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SUBJECT: THE SODIUM HYDROXIDE - SODIUM HYDRIDE SYSTEM

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THE SODIUM HYDROXIDE - SODIUM HYDRIDE SYSTEM

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Portions of the sodium hydroxide - sodium hydride phase diagram have been studied by means of differential thermal analysis. Under certain conditions sodium hydride will either react with sodium hydroxide according to the equation $NaH + NaOH \rightleftharpoons Na_2O + H_2$; or thermally dissociate according to the equation $NaH \rightleftharpoons Na + 1/2H_2$. Both of these reactions are suppressed by a high hydrogen pressure[1], however, and in the investigations reported here,

(1) H. C. Kelly, E.A. Sullivan, and S. Johnson, THIS JOURNAL, 00, 0000 (1957).

sodium hydride neither reacts nor dissociates to an extent sufficient to affect the results reported. This was evidenced by the fact that changing the hydrogen pressure above the system in the range indicated in Table I did not change, within the limit of error of the experiments ($\sim \pm 5°$), the temperature at which a phase change was started or completed. Therefore the concentrations of sodium and sodium oxide present in the samples must have been small in all cases, a conclusion which is substantiated by the work of Kelly, Sullivan, and Johnson.[1] Under a high hydrogen pressure, therefore, the system may be considered as essentially binary, consisting of sodium hydroxide and sodium hydride.

Data from this study are given in Table I and the most reasonable interpretation of these data in terms of a phase diagram is presented in Figure I. In the notation of Figure I, S_1 represents a solid solution of sodium hydroxide in a sodium hydride matrix, and S_2 and S_3 represent solid solutions of sodium hydride in β- and α- sodium hydroxide matrices, respectively. The boundaries of the regions designated as S_1 and S_3 are completely arbitrary, in that no investigation was made in those composition ranges. It is quite possible that these regions are vanishingly small, in which case S_1 would be essentially pure sodium hydride, and S_3 essentially pure α-sodium hydroxide.

TABLE I

SODIUM HYDROXIDE - SODIUM HYDRIDE SYSTEM PHASE CHANGES

Mole % NaOH-NaH	Transition (°C)	Solidus (°C)	Liquidus (°C)	H_2 Pressure (p.s.i.)
100.0--0.0	292.8*	319.1*	319.1*	
92.7--7.3	268	325	340	600-800
83.1-16.9	235	350	375	550-800
74.8-25.2	203	371	412	700-800
67.2-32.8	209	398	466	750-850
61.2-38.8	209	447	525	800-950

* Reference 3

The most interesting feature of the phase diagram would seem to be the series of solid solutions which are formed between sodium hydroxide and sodium hydride, indicating that the melting point of sodium hydroxide is not depressed by the addition of sodium hydride, as might be expected. A similar phenomenon has been observed in the case of the sodium hydroxide-sodium fluoride system.[2] The similarity is not surprising since the fluoride and

(2) O. Scarpa, Atti reale accad. Lincei, 24 I, 955 (1915).

hydride ions are of comparable sizes. Sodium chloride also has been reported to form solid solutions with sodium hydroxide, but sodium bromide and sodium iodide cause a depression in the melting point of sodium hydroxide, with the formation of eutictics at approximately 80 mole % sodium hydroxide[2].

Although sodium hydride does not depress the melting point of sodium hydroxide, it does cause a lowering of the α-β transition temperature. Using the data of Table I, a plot of the log N_{NaOH} vs. 1/T for the transition temperature gives a straight line fitting the equation log $N_{NaOH} = -379.3/T + 0.6687$. Assuming the Clausius-Clapeyron equation is applicable, a value of 1736 cal./mole if obtained for the heat of transition, in reasonable agreement with the very accurate value of 1519 cal./mole obtained by Douglas and Dever[3] from

(3) T. B. Douglas and J.L. Dever, J. Research Natl. Bur. Standards, 53, 81 (1954).

cryoscopic measurements. While the experimental error in the present study is of such a magnitude that the discrepancy is not regarded as significant, it should be noted that exact agreement is not to be expected necessarily, since the transition occuring is actually S_2 changing to S_3, rather than β-sodium hydroxide changing to α-sodium hydroxide.

At 61.2 and 67.2 mole % sodium hydroxide, phase changes were observed at 130° and 167°, respectively. The significance of these is not understood. Phase changes below the transition temperature could not be observed with the 83.1 and 92.7 mole % sodium hydroxide samples, because any changes which may have occured were masked by solidification of the sodium hydroxide-potassium hydroxide mixture which was used in the reference container for the studies at these compositions. Sodium chloride was used in the reference container at the other concentrations.

Experimental

Materials.- Sodium hydroxide. The sodium hydroxide used in these experiments was a specially dehydrated preparation. Analyses indicated 100.0% purity by alkalinity; 0.07% sodium carbonate.

