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PROBLEMS PERTAINING TO THE DEHYDRATION OF SODIUM HYDROXIDE BY VOLATILIZATION OF WATER

G. P. Smith

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METALLURGY DIVISION

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DATE ISSUED

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PROBLEMS PERTAINING TO THE DEHYDRATION OF SODIUM HYDROXIDE BY VOLATILIZATION OF WATER

G. P. Smith

ABSTRACT

Water, a ubiquitous contaminant of sodium hydroxide, has an effect on many reactions conducted in sodium hydroxide melts. Consequently, suggestions have been made in the literature on ways to remove it, but some of the suggestions are conflicting and nearly all are unsupported by experimental data. Dehydration by volatilization at temperatures approaching 800°C is impractical because of self-dissociation, but very little has previously been published on dehydration at lower temperatures.

The experiments described herein showed that volatilization of water from sodium hydroxide is exceptionally rapid in two widely separated temperature ranges, one in the neighborhood of 60 to 70°C and the other beginning a little below the melting point of the hydroxide. The high rate of water evaporation in the low-temperature range is attributed to melting of the monohydrate layer found at the surface of a hydroxide particle which had been exposed to a moist gas. Volatilization of water from the fused hydroxide takes place most rapidly by formation of water-vapor bubbles, but pronounced superheating was found. This superheating was enhanced by well-known devices, such as application of a gas pressure over the melt, and is believed to be a consequence of the high surface tension of the melt.

INTRODUCTION

Water is a ubiquitous contaminant of sodium hydroxide in even the fused state. It is generally recognized that reactions conducted in fused hydroxide media are frequently affected by water contamination; for example, polarization of an oxygen electrode in fused sodium hydroxide is markedly affected by small amounts of water (*2*), as are other electrode reactions in a hydroxide melt (*3*). Reactions between many oxides and fused sodium hydroxide involve water (*4,5*), as do reactions between metals and sodium hydroxide under certain conditions (*6,7*). The general aspects of the role of water in a variety of reactions in fused hydroxide media have been discussed (*8*).

At least nominal efforts have been made (*1–9*) to remove water from fused sodium hydroxide, such as by volatilization into a vacuum or stream of dry gas, but there is some divergence of opinion as to the conditions necessary to achieve dehydration. Neumann and Bergve (*3*) felt that 6 to 7 hr at a red heat was required, and D'Ans and Löffler (*4*) heated to 800°C. However, most workers have proposed that much less vigorous treatment would be satisfactory. Wallace and Fleck (*9*) heated for 1 hr at 500°C, Williams and Miller (*6*) dehydrated for an unspecified time at 400°C under a diffusion pump vacuum, while Agar and Bowden (*2*) proposed that most of the water contamination could be removed by heating for a few hours at 350 to 400°C with the use of a stream of dry oxygen which bubbled through the melt.

None of the workers cited present data to substantiate their statements regarding the completeness of water removal; presumably they used as a criterion the cessation of water evolution as determined by weighing a water absorbent in the system. Agar and Bowden (*2*) used an elegant

electrochemical technique to measure the pronounced effect that small amounts of water have on the overpotential of an oxygen electrode in a sodium hydroxide melt; they undoubtedly also applied this technique in determining the completeness of dehydration.

Although the escaping tendency of water in a hydroxide melt no doubt increases with increasing temperature, thereby facilitating dehydration at the highest temperature available, establishing a well-defined upper limit on the temperatures available for practical volatilization is hampered by two factors:

1. Very few container materials remain reasonably inert toward a hydroxide melt at high temperatures. Nickel, a relatively inert and widely used container material for hydroxide melts, reacts measurably with sodium hydroxide at 475°C and quite rapidly above 700°C in the absence of an overpressure of hydrogen (*6*). Most other metals, and nearly all ceramics which have been tested, react at temperatures at least as low as 700°C (*6,8*). Many of these reactions produce water. The only structural material which has been found to be reaction-resistant under conditions encountered in dehydration at high temperatures is binder-free magnesium oxide (*8*).

