Thermal Decomposition of Potassium Chlorate

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The thermal decomposition of potassium chlorate has been investigated mostly by measuring the volume of oxygen gas evolved[1-4]. The present author has studied this reaction from the viewpoint of the loss in weight (x), due to oxygen gas released in the progress of the decomposition. The measurement of loss in weight was made at definite intervals of 45 sec. with a thermal balance of automatic recording type. Plots of dx/dt against time (t) were obtained accurately.

Experimental

Commercial guaranteed potassium chlorate was recrystallized four times from water. A single crystal and a polycrystal were selected from the recrystallized samples under a microscope. A powdered sample was obtained by carefully squeezing the recrystallized sample in an agate mortar with a pestle. The detail of the thermal balance was already described in a previous report[5]. This balance was modulated to be able to indicate distinct differences of 0.022 mg. on a recording chart.

Results

When the temperature of the powdered sample was raised at constant rate, 250°C per hour, it decomposed at 500°C, evolving oxygen gas. Although the measurements were made for the powdered samples of different weights and also at different rates of heating, these samples decomposed at the same temperature of 500°C which was higher than the decomposition temperature obtained by Vitoria[6]. Since the melting point of potassium chlorate has been found to be 352[7] or 356°C[6], it is reasonable to consider that the thermal decomposition of potassium chlorate takes place in liquid state.

The kinetic measurements were made at several temperatures above 500°C. The reactant sample could reach these constant temperatures within five minutes. Fig. 1 shows the plots of dx/dt against t for the powdered samples of 12.0 mg. at 565, 570 and 575°C, respectively. The time of zero in Fig. 1 was set at the point where half of the weight of the sample was decomposed. In the figure, the acceleratory period is extremly short in comparison with the decay period. From the curves of dx/dt

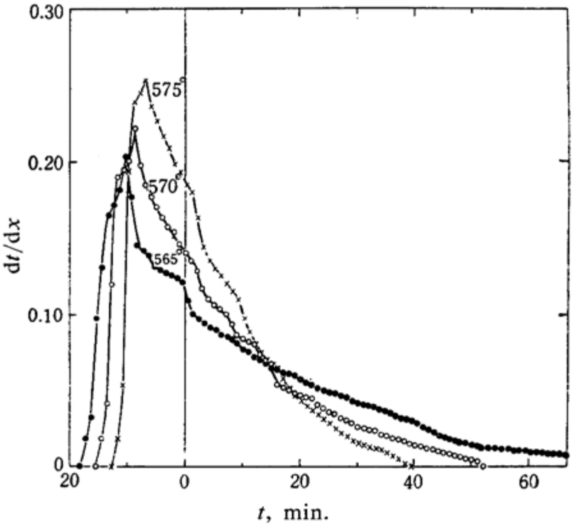

Fig. 1. Plots of dx/dt against time for the powdered samples (12.0 mg. in weight).

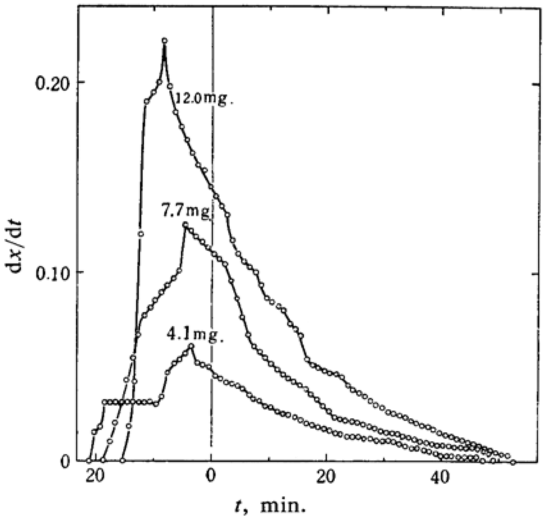

Fig. 2. Plots of dx/dt against time for the powdered samples at 570°C.

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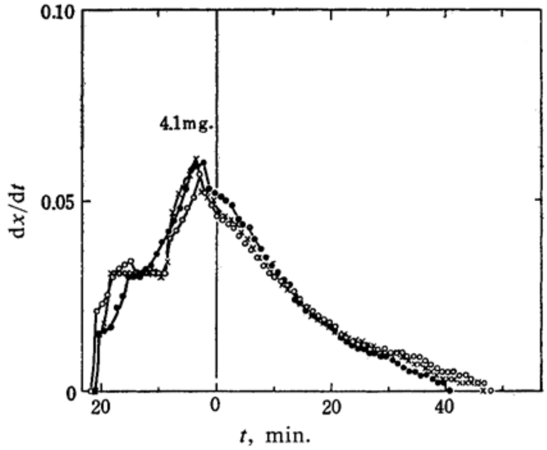

Fig. 3. Plots of dx/dt against time at 570°C.
—○—: Single crystal,
—●—: Polycrystal,
—×—: Powdered sample.

against t at the same temperature in Fig. 2, it is seen that, as the weight of the sample decreases, the acceleratory period becomes long and the shape of the curve of dx/dt against t in the acceleratory period becomes complicated. Fig. 3 shows the plots of dx/dt against t for the single crystal, the polycrystal and the powdered sample, all in the same weight of 4.1 mg. at the same temperature, 570°C. In the figure, the curves of dx/dt against t for the three samples show different shapes in the acceleratory period, while the curves in the decay period show analogous shapes. In each measurement, total losses in weight, due to the exhausted decomposition, agreed with the amount of oxygen calculated from the equation, $2KClO_3=2KCl+3O_2$, within the error of about one per cent.

Discussion

As shown in Figs. 1, 2 and 3, each curve of dx/dt against t shows a complicated shape, and such complication tends to disappear as the decomposition progresses. It has been reported by Otto et al.[3] that the reaction, $2KClO_3 \rightarrow 2KCl+3O_2$, is a monomolecular reaction. Glasner et al.[4] have also stated that the decomposition at high temperature is of the first order. However, as is evident from Figs 1, 2 and 3, the thermal decomposition of potassium chlorate is so complicated that a rate-equation can not be determined.

In a microscopic study of the sample undergoing the thermal decomposition, zig-zag bubbles of oxygen gas were observed in the liquid. Moreover, by visual observation of a reaction vessel at the end of the experiment, specks which were considered to be owing to the splashing of the liquid, were recognized along the wall. The bubbling of gas causes the splashing of the liquid. On the liquid-phase decomposition of potassium perchlorate, Bircumshaw et al.[8] have stated that the composition of the liquid which consists of perchlorate, chlorate and chloride, will not be constant on account of the spreading of the liquid along the tube, owing to bubbling, and thus variations in the rate of evolution of gas may be expected, depending on how much splashing takes place. On the thermal decomposition of potassium chlorate, it has been known that the reaction system consists of chlorate, chlorite, perchlorate and chloride, and that the chlorate, the chlorite and the perchlorate convert into chloride with the evolution of oxygen gas[9]. The bubbling and splashing under such a complicated condition will take place very irregularly. The complication of the curves of dx/dt against t may, therefore, be associated with the irregularities of the bubbling and splashing. As the decomposition progresses, the bubbling and splashing will become difficult to take place on account of the accumulation of chloride in the liquid. Consequently, the complication of the curves of dx/dt against t may be expected to disappear.

Summary

The curves of dx/dt against t were obtained with accuracy; in consequence, the complication of the curves appeared, and the complication may be associated with the irregularities of the bubbling and splashing.

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