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1965

SovietRxiv

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UDC 546.271 + 546.171.5 + 541.123.2

CHEMISTRY

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THERMAL ANALYSIS OF THE SODIUM BOROHYDRIDE–HYDRAZINE SYSTEM

(Presented by Academician I. I. Chernyaev, March 24, 1965)

Sodium borohydride is finding ever-increasing application in various fields of technology and scientific research. Its relation to solvents, however, has been systematically studied only for diglyme ([1]), water ([2]), liquid ammonia ([3]), pyridine ([4]), and dimethylformamide ([5]). Hydrazine is a good solvent for sodium borohydride. There are reports on the use of solutions of sodium borohydride in hydrazine as a high-calorie fuel ([6]), for the preparation of certain derivatives of borohydrides ([7]), etc. It is known, however, only that a saturated solution of sodium borohydride in hydrazine, containing 20.2 wt.% $NaBH_4$ at 25° and having a vapor pressure of 20 mm Hg, forms a eutectic at −26° ([8]). From this solution sodium borohydride crystallizes in the form of a solvate, presumably with two molecules of hydrazine. The present work gives the results of a study of phase equilibria in the sodium borohydride–hydrazine system over the temperature range from −120° to 80°.

For the study, sodium borohydride preparations containing 99.5 wt.% of the principal substance were used. The hydrazine samples contained 99.5 wt.% N_2H_4 and melted at 1.5°. Phase equilibria were studied by the differential-thermal method, with both cooling curves and heating curves being recorded. The rate of temperature change was 1–2° per minute. The accuracy of temperature measurement was $±$0.5°.

Phase equilibria in the sodium borohydride–hydrazine system were studied in the concentration range from 0 to 85.5 wt.% $NaBH_4$. The results of the investigations are presented in Fig. 1.

Four compounds were found in the system studied: $NaBH_4 \cdot 2N_2H_4$; $2NaBH_4 \cdot N_2H_4$; $NaBH_4 \cdot N_2H_4$ and $NaBH_4 \cdot 6N_2H_4$. The first of these compounds melts congruently at 53°. The eutectic between $NaBH_4 \cdot 2N_2H_4$ and hydrazine contains 15 wt.% $NaBH_4$ and melts at −22°. The eutectic between $NaBH_4 \cdot 2N_2H_4$ and $2NaBH_4 \cdot N_2H_4$ contains 46 wt.% $NaBH_4$ and melts at 44°. The compound $2NaBH_4 \cdot N_2H_4$ crystallizes from solutions containing 46–54 wt.% $NaBH_4$. At 56° it decomposes by a peritectic reaction into a solution containing 54 wt.%

Fig. 1. Phase diagram of the $NaBH_4$–N_2H_4 system

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$NaBH_4$ and unsolvated sodium borohydride. The branch of the curve corresponding to the solubility of unsolvated sodium borohydride rises very steeply upward, so that it could not be traced by the method of thermal analysis. Some lowering of the temperature of the eutectic arrests for mixtures far from the eutectic composition is apparently associated with the nonequilibrium character of crystallization, caused by the high viscosity of the solutions at these temperatures.

In addition to the thermal effects corresponding to the phase transitions listed above, a number of endothermic effects were observed on the heating curves and, correspondingly, exothermic effects on the cooling curves; these should be attributed to transformations in the solid phase. In the concentration range from 19 to 30 wt.% $NaBH_4$ a similar effect is observed at −5°, which we attribute to a polymorphic transformation of the solvate $NaBH_4 \cdot 2N_2H_4$.

The absence of this effect in the concentration range from 30 to 54.1 wt.% $NaBH_4$ is probably due to the fact that the transition from one crystalline modification of $NaBH_4 \cdot 2N_2H_4$ to another readily occurs only in the presence of a sufficient amount of liquid phase. Halts on the cooling and heating curves at −83° in the region of crystallization of unsolvated sodium borohydride correspond to the known polymorphic transformation of the latter (9-11). The same halt at −83° is observed in

Fig. 1. Phase diagram of the $NaBH_4$–N_2H_4 system

the concentration range 55-70.2 wt.% $NaBH_4$, which is apparently associated with the nonequilibrium course of the peritectic reaction, as a result of which part of the unreacted sodium borohydride remains in the solid phase. The halts on the heating curves at 9° in the concentration interval from 37.2 to 70.2 wt.% $NaBH_4$ should be attributed to the decomposition of the compound $NaBH_4 \cdot N_2H_4$ in the solid state into $NaBH_4 \cdot 2N_2H_4$ and $2NaBH_4 \cdot N_2H_4$. This interpretation of the indicated effects is based on the results of constructing the Tammann triangle and on the character of the heating curves of mixtures, for which the thermal halts were maximal in the concentration region containing 54.1 wt.% $NaBH_4$. It should be noted that the halts on the cooling curves corresponding to the formation of $NaBH_4 \cdot N_2H_4$, as well as to the polymorphic transformation of $NaBH_4 \cdot 2N_2H_4$, were observed with considerable supercooling. Thermal effects at −43° in the concentration region from 0 to 37.2 wt.% $NaBH_4$ were observed only on the heating curves. These halts were preceded by an exothermic effect near −71°, associated with the release of excess internal energy of the system and indicating nonequilibrium crystallization processes in this concentration interval. The sodium borohydride content at which the halt at −43° is maximal is equal to 16.5 wt.% $NaBH_4$, which corresponds to the composition $NaBH_4 \cdot$

$6N_2H_4$. This gives grounds to suppose that the halts at −43° may be attributed to the decomposition of the compound $NaBH_4 \cdot 6N_2H_4$. The latter is formed upon crystallization of supercooled solutions at a temperature of about −71°. Above −43° the compound $NaBH_4 \cdot 6N_2H_4$ decomposes into solid hydrazine and solid $NaBH_4 \cdot 2N_2H_4$.

The strong supercooling of mixtures of the system and the exothermic effect on the heating curves make it possible to assume that, upon cooling, the sy-

the system as a whole is prone to nonequilibrium crystallization; therefore, in constructing the phase diagram of sodium borohydride–hydrazine, we used the temperatures of phase transitions on the heating curves, rather than the cooling curves, as our guide. Evidently, it is precisely because of supercooling phenomena that some differences are observed between our data (the solubility at 25° is 23.5 wt.% $NaBH_4$, and the eutectic melts at −22°) and the data given in ([8]).

Received
19 III 1965

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