The Kinetics of the $2\text{Al(l)} + \text{AlCl}_3\text{(g)} = 3\text{AlCl(g)}$ Reaction in the Subhalide Process of Aluminum*

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The kinetics of a fundamental reaction of the aluminum subhalide process, $2\text{Al(l)} + \text{AlCl}_3\text{(g)} = 3\text{AlCl(g)}$, was studied by the flow method under a reduced pressure of trichloride at 900~1100°C.

The reaction rate increased with the increase in the flow rate of trichloride, namely its pressure. As a result of the present experiment, the reaction rate was expressed by the following equation :

$$V = 1.28 P_{\text{AlCl}_3}^{4/3} e^{-11800/RT} \quad (\text{Al g/cm}^2 \cdot \text{min}).$$

The apparent activation energy of this reaction was 11.8 kcal/mol. The reaction ratio of AlCl_3 increased with rising temperature and lowering trichloride pressure.

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I. Introduction

A number of reports have recently been published on the subhalide process as a refining method of aluminum by a means other than electrolysis of its oxide.

As a part of the research on this process, the present authors measured the equilibrium of the subchloride reaction, $2\text{Al(l)} + \text{AlCl}_3\text{(g)} = 3\text{AlCl(g)}$ previously⁽¹⁾. This paper describes the kinetics of the above reaction.

The kinetic studies of this process are considered to be important, whereas only a few reports by Yerkes⁽²⁾, Hirschwald⁽³⁾ and Tanabe⁽⁴⁾ have hitherto been published on this problem.

Hirschwald⁽³⁾ measured the reaction rate in a closed vessel, but this type of the reaction tube has the following difficulty as suggested by Schäfer⁽⁵⁾; that is, diffusion and thermal convection occur on the chemical reaction as the pressure of the system is increased. Furthermore, there is another disadvantageousness because of the difficult treatment of raw materials and the incomplete separation between the deposition zone and charged aluminum.

In the present work, therefore, aluminum trichloride was supplied to the reaction tube under the vacuum condition, and the intermediate reaction product, AlCl , was transferred to the opposite direction rapidly.

II. Experimental Apparatus and Procedures

1. Experimental apparatus

Figure 1 shows the experimental apparatus consisting of an aluminum trichloride evaporator, a reaction tube,

Fig. 1 Experimental apparatus.

A : Kanthal furnace B : AlCl_3 C : Nichrome ribbon heater
D : Silicone oil manometer E : Silica reaction tube F : Alumina tube G : Siliconit furnace H : Pt-PtRh thermocouple I : Al J~M : AlCl_3 condenser N : Vacuum pump

a trichloride condenser and a vacuum pump.

The reaction tube was a silica pipe (40 mm in inner diameter, 800 mm in length), and the inserted tube was an alumina pipe (35 mm in inner diameter, 700 mm in length). The Siliconit furnace was employed for heating, and the uniformity of the temperature was within $\pm 5^\circ\text{C}$ in the range of 12 cm at 1000°C.

The temperature was measured by a calibrated Pt-Pt-Rh thermocouple mounted on the outside wall of the reaction tube just above the position of the aluminum boat, while no temperature difference was found between the inside and the outside of the tube.

The gaseous mixture of aluminum trichloride decomposed by the disproportionation reaction and unreacted trichloride was discharged from the reaction tube from the opposite end, and it was trapped in the silica condenser cooled with liquid nitrogen. Aluminum charged

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was 99.99% in purity, and it was previously machined to fit to the shape of the boat.

2. Experimental method

Aluminum trichloride was charged into the evaporator quickly and weighed, then the evaporator was connected with the reaction tube. The boat for melting aluminum was made up of a high-alumina grade (Al_2O_3 : 98.8~99.2%, SiO_2 : 0.3~0.4%) to minimize contamination of impurities. In a sectional view, its bottom was made semicircular to fit to the inserted pipe, and two-thirds of the depth was made rectangular to maintain a constant area even if the decrease of aluminum took place due to the reaction.

The aluminum boat was first set in the uniform temperature zone. Then the evaporator and the reaction tube were connected and evacuated to 10^{-3} mmHg. When the furnace temperature reached a desired value, the aluminum trichloride evaporator was immersed in a furnace held at a desired temperature.

The partial pressure of aluminum trichloride was measured by a silicone-oil manometer (specific gravity, 1.05: KF 54 oil made by Shinetsu Kagaku Co.) every five minutes.

Aluminum trichloride sublimed slowly at the beginning, then increased and became almost constant. Therefore, the reaction time was corrected by leveling of the slow period in the flow rate. Thus, vapor pressure of trichloride was evaluated from the decreased amount and the corrected evaporating time.

