The P,T-State Diagram and Solid Phase Synthesis of Aluminium Hydride

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The P,T-diagram for aluminium hydride obtained at pressures 0.5–6.5 GPa and temperatures 100–700 °C indicates that the decomposition of AlH3 is reversed at high pressures and the compound can be prepared from the elements at pressures above 2.5 GPa. However, synthesis of AlH3 via the solid-state exchange reactions of LiAlH4 or LiH with AlCl3 under quasi-hydrostatic conditions is more advantageous. The synthetic P,T-conditions are limited by two straight lines that correspond to the decomposition of AlH3 into elements and the phase transition α-LiAlH4 → β-LiAlH4. Similar reaction of α-LiAlH4 with aluminium chloride does not occur at all, while reactions with α- and β-LiAlH4 lead to complete decomposition of the starting compounds. The reaction of AlCl3 with LiH to give AlH3 proceeds only at P > 5.6 GPa and T > 550 °C. Only the most compact α (hexagonal) modification of AlH3 is formed under the P,T-conditions studied.

Introduction

Covalent electronodeficient beryllium, aluminium and gallium hydrides are the most interesting and at the same time hardly available compounds in the series of binary nontransition metal hydrides. This is mostly due to the thermodynamic instability of the compounds (ΔGo[BeH2] = 3.68, ΔGo[AlH3] = 11.11 kcal mol⁻¹) which accounts for many previous unsuccessful attempts to prepare these compounds from elements under the conditions used for the synthesis of alkaline or alkaline earth metal hydrides (the P,T-conditions). Al, Be and Ga hydrides were obtained by multistep indirect routes associated with pyrolysis of beryllium organometallic dissociation of AlH3 and to evaluate the conditions for its dissociation of other from AlH3 Et2O or exchange reactions between (H2-BeCl2) or dimers [GaH3]2⁺ in which metals form a complicated system of M-H-M bridges. Crystalline Al and Be hydrides decompose into elements were slowly and are rather stable under ambient conditions. The compounds are, however, destroyed very rapidly even on mild heating. An increase in the hydrogen pressure in the systems M(H2) increases the stability. It has been shown¹¹ that eq 1 is completely shifted to the left at pressures ca. 2 GPa.

\[
\text{AlH}_3(s) \rightleftharpoons \text{Al}(s) + \frac{3}{2}\text{H}_2(g) \tag{1}
\]

Our goal was to find the exact P,T-conditions of equilibrium dissociation of AlH3 and to evaluate the conditions for its

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Footnotes:


(1) Termodinamicheskie konstanty veshchestv (Thermodynamic constants of substances); Glushko, V. P. Ed.; Moscow, 1979, p 14.


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Figure 1. Construction of the high-pressure device: 1 – Bridgman anvils (WC); 2 – ring from lithographic stone (douter = 18 mm, dcenter = 30 mm); 3 – container from lithographic stone (douter = 12 mm, dcenter = 18 mm); 4 – graphite heaters with caps (dcenter = 10 mm); 5 – holder with a sample (A) and standard (Al(OH)) from NaCl; 6 – thermocouple unit from NaCl; 7 – thermocouples (d = 3 mm); 8 – thermoslators from lithographic stone; 9 – graphite leads.

synthesis both from the elements and by exchange reactions in the absence of donor solvents. To achieve this, we have studied the P,T-state diagrams of {AlH3}, under the quasi hydrostatic pressures 0.5–6 GPa in the temperature range 20–700 °C. The main problem of investigation under such conditions is to determine the temperature and pressure in a high-pressure cell. We have solved it by modification of the differential thermal analysis such that it became possible to obtain data up to 8 GPa and 1000 °C. This was achieved by using tin as the internal standard which allowed an increase in the precision of obtaining the P,T-parameters.

Experimental Section

The P,T-state diagrams were obtained on a device consisting of a hydraulic press (2000 ton), two Bridgman anvils, and a high-pressure apparatus of the “lens”-type made of lithographic stone. A principal diagram of the apparatus is shown in Figure 1. A cylinder-shaped individual sample or a mixture with Al2O3 as standard (diameter 4 mm, height 3 mm) was placed into brass “glass-in-glass” capsules, sealed in a press-form, installed into the specially designed holder made from NaCl and equipped with a thermocouple.
and then heated at a constant rate of 10 deg min⁻¹. Heat effects were recorded after amplification by an H-308 XY-recorder. All operations on assembling and separating the capsule were carried out in a box filled with dry nitrogen.

