# THERMODYNAMICS OF THERMAL DECOMPOSITION
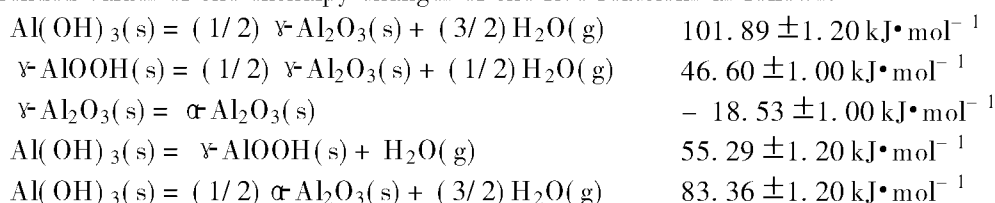# OF ALUMINUM HYDROXIDE [①]

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**ABSTRACT**   Of the following five reactions, the enthalpy changes of the first three reactions were calorimetrically determined, respectively. Combination of these results with the values from literature led to the recommended values of the enthalpy changes of the five reactions as follows:

$$Al(OH)_3(s) = (1/2)\ \gamma\text{-}Al_2O_3(s) + (3/2)H_2O(g) \qquad 101.89 \pm 1.20\,kJ\cdot mol^{-1}$$
$$\gamma\text{-}AlOOH(s) = (1/2)\ \gamma\text{-}Al_2O_3(s) + (1/2)H_2O(g) \qquad 46.60 \pm 1.00\,kJ\cdot mol^{-1}$$
$$\gamma\text{-}Al_2O_3(s) = \alpha\text{-}Al_2O_3(s) \qquad -18.53 \pm 1.00\,kJ\cdot mol^{-1}$$
$$Al(OH)_3(s) = \gamma\text{-}AlOOH(s) + H_2O(g) \qquad 55.29 \pm 1.20\,kJ\cdot mol^{-1}$$
$$Al(OH)_3(s) = (1/2)\ \alpha\text{-}Al_2O_3(s) + (3/2)H_2O(g) \qquad 83.36 \pm 1.20\,kJ\cdot mol^{-1}$$

**Key words**   $Al(OH)_3$   thermal decomposition   thermodynamics

## 1  INTRODUCTION

The thermal decomposition of $Al(OH)_3$ is the final technological stage of industrial production of alumina. Therefore, it is important to investigate the thermodynamics of thermal decomposition of $Al(OH)_3$ for the improvement of technological process and energy saving. Up to date, there have been few studies on the thermodynamics in the process of thermal decomposition of $Al(OH)_3$, although many studies on this thermal decomposition process have been made[1]. In the present work, the enthalpy changes of reaction for three main reactions in the process of thermal decomposition were measured by using a calorimetric method.

## 2  EXPERIMENTAL

### 2. 1   Preparation of samples of gibbsite, boehmite, and $\gamma\text{-}Al_2O_3$

The samples of the synthetic gibbsite ($Al(OH)_3$) used in the present experiments were prepared by using the method of Chen et al[2]. The pure boehmite ($\gamma\text{-}AlOOH$) samples were prepared by the hydrothermal reaction of $Al(OH)_3$ at the temperature $T = 473\,K$ and stirring for 4h with addition of water up to the ratio of 4~5 (liquid: solid)[3]. The samples of $\gamma\text{-}Al_2O_3$ for determination were prepared from pure synthetic $\gamma\text{-}AlOOH$ powder. Boehmite powder was calcined at 550 ℃ for 10h, and then cooled to room temperature. The samples of synthetic gibbsite, boehmite and $\gamma\text{-}Al_2O_3$ were confirmed as pure synthetic gibbsite, beohmite and $\gamma\text{-}Al_2O_3$ by thermogravimetry and differential thermal analysis and by X-ray diffraction.

### 2. 2   Enthalpy changes of decomposition of gibbsite, boehmite and $\gamma\text{-}Al_2O_3$

A Tian-Calvet twin-vessel high-temperature microcalorimeter (HT1000, Setaram, France) was used for the determination of the enthalpy changes of decomposition of gibbsite and boehmite. The temperature scale and sensitivity of the calorimeter were calibrated before experi-

ments as described in our previous paper[4].

A little corundum powder was put into both the reaction cell and the reference cell of the calorimeter HT1000. The temperature of the calorimeter was kept stable at 298. 15 K with a suitable heat-flow signal range and proper amplifying scale. A given mass of the sample was dropped into the reaction cell after the heat-flow base line became stable. A personal computer was used to collect the calorimetric results on line. An X-ray diffraction analysis on materials produced indicated that all the gibbsite and boehmite samples had been transformed to Y-Al$_2$O$_3$. The experimental results are listed in Table 1 and Table 2, respectively.