2. Sodium hydroxide self-dissociates into sodium oxide and water and hence must be considered as a two-component system, with water being an admissible component. There are very little data to indicate at what temperature this two-component nature of sodium hydroxide becomes important, but Steidlitz and Smith (*10*), in preliminary measurements of the rate of water evaporation from sodium hydroxide held in vessels machined from large single crystals of magnesium oxide, report a rapid rate of self-dissociation at 800°C and a very slow rate at 400°C.

This report presents some data pertaining to the processes involved in dehydration by volatilization and, based on these data, an analysis of some of the problems encountered in dehydration.

PROCEDURE AND RESULTS

The apparatus used for measurement of the rate of water evolution consisted of a nickel tube, 1.25 cm in diameter and 30 cm in length, closed off at one end and fitted with a ground joint at the other end. During measurement this tube was held vertically, and its closed-off end, containing hydroxide, was heated by an electric tube furnace. The other end of the tube was attached by means of the ground joint to a large-diameter vacuum line containing a liquid nitrogen cold-trap and was pumped by a mechanical vacuum pump. Pressure in the vacuum line near the nickel tube was measured by means of a Pirani gage which had been calibrated for water vapor. Without hydroxide in the system, a reproducible background pressure of 2 μ Hg was quickly attained. The temperature was measured to within 5°C by means of a Chromel-Alumel thermocouple fastened to the outer side of the nickel tube. For each experiment, 10 g of cp-grade sodium hydroxide pellets was weighed in a closed tube, and then the pellets were transferred in air to the nickel tube, which was then attached to the vacuum line. Vacuum pumping was begun at once, and as soon as the pressure in the system reached a steady level, the hydroxide was heated. Throughout the heating period the pressure and the furnace temperature were recorded. The pellets used in the experiment had been exposed to moisture for varying periods of time and at varying concentrations of water vapor, and the furnace temperature was raised at various rates.

The more important features of the results obtained for all these experiments are illustrated in Fig. 1, which shows the pressure and temperature curves for an experiment in which the temperature was raised at a slow and uniform rate. At a relatively low temperature a pronounced peak occurred in the pressure curve, after which the pressure returned to a low value and remained there until, at a temperature somewhat below the melting point of pure sodium hydroxide, another pressure surge occurred. This second surge was accompanied by a rapidly fluctuating pressure in which the excursions were irregular and much too rapid to indicate individually on the scale of Fig. 1. The shaded regions on the pressure curve indicate the approximate limits of these rapid pressure fluctuations. At a temperature above the melting point of sodium hydroxide, but below 400°C, the pressure surge ceased and the pressure fell rapidly to the background pressure of 2 μ. As the temperature increased, there was no further evidence of gas evolution until the temperature was raised to about 450°C; then the reaction between sodium hydroxide and nickel became appreciable and hydrogen was evolved. Samples

