



# Thermodynamic measurement of aluminium phosphate by double Knudsen cell mass spectrometry

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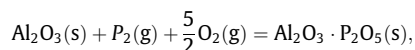
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## ABSTRACT

The ion currents of gaseous phosphorus oxides in equilibrium with a mixture of  $\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3$  at  $T = (1473 \text{ to } 1573) \text{ K}$  were measured by double Knudsen cell mass spectrometry. The Gibbs free energy changes of the following reactions estimated in comparison with the ion currents from a mixture of  $(\text{MgO})_3 \cdot \text{P}_2\text{O}_5$  and  $\text{MgO}$  are as follows:

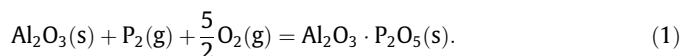


$$\Delta G^\circ / \text{J} = -1970000 + 574T / \text{K} (\pm 28000) \text{ for } (1473 < T / \text{K} < 1573).$$

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## 1. Introduction

Thermodynamic information on the  $(\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5)$  binary system at high temperature is important for various high temperature processes in ceramics, glass, and metallurgical industries, but the information available is extremely limited [1–5]. Aluminium phosphate ( $\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ ) is an intermediate compound of this system [1]. Miyamoto and Iwase [2] investigated this compound with an electrochemical technique, which is an electromotive force measurement using a galvanic cell, and estimated the Gibbs free energy change of reaction (1),  $\Delta G_1^\circ$ , for  $T = (1423 \text{ to } 1573) \text{ K}$ . The energy change for the region below  $T = 1200 \text{ K}$  is in the data book edited by Yungman *et al.* [3], however, there is considerable difference between these values



In this study, double Knudsen cell mass spectrometry was applied to measure the thermodynamic properties of  $\text{P}_2\text{O}_5$  in the  $(\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5)$  system and to estimate the Gibbs free energy change of reaction (1),  $\Delta G_1^\circ$ , since the authors have been successful in estimating thermodynamic properties of calcium phosphates by this method [6,7].

## 2. Experimental

### 2.1. Double Knudsen cell mass spectrometry

Knudsen cell mass spectrometry is developed to measure vapour pressures in equilibrium with a condensed phase. In this method, vapour pressure is measured by a mass spectrometer as ion current which is proportional to the pressure. The pressure,  $p_i$ , and ion current of  $i$ -species,  $I_i$ , measured by mass spectrometer are related through the following fundamental equation [8]:

$$p_i = \frac{T}{S_i} I_i, \quad (2)$$

where  $T$  is the absolute temperature of a specimen and  $S_i$  is the device dependent constant which includes such factors as ionization cross-section and efficiency of the ion detector. The usual accuracy of the data determined by single Knudsen cell mass spectrometry is not always adequate, since the constancy of the device dependent constant  $S_i$  is difficult to maintain over a long period and reproducibility of each experimental run may not be adequate. To overcome this problem, a technique using double Knudsen cells has been developed. The double Knudsen cells allow the measurement of ion currents of evaporated species from two specimens under identical conditions in a single experiment: one is an experimental specimen and the other is taken as a reference.

Details of the equipment for double Knudsen cell mass spectrometry are described elsewhere [9,10], and therefore, are

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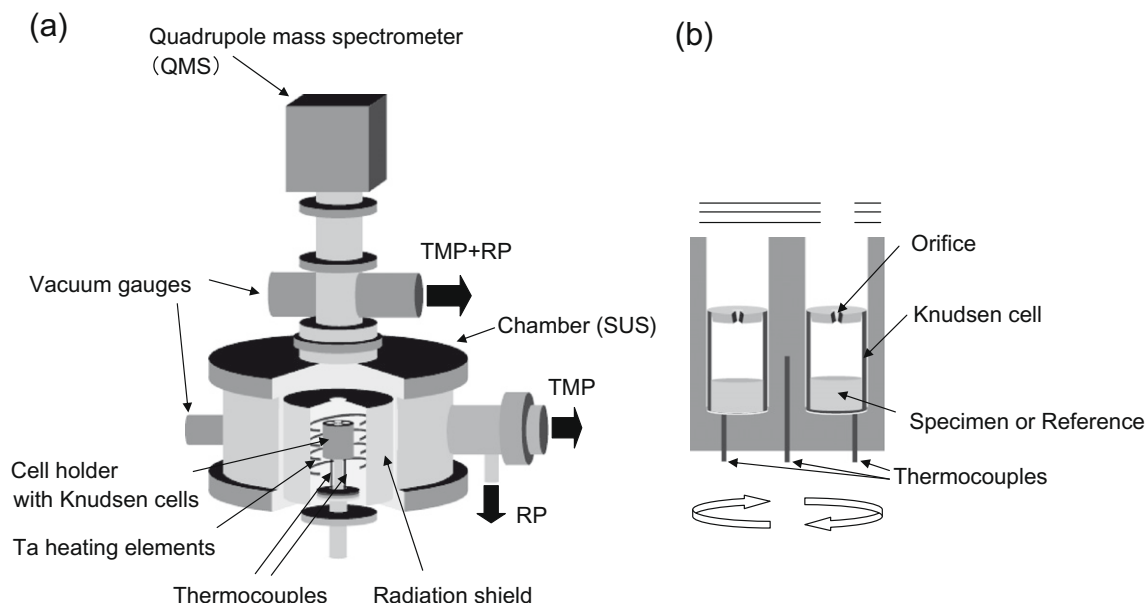