Yet another high-temperature calorimeter (HT1500, Setaram, France) was used to determine the enthalpy change of transformation from Y-Al$_2$O$_3$ to α-Al$_2$O$_3$. Three parallel measurements of the enthalpy change of decomposition of boehmite were also made. The temperature and sensitivity of the calorimeter were calibrated as described in our previous paper[4].

The sample cell of the calorimeter HT1500 was filled with some corundum powder. Then a sample was put onto the corundum powder. The reference cell was also filled with corundum powder. After the baseline of the heat-flow curve became stable, the sample cell and the reference cell were heated simultaneously at a rate of 0. 08 K/s for boehmite and 5 ℃/min for Y-Al$_2$O$_3$. A personal computer was used to collect and process the signals. An X-ray diffraction analysis on the yielded materials showed that all the Y-Al$_2$O$_3$ sample had been transformed to α-Al$_2$O$_3$ and all the boehmite sample had been transformed to Y-Al$_2$O$_3$. The experimental results are shown in Table 3 and Table 2, separately.

## 3   RESULTS AND DISCUSSION

The decomposition of Al(OH)$_3$ can be expressed as

$$Al(OH)_3(s) = (1/2) \text{ Y-}Al_2O_3(s) + (3/2) H_2O(g) \qquad (1)$$
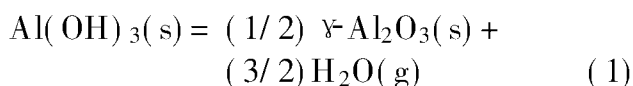
Using the relations between molar heat capacity and temperature of Y-Al$_2$O$_3$(s)[5, 6],

H$_2$O(g)[7] and Al(OH)$_3$[6], we have

$$\Delta C_{p, m}(J/K \cdot mol) = 52. 32 - 152. 83 \times 10^{-3} T - 5. 75 \times 10^5 T^{-2} \qquad (2)$$

According to reaction (1) and the data of Table 1, the molar enthalpy change of decomposition of Al(OH)$_3$ at 298. 15 K was calculated as 101. 89 kJ/mol with uncertainty estimated as 1. 20 kJ/mol. Roth[8] used his enthalpies of solution to calculate the molar enthalpy change of decomposition of Al(OH)$_3$ at 293. 15 K and got the result of 101. 67 kJ/mol, which is in excellent agreement with our result.

**Table 1   Measured results for molar enthalpy change of decomposition of given mass of Al(OH)$_3$(gibbsite)**

| $T$ /K | $m$ /mg | $\Delta H_m$(total) /kJ·mol$^{-1}$ | $\Delta_{dec}H_m$ /kJ·mol$^{-1}$ | $\langle \Delta_{dec}H_m \rangle(T)$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|
| 958 | 175. 134 | 176. 94 | 71. 95[1] | |
| 958 | 169. 517 | 176. 31 | 71. 32[1] | 1. 73 ±0. 36 |
| 958 | 173. 819 | 176. 91 | 71. 92[1] | |

1) The molar enthalpies of decomposition of Al(OH)$_3$ after deduction of the positive enthalpy changes (104. 99 kJ/mol) caused by its heat capacity[3].
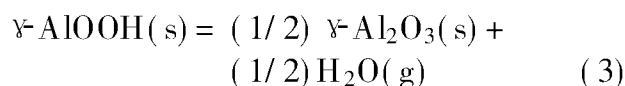
**Table 2   Measured results for molar enthalpy change of decomposition of given mass of Y-AlOOH(boehmite)**

| Calori- meters | $T$ /K | $m$ /mg | $\Delta H_m$(total) /kJ·mol$^{-1}$ | $\Delta_{dec}H_m$ /kJ·mol$^{-1}$ | $\langle \Delta_{dec}H_m \rangle(T)$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|---|
| HT1000 | 830 | 40. 637 | 86. 50 | 45. 63[1] | |
| | 830 | 42. 135 | 86. 34 | 45. 47[1] | 5. 71 ±0. 29 |
| | 830 | 43. 721 | 86. 90 | 46. 03[1] | |
| HT1500 | 816[2] | 547. 428 | | 45. 56 | |
| | 815[2] | 521. 566 | | 44. 93 | 5. 27 ±0. 32 |
| | 817[2] | 553. 912 | | 45. 32 | |

1) The molar enthalpies of decomposition of Y-AlOOH after deduction of the positive enthalpy changes (40. 87 kJ/mol) caused by heat capacity[3];
2) Peak temperatures.