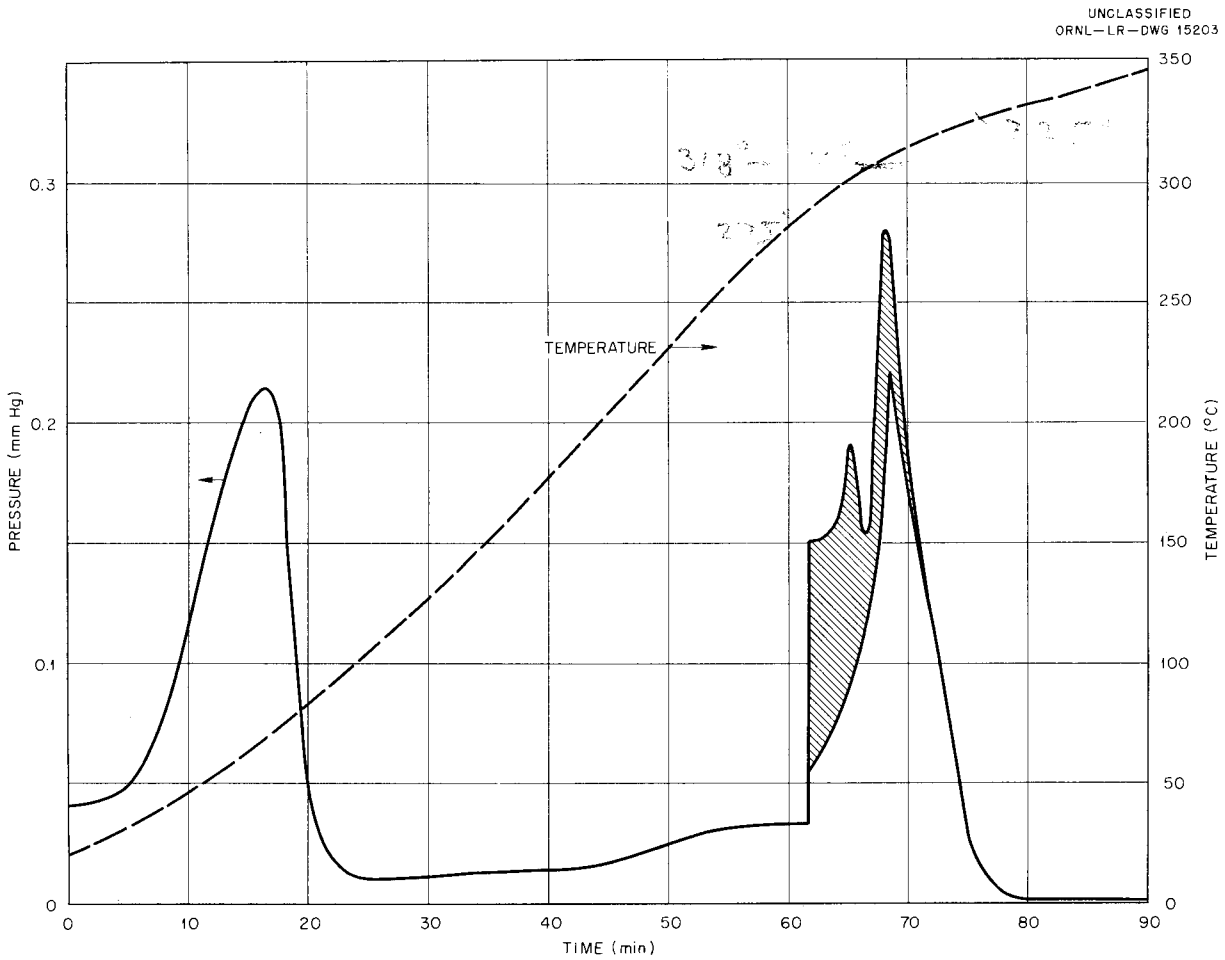

Fig. 1. Pressure of Water Vapor Formed Over Sodium Hydroxide During Dehydration by Volatilization into a Vacuum While Heating. The shaded area represents the limits of pressure excursions too rapid to show on the scale of the plot.

which had had the greatest exposure to water vapor before being heated gave especially large pressure surges, but the low-temperature surge always increased in magnitude with increasing exposure to water vapor much more than did the high-temperature surge.

A simplified apparatus was used for visually observing sodium hydroxide pellets subjected to the same heat and vacuum treatment as described above. Initially, the surfaces of the pellets were covered with a thin liquid film. After a few moments of evacuation at room temperature, this liquid film solidified. At a higher temperature, when the hydroxide melted, water evolution occurred in the form of bubbles, which nucleated on particles of unmelted hydroxide or on the walls of the vessel. When the fused hydroxide contained a great deal of water, as it did when the temperature was raised very rapidly to the melting point, bubbles of water vapor were produced in rather violent bursts, an action similar to the superheating of a liquid above its boiling point. When moisture-containing hydroxide was melted under 1 atm pressure of dry argon, bubble formation was inconspicuous below 400°C, but, when the pressure was reduced by evacuation, a vigorous ebullition ensued.