FIGURE 1. (a) Schematic configuration of equipment for double Knudsen cell mass spectrometry. (b) Cell holder.

explained only briefly here. Figure 1 shows a schematic configuration of the equipment. A chamber was evacuated by rotary pumps (RP) and turbo molecular pumps (TMP). The residual gas pressure in this chamber was kept below  $1 \cdot 10^{-4}$  Pa. A cell holder in the chamber held the two Knudsen cells. An experimental substance and a reference substance were separately charged in the Knudsen cells and they were installed in a high vacuum chamber. Two Knudsen cells at a time were set and heated in this chamber. One of them was used for the measured substances, and one was for reference. A quadrupole mass spectrometer (QMS, Leybold Inficon H200M), which was installed on top of the chamber, detected the atomic beam of evaporated species from the Knudsen cells. The cells were heated by a Ta electric resistance heating element in a vacuum chamber. The temperature was controlled using a thermocouple placed in a nearby heating element and a PID-type thermo-regulator. Temperatures of cells and samples were measured by three thermocouples placed in holes drilled at the bottom of the cell holder. Knudsen cells were made of molybdenum. Dimensions of the outer cell were 10 mm o.d., 8 mm i.d., and 18 mm height. The lid of the outer cell had an orifice with a diameter of 0.4 mm.

## 2.2. Specimen preparation

Aluminium phosphate ( $\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ ) was prepared by mixing alumina ( $\text{Al}_2\text{O}_3$ , mass fraction purity 0.999) and diammonium hydrogen phosphate ( $(\text{NH}_4)_2\text{HPO}_4$ , mass fraction purity 0.99) to yield a mole ratio of  $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5 = 1/1$ . The mixture charged in a platinum crucible was dehydrated on a hot plate at *ca.*  $T = 473$  K, then heated very slowly to  $T = 1473$  K and kept 2 h or 8 h at this temperature in an inert argon atmosphere by an electric resistance furnace.

The X-ray diffraction (XRD) pattern of the product, which was heated at  $T = 1473$  K for 2 h, is shown in figure 2. All diffraction peaks in this pattern could be assigned to  $\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3$ , indicating that the sample was composed of these two substances. Almost the same pattern was observed in the products treated for 8 h. The phase diagram of the binary system between  $\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3$  was given only by Tananaev *et al.* [1]. Their study is based on visual observation of the measurement of liquids at temperatures between (2073 and 2373) K. They mentioned that exist-

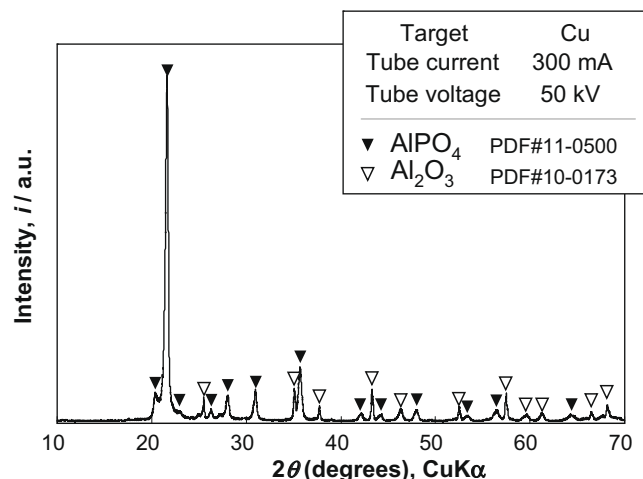


FIGURE 2. XRD pattern of the product.

tence of the intermediate compound  $(\text{Al}_2\text{O}_3)_2 \cdot \text{P}_2\text{O}_5$  was confirmed by XRD, although the pattern was not given in their paper. However, in the phase diagrams of ternary systems  $\text{Al}_2\text{O}_3$ – $\text{P}_2\text{O}_5$ – $\text{MgO}$  [11] and  $\text{Al}_2\text{O}_3$ – $\text{P}_2\text{O}_5$ – $\text{CaO}$  [12], the existence of  $(\text{Al}_2\text{O}_3)_2 \cdot \text{P}_2\text{O}_5$  was not detected. In the present study, based on XRD analysis, it was found that a 2-phase mixture of  $\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3$  was obtained if a mixture of  $\text{Al}_2\text{O}_3$  and  $(\text{NH}_4)_2\text{HPO}_4$  in a mole ratio of  $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5 = 2/1$  was heated. Miyamoto [2] and Iwase [13] also confirmed that  $(\text{Al}_2\text{O}_3)_2 \cdot \text{P}_2\text{O}_5$  does not exist below  $T = 1723$  K.

## 2.3. Principle of measurement

Thermodynamic data of  $\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$  would be estimated by measuring pressures of one or more gases in equilibrium with the mixture of  $\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3$ . According to “Thermochemical Data of Pure Substance” [14], P,  $\text{P}_2$ ,  $\text{P}_4$ , PO,  $\text{PO}_2$ ,  $\text{P}_4\text{O}_6$ , and  $\text{P}_4\text{O}_{10}$  can be in equilibrium with the mixture within at the experimental temperature of (1473 to 1573) K. It was reported that  $\text{P}_2$ , PO, and  $\text{PO}_2$  in equilibrium with  $\text{P}_2\text{O}_5$  in some oxide systems such as  $(\text{CaO} + \text{P}_2\text{O}_5)$  [6,7],  $(\text{Fe}_2\text{O}_3 + \text{P}_2\text{O}_5)$ , and  $(\text{PbO} + \text{P}_2\text{O}_5)$  [15] were

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