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THE SODIUM HYDROXIDE - SODIUM OXIDE - SODIUM -
SODIUM HYDRIDE - HYDROGEN SYSTEM

By: Henry C. Kelly, Edward A. Sullivan, and Sidney Johnson

ABSTRACT

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Sodium hydride dissolves in and reacts with molten sodium hydroxide to give an equilibrium mixture of sodium hydride, sodium hydroxide, sodium oxide, sodium, and hydrogen. In the case where there is a gaseous phase (hydrogen) and only one condensed phase, the system is defined by the temperature, pressure, and one composition variable. The equilibrium hydrogen pressure, which is a measure of the hydrogen activity within the melt, was determined as a function of the composition of the condensed phase(s) at 600°, 700°, and 800° for equilibrium mixtures with original compositions of 2.5 - 97.5, 5.0 - 95.0, 10.0 - 90.0, and 20.0 - 80.0 mole % sodium hydride - sodium hydroxide. The equilibrium hydrogen pressure - composition isotherms obtained by removing measured increments of hydrogen were reproduced by reabsorbing hydrogen. Results for the 5.0 mole percent sodium hydride mixture were duplicated by starting with an equivalent quantity of either sodium in sodium hydroxide or sodium oxide in sodium hydroxide, and reacting with measured increments of hydrogen. The system is discussed in relation to the interdependent reactions involved, the phase rule, the thermodynamics of certain reactions, and experimental techniques employed.

Interaction between sodium and sodium hydroxide was first observed by Davy¹

(1) H. Davy, Trans. Roy. Soc. (London), A98, 1 (1808)

in his classical experiments, during which he discovered and isolated sodium by electrolyzing fused sodium hydroxide. During the following century, many workers made observations on portions of the system under consideration. In 1909 von Hevesy² studied the solubility of sodium in sodium hydroxide, assuming the latter

(2) G. von Hevesy, Z. Elektro Chem., 15, 529 (1909)

to be an inert solvent. The true nature of the species present in the system was first recognized by Halla and Tompa³ and the first attempt to investigate

(3) F. Halla and H. Tompa, Z. anorg. allgem. Chem., 219, 321 (1934); 221, 18 (1934)

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the system in its entirety was reported by Klemenc and Svetlik⁴ as recently as

(4) A. Klemenc and E. Svetlik, Z. anorg. allgem. Chem., 269, 153 (1952)

1952. The latter investigators measured the equilibrium hydrogen pressure as a function of composition at 351, 377, and 445° in experiments similar in principle to the present study.

In the present investigation, various sodium hydride-sodium hydroxide mixtures were heated under hydrogen to give equilibrium mixtures of sodium hydride, sodium hydroxide, sodium oxide, sodium, and hydrogen. At equilibrium, the activity of each constituent will depend, in part, on the relative contribution of each of the following reactions to the overall equilibrium state of the system.

These are interdependent reactions, any one of which may be expressed in terms of two others. Reaction (1) represents sodium hydride and sodium hydroxide in equilibrium with sodium oxide and hydrogen. This may be considered the summation of reaction (2) (undissociated sodium hydride in equilibrium with sodium and hydrogen) and reaction (3) (equilibrium of sodium and sodium hydroxide with the oxide and hydrogen). Reaction (4) is another possible contributing equilibria involving these species.

From the standard heats, free energies and entropies of formation at 25°, as well as the heat capacities, and thermal data accompanying phase changes of the species, equilibrium constants of the reaction $\text{Na} + \text{NaOH} = \text{Na}_2\text{O} + 1/2 \text{H}_2$

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were calculated at elevated temperatures. Values of 0.93, 0.77, and 0.66 were obtained at 600, 700, and 800°, respectively. Pertinent data for NaH(c), such as the heat capacity at constant pressure and the entropy of formation at 25°, were either unknown, or involved such limits of error, that extended calculations of this type toward reactions involving NaH(c) as a constituent would result in limits of uncertainty too great to be of practical value.

