Vapor Pressures in the Al(l) + Al2O3(s) System:

Reconsidering Al2O3(s) Condensation

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Abstract

The vaporization behavior of the Al-O system has been studied on numerous occasions but significant uncertainties remain. The origin of this uncertainty must be understood before Al-O vaporization behavior can be accurately determined. The condensation of Al2O3 and clogging of the effusion orifice is a difficult problem for the Knudsen effusion technique that influences the measured vaporization behavior but has only received limited attention. This study reconsiders this behavior in detail. A new theory for Al2O3 condensation is proposed together with procedures that will improve the measured thermodynamic properties of Al-O vaporization.

Keywords: Al(g) and Al2O(g) vaporization; Al2O3(s) condensation; improving thermodynamic measurements; multiple effusion cell mass spectrometry.

1. Introduction

The vaporization behavior of the Al-O system has been investigated in numerous studies since the early 1950's. These studies used the effusion method, in its various forms, to sample the vapor phase in equilibrium with Al(l) + Al2O3(s) [1-4] and Al2O3(s) [1, 5, 6] in a range of container materials. In spite of this level of investigation, some vapor species and the thermodynamics of vaporization are still not fully understood. Recently there has been renewed interest in Al-O vaporization [7-9]. Improving the thermodynamic data of the Al-O system will allow more accurate measurements of the alloy + oxide equilibrium in the Ni-Al, Ti-Al and Fe-Al systems [10]. This information will improve our understanding
of high-temperature oxidation behavior of these systems which rely on the formation of a protective $\text{Al}_2\text{O}_3(\text{s})$ surface-layer by reaction with oxygen containing atmospheres. To do this, however, a more fundamental investigations of $\text{Al}^\text{(l)} + \text{Al}_2\text{O}_3(\text{s})$ vaporization is needed.

A range of vapor species have been identified in the Al-O system: $\text{Al}^\text{(g)}$, $\text{Al}_2\text{O}(\text{g})$, $\text{Al}_2\text{O}_3(\text{g})$, $\text{AlO}(\text{g})$, $\text{Al}_3\text{O}_2(\text{g})$, $\text{Al}_2\text{O}_3(\text{g})$, $\text{O}(\text{g})$ and $\text{O}_2(\text{g})$ [1-6]. Questions remain about the existence of $\text{Al}_2\text{O}_3(\text{g})$ [8]. The composition of the vapor depends on the oxygen partial pressure. At low $p(\text{O}_2)$, when $\text{Al}(\text{s,l})$ and $\alpha$-$\text{Al}_2\text{O}_3(\text{s,l})$ are stable, $\text{Al}^\text{(g)}$ and $\text{Al}_2\text{O}(\text{g})$ dominate while at higher $p(\text{O}_2)$, when $\alpha$-$\text{Al}_2\text{O}_3(\text{s,l})$ is stable, $\text{O}^\text{(g)}$, $\text{Al}^\text{(g)}$ and $\text{AlO}^\text{(g)}$ typically dominate. To quantify the uncertainty in Al-O vaporization reaction enthalpies measured by this author are compared to the accepted values [11-13] in table 1. The details of these new measurements will be discussed in a subsequent paper. While these results differ significantly, it is not constructive to propose changing generally accepted thermodynamic properties without first investigating possible reasons for the discrepancies and suggesting improved experimental procedures. Accordingly, two likely sources of error are: 1) reaction between Al(l) and the effusion-cell material, and 2) clogging the effusion orifice at high temperatures with the condensation of $\text{Al}_2\text{O}_3(\text{s,l})$.