DISCUSSION

The above experiments showed that volatilization of water from sodium hydroxide is exceptionally rapid in two widely separated temperature

ranges, one in the neighborhood of 60 to 70°C and the other beginning a little below the melting point of the hydroxide; that a great deal of the water absorbed by sodium hydroxide pellets at room temperature can be removed readily by volatilization into a vacuum at temperatures in the neighborhood of 60 to 70°C; and that volatilization of water above the melting point of the hydroxide is subject to the phenomenon of superheating associated with bubble formation.

The characteristic features of the pressure curves found in these experiments can be related to phase equilibria in the sodium hydroxide–water system. These two substances form only one compound which has a melting point above room temperature, the monohydrate with a congruent melting point of 64.2°C (*11*). This compound forms a eutectic with sodium hydroxide that has a composition near that of the monohydrate and a melting point of about 62°C. The solid-phase solubility of water in sodium hydroxide has not been determined but is known to be small.

The hydroxide pellets used in this work had been exposed for various periods to water vapor both during packaging and at the beginning of each experiment. From the phase relations and the assumption that sodium hydroxide and water form a normal diffusion couple, it can be deduced that the absorbed water was contained in a surface layer of monohydrate, which, in turn, was coated with a thin layer of aqueous solution of hydroxide. Additional water was, no doubt, contained in each pellet as a result of incomplete dehydration in manufacture. The phase relations indicate that this additional water was in the form of small crystals of monohydrate which had been entrapped when the pellet was frozen.

In the dehydration experiments the apparatus was first evacuated at room temperature, which, as shown by visual observation, caused the pellets to lose their surface layer of aqueous solution and led to a constant pressure being attained. Phase relations show that the hydroxide in the solution precipitates out as the monohydrate.

The dehydration apparatus was capable of attaining a pressure of 2 μ, which was, undoubtedly, well below the decomposition pressure of the monohydrate. Thus, in principle, it would have been possible to remove most of the water from the monohydrate layer at room temperature. However, water could escape under these conditions only by solid-state diffusion. Hence it was not surprising to find that vacuum pumping at room temperature generally gave a steady-state water-vapor pressure of 20 to 50 μ, which does not represent a particularly rapid rate of water evolution.

When the melting point of the monohydrate was reached, the surface layer became liquid. The rate of gas evolution from a liquid is much greater than that from a solid because of enhanced material transport rates and bubble formation. Consequently there was a surge of water evolution which produced the prominent peak found in every pressure curve at a temperature below 100°C.

In like manner the second surge in water-vapor pressure was undoubtedly associated with the melting of the hydroxide. However, this second surge usually began appreciably below the melting point of the hydroxide (except when the furnace temperature was raised at such a rapid rate that thermal equilibrium was not even approximately achieved within the mass of pellets). This phenomenon was undoubtedly associated with the lowering of the melting point of the hydroxide by the water which was present, a complex mechanism which will be discussed.

At a temperature above the melting point of the monohydrate but below the melting point of the hydroxide, the particles of what had been entrapped monohydrate became liquid nodules of water saturated with sodium hydroxide. Therefore the water in these nodules can escape into the vacuum only by the relatively slow process of solid-state diffusion or when some event opens a continuous path between liquid and vacuum. At temperatures well below the melting point of the hydroxide a few such events are to be expected, because there are several sources of crack-producing stresses within the pellets. For example, with increasing temperature the phase relations require that the aqueous nodules grow by dissolving hydroxide. The volume of these growing nodules was slightly greater than the volume of the hydroxide dissolved. It is possible that all this volume increase can be absorbed by mechanical deformation of the solid matrix or that a portion will not be absorbed and will thereby produce cracking. At a relatively high temperature but still appreciably below the melting point of pure hydroxide, a cataclysmic breakdown of the solid matrix must have occurred as the growing nodules began to intersect one another and the surface. At this time the geometry of the

heterogeneous system changed from that of liquid entrapped in a continuous solid matrix to that of solid particles within a continuous liquid matrix. Such an event is not a unique point on the phase diagram and is not accompanied by any special thermal effects but is accompanied by a greatly enhanced rate of water evolution. The temperature at which this occurs will depend not only on the water content but also on the geometry of the solid-liquid system.