Sodium hydride.- The sodium hydride used was a commercial product of Metal Hydrides Incorporated. Analysis indicated 99.5% purity by hydrogen evolution.

Thermal measurements.- The sample was loaded and sealed in a nickel liner, using techniques previously described. This was placed, along with a reference nickel liner, in a high temperature, high pressure, stainless steel pressure vessel, equipped to contain hydrogen pressure up to 1000 p.s.i. A differential thermocouple was affixed to the nickel liners, and a reference thermocouple to the liner containing the sample. The reference thermocouple was connected to a standard recording potentiometer and the differential thermocouple to a recording potentiometer of high sensitivity having a 1.1 millivolt range over an 11 inch scale. The rate of heating or cooling was governed by a program controller so that the rate was approximately one to two degrees per minute.

Acknowledgment

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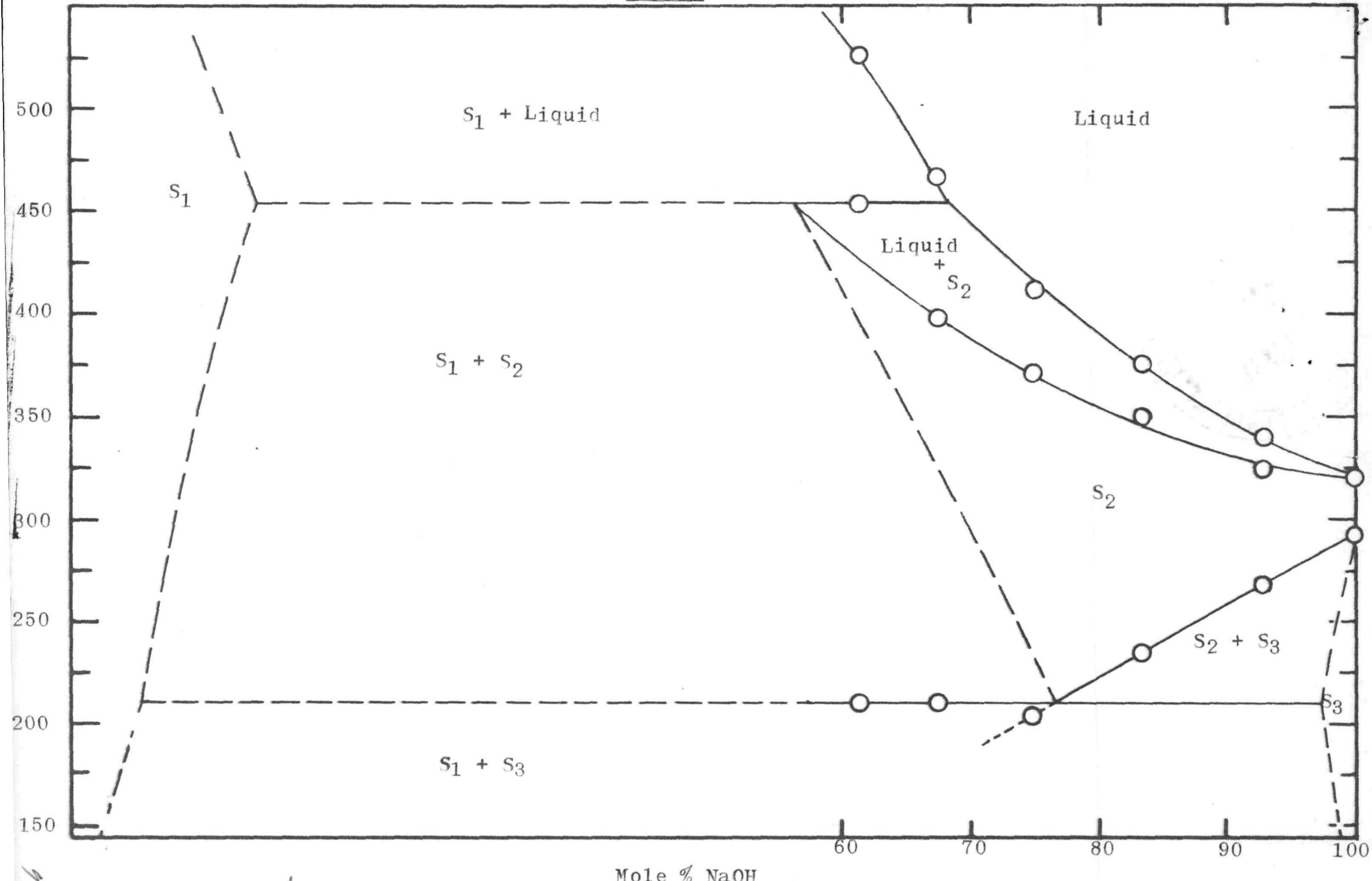

Fig. 1. Sodium hydroxide-Sodium Hydride phase diagram