**TABLE 1**

Comparison of Reaction Enthalpies in Al-O system, $\Delta_h^\text{P}(298.15K)$

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>$\text{Al}(\text{s,l}) = \text{Al}(\text{g})$</td>
<td>-</td>
<td>336.0±3.0</td>
<td>329.7±4.2</td>
</tr>
<tr>
<td>$4/3\text{Al}(\text{s,l}) + 1/3\text{Al}_2\text{O}_3(\text{s}) = \text{Al}_2\text{O}(\text{g})$</td>
<td>-</td>
<td>409.04±56</td>
<td>413.4±50</td>
</tr>
<tr>
<td>$4/3\text{Al}(\text{g}) + 1/3\text{Al}_2\text{O}_3(\text{g}) = \text{Al}_2\text{O}(\text{g})$</td>
<td>-</td>
<td>-30.0±4.3</td>
<td>-26.2±3.0</td>
</tr>
<tr>
<td>$2\text{Al}(\text{g}) + \text{O}(\text{g}) = \text{Al}_2\text{O}_3(\text{g})$</td>
<td>-</td>
<td>-1057.0±20</td>
<td>-1053.7±150</td>
</tr>
</tbody>
</table>

Identifying a suitable container material is important for all thermodynamic measurements and a range of materials (i.e., BeO, TaC, ZrO$_2$, Al$_2$O$_3$, Mo and W) have been used in Al-O vaporization studies. Brewer and Searcy used BeO and TaC effusion-cells but Al(l) reacted with both materials [1]. Porter et al., used a ZrO$_2$-liner in a Ta effusion-cell without reporting any significant reaction [2]. Motzfeldt et al., successfully used a Al$_2$O$_3$ effusion-cell [3, 4]. Mo and W have been used extensively to study the vaporization of Al$_2$O$_3$ but both are unsuitable for Al(l). According to the condensed phase diagrams, Al-O
[15], Al-Zr-O [16], and Al$_2$O$_3$-ZrO$_2$-Y$_2$O$_3$ [17, 18]. Al$_2$O$_3$ is best suited for studying the vaporization of Al(l) + Al$_2$O$_3$(s) as ZrO$_2$-based containers will react with Al(l). The effect of a ZrO$_2$-based effusion-cell was recently considered by directly comparing the vapor pressures of Al(g) and Al$_2$O(g) in equilibrium with Al(l) in a ZrO$_2$ effusion-cell and Al(l) in a Al$_2$O$_3$ effusion-cell [7]. These results showed Al(l) remained pure and a Al$_2$O$_3$-layer formed on the inner surface of the ZrO$_2$ effusion-cell, effectively transforming it into an Al$_2$O$_3$ effusion-cell and making it thermodynamically identical to Al(l) + Al$_2$O$_3$(s). While interesting, this result showed that a ZrO$_2$ effusion-cell does not change the measured vaporization behavior in the Al-O system. This leaves the difficult problem of Al$_2$O$_3$ condensation.

Al$_2$O$_3$ condensation has been observed by this author while measuring the vaporization behavior of Al(l) + Al$_2$O$_3$(s) and γ-TiAl(s) + Y$_2$O$_3$(s) and was previously observed for Al(l) + Al$_2$O$_3$(s) by Motzfeldt et al. [3, 4] and for Al$_2$O$_3$(l) by Drowart et al. [5]. It occurs on the outer edge of the orifice, is more pronounced for small diameter orifices (less than about 1.0 mm) and is usually only noticed at temperatures above about 1500 K. Condensation of Al$_2$O$_3$ will influence the measured vaporization behavior by changing the shape of the effusion orifice and therefore the rate of effusion independent of the partial pressures inside the effusion-cell. This behavior appears to be typical for systems with high aluminum activity, and it is surprising that it has only received limited discussion. Motzfeldt et al. appears to be the only research to consider this problem and their experiments and discussion are reviewed.

1.2 Motzfeldt's investigation of Al$_2$O$_3$-condensation

This problem was considered on two occasions while studying the vaporization of Al(l) + Al$_2$O$_3$(s) in an Al$_2$O$_3$(s) effusion-cell by a classical effusion method with continuous thermogravimetric monitoring of the rate of mass loss. The first study was conducted at 1585 and 1623 K in a tube furnace with a graphite heating element and with effusion orifices ranging from 0.8 to 8.0 mm in diameter [3]. The second study was at 1556 K in a furnace with a molybdenum heating element and with effusion orifices ranging from 0.6 to 2.9 mm in diameter [4]. In all experiments, pure Al(s) with excess Al$_2$O$_3$(s) was loaded into Al$_2$O$_3$ effusion-cells. From previous mass spectrometric studies [2, 5, 6] Al(g) and Al$_2$O(g) were assumed to be the dominant vapor species and it was explicitly assumed that there was no mass loss due to vaporization of
the outer surface of the Al₂O₃ effusion-cell and implicitly assumed that the effusion cell did not gain mass by reaction with the furnace environment. Following these assumptions the measured mass loss for the system (sample + effusion cell) was due solely to the effusion of Al(g) and Al₂O(g) at partial pressures \( p(\text{Al}) \) and \( p(\text{Al}_2\text{O}) \), according to the vaporization reactions Eq. (1) and Eq. (2). This occurs at a rate \( (\text{mol} \cdot \text{s}^{-1}) \) for each species according to the Hertz-Knudsen relation Eq. (3):