The decomposition of Y-AlOOH can be expressed as

$$\text{Y-}AlOOH(s) = (1/2) \text{ Y-}Al_2O_3(s) + (1/2) H_2O(g) \qquad (3)$$

By using the relations between molar heat capacity and temperature of Y-Al$_2$O$_3$ (s)[5, 6], H$_2$O(g)[7] and Y-AlOOH(s)[6], we obtain:

$$\Delta C_{p, m}(J/K \cdot mol) = 10. 94 - 23. 37 \times 10^{-3} T +$$

$$0.14 \times 10^5 \, T^{-2} \qquad (4)$$

**Table 3　Measured results for molar enthalpy changes of transformation from $\gamma$-Al$_2$O$_3$ to $\alpha$-Al$_2$O$_3$**

| $T$ / K | $m$ / mg | $\Delta_{trs}H_m$ / kJ·mol$^{-1}$ | $\langle \Delta_{trs}H_m \rangle (T)$ / kJ·mol$^{-1}$ |
|---|---|---|---|
| 1 470[1] | 760.218 | − 27.25 | |
| 1 468[1] | 762.751 | − 26.57 | − 26.78 ±0.41 |
| 1 471[1] | 763.198 | − 26.52 | |

1) Average value of the start temperature and the end temperature of peak.

In accordance with reaction ( 3) and the data of Table 2, the molar enthalpy change of decomposition of $\gamma$-AlOOH at 298.15 K was computed as 46.87 and 46.32 kJ/ mol, respectively.

Using the method of solution calorimetry Roth[8] measured the molar enthalpy change of the decomposition of $\gamma$-AlOOH at 293.15 K as 42.05 kJ/ mol. Russel *et al*[9] determined the molar enthalpy change of decomposition of the following reaction at 298.15 K as 51.46 kJ/ mol using the method of equilibrium:

$$\mathrm{Al(OH)_3(s) = AlOOH(s) + H_2O(g)} \qquad (5)$$

In terms of the molar enthalpy change of decomposition of reaction ( 1) ( 101.89 kJ/ mol) , the molar enthalpy change of decomposition of $\gamma$-AlOOH was calculated as 50.43 kJ/ mol. Our results lie between the calorimetric result obtained by Roth[8] and the equilibrium result determined by Russel *et al*[9], and ours are very consistent with each other.

Therefore, an average value of our calorimetric results, 46.60 kJ/ mol, was taken as the recommended value of the molar enthalpy change of decomposition of $\gamma$-AlOOH with uncertainty estimated as 1.00 kJ/ mol.

Combining the heat capacity values of $\alpha$-Al$_2$O$_3$[6] and $\gamma$-Al$_2$O$_3$[5, 6] gives an expression for the relationship between temperature and $\Delta C_{p, m}$ for the reaction

$$\gamma\text{-Al}_2\mathrm{O}_3(\mathrm{s}) = \alpha\text{-Al}_2\mathrm{O}_3(\mathrm{s}) \qquad (6)$$
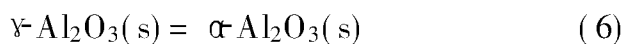
as

$$\Delta C_{p, m}(\mathrm{J/ K \cdot mol}) = 0.13 - 7.19 \times 10^{-3} \, T - 3.15 \times 10^5 \, T^{-2} \qquad (7)$$

By using equation ( 7) , the molar enthalpy change of transformation obtained above was calibrated to 298.15 K as − 18.64 kJ/ mol.

Yokokawa and Kleppa[10] indirectly measured the molar enthalpy change of the transformation from $\gamma$-Al$_2$O$_3$ to $\alpha$-Al$_2$O$_3$ at 928 K as − 22.18 kJ/ mol. Calibrating to room temperature with equation ( 7) leads to the value of − 18.41 kJ/ mol, which is only 0.23 kJ/ mol higher than our result. Therefore, the average value of Yokokawa, Kleppa[10] and ourselves ( − 18.53 kJ/ mol) is recommended as the molar enthalpy change of transformation from $\gamma$-Al$_2$O$_3$ to $\alpha$-Al$_2$O$_3$ with uncertainty estimated as 1.00 kJ/ mol. Reaction ( 1) minus reaction ( 3) results in the molar enthalpy change of decomposition of the following reaction as 55.29 kJ/ mol with uncertainty estimated as 1.20 kJ/ mol.

$$\mathrm{Al(OH)_3(s) = \gamma\text{-}AlOOH(s) + H_2O(g)} \qquad (8)$$
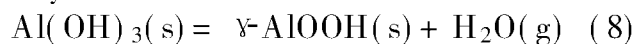
In the same way, reaction ( 6) plus reaction ( 1) leads to the molar enthalpy change of decomposition of the following reaction as 83.36 kJ/ mol with uncertainty estimated as 1.20 kJ/ mol.

$$\mathrm{Al(OH)_3(s) = (1/2)\ \alpha\text{-}Al_2O_3(s) + (3/2)H_2O(g)} \qquad (9)$$
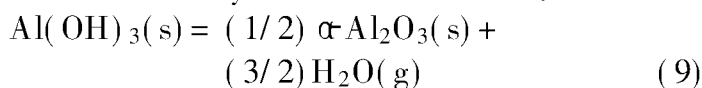
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