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Abstract

Full Text

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ON THE THERMAL STABILITY OF POTASSIUM ALUMINUM HYDRIDE

(Presented by Academician I. I. Chernyaev, 8 VII 1963)

The discovery of a highly economical method for obtaining aluminum hydrides of the alkali metals ($^{1-4}$) by the reaction

$$\mathrm{M + Al + 2H_2 \rightarrow MAlH_4} \quad (\mathrm{M = Li;\ Na, K}) \tag{1}$$

makes these valuable compounds available for broad use in chemical practice. The conditions for their preparation, as well as the possibility of using the aluminum hydrides, are directly dependent on the limits of their thermal stability. The nature of the phase transformations occurring upon heating lithium and sodium aluminum hydrides is described in detail in the literature ($^{5-7}$). Zakharkin and Gavrilenko (^{10}) describe potassium aluminum hydride as a non-melting substance that decomposes above 260°, but they do not give the content of potassium aluminum hydride in the sample studied.

Fig. 1. Heating curves (a, b) and cooling curves (a', b') of $KAlH_4$, combined with the polytherm of hydrogen evolution (v)

The preparation of potassium aluminum hydride used in the present work was obtained by the reaction of potassium, aluminum, and hydrogen and contained 99% of the principal substance.

The behavior of potassium aluminum hydride on heating was studied by the differential-thermal method on an N. S. Kurnakov pyrometer with photographic recording of the simple and differential curves. One junction of the combined thermocouple was introduced into the sample of the preparation, and the other into aluminum oxide, taken as the standard; both were placed in balanced caps of stainless steel. The caps, in turn, were located in quartz test tubes. The test tube containing the sample of the substance was connected to a gasometric apparatus. The system was carefully evacuated and filled with dry argon. The substance and eta-

lon was heated to 750° at a rate of about 5 deg/min., after which the furnace was switched off and the system cooled. The changes in thermo-e.m.f. arising in the circuits of the simple and differential thermocouples were transformed by means of mirror systems into light beams, the paths of which were recorded on photographic paper. At the same time, the change in the volume of the evolved hydrogen was noted.

Figure 1 shows the result of an experiment on the thermal decomposition of 0.89 g of potassium alumohydride.

The phase transformations of the substance that occur during heating and are recorded on the thermal curves are endothermic in character. Comparison of the thermogram with the course of the polytherm of hydrogen evolution shows that the first three effects, in the intervals 292–315°, 335–355°, and 425–430°, are associated with vigorous hydrogen evolution. At temperatures of 315–335° a sharp slowing is observed, and at 355–425° a complete cessation of hydrogen evolution; these correspond to a break and a distinct step on the gas-evolution curve. The subsequent transformations of the substance correspond to effects in the intervals 664–665°, 720–730° and are not accompanied by hydrogen evolution. On the cooling curve one exothermic effect is noted at 635°.

Fig. 2. Curves of partial heating and subsequent cooling of $KAlH_4$. The designations are the same as in Fig. 1.

It was natural to expect that potassium alumohydride melts, like sodium alumohydride (^{9}). However, recording the curves of partial heating and subsequent cooling of the substance (Fig. 2) did not show a reverse effect on the cooling curve. At the same time, visual observation confirmed that under atmospheric-pressure conditions potassium alumohydride decomposes without melting.

Thus, the nature of the first three transformations occurring upon heating $KAlH_4$ up to 430° consists in stepwise decomposition of the substance and ends with complete loss of hydride hydrogen. The halt on the heating curve at 664-665° corresponds to melting of the metallic aluminum obtained as a result of pyrolysis. The reverse phenomenon—the solidification of aluminum—is reflected by an exothermic effect on the cooling curve at 635°. The nature of the effect on the heating curve at 720–730° remains unclear.

Table 1

Hydrogen evolution during thermal decomposition of potassium alumohydride

T-ra, °C	v_{H2}, cm^{3*}	$v_1 : v_2 : v_3 : v_4$
292–315	290	290 : 145 : 145 : 580 = 2 : 1 : 1 : 4

T-ra, °C	v_{H2}, cm^{3}*	$v_1 : v_2 : v_3 : v_4$
335-355	145	$290 : 145 : 145 : 580 = 2 : 1 : 1 : 4$
425-430	145	$290 : 145 : 145 : 580 = 2 : 1 : 1 : 4$
292-430	580	$290 : 145 : 145 : 580 = 2 : 1 : 1 : 4$

* Volumes are indicated without reduction to normal conditions.

Comparison of the volumes of hydrogen evolved at the individual stages of decomposition and as a whole shows that they are related to one another as simple whole numbers (see Table 1).

The reduced volume of pyrolytic hydrogen can serve as a criterion of the purity of the substance. In the present case it is 515.71 cm^3, or 637.47 cm^3/g. The calculated amount of pyrolytic hydrogen for $KAlH_4$

is equal to 639.41 cm^3/g. Hence the content of $KAlH_4$ in the product studied is

$$\frac{637.47 \cdot 100}{639.41} = 99.7\%.$$

The distinct stepwise character of gas evolution and the multiplicity of the volumes of hydrogen liberated in the individual steps make it possible to conclude that the following reactions occur during the pyrolysis of $KAlH_4$:

$$KAlH_4 \rightarrow KAlH_2 + H_2 \ (292\text{—}315^\circ), \tag{2}$$

$$KAlH_2 \rightarrow KH + Al + \tfrac{1}{2}H_2 \ (335\text{—}355^\circ), \tag{3}$$

$$KH \rightarrow K + \tfrac{1}{2}H_2 \ (425\text{—}430^\circ). \tag{4}$$

In all, above 430°:

$$KAlH_4 \rightarrow K + Al + 2H_2. \tag{5}$$

The thermal decomposition of potassium hydride formed during the pyrolysis of $KAlH_4$ (equation (4)) occurs at a temperature of 425—430°, which agrees with the temperature indicated for the thermal decomposition of pure potassium hydride ([11]).

Thus, potassium alumohydride belongs to the group of thermally rather stable complex hydrides, with a temperature-stability limit of 292°. Above 292°,

$KAlH_4$ decomposes without melting, losing hydrogen in stages. The final products of its decomposition are potassium, aluminum, and hydrogen.

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