\[
\text{Al}(l) = \text{Al}(g) \tag{1}
\]

\[
4\text{Al}(l) + \text{Al}_2\text{O}_3(s) = 3\text{Al}_2\text{O}(g) \tag{2}
\]

\[
\frac{dn_i}{dt} = p(i)A_oW_o\left(\frac{2\pi RM_i T}{M_i}\right)^{1/2} \tag{3}
\]

where \( n_i \) is number of moles, \( p(i) \) is the partial pressure, \( A_o \) is the area of the orifice, \( W_o \) is the Clasing factor or the orifice, \( R \) is the gas constant, \( M_i \) is the molar mass and \( T \) is the absolute temperature. The total mass loss, \( \Delta q \), is due to consumption of \( \text{Al}(l) \) and \( \text{Al}_2\text{O}_3(s) \) in the cell ( \( \Delta q = \Delta n_{\text{Al}} \cdot M_{\text{Al}} + \Delta n_{\text{Al}_2\text{O}_3} \cdot M_{\text{Al}_2\text{O}_3} \) ).

The moles of \( \text{Al}(l) \) consumed, \( \Delta n_{\text{Al}} \), were determined by measuring how much \( \text{Al}(l) \) remained while \( \text{Al}_2\text{O}_3(s) \) consumption, \( \Delta n_{\text{Al}_2\text{O}_3} \), was determined by the difference between the total mass loss and measured \( \text{Al}(l) \) consumption ( \( \Delta q = \Delta n_{\text{Al}} \cdot M_{\text{Al}} / M_{\text{Al}_2\text{O}_3} \) ). For each mole of \( \text{Al}_2\text{O}_3 \) four moles of \( \text{Al}(l) \) were consumed due to the effusion of three moles of \( \text{Al}_2\text{O}(g) \) according to Eq. (2). The excess moles of \( \text{Al}(l) \) lost were attributed to reaction (1) and the effusion of \( \text{Al}(g) \). In this way the number of moles \( \text{Al}_2\text{O} \), \( n_{\text{Al}_2\text{O}} \), and \( \text{Al}_2\text{O}(g) \), \( n_{\text{Al}_2\text{O}} \), lost by effusion during the experiment were determined and used to calculate \( p(\text{Al}) \) and \( p(\text{Al}_2\text{O}) \) according to Eq. (3). The total rate of mass loss (g·s⁻¹) is the sum of the effusion of \( \text{Al}(g) \) and \( \text{Al}_2\text{O}(g) \), Eq. (4), and is constant at a fixed temperature.

\[
\frac{dq}{dt} = A_oW_o\left(\frac{2\pi RT}{M_i}\right)^{1/2}\left(p(\text{Al})\left(M_{\text{Al}}\right)^{1/2} + p(\text{Al}_2\text{O})\left(M_{\text{Al}_2\text{O}}\right)^{1/2}\right) \tag{4}
\]

