

Anhydrous Sodium Hydroxide: The Heat Content From 0° to 700° C, the Transition Temperature, and the Melting Point*

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Samples of sodium hydroxide, whose purity as indicated by analyses was approximately 99.3 percent, were sealed in pure silver. Cryoscopic measurements indicated a transition temperature of 293° C. Using a "drop" method and a Bunsen ice calorimeter, the enthalpy¹ change between 0° and each of 11 temperatures up to 700° C was measured. With reasonable simplifying assumptions, the thermal measurements near the freezing point were used to correct for the impurity, giving for pure sodium hydroxide a melting point of 319° C and the same value, 159 absolute joules per gram, for the heat of fusion and the heat of transition. The heat capacity derived for the liquid is estimated to be correct within 2 percent, whereas the derived heats of fusion and transition may be in error by as much as 5 percent. Values of heat capacity, entropy, relative enthalpy, and relative free energy are tabulated at regular intervals from 298° to 1,000° K.

1. Sample and Containers

As a container material for the sodium hydroxide, oxygen-free silver was selected, as tests made elsewhere² indicate that this material is attacked only slightly by molten sodium hydroxide at the high temperatures to be used. Any disintegration of the silver surface, which is thought to be the only interaction that would occur, was not expected to affect the total enthalpy of such a sample. An examination of two of the silver containers after exposure to molten sodium hydroxide at 700° and 800° C is described in section 3.

Silver of 999.5 fineness that had been cast in an inert atmosphere to remove the oxygen was obtained from the American Platinum Works, of Newark, N. J., in the form of tubing 0.015 in. thick and of $\frac{3}{8}$ -in. diameter. Each container was fabricated from a length of this tubing by drawing down one end by dies to a neck of 2 in. in length and $\frac{1}{4}$ -in. diameter. After turning down the neck to an average wall thickness of 0.012 in. (to decrease heat conduction and so facilitate the subsequent sealing off), the larger open end was closed by welding to it a silver cap of 0.02-in. thickness.

Four such containers were loaded with solid sodium hydroxide (about 4 g each) in a dry box continuously swept out with argon dried by activated alumina. They were then promptly evacuated to a pressure of 1 mm or less. Under an internal pressure of 25 mm of helium (added for good heat transfer during the subsequent measurements), their necks were then flattened and sealed off in a gas-oxygen flame. That the samples to be used were gas-tight was confirmed by evacuating the surrounding space and then surrounding them by helium. If they had not been tight, the air that had consequently leaked in (several milligrams) would have been replaced by

helium. However, there was no detectable decrease in weight. The part of the final mass of each sample due to silver and the part due to sodium hydroxide were easily obtained using the masses of the empty silver vessel and of the silver removed on sealing. Preliminary tests had shown that consistently about 1 mg of silver was lost during such a sealing process.

The stock of sodium hydroxide used had been obtained from the Oak Ridge National Laboratory, which gave as its analysis "100.0 percent ($\pm 0.05\%$) alkalinity, calculated as NaOH; 0.05 percent Na_2CO_3 ." Simultaneously with filling the silver vessels, three additional samples were taken in the dry box, and were sealed and stored in a desiccator over solid potassium hydroxide. Two of these samples were titrated at the Bureau, using both phenolphthalein and methyl orange as indicators, in the presence of barium chloride and using standardized normal hydrochloric acid. These analyses gave the following results.

| Sample | NaOH | Na_2CO_3 |
|--------|-----------|--------------------------|
| 1 | % 99.2 | % 0.33 |
| 2 | 99.4 | .27 |

It seems likely that the remaining approximately 0.4 percent was largely water. A considerable portion of the impurities may have entered during handling in the dry box.

2. Cryoscopic Measurements

Careful measurements of the temperatures of halt during cooling were undertaken in order to determine the freezing and transition points of the two samples on which nearly all of the enthalpy measurements were made. Measuring the equilibrium temperatures during freezing provided also an estimate of the amount of impurity in the samples. The general

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¹ The terms *enthalpy* and *heat content* are used interchangeably to designate the same thermodynamic property, which is symbolized by *H*.

L. G. Overholser, Oak Ridge National Laboratory, private communication.

method and type of apparatus used have been described in detail elsewhere[1].³ Because higher temperatures are involved here, it was necessary to construct a new apparatus held together by silver solder instead of tin.

The apparatus used is shown in figure 1. The sample container was surrounded by a close-fitting gold-plated copper cylinder suspended in the silver surrounded furnace core that was later used with a Bunsen ice calorimeter for the enthalpy measurements. A single-junction thermocouple (chromel P versus constantan) measured the difference in

temperature between the furnace wall and the sample, whereas a platinum resistance thermometer accurately measured the furnace temperature. The method used was entirely similar to the conventional cooling-curve technique, except that after a desired amount of cooling (usually 1 deg), the enviroing furnace was then held constant at a temperature sufficiently close to that of the sample to halt most of the cooling and so to permit a dependable evaluation of the sample temperature. (Because the thermal conductivity of sodium hydroxide is so much smaller than that of metals, it was found in preliminary trials that the conventional dynamic cooling-curve method led to such large thermal lags as to be entirely useless here.)

The technique adopted consisted in melting all the sample and then cooling it in stages by lowering the furnace temperature 1 deg at a time. After a small amount of freezing had occurred, the furnace temperature was held constant and the thermocouple was read until steady. Subsequent raising of the furnace temperature and then maintaining it constant slightly above the sample temperature, gave another set of data that provided a direct empirical determination of the thermocouple sensitivity for measuring the difference in temperature between the furnace and the NaOH solid-liquid interface, assuming that the temperature of the latter had not changed appreciably. As this sensitivity was considerably lower than such a thermocouple would ordinarily give, it was evident that the thermocouple was measuring only a fraction of the desired temperature difference, owing to an unavoidable thermal resistance between the thermocouple junction and the NaOH solid-liquid interface. The calibration just referred to, however, should have eliminated most of the error from this source.

In order to estimate the amount of liquid-soluble, solid-insoluble impurity in the sodium hydroxide sample, the temperature of the furnace was maintained several degrees below that of the sample itself for the time necessary to freeze about half of it. After again raising the furnace temperature to slightly below and then to slightly above the sample, and repeating the readings described in the preceding paragraph, the temperature of the sample was found to have dropped from approximately 317.1° to 315.8° C. Approximately the same temperatures were found for both samples of sodium hydroxide. In the present investigation the solid-solid transition point was similarly determined and for both samples was found to be 292.8° C.