Calibration of the home-assembled set showed that the axial and radial temperature gradients measured by thermocouples did not exceed 0.1–1 °C/1 mm 100 °C and 0.5–1 °C/1 mm 100 °C, respectively. The pressure inside the camera was determined from the melting point of tin as described in ref 14. The pressure in the camera was thus determined with uncertainty lower than 0.1 GPa in the ternary point. It decreased to 0.05 GPa at higher and lower pressures. The error in determining the temperature was within 3–5 °C.

Samples of α- and γ-AlH₃ were prepared as described elsewhere. An X-ray powder analysis was performed after release of pressure on a DRON-2 diffractometer (Cu Kα irradiation).

Results and Discussion

As seen in Figure 2, the P,T-state diagram of aluminium hydride is rather simple. The solid line corresponds to the decomposition of α-AlH₃ on heating and the broken line corresponds to its synthesis on cooling. Thermograms of α-AlH₃ at pressures 0.5–2.0 GPa are characterized by one irreversible endothermal effect, Figure 3, which is due to decomposition of AlH₃ into elements. If the pressure is increased up to ca. 2.5 GPa, a broad (Δ = 100–120 °C), poorly resolved exothermal effect appears. Figure 3, which is then becomes endothermal. The latter is also due to decomposition of AlH₃ into elements, but equilibrium 1 is shifted to the left at pressures higher 2.5 GPa. If the samples then cooled, the corresponding thermal effect associated with the synthesis of α-AlH₃ is observed and the powder diffractogram of the product contains lines typical of α-AlH₃. As seen in Figure 2, the thermal hysteresis for the forward and backward reactions does not exceed 50 °C at pressures 2.5–6.0 GPa. The pressure required for the synthesis of AlH₃ from the elements can probably be as low as 1.7–2.0 GPa. However, the reaction rate may be lower than the rate of diffusion of hydrogen through the cell walls of the apparatus under these conditions. The yield of the hydride might not thus be that high.

It should be pointed out that the thermograms give no evidence for the presence of AlH₃ modifications other than α-AlH₃ in the pressure range 0.5–6.5 GPa. This means that in the pressure range 1–2 GPa γ-AlH₃ easily and irreversibly transforms into α-AlH₃ even at 50–80 °C. This is really remarkable since the crystallization from solution gives at least five different phases.

The nature of a weak exothermal effect that precedes the decomposition of α-AlH₃ at pressures higher than 2.5 GPa is unclear, Figure 3. Other regimes of the thermal treatment (short or prolong annealing, gradual variation of temperature or "quenching") provided only α-AlH₃ according to the powder diffraction data. It might be assumed that at pressures higher than 2.5 GPa polymeric crystalline aluminium hydride becomes amorphous before the decomposition due to partial cleavage of the M–H–M bridges.

On addition of 1–3% LiH to BeH₂, the formation of the crystalline phases (α- and β-BeH₂) occurs under milder P,T-conditions. There is no similar effect, however, in the case of α-AlH₃ and the P,T-diagram of AlH₃ does not change (i.e. there are no new modifications). At higher concentrations of LiH, additional reflexes appear on the diffractograms ascribed to tetrahydridoaluminate. This is indicative of a reaction between LiH and AlH₃. However, this process proceeds rather slowly at higher temperatures (200–400 °C, 3–5 GPa), since it involves the cleavage of bridging H–Al–H bonds. At higher temperatures AlH₃ decomposes into elements.

The P,T-state diagram suggests that the synthesis of AlH₃ from the elements becomes feasible in the temperature range 280–300 °C at pressures higher than 2.5 GPa. This is in agreement with the data of Baranovski, et al. Two important observations should, however, be taken into account. First, hydrogen reacts with a fine nonoxidized Al powder obtained by thermal decomposition of AlH₃. If Al powders obtained by conventional routines and, therefore, have oxidized surface are used, the synthesis must probably be carried out under more rigorous conditions. Second, a leakage of H₂ through the walls of the high-pressure cell due to diffusion is inversely dependent on the time of keeping the sample under the P,T-conditions above the curve of AlH₃ decomposition; i.e. the longer high-temperature exposure, the lower is the yield of the hydride.

