that the change from heat evolved to heat absorbed occurred at about $NaOH \cdot 20H_2O$.

This change in the curve was studied by diluting a solution corresponding to the composition of $NaOH \cdot 10H_2O$ to many stages of dilution ($NaOH \cdot 11H_2O$ to $25H_2O$). The values thus obtained for 20° are presented in the small inset of Fig. 1.

This graph depicts the result of the different influences involved in dilution. It is also clear that if a solution of $NaOH \cdot 10H_2O$ were diluted to about $NaOH \cdot 35H_2O$ there would be no heat change. The ordinates thus form a series of "isothermal lines" up to $NaOH \cdot 200H_2O$.

Specific Heat of Concentrated Solutions.—From the temperature coefficients for the above heats of dilution the specific heats of the concentrated solutions can be calculated by the Person–Kirchhoff Law, using the specific heat of $NaOH \cdot 25H_2O$ as the basis.

In a similar way the specific heat of $NaOH \cdot 17.87H_2O$ can be calculated from the temperature coefficient of the dilution $NaOH \cdot 17.87H_2O$ to NaOH·-

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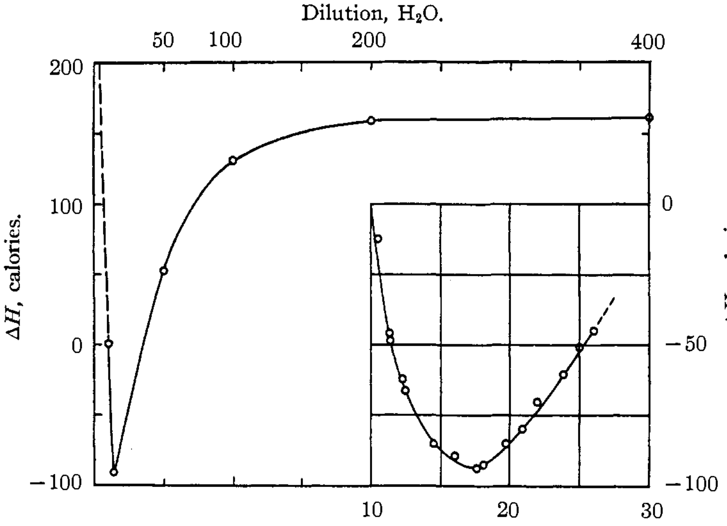
[6] Thomsen, "Thermochemische Untersuchungen," Leipzig, **1883**, Vol. III, p. 83.

TABLE II

HEAT CAPACITIES AND SPECIFIC HEATS OF $NaOH\cdot 10H_2O$

Temperature, °C.	16	18	20
Heat capacity, mayers	3.630	3.619	3.641
Specific heat	0.865	0.868	0.871

$25.00H_2O$ as 0.8962 at 18°. If the value found for the specific heat of $NaOH\cdot 10H_2O$ is used as a basis in the dilution of $NaOH\cdot 10.00H_2O$ to $NaOH\cdot 17.87H_2O$, the specific heat value 0.8966 is obtained. These values agree well with that interpolated from the graph for specific heats at 18° plotted against dilution, 0.8965.



Dilution, moles H_2O per mole of NaOH.

Fig. 1.

Recalculation of Earlier Data.—As was pointed out in a note in the article by Richards and Hall,[3b] the value for the specific heat of $NaOH\cdot 10H_2O$, 0.855, which was used by Richards and Rowe[7] as the basis of calculation, was too low. The recent accurate determination for the specific heat of sodium hydroxide solutions permits the recalculation of the heats of dilution and specific heats published in 1921. These recalculations are summarized in Tables III and IV.

For comparison with the results of Richards and Gucker[2] these values are calculated for the dilution of an initial solution of $NaOH\cdot 25H_2O$ in Table IV.

The good agreement between the recalculated values of Richards and Rowe and those recently published by Richards and Gucker is of particular importance as the stages of dilution in the two researches were quite dif-

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[7] Richards and Rowe, THIS JOURNAL, **43**, 770 (1921).

TABLE III

HEATS OF DILUTION OF SODIUM HYDROXIDE

From the data of Richards and Rowe, THIS JOURNAL, **43**, 779 (1921).