In order to estimate how long to cool the sodium hydroxide so as to freeze a certain fraction of it, it was necessary to establish the heat-leakage rate of the sample in the given experimental environment. This rate was measured by substituting a sealed sample of sodium metal, in which the thermal gradients could be assumed negligible, and following the rate of change in the difference between the temperature of the completely melted sodium and that of the furnace. As in all cases, the differential thermocouple readings were corrected by the reading obtained after the two were known to have reached

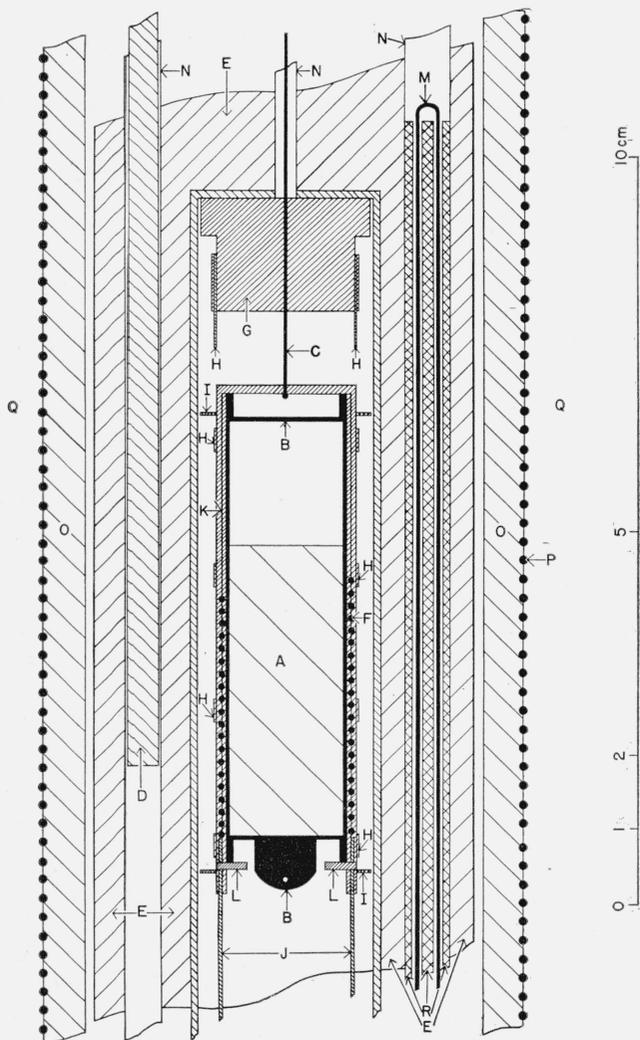


FIGURE 1. Cryoscopic apparatus.

A, Sample of sodium hydroxide; B, sealed container for sample (silver) (shown slightly different in shape from that actually used); C, suspension wire (nichrome V); D, platinum resistance thermometer; E, isothermal jacket (silver); F, heater or sample (glass-covered constantan); G, thermocouple reference block (gold-plated copper); H, thermocouple junctions (silver bands); I, spacers (nichrome-V wire); J, heater leads (copper); K, jacket for sample container, and heater cover (gold-plated copper); L, pins for supporting sample container; M, auxiliary heater for silver jacket (nichrome); N, Inconel tubing; O, Alundum tube; P, main furnace heater (platinum); Q, furnace insulation (silica powder); R, porcelain tube.

the same temperature. The heat-leakage rate was readily calculated from the known masses and specific heats of the component parts of this system.

Table 1 summarizes the data obtained in measuring the transition and freezing points of the two samples of sodium hydroxide.

The obvious small inconsistencies in table 1 between the fractions frozen and the corresponding sample temperatures indicate that these measurements can be only roughly correct. Fortunately, the enthalpy measurements later made in this temperature region furnish independent data for determining the same relationships, and an estimate of the amount of impurity present will thus be deferred to section 4.

TABLE 1. *Equilibrium temperatures during transition and freezing of two samples of sodium hydroxide*

| Sample | Furnace temperature | | Temperature of sample holder relative to furnace | Interpolated temperature of sample | Phase change involved | Estimated fraction frozen | Effective sensitivity of differential thermocouple |
|--------|---------------------|---------------|--|------------------------------------|-----------------------|---------------------------|--|
| | $^{\circ}C$ | μ° | | | | | |
| 3 | 292.8 | -30 | 292.8 | Transition | ----- | 42 | |
| | 293.75 | -40 | | | | | |
| | 292.25 | +23 | | | | | |
| | 293.65 | -20 | | | | | |
| 3 | 316.35 | +18 | 316.9 | Freezing | 0.04 | 27 | |
| | 317.8 | -20.5 | | | | | |
| | 316.4 | +15 | | | | | |
| | 316.9 | -4 | | | | | |
| 3 | 316.4 | +20 | 317.2 | do | .05 | 24 | |
| | 317.8 | -14 | | | | | |
| | 314.25 | +54 | | | | | |
| | 316.4 | -26 | | | | | |
| 3 | 315.6 | +8 | 315.8 | do | .60 | 38 | |
| | 316.5 | +11.5 | | | | | |
| | 317.8 | -28 | | | | | |
| | 316.5 | +28.5 | | | | | |
| 4 | 315.6 | +8.5 | 315.8 | do | .44 | 41 | |
| | 292.3 | +20 | | | | | |
| | 291.4 | +54 | | | | | |
| | 292.8 | ----- | | | | | 292.8 |

3. Enthalpy Measurements

The method of enthalpy measurement and apparatus used were described in detail in two early papers [2]. Two more recent publications [3,4] describe the improved apparatus used in the present investigation. Briefly, the sample is heated in a silver-core furnace to a known temperature, and is then dropped into a Bunsen ice calorimeter that measures the heat evolved by the sample in cooling to $0^{\circ}C$. Repetition at a number of furnace temperatures enables the heat capacity to be derived over a temperature range. Carrying out such measurements also on the empty container gives "blank" values that correct for the heat evolved by the container.