Visual observations on the dehydration of just-melted sodium hydroxide showed that water evolution occurred in the form of bubbles which nucleated on particles of solid hydroxide or on the walls of the vessel. The rapid pressure fluctuations represented by the shaded region in Fig. 1 were no doubt associated with the bursting of bubbles of water vapor at the surface of the hydroxide. When the fused hydroxide contained a great deal of water, bubble evolution came in bursts which produced irregular peaks in the average pressure curve. Similar evidence of superheating was obtained when water-laden sodium hydroxide was heated under 1 atm pressure of argon, and then the pressure rapidly reduced after the hydroxide melted. Williams and Miller (*6*) point out that it is difficult to dehydrate fused sodium hydroxide in vessels of Teflon, which the hydroxide does not wet. These facts agree with a general picture of dehydration of the liquid by nucleation of bubbles of water vapor.

The removal of water vapor from sodium hydroxide by volatilization necessitates the migration of water across a gas-liquid interface, whether this be the external liquid surface or the surface of the bubble. Obviously, the greater the area of the gas-liquid interface, the faster the rate of water evolution. In addition the net flux of water across a hydroxide interface will be an increasing function of $(p_l - p_g)$, where p_l is the partial pressure of water which would be in equilibrium with the concentration of water in the bulk of the hydroxide and p_g is the partial pressure of water vapor which exists in the bulk of the gas phase. The exact functional relation should be quite complex inasmuch as it involves a series diffusion path (liquid-phase diffusion followed by gas-phase diffusion) and to some extent a chemical change at the interface corresponding to the breakdown of ion-dipole forces in the melt.

Several factors contribute to the difficulty of achieving bubble nucleation in the liquid, the one causing the most difficulty being interfacial tension. The surface tension of fused sodium hydroxide has not been measured, but it is known to be quite large because of especially strong capillary activity (*8*). This surface tension not only inhibits the nucleation of bubbles but also restricts their rate of growth by forcing p_g within the interior of the bubble to be greater than it would otherwise have to be.

Artificially increasing the liquid surface area by various well-known means such as bubbling a dry gas through the melt will obviously assist dehydration; this procedure, however, has been ignored by all experimenters except Agar and Bowden (*2*). Although it has been a popular dehydration procedure, inhibiting the spontaneous increase of the liquid surface by applying a gas pressure without bubbling is to be avoided because it inhibits spontaneous bubble formation.

The above data and discussion serve to illustrate the complexity of the problem of removing water from fused sodium hydroxide by volatilization and show why there are conflicting claims about the conditions necessary for dehydration.

Finally, there is the problem of ascertaining the concentration of water in a hydroxide melt which is at equilibrium with a specified partial pressure of water in the gas phase. This relation enters the dehydration problem in two ways. First, it determines the limiting concentration of water in the liquid phase imposed by the degree of dryness of the gas phase; second, it enters into the kinetics of dehydration as being one way of expressing activity coefficients of water in a melt, and the activity coefficients in turn enter into diffusional processes by virtue of the driving force for the latter being the gradient of the chemical potential. The work of numerous investigators (*12*) on the partial pressure of water over sodium hydroxide–water mixtures has been assembled (Fig. 2) for temperatures up to 350°C. If it is assumed that 1 mole of sodium hydroxide dissolves in water to form 1 mole of particles, these data do not approach, even at low hydroxide concentrations, Raoult's law in the approximate form $p = p^{*}N$, where p is the partial pressure of water over the melt, p^{*} is the vapor pressure of pure water at the temperature in question, and N is the mole