The equilibrium hydrogen pressure, which is a measure of the hydrogen activity within the system, was determined as a function of the composition of the condensed phase(s) at 600, 700, and 800° for equilibrium mixtures of varying initial sodium hydride-sodium hydroxide concentration. Four mixtures studied in this manner consisted of 2.5-97.5, 5.0-95.0, 10.0-90.0, and 20.0-80.0 mole % NaH-NaOH. Results of these isothermal studies are shown in Figures 1-4.

Insert Figures 1,2,3,4

LEGEND

<u>Symbol</u>	<u>Isotherm</u>	<u>Starting Mixture</u>
○	600°	NaH - NaOH
◐	700°	NaH - NaOH
●	800°	NaH - NaOH
▲	600°	Na - NaOH
△	600°	Na ₂ O - NaOH

For a given composition, a higher equilibrium pressure is exhibited with increasing temperature. Since the composition variable concerns the relative quantity of evolvable hydrogen in the condensed phase(s), the composition is expressed as $100 H_{ev} / H_{ev}^{max}$, where H_{ev} is the evolvable hydrogen actually present in the condensed phase(s), and H_{ev}^{max} is the quantity of hydrogen available for evolution which would exist in the condensed phase(s) if sodium and sodium oxide

were not present in the system. Thus, H_{ev}^{max} represents the maximum quantity of hydrogen which could be evolved via reactions (1) (2) or (3), provided these reactions were initially displaced entirely to the left. The solubility of hydrogen in sodium hydroxide is known to be small,⁵ and, if assumed neglig-

(5) E.A. Sullivan, S. Johnson and M.D. Banus, J. Am. Chem. Soc., 77, 2023 (1955)

ible, H_{ev}^{max} is equal to two times the maximum hydride-hydrogen content. Thus at 100.0 on the composition axis, the condensed system contains sodium hydride and sodium hydroxide; at 0.0, sodium oxide and sodium hydroxide; and at intermediate values, equilibrium mixtures of sodium hydride, sodium hydroxide, sodium oxide, and sodium.

The majority of data were obtained by desorption of hydrogen from the given sodium hydride-sodium hydroxide mixture. In studies of this type, measured increments of hydrogen are removed from the system in stages and equilibrium conditions established at each stage. These curves are reproduced by reabsorbing hydrogen in similar stages following completion of the corresponding desorption run. Complete reversibility of the system is indicated by equilibrium data obtained at 600° on absorption of hydrogen into starting mixtures consisting of 5.0 mole % Na - 95.0 mole % NaOH; and 5.3 mole % Na₂O - 94.7 mole % NaOH (Fig. 2). The composition of these mixtures was selected so that upon complete absorption of hydrogen, the resultant mixtures would consist of 5.0 mole % NaH and 95.0 mole % NaOH.

An increase in the original sodium hydride concentration results in a considerable increase in the equilibrium hydrogen pressure for a given temperature and composition. All isotherms approach the 100.0 composition axis asymptotically; a small change in composition resulting in a very rapid change in equilibrium pressure in the vicinity of the 100.0 composition ordinate.

In conjunction with isothermal studies, a series of pressure-temperature studies were conducted on similar sodium hydride-sodium hydroxide starting mixtures. Utilizing the same experimental equipment, these mixtures were heated under given starting pressures to a series of increasing temperatures to produce curves of the type shown in Fig. 5.

Fig. 5 Insert

When a given sodium hydride-sodium hydroxide mixture is treated in this manner, a pressure-temperature curve similar to AC is obtained. The initial portion, AD, is linear (within limits of experimental error), and the slope corresponds to that expected for a fixed quantity of hydrogen obeying the gas laws. The expected pressure increase is shown as ADB, and the rise above this line is due to the evolution of hydrogen from the condensed phase. Since the line from C to D approaches the line AB asymptotically, the position of D is actually dependent on the sensitivity of the pressure recording instrument. The significance of D is that it represents a point beyond which a measurable quantity of hydrogen is evolved from the condensed phase. It would be expected then that this point should correspond to a point on the 100.0 composition axis of an isotherm (of similar sodium hydride-sodium hydroxide content), whereupon reduction in pressure results in the first measurable evolution of hydrogen from the condensed phase. This was indeed found to be true (i.e., a 5.0 mole % NaH - 95.0 mole % NaOH mixture treated as described revealed, in the case where D corresponds to a temperature of 600° , an equilibrium pressure in excellent agreement with that obtained on the 600° isotherm below which the evolution of hydrogen becomes a measurable quantity). Excellent agreement was obtained between isothermal investigations and pressure-temperature studies at 600, 700, and 800° for the four starting mixtures concerned.