The sealed silver vessel was contained in an outer vessel, partly for mechanical support at the high temperatures where silver becomes quite soft and partly to protect the apparatus in case the silver container bursts open. The outer vessels used were evacuated, filled with helium, and closed (almost tight) by a screw lid before insertion into the furnace. Three such outer vessels were used, two of com-

mercial nickel and the other of a stainless-steel type 446. The use of a nickel container at 500° and 600° was dictated by earlier work by the authors with the stainless-steel type-446 containers, which were found to give results of inferior reproducibility in this range of furnace temperatures, owing to a transition in the steel.

Beside each sample of sodium hydroxide measured was placed a small piece of annealed silver such as to make the total mass of silver exactly 12 g. In measuring the blanks, a 12-g annealed piece of the same pure silver was put into the appropriate empty outer container. In this way the results were made independent of the explicit heat capacity of silver alone. Small corrections were applied to place the results for containers with and without sodium hydroxide on the basis of the same mass of each material entering the calorimeter. The corrected values of enthalpy obtained in individual runs are given in table 2. No corrections for the effects of impurities are included in the results in table 2; these corrections are large at a few of the temperatures, as shown in section 4.

TABLE 2. *Enthalpy measurements*

| Furnace temperature ($^{\circ}C$) | Outer container No. | Sample No. | Mass of sample g | Measured heat | | $H_i - H_0^{\circ}$, net for sample |
|-------------------------------------|---------------------|------------|--------------------|--|--|--------------------------------------|
| | | | | With sample | Empty containers | |
| 100.00 | 3 | 4 | 4.1074 | $abs\ j$ | $abs\ j$ | 152.8 |
| | | | | 1720.6 1725.5 1722.8 3593.7 3597.1 3596.7 3603.1 | 1093.4 1094.4 1098.8 2271.6 2274.2 2274.0 | |
| 200.00 | 3 | 4 | 4.1074 | 3603.1 | 2274.0 | 322.4 |
| | | | | 5316.0 5316.1 | 3437.4 3438.2 | |
| 280.00 | 3 | 3 4 | 4.2007 4.1074 | 3270.8 3271.4 | 3438.2 | 486.5 |
| | | | | 5268.9 5268.7 | 3438.2 | |
| 298.00 | 2 | 3 | 4.2007 | 6326.3 6327.3 | 3438.2 b(3625.5) | 687.7 |
| | | | | 6790.3 6789.5 | 3612.3 3609.7 3614.1 3610.2 | |
| 313.00 | 2 | 3 | 4.2007 | a(7137.4) a(7156.5) | 3711.6 3712.6 | 822.5 |
| | | | | 7165.3 7169.3 7497.5 | 3859.1 | |
| 316.00 | 1 | 3 | 4.2007 | 7505.8 7502.4 7505.8 | 3863.6 3859.5 3857.7 | 886.9 |
| | | | | 8986.4 8988.3 8991.3 8988.3 | 4678.5 4675.7 4676.9 4675.8 | |
| 400.00 | 2 | 4 | 4.1074 | 11099.1 11104.6 11101.8 | 5923.0 5924.7 5923.1 | 1260.8 |
| | | | | 13258.3 13259.0 13260.4 | 7205.6 7204.8 7205.2 | |
| 500.00 | 2 | 4 | 4.1074 | 9684.9 9682.4 9693.8 9695.2 9687.3 9692.8 | 8546.0 | 1473.9 |
| | | | | 11099.1 11104.6 11101.8 | 5923.0 5924.7 5923.1 | |
| 600.00 | 2 | 4 | 4.1074 | 13258.3 13259.0 13260.4 | 7205.6 7204.8 7205.2 | 1473.9 |
| | | | | 11099.1 11104.6 11101.8 | 5923.0 5924.7 5923.1 | |
| 701.2 | 3 | 4 | 4.1074 | 16615.6 | 8546.0 | 1686.3 |
| | | | | 16615.6 | 8546.0 | |
| 701.2 | 2 | 5 | 4.1840 | 15610.4 | 8556.1 8553.1 8556.4 | 1686.8 |
| | | | | 15610.4 | 8556.1 8553.1 8556.4 | |

^a These two results were rejected because the lengths of time the sample was held in the furnace (92 and 86 min, respectively) were thought inadequate for equilibration under these particular conditions. In the third and fourth runs at 316° the sample was in the furnace for 142 and 116 min, respectively.

^b Rejected for lack of precision.

As will be noted from table 2, measurements were made on two samples of sodium hydroxide at each of the furnace temperatures 280° and 701.2°. The agreement within 0.03 percent at 701.2° is considered somewhat fortuitous, in view of the precision and of the uncertainties in several corrections applied. Two samples were run at 280° to check on the accuracy of the sample masses, a large error in which would otherwise go undetected. The two runs on each sample at 280° agree closely, so that the difference between the means for the two samples (only 0.1 percent in that part of the enthalpy change attributed to the sample) furnishes evidence that the two sample masses were not much in error. There may thus be a 0.1-percent discrepancy between the masses of the two samples. However, this interpretation of the discrepancy at 280° is uncertain, as it rests on the assumption that the concentration of impurity is practically the same in the two samples. Actually, the corrections derived in section 4 show that at 280° the measured enthalpy of each sample is about 2 percent too high because of the impurity.

The silver vessel containing the sample (No. 5) opened during the second run at 701.2°. There proved to have been no loss of sample, however, so the heat measurement was accepted. On the other hand, in an effort to extend the measurements above 700° two runs were made on a different sample at a furnace temperature near 800° C. A considerable quantity of sodium hydroxide escaped not only from the silver container but from the outside container as well, so that the calorimetric results for 800° are of no value and were discarded.

The reason for the consistent escape of sodium hydroxide from the sealed silver vessels at approximately 700° and 800° is not known. The partial pressure of water, present as an impurity, may have become sufficiently high to blow open the relatively soft silver. Or the experience of two earlier investigators [5] may have been repeated. They found that after prolonged contact of the two substances near 700°, silver was no longer impervious to molten sodium hydroxide.

