# *Hydrothermal Reaction of Aluminumtrihydroxides*

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Recently, many studies of thermal transformation of the aluminumtrihydroxides have been reported¹⁾ and we have got details of the mechanism of thermal change. Moreover, there are many experiments dealing with the digesting of gibbsite in an autoclave, but there is no consistent theory of the mechanism of the digesting reaction. The present authors studied and tried to explain the mechanism of hydrothermal reaction of aluminumtrihydroxides. Details are shown as follows.

## Experimental

**Materials.** — The aluminumtrihydroxides employed in this experiment were gibbsite and bayerite. The gibbsite was a commercial product. It was washed with pure water. Ignition loss was 34.40%. The bayerites were prepared by three methods. The details of the methods had already been reported by the authors²⁾. Three bayerites are named bayerite-*a*, -*b* and -*c*. In this study, the *a* was prepared by aging alumina-gel in ammonia water, the *b* was precipitated from sodium aluminate solution by means of a current of carbon dioxide, and the *c* was prepared by auto-precipitation from sodium aluminate solution. The main impurity was sodium oxide of 0.10∼0.50%. The crystallinities of bayerites were quite different according to their processes of preparation. They were identified by X-ray analysis.

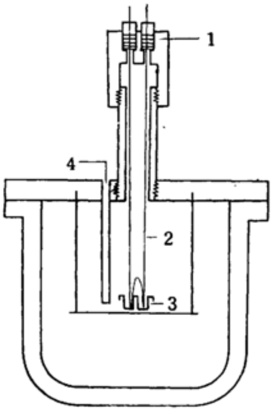

Fig. 1. Diagram of autoclave for DTA in saturated vapor.
(1) Teflon packing, (2) double thermocouples, (3) sample holders, (4) thermometer.

**Apparatus and Procedure.**—The authors devised an apparatus for differential thermal analysis in saturated vapor. The diagram is shown in Fig. 1. Air-tightness of the part 1 is kept by packing many thin Teflon sheets. This part is cooled in runs to protect the Teflon packings from thermal damage. Sample holders are silica vessels with 1 cm. diameter and 1.5 cm. depth.

The sample was about 1.5 g. in weight, and soaked with 1.5 cc. of water or alkali solutions of various concentrations. In some cases samples were mixed with boehmite. The reaction products were checked by X-ray diffraction.

TABLE I. GIBBSITE

| The concn. of alkali added (%) | The contents of boehmite added (%) | Peak temp. (°C) | The breadth |
|---|---|---|---|
| — | — | 218 | 5 |
| 0.5 | — | 217 | 6 |
| 5.0 | — | 212 | 8 |
| 20.0 | — | 207 | 8 |
| — | 5 | 210 | 9 |
| — | 10 | 205 | 9 |
| — | 20 | 203 | 10 |
| — | 30 | 200 | 17 |
| | Bayerite-*a* | | |
| — | — | 190 | 14 |
| 0.5 | — | 167 | 14 |
| 5.0 | — | 153 | 12 |
| 20.0 | — | 145 | 10 |
| — | 30 | 185 | 13 |
| | Bayerite-*b* | | |
| — | — | 205 | 8 |
| 0.5 | — | 202 | 10 |
| 5.0 | — | 192 | 11 |
| 20.0 | — | 190 | 11 |
| — | 30 | 194 | 11 |
| | Bayerite-*c* | | |
| — | — | 206 | 6 |
| 0.5 | — | 200 | 8 |
| 5.0 | — | 187 | 10 |
| 20.0 | — | 185 | 9 |
| — | 30.0 | 194 | 6 |

