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Abstract

Full Text

Chemistry

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On Solid Solutions of Sodium and Potassium Hydrides in Their Hydroxides

(Presented by Academician I. I. Chernyaev, 13 XII 1961)

Alkali-metal hydroxides are capable of dissolving alkali-metal hydrides. Solutions of 1.5-2% sodium hydride in sodium hydroxide, for example, are already used for removing oxides from the surface of metals ([1,2]). There are qualitative indications of the mutual solubility of sodium hydride and sodium oxide in sodium hydroxide ([3,4]). However, a quantitative study of the solubility of alkali hydrides in their hydroxides at various temperatures has not been reflected in the literature. In the present

Fig. 1. Sodium hydroxide—sodium hydride system (A); potassium hydroxide—potassium hydride system (B). *a*—single-phase structure, *b*—two-phase structure, according to X-ray phase-analysis data

work, sodium and potassium hydrides containing 97-98% of the main substance, obtained by direct hydrogenation of sodium and potassium ([5,6]), and sodium and potassium hydroxides dehydrated by prolonged heating at 500°, were used as starting materials.

Samples with a hydride content of up to 30% were also obtained by direct hydrogenation of mixtures of dehydrated hydroxide and alkali metal in an autoclave with a mechanical stirrer. The analysis of hydrides and hydride-alkali melts was carried out by measuring the volume of hydrogen evolved when a sample of the preparations was treated with water ([5,6]).

The principal methods of investigation were thermal analysis on an N. S. Kurnakov pyrometer and powder X-ray phase analysis using copper radiation with a high-temperature chamber.

The NaOH–NaH system was studied by thermal analysis up to 60% NaH (Fig. 1A), and the KOH–KH system up to 48% KH (Fig. 1B). The data

of these contents of alkali hydride, its intensive thermal decomposition already begins.

Comparison of the volume of hydrogen evolved during thermal analysis (V_1, $cm^3/0.1$ g) with the volume of hydrogen corresponding to complete decomposition of the hydride (V_2, $cm^3/0.1$ g) shows that solid solutions with a lower hydride concentration are practically stable up to 600–650°. In the two-phase region, dissociation of the samples under the same conditions increases considerably and approaches completion at a hydride content of 70–80%. However, the amount of hydrogen evolved, V_1 $cm^3/0.1$ g, even at the highest temperatures does not exceed the theoretical amount calculated for complete dissociation of the hydride according to the equation

$$2MeH = 2Me + H_2,$$

which indicates the absence, up to 600°, of chemical interaction of the components ([3,4]) according to the equation

$$MeOH \pm MeH \leftrightarrow Me_2O + H_2.$$

As the concentration of hydrides in the hydroxides increases, there is a continuous rise in the melting temperature and a lowering of the temperature of the polymorphic transformation of the initial hydroxides, which indicates the formation of solid solutions based on the latter. Both systems, in the hydroxide-rich part, can be characterized by a peritectic diagram with a limited region of solid solutions based on the hydroxides (Fig. 1). The magnitude of the solubility of the hydrides at different temperatures and the properties of the solutions differ somewhat for the two systems.

In the system NaOH–NaH, below the line of the polymorphic transformation there is a region of α-solid solutions, extending, according to X-ray phase analysis, to 18, 30, and 40% NaH, respectively, at room temperature, 300°, and 460°. In the system KOH–KH the boundary of existence of α-solid solutions at room temperature is located at about 14% KH and increases somewhat at higher temperatures.

Chemical analysis of the solid solutions after thermal analysis shows a significant increase in the thermal stability of the hydrides dissolved in the hydroxides in comparison with the initial pure hydrides. For example, a solution with 18.5% NaH after heating to 530° contained 12.4% NaH, and a solution with 20% KH contained 17% KH, whereas the dissociation pressure of the pure hydrides already reaches atmospheric pressure for NaH at 421° and for KH at 428°.

Thus, dissolution of alkali hydrides in their hydroxides raises the upper temperature limit of existence of the alkali hydrides, which is undoubtedly of practical interest for the use of the latter as reducing agents for refractory compounds.

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