The two silver containers that opened after a few hours at high temperatures were later examined for any apparent action on them by the sodium hydroxide. Neither container showed any visible signs of having been attacked. However, the silver that had been heated to 800° C was very brittle; it was not possible to remove it quantitatively for weighing. But the silver that had been in contact with sodium hydroxide only up to 700° (and for a shorter time) appeared to be no more brittle than pure annealed silver; after washing and drying, its weight was within 1 mg (0.01 percent) of that before filling with sodium hydroxide and sealing. Thus it appears that under this limited treatment near 700° no appreciable silver loosened and became dispersed in the molten sodium hydroxide.

The same nickel container was used as an outer vessel for both these silver containers at their highest temperatures. There was no detectable loss of nickel at 700°. But at 800° a hole developed in the

nickel at one point where the silver had apparently been in contact with it. According to the literature [6], nickel and silver form a nickel-rich solid alloy, but no liquid phase, at this temperature. On the other hand, nickel and silver may have formed an electrochemical couple in the presence of the sodium hydroxide. Otherwise the nickel appeared unattacked, except for a thorough removal of its thin oxide coating where it had come in contact with sodium hydroxide.

4. Correction for Impurity: Final Values

It has been known for a long time that anhydrous sodium hydroxide undergoes a solid-solid first-order transition at some temperature between 290° and 300° C, the high-temperature crystalline form melting in the neighborhood of 320°. Accurate enthalpy measurements on a pure sample of this substance at enough temperatures in the range of the present investigation, 0° to 700°, should obviously be sufficient to determine the heat capacities of the two crystalline forms and the liquid (over the respective temperature ranges in which they are stable), as well as the heats of transition and fusion.

The unexpectedly large amounts of impurities found in the samples analyzed (section 1) make it necessary to consider carefully the errors thereby introduced into the thermal results and to correct for these undesired effects as well as possible. The impurities will for the present be taken as consisting of 0.3 percent of sodium carbonate, as found by chemical analyses, and 0.4 percent not accounted for but assumed to be water. The sources of error thereby created in the measured heat capacities are three: (1) differences between the heat capacity per unit mass of the impurities and that of the sodium hydroxide, (2) the extra heat absorbed or evolved in evaporating or condensing water in the gas space available, and (3) the extra heat absorbed below the melting point because of "premelting" of part of the sodium hydroxide caused by the impurities.

The first is a minor source of error here. Using an estimated heat-capacity equation of Kelley [7] for crystalline sodium carbonate given for the temperature range 25° to 225° C, it was estimated that 0.3 percent of sodium carbonate contributes in this way an error in heat capacity no greater than about 0.1 percent. The apparent specific heat of water (when saturated with sodium hydroxide below the freezing point of the sample) is probably comparable to that of sodium hydroxide and may contribute in this way no greater error than that due to the sodium carbonate.

The second source of error also is of minor importance below the melting point, as the gas space is only about 1 cm³/g of sample, and the partial pressure of water vapor over saturated aqueous sodium hydroxide solutions does not exceed approximately one-third atmosphere at any temperature [8]. As the temperature rises above 260° C, this partial pressure decreases rapidly, and in the present case is very small, possibly of the order of 0.001 mm, at the freezing point of the sample.

Above the freezing point the concentration of water in the liquid sodium hydroxide cannot become smaller through melting of additional crystalline phase, and as the temperature rises the partial pressure of water vapor must increase many-fold. How great this pressure becomes at the highest temperature of the present measurements, 700° , is difficult to estimate even approximately from the data referred to above [8], as such an estimation involves extrapolating to much higher temperatures and much lower concentrations of water than covered by the data. An estimate made it seem probable, however, that not enough water evaporated up to 700° from the samples measured to contribute an error as great as 2 percent in any smoothed value of heat capacity of liquid sodium hydroxide obtained in the present investigation. This conclusion is supported by two additional facts: (a) One sample that became unsealed in a 700° run was found afterward to have lost in mass, if any, not more than 5 mg that might be water, instead of the 15 mg or so that was inferred from chemical analyses as having been present originally, and (b) it will be seen later in this paper (fig. 3) that the relative enthalpies measured in the liquid range give by difference four "observed" heat-capacity values that fit randomly the adopted linear variation of heat capacity with temperature within about 1 percent, instead of showing the upward curvature that would certainly be expected if the partial pressure of water increased so fast with rising temperature as to evaporate most of the water at or below 700° .

The third source of error, that involving an extraneous "heat of premelting" below the melting point, obviously caused no error in the values obtained for liquid sodium hydroxide. However, the errors in some of the enthalpy values obtained below the melting point are large. These will now be corrected for, by a procedure that makes no assumption as to the identity, the amounts, or the effective molecular weights of the impurities present. Three reasonable simplifying assumptions are made, as follows:

(1) The crystalline form of sodium hydroxide that is stable below the transition temperature will be designated as "alpha," and that stable above as "beta."⁴ It will be assumed that at equilibrium at any temperature except the transition temperature, all the crystalline sodium hydroxide present in the sample is in the form of one of these two pure phases. (In this circumstance the transition point found, 292.8°C (section 2), is uninfluenced by the impurities.) In a careful study of the NaOH- Na_2CO_3 system [9] an earlier investigator was unable to detect any solubility of Na_2CO_3 in crystalline NaOH; and according to the literature, no solid hydrate of sodium hydroxide is stable above 60°C [8]. The existence of a solid solution of sodium hydroxide and water seems even less likely.

(2) The liquid solutions formed by sodium hydroxide and the impurities soluble in it will be assumed to obey Raoult's law, and therefore also to exhibit

no heat of mixing as liquids. It thus becomes a simple matter of deducing from the thermal data the fraction of the sodium hydroxide in liquid solution with the impurities at each temperature (fraction "premelting"), and of identifying the extra enthalpy (which the sample possesses) with the heat of fusion of that amount of liquefied sodium hydroxide. Below the transition temperature this heat of fusion is then actually the true heat of fusion (of the "beta" form) plus the heat of transition.

It is claimed [9] that liquid sodium hydroxide forms nearly ideal solutions with sodium carbonate. On the other hand, the solutions with water are certainly far from ideal, as shown by the partial-pressure data [8]. Nevertheless, from the foregoing treatment it may be shown that between the transition and melting points the mole fraction of sodium hydroxide in the liquid solution is not less than about 0.95, so that the deviations from Raoult's law are probably minor. At lower temperatures the deviations from this law become increasingly greater, of course, because of the larger proportions of water; but the thermal corrections become much smaller, so that errors in them are correspondingly less consequential. The data on the NaOH- H_2O system [8] seemed too inconsistent to allow any estimate of the error due to this lack of ideality, beyond leading to the belief that most of the thermal corrections to be deduced are in error by not more than a few percent of themselves.