Factors	Product	$-\Delta H_{16^\circ}$, Joules	Cal.	$-\Delta H_{20^\circ}$, Joules	Cal.	Mayers	$-\Delta C_p$, Cal.
$NaOH\cdot 10H_2O + 15H_2O$	$NaOH\cdot 25H_2O$	+ 6	+ 1.4	+237	+ 56.7	57.8	13.8
$NaOH\cdot 10H_2O + 40H_2O$	$NaOH\cdot 50H_2O$	− 608	−143	−228	− 54.8	95	22.7
$NaOH\cdot 10H_2O + 90H_2O$	$NaOH\cdot 100H_2O$	− 999	−239	−532	−127	117	27.9
$NaOH\cdot 10H_2O + 190H_2O$	$NaOH\cdot 200H_2O$	−1204	−288	−652	−156	138	33
$NaOH\cdot 10H_2O + 390H_2O$	$NaOH\cdot 400H_2O$	−1242	−297	−674	−161	142	34

TABLE IV

COMPARISON OF HEATS OF DILUTION IN 20° CALORIES

Factors	Products	R. and R.		R. and G.	
		$-\Delta H_{16^\circ}$	$-\Delta H_{20^\circ}$	$-\Delta H_{18^\circ}$	$-\Delta H_{20^\circ}$
$NaOH\cdot 25H_2O + 25H_2O$	$NaOH\cdot 50H_2O$	−147	−111	−141	−105
$NaOH\cdot 25H_2O + 75H_2O$	$NaOH\cdot 100H_2O$	−240	−184	−240	−184
$NaOH\cdot 25H_2O + 175H_2O$	$NaOH\cdot 200H_2O$	−289	−213	−286	−213
$NaOH\cdot 25H_2O + 375H_2O$	$NaOH\cdot 400H_2O$	−299	−218	−298	−216
$NaOH\cdot 25H_2O + \infty$	....	...	...	−257	−163

ferent and as the methods were also sufficiently diverse to provide an excellent independent check.

Comparison of Specific Heat Values.—The recalculated heats of dilution make possible comparisons of the specific heat values determined by the two different methods of dilution, by direct measurement, and by other methods of experimentation.

TABLE V

SPECIFIC HEATS OF SODIUM HYDROXIDE SOLUTIONS AT 18° REFERRED TO WATER AT THE SAME TEMPERATURE

Solution	Richards and Hall, by direct detn.	Richards and Gucker, from heats of dilution	Richards and Rowe, from heats of dilution	Thomsen, directly	Others by various methods
$NaOH\cdot 10H_2O$	[0.8682][a]	.....	0.8680	(0.858)[b]	....
$NaOH\cdot 17.87H_2O$	[.896][a]	.....	....	(.888)[b]	....
$NaOH\cdot 25H_2O$	.91272	(0.91272)	(0.9127)	(.908)[b]	....
$NaOH\cdot 50H_2O$	.946	.94654	.9450	.942	....
$NaOH\cdot 100H_2O$	.96904	.96906	.9691	.968	0.9664[c]
$NaOH\cdot 200H_2O$	.....	.98319	.9830	.983	.9827[c]
$NaOH\cdot 400H_2O$	.....	.99122	.9913	...	....

[a] Calculated by the Person-Kirchhoff law from heat of dilution.

[b] By interpolation.

[c] Richards and Rowe, *Proc. Am. Acad.*, **49**, 178 (1913). The error for the value 0.9664 is unexpectedly and inexplicably large. Its cause is not apparent.

It is interesting to note in connection with these comparisons that in the cases of solutions of other substances other experimenters have more recently obtained values consistent with those found by Richards and Rowe. Maass and others[8] have found by an entirely different method essentially identical values for the heat of dilution of sodium chloride.

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[8] Lipsett, Johnson and Maass, THIS JOURNAL, **49**, 925, 1940 (1927).

Lange,[9] working with others, has found confirming values for a number of salts by yet another method. The objection made by Lange[10] to the method of calculation used by Richards and Rowe, has since been courteously withdrawn.[11]

Recalculation of Heats of Neutralization.—The newer values for heats of dilution and specific heat make possible a still more accurate calculation of the heat of neutralization when sodium hydroxide solutions react with strong acids.[12] These new values improve considerably the extrapolation to infinite dilution for the curves plotted for heat of neutralization against dilution.[13]

TABLE VI

HEAT OF NEUTRALIZATION OF $NaOH\cdot 100H_2O$[a]

	18° Cal.	20° Cal.	Kj.
$HCl\cdot 100H_2O$	13,919	13,924	58.21
$HBr\cdot 100H_2O$	13,851	13,856	57.93
$HI\cdot 100H_2O$	13,792	13,797	57.68
$HNO_3\cdot 100H_2O$	13,846	13,851	57.90

[a] This table replaces part of Table IV, THIS JOURNAL, **44**, 699 (1922).