In both studies, however, the rate of mass loss was not constant but decreased with time. This was more pronounced for smaller effusion orifices and occurred at a faster rate in the first study. This behavior
was attributed to \( \text{Al}_2\text{O}_3 \) condensation on the outer edge of the orifice that reduced the orifice area, \( A_{o} \), and changed the Cavling factor, \( W_{c} \), during the course of each experiment. A temperature gradient was ruled out because no condensation was observed inside of the cell lid and a significant effort was made to ensure an isothermal condition. No explanation was proposed for \( \text{Al}_2\text{O}_3 \) condensation in the first study but it was noted that the ratio of the partial pressures of the species, \( F \), was related to the effusion orifice area. It was suggested that this could be due to \( \text{Al}_2\text{O}_3(g) \) reacting with the graphite heating element and the formation of excess \( \text{Al}(g) \) outside the effusion-cell, according to reaction (6). The excess \( \text{Al}(g) \) could then react with the outside of the effusion-cell resulting in an increased loss of \( \text{Al}_2\text{O}_3(s) \), according to reaction (7). To test this a molybdenum heating element was used in the second study. Data was obtained by extrapolating the measured rate of mass loss to the start of the experiment when the shape of the orifice was known.

\[
F = \frac{p(\text{Al}_2\text{O}_3)}{p(\text{Al})} = \frac{n_{\text{Al}_2\text{O}_3}}{n_{\text{Al}}} \left( \frac{M_{\text{Al}_2\text{O}_3}}{M_{\text{Al}}} \right)^{1/2} / \left( \frac{M_{\text{Al}}}{M_{\text{Al}_2\text{O}_3}} \right)^{1/2}
\]

\[
\text{Al}_2\text{O}_3(g) + C(s) = 2\text{Al}(g) + \text{CO}(g)
\]

\[
4\text{Al}(g) + \text{Al}_2\text{O}_3(s) = 3\text{Al}_2\text{O}(g)
\]

The second study [4] used the same analysis procedure and similar behavior was observed but the rate of orifice clogging and the increase in \( F \) with orifice area was less pronounced. The variation in \( F \) with orifice area was accepted as real but unrelated to the heating element material. A complex calculation procedure was developed to consider an average effective orifice area, \( A_{\text{eff}} \), to correct for the decreasing orifice area with time. In addition, the concept of “sintered” vaporization for \( \text{Al}(g) \), \( \alpha_{\text{vap}}(\text{Al}) < 1 \), from \( \text{Al}_2\text{O}_3(s) \) was introduce to explain the apparent decrease in measured \( p(\text{Al}) \) with increasing orifice area (while \( p(\text{Al}_2\text{O}) \) was assumed to be independent of orifice area). This was used, with reaction (7), to explain the “unavoidable” \( \text{Al}_2\text{O}_3 \) condensation. The reduced \( p(\text{Al}) \) in the effusion orifice acts to shift the equilibrium in reaction (7) to the left, resulting in condensation of \( \text{Al}_2\text{O}_3(s) \).

These studies clearly involved a large amount of detailed experimental work, however, there are several obvious problems in the interpretation of these results that need to be identified. The first problem is the mass balance analysis used to determine the number of moles of \( \text{Al}(l) \) and \( \text{Al}_2\text{O}_3(s) \) lost from the
system. The analysis technique did not allow the vaporization processes inside the cell and effusion from the cell to be treated separately from the condensation of Al₂O₃ on the outside of the cell. A portion of material transported from inside the effusion-cell did not leave the system but condensed as Al₂O₃ on the outside of the cell. Therefore the measured mass loss is less than the actual amount of Al(l) and Al₂O₃(s) removed from inside of the cell. In this situation the analysis procedure underestimates the moles of Al₂O₃(s) consumption which results in both a low p(Al₂O₃) and high p(Al). As the amount of Al₂O₃ condensation increases relative to the orifice area (as the orifice area decreases) F must decrease. Thus, the behavior observed for F can be explained without considering “hindered” vaporization of Al(g) and the best results should be obtained with the largest orifices where the relative amount of orifice clogging is the smallest. While a reduced vaporization coefficient for Al(g) from Al₂O₃(s) is possible, its effect would be difficult to observe with a Al(l) + Al₂O₃(s) mixture as Al(g) vaporization from Al(l) would dominate. As a general rule the more complex vapor species is more likely to experience hindered vaporization, that is \( \alpha_{vap}(Al₂O₃) < \alpha_{vap}(Al) \) [19]. Further, if a reduced \( \alpha_{vap}(Al) \) was the reason for Al₂O₃ condensation then as the effusion orifice clogs \( p(Al) \) would increase as it is more accurately sampled. This would shift equilibrium of reaction (7) to the right and limit further condensation, against the observation that Al₂O₃ condensation is more pronounced for smaller orifices. These problems raise uncertainty about Moizfeldt’s theory. An obvious test of this theory is to measure F with time as the effusion orifice clogs due to Al₂O₃ condensation. This is a relatively simple experiment for effusion cell vapor source coupled to a mass spectrometer, KEMS. This experiment is described and the results considered.