At this point it may be mentioned that the water in the sample is no doubt present at 0°C , the reference temperature of all the enthalpy values, in the form of hydrates of sodium hydroxide. Thermochemical data [10] indicate that for any of the several common hydrates the heat of hydration (referred to pure liquid water) amounts to approximately 4 joules for the 0.004 g of water that may be associated with each gram of sodium hydroxide. However, it seems reasonable to assume that as the temperature rises the heat of dehydration will be more or less balanced by a heat of mixing, as dehydration in the liquid phase is a more gradual process. Thus no corresponding correction seems in order here.

(3) The third assumption is that the heat capacities of the alpha, beta, and liquid forms of sodium hydroxide are equal and independent of temperature, the value taken being $2.15 \text{ abs j g}^{-1} \text{ deg K}^{-1}$, which is the observed heat capacity of the liquid extrapolated to the temperature region between the transition and melting points.

As the thermal corrections are large enough to make this assumption of consequence only between the transition and melting points, and as the heat capacities of the alpha and liquid forms would be found, regardless of this assumption, to be almost equal at the boundaries of this temperature region (fig. 3), the principal assumption being made here is essentially that the heat capacity of the beta form, otherwise entirely undetermined, is equal to that of the other two forms. This assumes without proof that the enthalpy of the beta form increases between

⁴ Some authors have used these names in the reversed sense as applied to sodium hydroxide.

the transition and the melting point by approximately 57 j/g—a substantial amount of heat. However, it seems unlikely that this is considerably in error, as the heat capacities of most substances change by only a few percent on passing the melting point. Enough data were obtained to determine in principle a value for the heat capacity of the beta form; but, as was anticipated, such an indirect method is so sensitive to small errors in the thermal data (aside from deviations from the ideal solution laws) that these errors were sufficient to lead to an incredible value for this constant (actually a negative value).

This third assumption is equivalent to treating the heats of transition and fusion as independent of temperature.

The symbols used in the subsequent quantitative treatment will first be defined:

- t = temperature ($^{\circ}\text{C}$)
- T = temperature ($^{\circ}\text{K}$) ($=t+273.2$)
- T_m = melting point of pure sodium hydroxide ($^{\circ}\text{K}$)
- T_t = transition point of pure sodium hydroxide ($^{\circ}\text{K}$)
- T_f = freezing point of the sample measured ($^{\circ}\text{C}$) (that is, temperature at which $m=1$)
- L_f = heat of fusion of pure (beta) sodium hydroxide (abs j g^{-1})
- L_t = heat of transition of pure sodium hydroxide (abs j g^{-1})
- n = total moles of liquid-soluble impurity in sample measured, per gram of sodium hydroxide present
- m = grams of sodium hydroxide in liquid solution at temperature T , per gram of total sodium hydroxide
- a_1 = activity of alpha sodium hydroxide relative to the pure liquid at the same temperature
- a_2 = activity of beta sodium hydroxide relative to the pure liquid at the same temperature
- M = effective molecular weight of sodium hydroxide vapor in any given case
- R = gas constant ($=8.3144$ abs j mole $^{-1}$ deg K^{-1})
- H = observed enthalpy (at a given temperature T) of sample measured, above that at 0°C (abs j g^{-1})

The variation of activity with temperature for the two crystalline forms of sodium hydroxide is given by the two equations [11]:

$$d \ln a_1/dT = M(L_t + L_f)/RT^2 \quad (1)$$

$$d \ln a_2/dT = ML_f/RT^2 \quad (2)$$

Integration of eq (1) and (2) and imposition of the conditions that when $T=T_m$, $a_2=1$, and when $T=T_t$, $a_1=a_2$, lead to the equations

$$\ln a_1 = -[M/R][L_t(1/T-1/T_t) + L_f(1/T-1/T_m)] \quad (3)$$

$$\ln a_2 = -[M/R][L_f(1/T-1/T_m)]. \quad (4)$$

The activity of each solid is equal to that of the sodium hydroxide in the liquid solution with which the solid is in equilibrium, and this in turn is, accord-

ing to Raoult's law, equal to the mole fraction of sodium hydroxide in the solution, $1-n/(m/M+n)$. As n is relatively small here, it proves sufficiently accurate to replace $\ln[1-n/(m/M+n)]$ by $-nM/m$, which, when substituted for the left-hand members of eq (3) and (4), gives two equations independent of M :

$$nR/m = L_t(1/T-1/T_t) + L_f(1/T-1/T_m) \quad (T \leq T_t) \quad (5)$$

$$nR/m = L_f(1/T-1/T_m) \quad (T_t \leq T \leq T_f) \quad (6)$$

When $T=T_f$, $m=1$. Substituting into eq (6),

$$nRT_mT_f = L_f(T_m - T_f) \quad (7)$$

Before proceeding further, smoothed values of the relative enthalpy of liquid sodium hydroxide, based on the results of this investigation, will be obtained. The last six values of relative enthalpy in the last column of table 2 (section 3) gave by the method of least squares the equation (in abs j g^{-1} at $t^{\circ}\text{C}$):

$$H_t(\text{liquid}) - {}_0^{\circ}H(\text{alpha}) = 180.6 + 2.1990t - 7.31(10^{-5})t^2 \quad (319^{\circ} \text{ to } 700^{\circ} \text{ C}) \quad (8)$$

The smoothed values given by this equation differ from the observed values on which the equation is based by the amounts shown in table 3. (The temperature of the melting point, T_m , is anticipated from the calculations that follow.) The differentiation of eq (8) gives for the heat capacity of liquid sodium hydroxide the equation (in abs j g^{-1} deg C^{-1} at $t^{\circ}\text{C}$):

$$C_p = 2.199 - 1.46(10^{-4})t \quad (319^{\circ} \text{ to } 700^{\circ} \text{ C}) \quad (9)$$

