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Abstract

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MELTING DIAGRAM OF THE SYSTEM POTASSIUM HYDROXIDE HYDRATE–POTASSIUM BOROHYDRIDE

(Presented by Academician N. I. Chernyaev, 11 IX 1961)

Borohydrides of the alkali metals are powerful reducing agents for organic and inorganic compounds (1–3). The stability of their aqueous solutions opens up the possibility of their use in analytical chemistry (4). However, the use of borohydrides for the reduction of inorganic compounds would be still more effective under conditions of reaction in a medium permitting reactions to be carried out at higher temperatures. For this purpose it was necessary to obtain melting diagrams of systems based on low-melting inorganic compounds with alkali-metal borohydrides as components. The present work is the first attempt in this direction.

Potassium borohydride was obtained by the interaction of an aqueous solution of technical sodium borohydride with potassium hydroxide according to the reaction

$$NaBH_4 + KOH \rightarrow KBH_4 + NaOH. \quad (1)$$

After thorough drying by washing with ethyl alcohol and subsequent prolonged evacuation at 80°, the preparation contained, according to analysis for active hydrogen, 99.5% KBH_4. Anhydrous potassium hydroxide hydrate was prepared from a chemically pure preparation by prolonged holding in the molten state under vacuum.

All manipulations connected with grinding, weighing, and transferring the substance into the apparatus for thermal analysis were carried out in an atmosphere of dry nitrogen.

Weighed portions of mixtures of specified composition, in a tall stainless-steel crucible, were placed in a quartz test tube connected to a vacuum system for

Fig. 1. Fusibility diagram of KOH–KBH4

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filling with inert gas and to a gasometric burette for measuring the gases evolved upon heating. The heating and cooling curves were recorded on a pyrometer of the N. S. Kurnakov system using a platinum-platinum-rhodium thermocouple.

On the heating curve potassium borohydride shows three endothermic effects, corresponding to melting at 640° (reversible); intense thermal decomposition at 690-700°; and the beginning of reaction of the alkaline melt with the crucible material at 780-800°. Anhydrous caustic potassium is characterized by reversible thermal effects at 275 and 385°, corresponding to its polymorphic transformation and melting.

The heating curves and cooling curves of binary mixtures show the same reversible thermal effects. However, on the heating curves of all mixtures there are also irreversible effects associated with the removal of traces of adsorbed water at about 100° and with the occurrence of intermediate stages in the establishment of phase equilibrium in the solid and partly in the liquid state. Therefore, the cooling curves of the mixtures were taken as the basis for constructing the melting diagram, provided they were heated no higher than the temperature at which decomposition of potassium borohydride begins.

The melting diagram of the system potassium hydroxide hydrate–potassium borohydride (Fig. 1) is characterized by two crystallization branches of potassium hydroxide hydrate and

of potassium borohydride, intersecting at the eutectic point at 347° and a concentration of 5.3% KBH_4. In the part of the system rich in potassium hydroxide hydrate, temperature arrests are observed corresponding to its polymorphic transformation at about 245°. Their constancy indicates the absence, in this system, of solid solutions based on potassium hydroxide hydrate.

Observation of KOH—KBH_4 mixtures during heating shows a slight evolution of hydrogen from them in the temperature region 450–550°, the maximum of which corresponds to an equimolecular ratio of the components.

Fig. 1. Fusibility diagram of KOH—KBH_4

Dissolution of the melts in water is also accompanied by a slight evolution of hydrogen, sometimes even with a flash. The intensity of this effect is greatest for melts from the middle part of the system. These phenomena, which are characteristic neither of potassium borohydride nor, still less, of potassium hydroxide hydrate, we believe to be associated with the partial occurrence of an exchange reaction

$$KBH_4 + KOH \rightarrow KBH_3OH + KH, \qquad (2)$$

with the formation of the compound KBH_3OH, previously isolated by us from the products of hydrolysis of magnesium boride (5), and potassium hydride. The dissociation elasticity of the latter reaches atmospheric pressure at about 428°, and vigorous reaction with water is accompanied by a flash (6).

Thus, the KOH—KBH_4 system is in fact a pseudobinary section of a quaternary reciprocal system corresponding to equation (2), and the binary melts of the middle part are, to some extent, carriers of the properties and activity of potassium hydride at temperatures considerably exceeding the region of its stable existence in the pure state.

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