2. Experimental

2.1. Materials

In this study about 0.5 g of Al(s) (99.9999 wt% purity) were loaded into an Al₂O₃ effusion-cell (99.99 wt% purity) shown schematically in figure 1. Prior to use the effusion cell was cleaned by baking at about 1800 K for 10 hours under vacuum (~10⁻³ Pa). In addition, a sample of Au (99.9999 wt% purity) was
placed in a graphite-liner inside a second Al₂O₃ effusion-cell, in the isothermal zone of the furnace, and
was used to check for temperature and instrument sensitivity during the experiment.

2.2. Apparatus and Experimental Procedure

These measurements were made with a Nuclide/MAAS/PATCO 12-90-HT single focus magnetic
sector mass spectrometer coupled to a multiple effusion-cell vapor source. The relative partial pressures of
Au(g), Al(g) and Al₂O(g) were determined indirectly by sampling their flux in a molecular beam (selected
from the distribution of effusing molecules) by electron impact resulting in Au⁺, Al⁺ and Al₂O⁺ ions and the
formation of a representative ion beam that was sorted according to mass-to-charge ratio by common mass
spectrometric techniques. An electron energy of about 25 eV was used and there was no evidence of
Al₂O(g) fragmentation. The partial pressures, \( p(i) \), in the effusion-cell is related to the measured intensity
of each ion, \( I_i \), and absolute temperature, \( T \), by Eq. (8) [20]:

\[
p(i) = I_i T / S_i
\]

\( S_i \) is the instrument sensitivity factor and is a complex function of the: intersection of the molecular and
electron beams, ion extraction efficiency, ionization cross-section, transmission probability of the mass
analyzer, detector efficiency and isotopic abundance. Absolute pressure measurements are difficult, as a
result \( S_i \) is typically assumed constant and relative partial pressures are considered (i.e., \( p(i) \propto I_i T \)). In
this way \( F \) was monitored directly by measuring the ion intensity ratio of Al₂O⁺ and Al⁺ with time, Eq. (9).

\[
F \propto I_{Al₂O⁺}/I_{Al⁺}
\]

The effusion cells were maintained at 1550±3.0 K over 8 hours during which time a consistent portion
of the effusing molecules from each cell were sampled at 45 minute intervals while the orifice of the cell
containing Al(l) partial clogged with the condensation of Al₂O₃. From Eq. (3) the rate and the distribution
of Al(g) and Al₂O(g) effusing from the orifice will change with time as the orifice closes. This will change their flux distribution in the molecular beam and therefore the rate of ion production independent of

\( p(Al_2O) \) and \( p(Al) \) in the effusion-cell, however, as both species are sampled with the same orifice the effect is identical.

The successful application of a multiple effusion-cell vapor sources requires that vapor pressure can be consistently sampled independent of the effusion-cell. This condition is obtained with the inclusion of two fixed apertures (field and source) between the effusion cell and ion source and accurate alignment of the orifice [14, 21-23]. The fixed apertures define an ionization volume independent of vapor source and the alignment of the orifice is monitored visually with a video camera mounted above the ion source that sights through the fixed apertures [14]. The temperature was measured with a pyrometer (Mikron M190V-TS) sighting a blackbody source (2.5 mm in diameter and 13.5 mm long) machined into the bottom of the effusion-cell and Mo-cell holder.