Using for the heat capacity a constant value of 2.15 abs j g^{-1} deg K^{-1} , which eq (9) gives at the temperatures between the transition and melting points, an equation may now be formulated giving the relation among the observed enthalpy H of the sample measured, the enthalpy at the same temperature if all were liquid, and the fraction of the sodium hydroxide remaining frozen (as beta) in the sample:

$$(1-m)L_f = 874.8 - 2.15(592.3 - T) - H. \quad (T_t \leq T \leq T_f) \quad (10)$$

TABLE 3. Enthalpy of liquid sodium hydroxide

| Temperature (t) | Relative enthalpy, $H_t(\text{liq}) - H_{0^{\circ}}(\alpha)$ | | |
|---------------------|--|------------------------|-----------------------|
| | Observed | Calculated from eq (8) | Difference |
| $^{\circ}\text{C}$ | abs j g^{-1} | abs j g^{-1} | abs j g^{-1} |
| *319.1 | 874.8 | 874.8 | 0.0 |
| 325.0 | 886.9 | 887.6 | -0.7 |
| 400.0 | 1049.8 | 1048.5 | +1.3 |
| 500.0 | 1260.8 | 1261.8 | -1.0 |
| 600.0 | 1473.9 | 1473.7 | +0.2 |
| 701.2 | 1686.6 | 1686.6 | 0.0 |

* Melting point.

Elimination of m and n among eq (6), (7), and (10) gives

$$T_m(T_f - T)L_f/[T_f(T_m - T)] = 874.8 - 2.15(592.3 - T) - H. \quad (T_i \leq T \leq T_f) \quad (11)$$

The successive substitution into eq (11) of the observed enthalpy values (last column of table 2) for 298°, 313°, and 316° C, together with the corresponding absolute temperatures, gives three equations whose simultaneous solution gives for T_f a value of 589.9° K (316.7° C). The independent cryoscopic measurements described in section 2 gave a freezing point of these samples of 317.1° C. Adopting as a mean 316.9° C ($T_f=590.1$), the three equations just referred to will give consistent values for the melting point of pure sodium hydroxide and the heat of fusion if the observed enthalpies H are altered by small amounts that are within the accuracy of the measurements: Increasing the observed enthalpy at 313° C by 2.5 abs j g⁻¹ and decreasing each of the observed enthalpies at 298° and 316° by half this amount lead to: $T_m=592.3$ (319.1° C); $L_f=158.9$. (These constants are very close to those that would have been obtained from the cryoscopically observed freezing point and only the two observed enthalpies at 298° and 313°.) These two values, together with the adopted value for T_f of 590.1, then give, when substituted into eq (7), a value for the impurity in the sample, in moles per gram of sodium hydroxide: $n=0.00012$.

A value for the heat of transition, L_t , may now be found. Substituting the values of the constants so far found, eq (6) gives, at the transition point ($T_f=566.0$), $m=0.080$, corresponding to 8.0 percent of the sodium hydroxide liquefied at this temperature. Equation (10) then gives an "observed" enthalpy at this temperature, with all the solid in the beta form, of 672.1 abs j g⁻¹. Removal as heat of 92.0 percent of the heat of transition per gram of pure sodium hydroxide should then give the "observed" enthalpy at the same temperature with all the solid in the alpha form. Extrapolation of the observed enthalpies at 100°, 200°, and 280° C (last column of table 2, section 3) gives for this enthalpy (at 292.8° C) a value of 525.9 abs j g⁻¹ (actually after a slight adjustment by means of a second approximation in order to make all the results entirely consistent). Thus

$$L_t = (672.1 - 525.9)/0.920 = 158.9.$$

Substitution into eq (5) then gives values of m at 100°, 200°, and 280° C, and when these are multiplied by the sum of the heats of transition and fusion and then subtracted from the observed enthalpies at these temperatures, three values of relative enthalpy of pure alpha sodium hydroxide are obtained that determine the empirical equation (in abs j g⁻¹ at t° C):

$$H_t(\text{alpha}) - H_{0^\circ\text{C}}(\text{alpha}) = 1.4764t + 2.195(10^{-4})t^2 + 1.968(10^{-6})t^3 \quad (0^\circ \text{ to } 292.8^\circ \text{ C}) \quad (12)$$

(As was intended, this equation gives at 292.8° C a value that is consistent with the "observed" value of 525.9 abs j g⁻¹ used above.)

It is of interest to solve eq (3) for the temperature at which $a_1=1$. This gives 305.7° C, which is the temperature at which the alpha form would melt if the beta form, which is the more stable at this temperature, did not appear. Such metastability is very important in the case of some substances; but only a slight amount (brief supercooling once at the transition point) was detected in all the present cryoscopic and thermal measurements on sodium hydroxide, and this is in accord with the report of another investigator [9].

Some of the results of the preceding treatment may now be compared with those found in the cryoscopic measurements (section 2) and by chemical analysis (section 1). It will be noted from table 1, section 2, that for the two samples the estimated fractions frozen at 315.8° show poor agreement, though the values found for the freezing points of the two samples approximately agree. This is thought to be due to the crude method of determining from time interval and average temperature difference the total heat passing from sample to furnace in such partial freezing, particularly as the solid-liquid interface of the sample was no doubt moving constantly toward the center of the sample, setting up an extra temperature gradient across the solid that for so poor a thermal conductor was difficult to estimate and allow for correctly. The above treatment, in comparison, gives at 315.8° a still somewhat lower fraction present as solid than the two cryoscopic figures, and hence a somewhat greater proportion of impurity in the sample, though of the same order of magnitude.

As shown above, the treatment of this section gives for the moles of impurity per gram of sodium hydroxide (n) a value of 0.00012. On the other hand the chemical analyses referred to in section 2 give a value approximately twice as great if the effective molecular weights of H₂O and Na₂CO₃ be taken equal to their formula weights. It is not known whether the last assumption is unjustified here or whether the samples chemically analyzed contained more impurity than the samples measured thermally.

At any rate, the samples contained several tenths of one percent of impurity, and the derived heats of transition and fusion are proportionately too low because this fact was not taken into account. The uncertainties due to the assumptions of the above treatment, however, are probably more serious and must be considered to render the derived heats of transition and fusion uncertain by perhaps as much as 5 percent. However, the observed enthalpy for liquid sodium hydroxide near the melting point should possess considerable accuracy. Thus the total enthalpy change in the conversion of pure sodium hydroxide from the alpha form at the transition point to liquid at the melting point should be given rather accurately by the results of the present investigation. And as this relatively large enthalpy change occurs over a range of only 26 degrees, its contribution can hardly produce much error in the

absolute entropy and free energy of the liquid, as tabulated in section 6.