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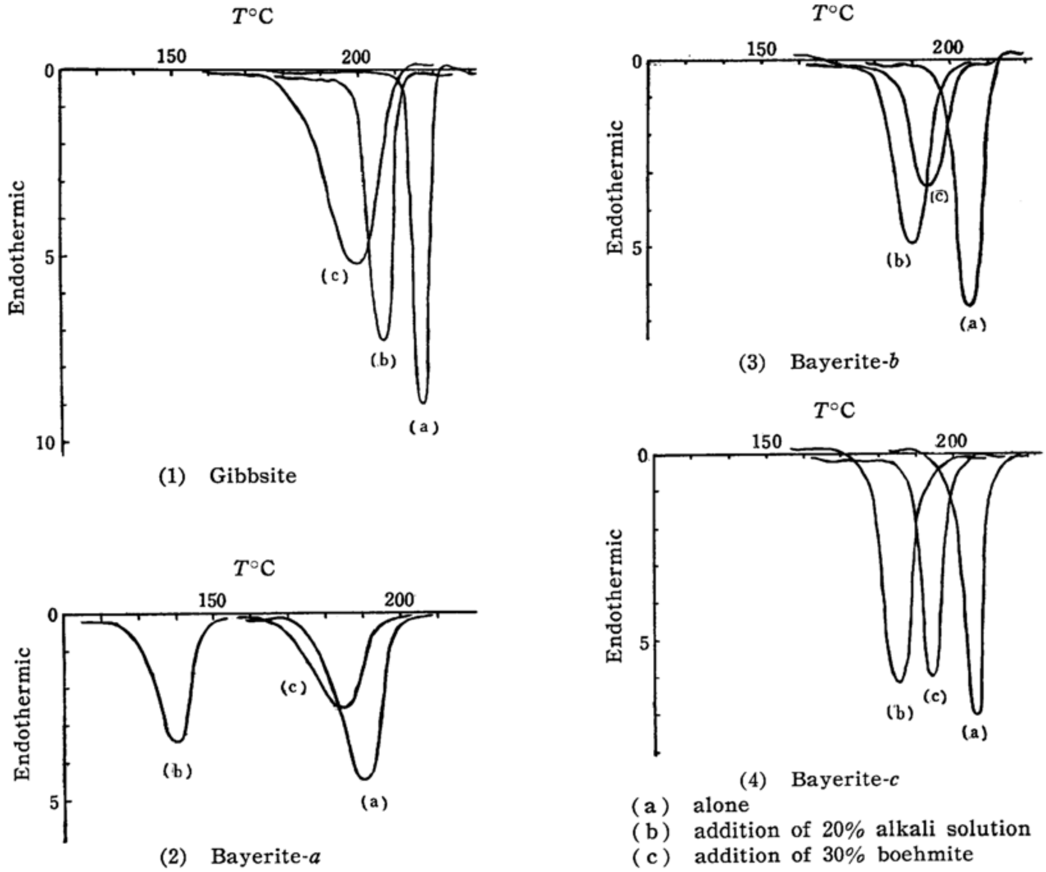
1) A. S. Russell et al., Technical Paper No. 10, Aluminum Company of America, Pittsburgh, Pennsylvania (1956).

2) G. Yamaguchi, K. Sakamoto and K. Shirasuka, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **61**, 307 (1958).



(1) Gibbsite

(2) Bayerite-*a*

(3) Bayerite-*b*

(4) Bayerite-*c*

(a) alone
(b) addition of 20% alkali solution
(c) addition of 30% boehmite

Fig. 2. DTA-curve of aluminumtrihydroxides.

## Result

The results of the differential thermal analysis were shown in Fig. 2 and Table I. Gibbsite decomposes endothermally into boehmite. When gibbsite is immersed in alkali solution the peak temperature shifts to a lower point and the breadth at the half value of the endothermic peak becomes greater. The fall in peak temperature and the widening in breadth are very striking at the mixture of gibbsite and boehmite. In the case of 30%-boehmite, the peak temperature lowers to 200°C and the breadth becomes as wide as 17°C. These facts indicate that the alkalinity and the existence of boehmite lower the transformation temperature, that is, accelerate the transformation velocity.

About bayerites, it is clear that they have different stabilities according to the process of preparation. The bayerite-*a* exhibited the lowest peak temperature, and the temperature at the beginning of the transformation is also low. The peak temperature of DTA-curve is lowered remarkably by the addition of alkali. This indicates that this type of bayerite dissolves faster than it does in water. On the other hand, boehmite has only a little effect on the transformation of bayerite-*a*. Bayerite-*b* and -*c* showed similar characters. Added alkali lowers the peak temperature of these two bayerites, and makes the breadth wider. Boehmite lowers also the peak temperature of these bayerites, but has a different effect upon their width. The width of DTA-curve for bayerite-*c* is not effected by the addition of boehmite but the width for bayerite-*b*, becomes wider.

## Consideration

Bauermeister and Fulda³⁾ and also Ginsberg and Koester⁴⁾ reported that the transformation of gibbsite to boehmite in an autoclave was accelerated by a small amount of alkali being added. Their

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3) B. Bauermeister and W. Fulda, *Aluminum*, **25**, 97 (1953).