By the disproportionation reaction, aluminum deposited as dendrites and molten particles in the cooler and hotter parts of the deposition zone, respectively, and aluminum trichloride was trapped in the condenser.

After the reaction, the evaporator and the reactor were rapidly cooled, and the reaction ratios of aluminum and aluminum trichloride were calculated from the weight decrease of these substances. The reaction temperature was 900, 1000 and 1100°C.

III. Experimental Results and Discussion

Figure 2 shows the relation between partial pressure of aluminum trichloride P_{AlCl_3} (mmHg) and its flow rate $[\text{AlCl}_3]$ (g/min), and the experimental points can be expressed by the relation, $[\text{AlCl}_3] = 0.7 P_{\text{AlCl}_3}^2$ (mmHg).

Figures 3 to 5 indicate the effect of the partial pressure of aluminum trichloride on the amount of aluminum reacted at 900, 1000 and 1100°C, respectively. As indicated in these figures, the reacted aluminum increases with increase in vapor pressure of aluminum trichloride and reaction time.

The relation between the reacted amount and the reaction time was obtained at a given partial pressure in the following way. Initially a certain partial pressure of aluminum trichloride was selected in Figs. 3 to 5, and amounts of the reacted aluminum at each temperature and the reaction time were obtained under the selected partial pressure. For instance, when a partial pressure of trichloride chosen was 1.0 mmHg in Fig. 3, reacted

Fig. 2 Relation between partial pressure of AlCl_3 and its flow rate.

Fig. 3 Relation between partial pressure of AlCl_3 and amount of reacted Al at 900°C.

amounts of aluminum were 0.12 g/cm² at 17 min, 0.21 g/cm² at 27 min and 0.38 g/cm² at 47 min, respectively.

Figure 6 shows the relation between the amount of the reacted aluminum and the reaction time at various temperatures. It seems that the reaction takes place with the same mechanism, in view of the fact that there is a linear relationship between the amount of reacted aluminum and the reaction time as shown in the figure.

The reaction of aluminum and aluminum trichloride has been confirmed spectroscopically by Bhaduri, Fowler⁽⁶⁾, and Foster, Russel et al.⁽⁷⁾

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Fig. 4 Relation between partial pressure of AlCl_3 and amount of reacted Al at 1000°C .

Fig. 5 Relation between partial pressure of AlCl_3 and amount of reacted Al at 1100°C .

On the other hand, the degree of dissociation of aluminum trichloride in the experimental temperature range was estimated using thermodynamic data of Kellogg⁽³⁾ and the present authors⁽¹⁾. The dissociation reaction is described as $\text{AlCl}_3(\text{g}) = \text{AlCl}(\text{g}) + \text{Cl}_2(\text{g})$, and the fractional dissociation was calculated to be 3.67×10^{-8} at 1000°C and the total pressure of 0.001 atm, and 1.43×10^{-6} at 1100°C and the same total pressure.

Furthermore, Foster and Russel detected the presence of AlCl and Cl_2 resulting from the dissociation of aluminum trichloride in the absence of aluminum, and its degree was almost equal to that of the above-described

Fig. 6 Relation between reaction time and amount of reacted Al.

Fig. 7 Reaction rate of Al vs. AlCl_3 pressure.

value. Since the dissociation is very slight, the reaction rate may be represented in consideration of the forward and reverse reactions of the above-mentioned chemical equation :

$$V = k_1(\text{Al})^m(\text{AlCl}_3)^n - k_2(\text{AlCl})^p, \quad (1)$$

where V is the reaction rate, k_1 and k_2 are the specific rate constants, (Al) , (AlCl_3) and (AlCl) are the concentrations or partial pressures of each substance. Since the surface area and the concentration of aluminum are constant or invariable during the reaction, eq.(1) may be rewritten as

$$V = k_1'(\text{AlCl}_3)^n - k_2(\text{AlCl})^p. \quad (2)$$

Figure 7 shows the reaction rate of aluminum as a function of partial pressure of aluminum trichloride in a logarithmic way. With reference to this figure, the relation between $\log V$ and $\log P$ is expressed as a straight line and consequently the second term in eq.(2) may be disregarded. This may be due to a fast supply of aluminum trichloride and a rapid removal of the reacted gas out of the reaction zone because of the low pressure and the flowing condition.