All these complications vanish by synthesis of aluminium hydride via the Schlesinger exchange reactions starting from

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Consider the thermogram of 3LiAlH₄ + AlCl₃ mixture at 3.6 GPa as an example. As shown in Figure 4, there are four thermal effects. The first, as in the case of pure LiAlH₄, should be attributed to interaction of LiAlH₄ with products of its partial hydrolysis or oxidation. Since these admixtures do not exceed 0.5% in fresh prepared LiAlH₄, we assume that the first effect does not influence the course of the major pathway. Therefore, it is not indicated in Figure 5. The second endothermal effect (325 °C) is due to the phase transition α-LiAlH₄ → β-LiAlH₄. Its P,T-conditions are shown by line I in Figure 5 and are identical to those for pure tetrahydridoaluminate. Exchange reaction 2 occurs only after this phase transition. Third exothermal effect corresponds to reaction 2 and has a maximum at 350 °C, but α-AlH₃ formed decomposes into elements at 400 °C (the fourth heat effect). Attention should be paid to a profile of curve III in Figure 5 which defines the P,T-conditions of reaction 2. It is a superposition of two curves which cross line II showing the thermobaric conditions of synthesis and decomposition of AlH₃. Above this curve, the reaction between LiAlH₄ and AlCl₃ proceeds via eq 5. As a result, the area of P,T-conditions suitable for synthesis of AlH₃ via reaction 2 becomes limited, Figure 5.

$$\text{3LiAlH}_4(s) + 3\text{AlCl}_3(s) \xrightarrow{P,T} 4\text{AlH}_3(s) + 3\text{LiCl}(s) \quad (2)$$

$$\text{Li}_3\text{AlH}_6(s) + 3\text{AlCl}_3(s) \xrightarrow{P,T} 2\text{AlH}_3(s) + 3\text{LiCl}(s) \quad (3)$$

$$3\text{LiH}(s) + \text{AlCl}_3(s) \xrightarrow{P,T} \text{AlH}_3(s) + 3\text{LiCl}(s) \quad (4)$$

The formation of AlH₃ in donor solvents occurs by successive substitution of halide ligands in AlX₃ by hydride via the intermediates AlH₃→XₐL (X = Hal; n = 0–2; L = Et₂O, THF, NR₃, etc.). No chloroalanes were found in the case of the solid state reactions. Chloroalanes also cannot be prepared via reactions 8–11.

$$\text{LiAlH}_4(s) + \text{AlCl}_3(s) \xrightarrow{P,T} 2\text{AlH}_2\text{Cl}(s) + \text{LiCl}(s) \quad (8)$$

$$\text{LiAlH}_4(s) + 2\text{AlCl}_3(s) \xrightarrow{P,T} 4\text{AlHCl}_2(s) + \text{LiCl}(s) \quad (9)$$


Solid Phase Synthesis of AlH₃

\[ \text{AlH}_3(s) + 2\text{AlCl}_3(s) \rightleftharpoons 3\text{AlHCl}_2(s) \quad (10) \]

\[ 2\text{AlH}_3(s) + \text{AlCl}_3(s) \rightleftharpoons 3\text{AlH}_2\text{Cl}(s) \quad (11) \]

All the data show the principal difference between the Schlesinger reactions in solution and in the solid state under high pressure. As seen in Figure 5, the formation of AlH₃ from LiAlH₄ and AlCl₃ is only observed after generation of β-LiAlH₄ (line I). Unfortunately, the structure of this compound has not been solved directly. It was mentioned however, that the structure is unusual in the series of related alkali metal tetrahydridoaluminates, i.e. aluminium has strongly distorted octahedral rather than tetrahedral environment. Since the main building blok of α-AlH₃ is the \{AlH₆\} octahedron, it can be assumed that the interaction between β-LiAlH₄ and AlCl₃ under the high pressure proceeds via the substitution of Li⁺ by Al³⁺ (arising from AlCl₃) which enters the hydride octahedron β-LiAlH₄ rather than by substitution of hydrido for chloro ligands. α-Li₂AlH₆ differs from β-LiAlH₄ in its stoichiometry and regular arrangement of the \{AlH₆\} octahedron. These are probably two reasons that make impossible the preparation of AlH₃ by the solid state reaction 3 in the pressure range studied (\(P < 4\) GPa). One cannot, however, exclude that the reaction 3 may occur at higher pressures. This suggestion finds a support in both the location of line IV which will cross Line II at \(P > 4.5\) GPa and the formation of AlH₃ at \(P > 5.6\) GPa via eq 4. In the latter case, β-LiAlH₄ might be an intermediate which interacts further with AlCl₃. Direct substitution of chloro-ligands by hydrido-ligands in reaction 4 is also possible at \(P > 5.6\) GPa as suggested by different features of reaction 2 in solution and the solid phase.

In conclusion, we have shown that thermodynamically unstable AlH₃ can be prepared under high pressure either directly from the elements or by the solid-state Schlesinger exchange reactions. The hexagonal modification of AlH₃ (\(\rho = 1.47\) g/cm³) was formed in both cases. This fact shows that α-AlH₃ is the most “stable” phase at the pressures and temperatures studied in comparison with other known modifications of aluminium hydride. However, this does not imply that other modifications of aluminium hydride are not available at pressures higher than 6.5 GPa or by other routes.

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