The accuracy of the treatment carried out in the present section cannot be expected to equal that of accurate enthalpy measurements on a highly pure sample, though such a treatment would give more accurate corrections the purer the sample measured. Nevertheless, it is believed that the present corrected results are more accurate than have been published to date for sodium hydroxide over this temperature range.

The final results for pure sodium hydroxide, based on the present investigation only, will now be summarized (with enthalpy in abs j g^{-1} and heat capacity in $\text{abs j g}^{-1} \text{ deg C}^{-1}$, at $t^\circ \text{C}$).

Alpha NaOH, 0° to 292.8° C

$$H_t - H_{0^\circ} = 1.4764t + 2.195(10^{-4})t^2 + 1.968(10^{-6})t^3$$

$$C_p = 1.476 + 4.39(10^{-4})t + 5.90(10^{-6})t^2$$

Transition, 292.8° C

Heat of transition, 158.9

Beta NaOH, 292.8° to 319.1° C

$$H_t(\beta) - H_{0^\circ}(\alpha) = 29.9 + 2.15t$$

$$C_p = 2.15$$

Melting, 319.1° C

Heat of fusion, 158.9

Liquid, 319.1° to 700° C

$$H_t(\text{liquid}) - H_{0^\circ}(\alpha) = 180.6 + 2.1990t - 7.31(10^{-5})t^2$$

$$C_p = 2.199 - 1.46(10^{-4})t$$

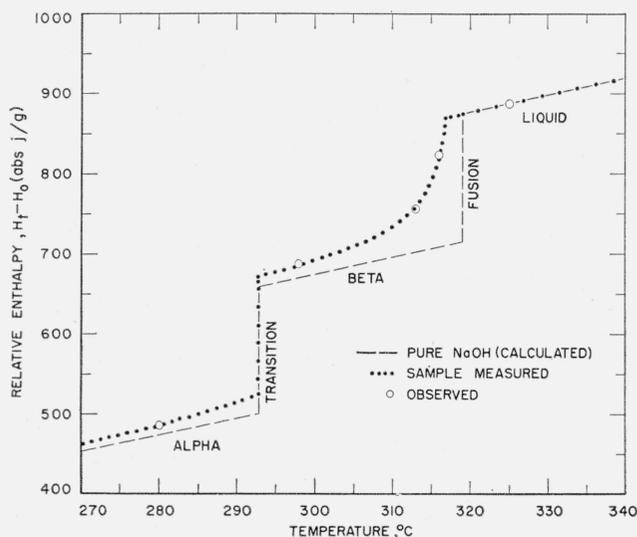


FIGURE 2. Observed and corrected enthalpy of sodium hydroxide.

It is interesting to compare the above (corrected) enthalpy-temperature relations with those observed on the samples measured. This comparison is shown in figure 2 for the temperature region in which the difference is significantly large. The dotted path deviates from the observed points to the extent necessary to make it consistent with the simplifying assumptions made in this section.

5. Comparison With Other Measurements

Various values for the transition and melting points of sodium hydroxide have been reported in the literature. Together with the values for these obtained in the present investigation, they are given in table 4. Some of these temperatures were apparently determined on samples containing considerable impurity whose effect was not allowed for.

The present work gives the same value, 159 abs j g^{-1} , for the heat of transition and the heat of fusion. The only values that were found in the literature are those of von Hevesy [12] and Seward [9]. Von Hevesy obtained from cooling curves 104 and 168 abs j g^{-1} , respectively. Seward did not attempt to measure the heat of transition, but calculated from the effect of sodium carbonate on the melting point a value of 175 abs j g^{-1} for the heat of fusion. Though Seward's measurements were apparently made with considerable care, his assumption of the effective molecular weight of Na_2CO_3 in these solutions being equal to the formula weight is open to question for so strong an electrolyte. His value for the heat of fusion of sodium hydroxide depends directly on this assumption.

A few investigators have measured the heat capacity of sodium hydroxide. Blümcke [17] obtained 3.26 $\text{abs j g}^{-1} \text{ deg C}^{-1}$ between 0° and 98°C , a value that is undoubtedly much too high. Terashkevich and Vishnevskii [18] covered the range 20° to 600°C , using samples of sodium hydroxide of 99 and 96 percent purity. Their results have been systematically formulated by Hulme [19]. Recently (1951) the enthalpy of the liquid from the melting point to 990°C was measured at the Oak Ridge National Laboratory using a Bunsen ice calorimeter [20]. The results of this work were expressed by an equation which when converted to terms of abs j g^{-1} is:

$$H_t(\text{liquid}) - H_{0^\circ}(\alpha) = 275.3 + 2.067t.$$

TABLE 4. Transition and melting points of sodium hydroxide

| Transition point | Melting point | Reference |
|-------------------|-------------------|---------------------|
| $^\circ \text{C}$ | $^\circ \text{C}$ | |
| 292.8 | 319.1 | This investigation. |
| 294 | 320 | [9] |
| 299.6 | 318.4 | [12] |
| 295 | 327.6 | [13] |
| ----- | 296 | [14] |
| ----- | 322 | [15] |
| ----- | 310 | [16] |

The corresponding heat capacity, 2.07 ± 0.08 abs $\text{j g}^{-1} \text{ deg C}^{-1}$, agrees within the precision with that of the present measurements over the entire temperature range covered by both; but the values of enthalpy referred to 0° differ considerably (by 60 j g^{-1} at 325°). Using an adiabatic calorimeter and sodium hydroxide said to be at least 99.84 percent pure, Kelly and Snyder [21] measured the heat capacity from 60° to 300° K .

The heat capacity, as measured in the present investigation and corrected below the melting point in section 4, is compared with the values of the other investigators in figure 3.