TABLE VII

HEATS OF NEUTRALIZATION AT VARIOUS CONCENTRATIONS IN 20° CALORIES (TEMP., 20°)[a]

Moles H_2O	In factors	25+25	50+50	100+100	200+200	400+400	∞
	In products	51	101	201	401	801	∞
Reaction	NaOH+HCl	14,260	14,026	13,924	13,854	13,794	13,640
	$NaOH+HNO_3$	14,034	13,902	13,851	13,804	13,769	13,640

[a] This table replaces part of the table on p. 702, THIS JOURNAL, **44**, (1922).

The values in Table VII for the heat of neutralization at infinite dilution were obtained by graphical extrapolation of the neutralization curves. Another method of finding this value is extrapolation of the heats of dilution of the factors and products to zero concentration and algebraic summation of these values. This may be done with least uncertainty in the case of the neutralization of hydrochloric acid. The dilution of sodium hydroxide has recently been discussed.[2] New values for the heat of dilution of hydrochloric acid recently determined in this Laboratory[14] indicate the evolution of 266 calories on dilution from $HCl\cdot 100H_2O$ to $HCl\cdot\infty H_2O$ at 20°. In order to obtain an extrapolated value for sodium chloride the heat of dilution measured by Richards and Rowe has[15] been combined

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[9] (a) Lange, *Z. physik. Chem.*, **116**, 337 (1925); (b) Wüst and Lange, *ibid.*, **116**, 162 (1925); (c) Lange and Dürr, *ibid.*, **118**, 129 (1925); (d) **121**, 361 (1926).

[10] Ref. 9 b, p. 189.

[11] Lange, *Z. physik. Chem.*, **117**, 336 (1925).

[12] Richards and Rowe, THIS JOURNAL, **44**, 684 (1922).

[13] *Cf.* ref. 12, p. 703.

[14] Richards, Mair and Hall, THIS JOURNAL, **51**, 727 (1929).

[15] Richards and Rowe, *ibid.*, **43**, 779 (1921).

with values found by Lipsett, Johnson and Maass[8] and also with those of Lange and Messner[16] at still smaller concentrations. The resulting curve is a regular one with an inflection at about $NaCl \cdot 500H_2O$; at lower concentrations than this a small amount of heat is evolved. Using these values for the factors and products, the following thermochemical equations are obtained.

$$\begin{array}{lclr}
NaOH \cdot 100H_2O + HCl \cdot 100H_2O & = & NaCl \cdot 201H_2O & 13{,}924\ \text{Cal.} \\
NaCl \cdot 201H_2O + (\infty - 201)H_2O & = & NaCl \cdot \infty H_2O & 15\ \text{Cal.} \\
HCl \cdot \infty H_2O & = & HCl \cdot 100H_2O + (\infty - 100)H_2O & -266\ \text{Cal.} \\
NaOH \cdot \infty H_2O & = & NaOH \cdot 100H_2O + (\infty - 100)H_2O & -20\ \text{Cal.} \\
\hline
 & & & 13{,}653\ \text{Cal.}
\end{array}$$

The agreement with graphical extrapolation is as good as could be hoped, with due consideration for the difficulties and uncertainties of extrapolations.

The authors take pleasure in acknowledging their indebtedness to the Carnegie Institution of Washington and to an anonymous benefactor of this Laboratory for essential financial assistance in carrying out this research.

Summary

1. The heat of dilution of $NaOH \cdot 10H_2O$ has been measured at 16 and 20°. The change from heat evolved to heat absorbed was found to be at $NaOH \cdot 17.5H_2O$ at 20°.
2. The specific heats of more concentrated solutions were calculated by the Person–Kirchhoff Law to be 0.868 at 18° for a solution of $NaOH \cdot 10H_2O$, and 0.896 at 18° for $NaOH \cdot 17.87H_2O$.
3. Earlier work with sodium hydroxide solutions on heats of dilution, specific heats and heats of neutralization has been recalculated and compared with recent researches.
4. The heat of neutralization at 20° of hydrochloric acid and sodium hydroxide is calculated to be 13.65 Cal. at infinite dilution.

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[16] Lange and Messner, *Naturwissenschaften*, **15**, 521 (1927).