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The system under consideration contains three components. Any three of the five constituents may be chosen, provided one is an oxygen-containing constituent. In accordance with the phase rule, in the case where there are two phases present (a gaseous hydrogen phase plus one condensed phase), there are three degrees of freedom, and the system is defined by the temperature, pressure, and one composition variable.

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EXPERIMENTAL PART

Experimentally, it is necessary to avoid two very serious sources of error inherent in many high temperature studies of metal hydrogen systems. These involve the solubility of hydrogen in the metal container system, and the loss of hydrogen via diffusion through the container walls. Individual investigations were conducted on the solubility of hydrogen in the specific metal containers, and corresponding corrections applied to the systems under consideration. Each mixture is contained in an inner chamber of a double-walled pressure vessel, the equilibrium pressure of the system being balanced at all times by maintaining an equivalent hydrogen pressure in the surrounding outer chamber. This prevents hydrogen diffusion losses through the walls of the inner chamber.

Due to the hygroscopic nature of the materials, extreme caution is observed to prevent contact with moisture and air. All mixtures are prepared in the inert atmosphere of an argon filled drybox. Samples are housed in nickel containers, the stems of which are welded gas tight. These containers are in turn enclosed in pressure vessels of type #304 stainless steel which are sealed by welding. A valve attached to the stem of each stainless steel chamber is connected to 1/8" diameter copper tubing, capable of maintaining vacuum as well as pressures in excess of 1000 psi. This tubing is connected to instruments which record the variation with time of pressures from 0 to 1000 psi. Drybox gas is then evacuated.

For all sodium hydride-sodium hydroxide mixtures, hydrogen is added until a pressure in excess of 500 psi is obtained. The system is heated to the desired temperature, and for pressure temperature studies, the pressure adjusted to an appropriate value. For isotherm investigations, the initial pressure is adjusted to a value high enough so that initial removal of an increment of hydrogen produces no measurable hydrogen evolution from the condensed phase(s). The absolute value ranges from 3500 to 5500 cm. Hg., depending upon the initial sodium-

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hydride-sodium hydroxide mole ratio. The composition at this pressure is assumed equal to 100.0, i.e., no sodium or sodium oxide present. The volume of the system is then determined from a knowledge of the temperature, the density of gaseous hydrogen at a series of temperatures and pressures, as well as the pressure drop occurring in the system upon removal of a known quantity of hydrogen into a previously calibrated volume.

Desorption is carried out by removing measured quantities of hydrogen from a starting composition of 100.0 and determining the equilibrium pressure and composition on attainment of equilibrium. Absorption studies are executed by addition of hydrogen in similar stages.

For sodium-sodium hydroxide and sodium oxide-sodium hydroxide absorption studies, measured quantities of hydrogen are added while the system is heated slowly to the desired temperature. Additional increments are added stepwise until pressures in excess of 4100 cm. Hg. are obtained, following which appropriate volume calibrations are carried out, and such data utilized to calculate the equilibrium composition at the various equilibrium pressures obtained upon each stepwise absorption. It is interesting that the initial absorption of hydrogen by a 5.3 mole % Na_2O - 94.7 mole % NaOH mixture was found to occur at 110°C. This is the temperature recorded by Klemenc and Svetlik⁴ for the absorption of hydrogen by sodium oxide.

All pressures are known to a precision limit of ± 2 psi. Temperatures are determined using a chromel-alumel thermocouple inserted into a well in the stainless steel container to a point adjacent to the sample, and are accurate to $\pm 1^\circ$.

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Fig. 1. 2.5-97.5 mole % NaH-NaOH isotherm data.

Fig. 2. 5.0-95.0 mole % NaH-NaOH isotherm data.

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Fig. 3. 10.0-90.0 mole % NaH-NaOH isotherm data.

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Fig. 4. 20.0-80.0 mole % NaH-NaOH isotherm data.

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Fig. 5. Typical pressure-temperature curve for NaH-NaOH mixture.

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