Therefore, eq.(2) is further simplified as

$$V = k_1'(\text{AlCl}_3)^n \quad (3)$$

Taking the Arrhenius equation for this rate,

$$V = A(\text{AlCl}_3)^n e^{-E_0/RT} \quad (4)$$

where A is the frequency factor and E_0 is the activation energy. By taking the logarithm of eq.(3), the relation between $\log V$ and $\log(\text{AlCl}_3)$ gives the inclination of the straight line in Fig. 7, i.e. the reaction order n .

The straight lines in this figure can be expressed by the method of least squares.

$$\text{at } 900^\circ\text{C}, \quad \log V = 1.33 \log P_{\text{AlCl}_3} - 2.08 \quad (5)$$

$$\text{at } 1000^\circ\text{C}, \quad \log V = 1.33 \log P_{\text{AlCl}_3} - 1.92 \quad (6)$$

$$\text{at } 1100^\circ\text{C}, \quad \log V = 1.31 \log P_{\text{AlCl}_3} - 1.76 \quad (7)$$

Hence the inclinations of these lines become $4/3$ approximately.

Furthermore, the activation energy and the frequency factor were obtained as follows. In Fig. 7, the intercepts on the ordinate at $\log P_{\text{AlCl}_3} = 0$ correspond to $\log A - E_0/RT$ written in the logarithmic form of eq.(4), and the relation between $\log A - E_0/RT$ and $1/T$ is shown in Fig. 8.

Fig. 8 Arrhenius plot showing effect of temperature.

When the points were connected by a straight line using the method of least squares, the activation energy was 11800 cal and the intercept of the extrapolated line on the ordinate at $1/T=0$, namely frequency factor was 1.28.

Therefore, the reaction rate of the subchloride reaction is given by

$$V = 1.28 P_{\text{AlCl}_3}^{4/3} e^{-11800/RT}. \quad (\text{Al g/cm}^2 \cdot \text{min})$$

From the practical standpoint, it may be useful to express the reaction rate using flow rate of trichloride $[\text{AlCl}_3]\text{g/min}$. Thus,

$$V = 1.86 [\text{AlCl}_3]^{2/3} e^{-11800/RT}. \quad (\text{Al g/cm}^2 \cdot \text{min})$$

In addition, the reaction ratio of aluminum trichloride is shown in Fig. 9 as a function of partial pressure of aluminum trichloride. As indicated in this figure, the reaction ratio decreases with increasing partial pressure and temperature.

Fig. 9 Relation between reaction ratio of AlCl_3 and partial pressure of AlCl_3 .

Tanabe et al.⁽⁴⁾ examined the effect of evacuating degree on the fractional reaction of aluminum trichloride. In this case, a mercury bottle was set between the reactor and the pump to control the evacuating degree. With reference to this report, we estimated the reaction order using the logarithm of trichloride flow rate (g/min) and the logarithm of aluminum reaction rate (Al g/min·surface). Under an atmosphere of 1 mmHg, the order was 0.6 at 900°C and 0.8 at 1000°C , respectively, which are close to 0.66 in the present work. Furthermore, the same tendency was reported that reaction ratio of trichloride decreased with increase in flow rate.

Hirschwald et al.⁽³⁾ carried out experiments at lower pressures of aluminum trichloride (0.007~0.676 mmHg) and lower temperatures ($670\sim 830^\circ\text{C}$) using a reaction vessel of closed type. They formulated the reaction rate as the first order of the partial pressure of trichloride. Hence it seems comparable to 1.3 obtained in the present work.

IV. Summary

As a fundamental research concerning the subchloride process of aluminum, the reaction rate of $2\text{Al(l)} + \text{AlCl}_3(\text{g}) = 3\text{AlCl(g)}$ was measured at reduced pressure and flow of aluminum trichloride.

(1) The reaction rate of aluminum depended upon the flow rate of aluminum trichloride $[\text{AlCl}_3](\text{g/min})$ or its partial pressure $P_{\text{AlCl}_3}(\text{mmHg})$ over the range of $900\sim 1000^\circ\text{C}$:

$$V = 1.28 P_{\text{AlCl}_3}^{4/3} e^{-11800/RT}, \quad (\text{Al g/cm}^2 \cdot \text{min})$$

$$V = 1.86 [\text{AlCl}_3]^{2/3} e^{-11800/RT}. \quad (\text{Al g/cm}^2 \cdot \text{min})$$

(2) The activation energy is about 12 kcal/mol, and it is considered to be reaction control.

(3) The reaction ratio of aluminum trichloride increased with increase in temperature and decreased with increase in flow rate, namely at higher partial pressure.

(4) Deposited aluminum was mostly small spherical particles in the high temperature zone and dendrites in the lower temperature zone.