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Abstract

Full Text

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ON THE THERMAL STABILITY OF SODIUM ALUMINUM HYDRIDE

(Presented by Academician I. I. Chernyaev, 9 X 1962)

To determine the conditions for obtaining, by the newest method, the aluminum hydrides of alkali metals from alkali metals (or their hydrides), aluminum, and hydrogen (1,2),

$$\mathrm{M} + \mathrm{Al} + 2\mathrm{H}_2 \rightarrow \mathrm{MAlH}_4; \qquad \mathrm{MH} + \mathrm{Al} + \tfrac{3}{2}\mathrm{H}_2 \rightarrow \mathrm{MAlH}_4,$$

it is necessary to know the limits of the temperature stability of the aluminum hydrides, as well as the nature of the phase transformations observed during their thermal decomposition. Knowledge of the nature of the thermal decomposition of aluminum hydrides is no less important for understanding the reactions proceeding with their participation.

Among the aluminum hydrides of alkali metals, up to the present time only the thermal stability of lithium aluminum hydride has been well studied (3–6). The data of Fingold and co-workers on the behavior of sodium aluminum hydride upon heating are only approximate, since the authors had at their disposal a substance containing aluminum halides (7).

In the present work we used a preparation of sodium aluminum hydride obtained by a somewhat modified Klassen method (1,2) and containing 98% NaAlH_4.

The behavior of sodium aluminum hydride upon heating was studied by the differential-thermal method on an N. S. Kurnakov pyrometer with differential-thermal photographic recording.

Fig. 1. Heating and cooling curves of NaAlH_4, simple (a) and differential (b), combined with the polytherm of hydrogen evolution (v)

Fig. 2

Figure 2: Fig. 2

One junction of the combined thermocouple was introduced into a sample of the preparation (0.3-0.5 g), placed in a stainless-steel cap; the other junction—into calcined aluminum oxide taken as the standard, which was in an identical steel cap. Both caps, in turn, were placed in a hermetic quartz tube connected to a gasometric burette. The system was carefully evacuated and filled with dry argon. Heating to 700–750° C was carried out by means of an electric unit at a rate of 4–5° per minute. The heating was then stopped and cooling curves were recorded down to 100–80° C.

In a typical experiment, simultaneously with recording the change in temperature of the sample on the pyrometer, the amount of hydrogen evolved was visually recorded (Fig. 1). All phase transformations of sodium aluminum hydride that occur upon heating and are indicated on the thermal curves, both simple (*a*) and differential (*b*), are endothermic in character.

The first effect in the interval 178-184° is associated only with a very small evolution of gas, as is evident from the course of the volume-change curve (*c*). To determine the nature of this transformation under the same conditions, but with the steel cap replaced by a transparent quartz one, a heating curve of the substance up to 200°C with subsequent cooling was recorded (Fig. 2). The direct and reverse effects recorded on the pyrometric curves correspond to visually observed transformations of the contents of the test tube—into a liquid on heating and into a solid state on cooling. Thus, at 178°C sodium aluminum hydride melts.

Fig. 2. Heating and cooling curves of $NaAlH_4$ at temperatures below the onset of thermal decomposition: simple (*a*), differential (*b*)

The loss of sodium aluminum hydride content in samples subjected to melting amounts, according to chemical analysis, to 2-3%, which agrees with the character of the gas-evolution curve (Fig. 1*c*). The effects in the intervals 290-298° and 422–432° are accompanied by vigorous gas evolution, whereas the transformation at 660-664° is not accompanied by a change in gas volume and has a reverse character (corresponding to the exothermic effect on the cooling curve at 660–658°).

From a comparison of the indicated thermal effects it is easy to see that the transformation in the interval 290–298° corresponds to the decomposition reaction of sodium aluminum hydride:

$$NaAlH_4 \rightarrow NaH + Al + {}^3/_2H_2;$$

the transformation at 422–432° corresponds to the dissociation of sodium hydride into the elements:

$$NaH \rightarrow Na + {}^{1}/_{2}H_2;$$

the phase transformation at 660-664° corresponds to the melting of the metallic aluminum liberated during the decomposition of sodium aluminum hydride.

It is characteristic that on the cooling curve of the sample, at 422-410°, a reverse effect is recorded—the formation of sodium hydride from the elements. In accordance with this, at the boundary of the hot and cold zones of the test tube the formation of a white deposit of extremely fine needles of sodium hydride is observed.

Thus, sodium aluminum hydride belongs to the class of complex hydrides that melt practically without decomposition (melting point 178°C). Heating sodium aluminum hydride above its melting point is accompanied at first by slow, and at 290° by vigorous, decomposition into sodium hydride, aluminum, and hydrogen. Ultimately, above 422°C, the decomposition products of sodium aluminum hydride are sodium, aluminum, and hydrogen.

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Note: Figure translations are in progress. See original paper for figures.