4) H. Ginsberg and M. Koester, *Z. anorg. u. allgem. Chem.*, **271**, 41 (1952).

results agree with the present results. Further Russell and his co-workers[5] reported that gibbsite transformed quickly to boehmite in a concentrated alkali solution. Bauermeister explained the transformation from gibbsite to boehmite as a dissolution change, but Ginsberg, and also Sato[6] supposed this reaction to be solid-decomposition. Now, the authors support the re-solution reaction through which the transformation proceeds. This reaction consists of two steps; the dissolution of trihydroxides and the crystallization of boehmite. We can represent this reaction as follows:

$$Al(OH)_3+(OH)^- \rightarrow Al(OH)_4^-$$

$$Al(OH)_4^- \rightarrow AlO(OH)+(OH)^-+H_2O$$

Thus, we can understand the effect of boehmite as the seed of the crystallization of boehmite. In this region boehmite is very stable, so it is unnatural to suppose that this boehmite reacts directly with aluminumtrihydroxide. This is quite analogous to the effect of gibbsite-seed in the Bayer-process.

About bayerites, it was found that their stabilities were quite different according to the process of their preparation. Also in reference to X-ray diffraction data, it is sure that stabilities of bayerites correspond to their crystallinities. So, the properties which bayerite-*a* exhibited, i.e., the low temperature of the beginning of the transformation and the broad width of the DTA-curve, are attributed to its poor crystallinity. This bayerite was prepared by aging an alumina gel in ammonia solution. So it is supposed that this bayerite consisted of components with different crystallinities. The stability of the composition with poor crystallinity is very small, so this part begins to change into boehmite at temperature as low as 165°C. When alkali solution was added to this bayerite the peak temperature lowered remarkably. This is explained as follows: The part with poor crystallinity dissolves faster in alkali solution than in water, then boehmite crystallizes quickly from this aluminate solution, so this boehmite acts as the seed for the following crystallization. Therefore, the peak temperature fell remarkably, and the width of the DTA-curve remained as before.

Finally, it is emphasized that the transition of aluminumtrihydroxides in saturated vapor does not proceed as an equilibrium transition but as the change from an unstable system to a stable one. This means that the transition velocity at the equilibrium state is very slow and the first phase exists unchanged. A sufficiently high temperature is necessary for rapid change of aluminumtrihydroxides. When this condition is fulfilled, the transition proceeds quickly and shows a sharp endothermic peak of DTA-curve. This was realized in the thermal analysis of trihydroxides without alkali and boehmite (Fig. 2). In this case, the endothermic peak is very sharp and seems to be the peak of a monovariant reaction. But this is attributed to the large velocities of dissolution of aluminumtrihydroxides and of crystallization of boehmite.

In general the change of the Gibbs free energy of any reaction is represented by the next formula

$$\Delta G=\Delta H-T\Delta S$$

In this experiment, the chemical change proceeds as follows:

$$Al(OH)_3+(OH)^- \rightarrow Al(OH)_4^-$$

$$Al(OH)_4^- \rightarrow AlO(OH)+(OH)^-+H_2O$$

in short

$$Al(OH)_3 \rightarrow AlO(OH)+H_2O$$

Under this condition, of course, $\Delta G$ must be negative. $\Delta H$ was found to be positive, and the entropy change is positive, because entropy increases at dehydration reaction. When this entropy term overcomes the enthalpy term, then the reaction proceeds. Russell and his co-workers studied the equilibrium constants to form aluminate ion from gibbsite and boehmite and found the transition temperature from gibbsite to boehmite in pure water to be 27°C. Also they found that the trihydrates transformed rapidly to $\alpha$-monohydrate at solution temperatures above 100°C. This is consistent with the present results.

## Summary

In saturated vapor, the aluminumtrihydroxides dissolve in the water and the velocity of dissolution of the trihydroxides becomes larger as the temperature rises. When this solution is supersaturated over the solubility of boehmite, transformation proceeds. The alkalinity and the boehmite added to the hydroxides accelerate

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[5] A. S. Russell et al., *J. Metal*, 7, 1123 (1955).

[6] T. Sato, Abstracts of the 11th Annual Meeting of Chemical Society of Japan, 296 (1958).

the transition. The former makes easy the dissolution of trihydroxides, and the latter acts as the seed and accelerates the velocity of the crystallization of boehmite.

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