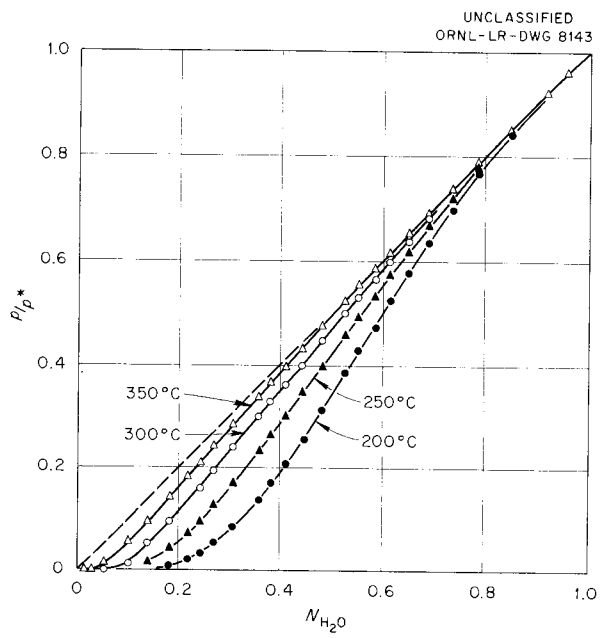

Fig. 2. Curves Illustrating the Affinity of Sodium Hydroxide for Water Vapor at Elevated Temperatures as Computed from Data in Ref. 12.

fraction of water in the liquid. However, if it is assumed that each mole of sodium hydroxide contributes 2 moles of particles (so-called "complete ionization" assumption), then it will be found that the data fit Raoult's law over a surprisingly wide range of concentrations at higher temperatures ($0.5 < N < 1.0$ at 350°C). Nevertheless, deviations become increasingly negative with decreasing water content. At the lowest water concentration for which data are given, the activity coefficient is less than 0.01 (standard states taken as the pure substances) and shows no sign of ceasing to decrease with decreasing concentration in accordance with Henry's law. (This may best be shown on a log p/p^* vs log N curve.)

CONCLUSIONS

1. Dehydration of sodium hydroxide by volatilization at temperatures approaching 800°C is not practical because of self-dissociation, but a limiting temperature cannot be specified at present.
2. Dehydration of fused sodium hydroxide at temperatures below 400°C is made difficult by a superheating phenomenon.
3. The adequacy of cessation of water evolution as a criterion for the completeness of dehydration is questionable because of superheating, except where a dry gas is bubbled through the melt.
4. The exceptionally high rate of water evolution found for temperatures in the neighborhood of 60 to 70°C is attributed to melting and subsequent decomposition of a monohydrate layer which formed at the surface of sodium hydroxide pellets because of exposure to moist air.
5. The affinity of sodium hydroxide for water vapor was shown by the use of existing data to be unexpectedly high even at 350°C.

BIBLIOGRAPHY

(1) M. LeBlanc and L. Bergmann, *Ber. deut. chem. Ges.* **42,** 4728 (1909); M. LeBlanc and O. Weyl, *ibid.* **45,** 2300 (1912).

(2) J. N. Agar and F. P. Bowden, *Proc. Roy. Soc.* (*London*) **A169,** 220 (1939).

(3) B. Neumann and E. Bergve, *Z. Elektrochem.* **21,** 143 (1915).

(4) J. D'Ans and J. Löffler, *Ber. deut. chem. Ges.* **63B,** 1446 (1930).

(5) B. A. Nekleevich, *Khim. Referat. Zhur.* **4,** 26, 27 (1941).

(6) D. D. Williams and R. R. Miller, *Thermal and Related Physical Properties of Molten Materials. Part II. High Temperature Reaction of Sodium Hydroxide,* WADC-TR-54-185 (Feb. 1955).

(7) R. S. Peoples, P. D. Miller, and H. D. Hannan, *Reaction of Nickel in Molten Sodium Hydroxide,* BMI-1041 (Sept. 27, 1955).

(8) G. P. Smith, *Am. Inst. Mining Met. Engrs., Inst. Metals Div., Spec. Rep. Ser.* **No. 2,** 71–94 (1956).

(9) T. Wallace and A. Fleck, *J. Chem. Soc.* **119,** 1839 (1921).

(10) M. E. Steidlitz and G. P. Smith, unpublished research.

(11) S. U. Pickering, *J. Chem. Soc.* **63,** 890 (1893).

(12) *International Critical Tables,* vol. 3, p 370, McGraw-Hill, New York, 1928.