The curve representing the present results for the alpha form fits fairly smoothly (above 25° C) to that obtained from the precise low-temperature measurements of Kelly and Snyder [21], and shows at higher temperatures an upward curvature similar to that found by the present authors for crystalline lithium fluoride near its melting point [4]. As has already been pointed out in section 4, the heat capacities of solid and liquid sodium hydroxide show the customary behavior of being roughly the same near the melting point. Finally, attention may be called to the gradually decreasing heat capacity of liquid sodium hydroxide with temperature, according to the present measurements. Such a gradual decrease not far above the melting point has been found for numerous other liquids whose heat capacities have been measured in this laboratory—for all liquid metals measured, and very recently for the eutectic

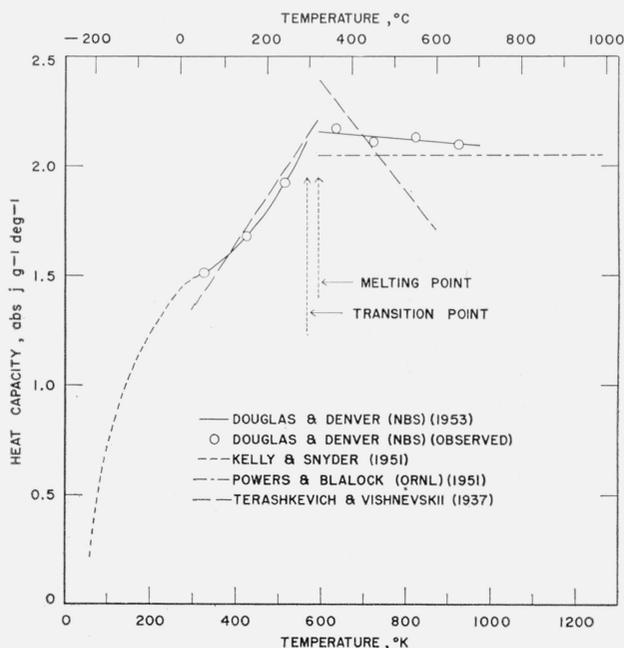


FIGURE 3. Heat capacity of sodium hydroxide.

mixture of lithium and potassium chlorides over a range of 450 deg above the eutectic temperature. The decrease of heat capacity with rising temperature has a theoretical basis in the case of simple liquids.

6. Thermodynamic Functions of Sodium Hydroxide, 298.2° to $1,000^\circ \text{ K}$

Using the corrected enthalpy results summarized at the end of section 4, together with Kelly and Snyder's value of $15.34 \pm 0.1 \text{ cal/mole-deg K}$ for the absolute entropy at 298.2° K [21]⁵, some of the common thermodynamic properties of sodium hydroxide (relative enthalpy, relative free energy, entropy, and heat capacity) were computed from 298.2° to $1,000^\circ \text{ K}$ and are given in table 5. It will be noted that the values of enthalpy and free energy given are relative to the enthalpy at 298.2° K , whereas the entropy as given is the absolute entropy (that is, relative to 0° K).

TABLE 5. Thermodynamic functions of sodium hydroxide^a

| Temperature | Physical state | $\frac{H^\circ - H_{298.2}^\circ}{T}$ | $-\left(\frac{F^\circ - H_{298.2}^\circ}{T}\right)$ | S° | C_p° |
|-------------------|----------------|---|---|---|---|
| $^\circ \text{K}$ | | $\text{cal deg}^{-1} \text{ mole}^{-1}$ | $\text{cal deg}^{-1} \text{ mole}^{-1}$ | $\text{cal deg}^{-1} \text{ mole}^{-1}$ | $\text{cal deg}^{-1} \text{ mole}^{-1}$ |
| 298.2 | Alpha | 0 | 15.34 | 15.34 | 14.26 |
| 300 | do | 0.086 | 15.34 | 15.43 | 14.27 |
| 325 | do | 1.184 | 15.40 | 16.58 | 14.49 |
| 350 | do | 2.144 | 15.52 | 17.66 | 14.77 |
| 375 | do | 2.998 | 15.69 | 18.69 | 15.13 |
| 400 | do | 3.769 | 15.91 | 19.68 | 15.56 |
| 425 | do | 4.477 | 16.16 | 20.64 | 16.05 |
| 450 | do | 5.135 | 16.44 | 21.57 | 16.62 |
| 475 | do | 5.756 | 16.73 | 22.49 | 17.26 |
| 500 | do | 6.349 | 17.04 | 23.39 | 17.97 |
| 525 | do | 6.921 | 17.37 | 24.29 | 18.75 |
| 550 | do | 7.478 | 17.70 | 25.18 | 19.60 |
| 566.0 | do | 7.829 | 17.92 | 25.75 | 20.18 |
| 566.0 | Beta | 10.513 | 17.92 | 28.43 | (20.56) |
| 575 | do | 10.670 | 18.09 | 28.76 | (20.56) |
| 592.3 | do | 10.959 | 18.41 | 29.37 | (20.56) |
| 592.3 | Liquid | 13.524 | 18.41 | 31.93 | 20.58 |
| 600 | do | 13.615 | 18.58 | 32.20 | 20.57 |
| 650 | do | 14.147 | 19.69 | 33.84 | 20.50 |
| 700 | do | 14.598 | 20.76 | 35.36 | 20.43 |
| 750 | do | 14.984 | 21.78 | 36.76 | 20.36 |
| 800 | do | 15.318 | 22.76 | 38.08 | 20.29 |
| 850 | do | 15.609 | 23.69 | 39.30 | 20.22 |
| 900 | do | 15.863 | 24.60 | 40.46 | 20.15 |
| 950 | do | 16.087 | 25.45 | 41.54 | 20.08 |
| 1,000 | do | 16.284 | 26.29 | 42.57 | 20.01 |

^a 1 calorie = 4.1840 abs j. Molecular weight of NaOH = 40.005. $0^\circ \text{ C} = 273.2^\circ \text{ K}$

The sodium hydroxide was supplied by members of the Oak Ridge National Laboratory. Credit is due several members of the National Bureau of Standards: To S. W. Clabaugh and J. W. Donovan for investigating means of preparing pure sodium hydroxide, as well as for analyses of samples; to J. M. Sherfey for making available a special dry box.

⁵ The other source of entropy data is the emf measurements of Shibata, who in two papers [22] gave values of 17.5 and 12.43 for this entropy. Kelley [23] lists 14.2 ± 1.5 , based on this work. Kelly and Snyder [21] gave a table of thermodynamic functions of sodium hydroxide from 60° to 300° K , based on their own measurements.

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