3. Results

\( \text{Al}_2\text{O}_3 \) condensed and clogged the effusion orifice over 8 hours at 1550±3 K and was observed visually and as a drop in the measured ion intensities of \( \text{Al}^+ \) and \( \text{Al}_2\text{O}^+ \) with time. In addition to growth on the outer edge of the effusion orifice, \( \text{Al}_2\text{O}_3 \) “needles or whiskers” also grew from other surfaces in the furnace in a direct line from the effusion orifice. These areas are identified in the cross section of the furnace shown in figure 2. The extent of clogging after 8 hours is shown in the SEM image of the outside of the orifice, shown in figure 3. The \( \text{Al}_2\text{O}_3 \) crystals have grown out of the plane of the orifice (30–60° to the normal) and range widely in thickness.

The temperature and instrument sensitivity were monitored during the experiment and the ion intensity of \( \text{Au}^+ \) from the effusion cell containing pure \( \text{Au} \) is shown in figure 4. Over 8 hours the furnace temperature slowly increased from 1547 K to 1552 K while \( I_{\text{Au}} \) remained consistent (5342±180 K). This indicates a small decrease in instrument sensitivity but this is not expected affect any other results. The variation in the measured ion intensities of \( \text{Al}^+ \), \( \text{Al}_2\text{O}^+ \) and \( F \), as the effusion orifice closed, are shown in figure 5. During an initial period, ~2 hours, the measured ion intensities of \( \text{Al}^+ \) and \( \text{Al}_2\text{O}^+ \) were constant.
This is expected to be due to a "restricted collimation" condition imposed by the fixed apertures that define the source area, \(A_s\), of the molecular beam that is smaller than the cross section of the effusion orifice, \(A_o\) [22, 23]. As a result the flux distribution of \(\text{Al}(g)\) and \(\text{Al}_2\text{O}_3(g)\) in the molecular beam remained relatively unchanged until the growth of \(\text{Al}_2\text{O}_3\) condensation encroaches into the source area, \(A_o\). Following this period, the measured ion intensities of \(\text{Al}^+\) and \(\text{Al}_2\text{O}_3^+\) dropped about 41% over 6 hours as the \(\text{Al}_2\text{O}_3\) crystals continued to grow. \(F\) remained consistent with only a small increase with time consistent with the measured temperature drift and the reaction enthalpies reported in table 1.

4. Discussion

Observing that the measured ratio of \(p(\text{Al}_2\text{O}_3)/p(\text{Al})\) remained consistent as the orifice closed provides direct evidence that hindered vaporization of \(\text{Al}(g)\) from \(\text{Al}_2\text{O}_3(s)\) inside the effusion cell is not the reason for the condensation of \(\text{Al}_2\text{O}_3\). The condensation of \(\text{Al}_2\text{O}_3\) can be easily understood when it is recognized that inside the effusion cell \(\text{Al}(g)\) and \(\text{Al}_2\text{O}(g)\) are in equilibrium with \(\text{Al}(l) + \text{Al}_2\text{O}_3(s)\) and this equilibrium also defines a partial pressure of \(\text{O}_2(g)\) in the order of \(10^{-42}\) to \(10^{-20}\) Pa (and \(\text{O}(g)\) \(10^{-24}\) to \(10^{-12}\) Pa) over the temperature range 1000 K to 1600 K. The environment outside the effusion cell in a furnace containing Ta can contain \(\text{O}_2(g)\) pressures up to \(10^{-20}\) to \(10^{-12}\) Pa [11]. This is many orders of magnitude higher than that in equilibrium with \(\text{Al}(l) + \text{Al}_2\text{O}_3(s)\) which allows the \(\text{Al}_2\text{O}_3\) effusion cell remain stable. Therefore as \(\text{Al}\) and \(\text{Al}_2\text{O}\) molecules leave the effusion cell they enter an environment with a greatly increased oxygen activity which results in a large driving force for \(\text{Al}_2\text{O}_3(s)\) formation. At reduced pressures (~\(10^{-4}\) Pa) a heterogeneous reaction between \(\text{Al}(g), \text{Al}_2\text{O}(g)\) and oxygen containing species (\(\text{O}_2(g), \text{O}(g), \text{H}_2\text{O}(g), \text{Al}_2\text{O}(g), \ldots\)) on a surface is more probable than homogeneous precipitation of \(\text{Al}_2\text{O}_3(s)\) in the vapor phase. Therefore it is proposed that \(\text{Al}_2\text{O}_3\) condensation occurs by heterogeneous growth by the reaction of impinging fluxes of \(\text{Al}(g)\) or \(\text{Al}_2\text{O}(g)\) molecules with oxygen containing species on a \(\text{Al}_2\text{O}_3\)-surface according to either:

\[
2\text{Al}(g) + 3\text{O(ads)} = \text{Al}_2\text{O}_3(s) \quad (10a)
\]

\[
\text{Al}_2\text{O}(g) + 2\text{O(ads)} = \text{Al}_2\text{O}_3(s) \quad (10b)
\]
It is unclear which reaction dominates the growth rate of $\text{Al}_2\text{O}_3(s)$. This would be difficult to determine and is outside of the scope of this investigation. In general terms, the growth kinetics depend on: the flux of $\text{Al}_2\text{O}_3(g)$, $\text{Al}(g)$ and oxygen containing species; their condensation coefficients; the adsorption process; and the crystallographic orientation of the $\text{Al}_2\text{O}_3$ relative to the vapor flux [24]. According to this theory, as the temperature is increased the growth rate of condensed $\text{Al}_2\text{O}_3$ will increase in proportion to $p(\text{Al}_2\text{O})$ and $p(\text{Al})$, provided there is an adequate supply of oxygen. Therefore the higher $\text{Al}_2\text{O}_3$ growth rate observed in Motzfeldt’s first study can probably be attributed to the higher temperatures (1585 K and 1623 K as opposed to 1556 K) rather than the different heating element materials (graphite and Mo).

Even though $\text{Al}(g)$ and $\text{Al}_2\text{O}(g)$ are reacting to form $\text{Al}_2\text{O}_3(s)$ this will not change the measured $p(\text{Al}_2\text{O})/p(\text{Al})$ ratio because only molecules that don’t reacted to form $\text{Al}_2\text{O}_3(s)$ reach the ion-source. The molecular beam will therefore retain the equilibrium $p(\text{Al}_2\text{O})/p(\text{Al})$ ratio defined by $\text{Al}(l) + \text{Al}_2\text{O}_3(s)$ inside the effusion-cell. Some vaporization will occur from the condensed $\text{Al}_2\text{O}_3(s)$ within the source area, $A_o$, of the molecular beam, however, the increased oxygen activity of the furnace environment mean $\text{Al}_2\text{O}(g)$ and $\text{Al}(g)$ no longer dominant. Therefore the contribution of $\text{Al}_2\text{O}(g)$ and $\text{Al}(g)$ vaporizing from the condensed $\text{Al}_2\text{O}_3(s)$ to the molecular beam would be insignificant compared to that coming from within the effusion cell, until the point when the orifice is almost completely closed. Therefore clogging of the orifice by $\text{Al}_2\text{O}_3$ condensation can be thought of solely as changing the effective orifice-area and the associated change in the distribution of effusing molecules. As orifice clogging is more pronounced at high temperatures, pressure measurements made at higher temperatures are more effected, reducing the measured enthalpies of vaporization of both $\text{Al}(g)$ and $\text{Al}_2\text{O}(g)$, as seen in table 1. Improving thermodynamic measurements in the Al-C system requires that the affect of $\text{Al}_2\text{O}_3$ condensation is reduced to a minimum.

### 4.1 Suggestions for improved thermodynamic measurements

According to this theory, the condensation of $\text{Al}_2\text{O}_3(s)$ must occur at all temperatures but it only occurs at an observable rate when $p(\text{Al})$ and $p(\text{Al}_2\text{O})$ are high enough to provide a significant molecular flux to the
Al₂O₃-surface for a given \( p(O_2) \). Therefore more accurate thermodynamic data in the Al-O system can be obtained by: 1) limiting measurements to temperatures below about 1450 K with the highest temperature measurement taken first, or 2) reducing the \( p(O_2) \) inside the furnace to levels that approach those in equilibrium with Al(l) + Al₂O₃(s). The first option may not initially appear satisfactory, however, the upper pressure-limit of the Knudsen-effusion technique (~1 Pa), imposed by molecular flow conditions, already limits the temperature to about 1600 K. Reducing \( p(O_2) \) to these levels requires the introduction of “oxygen-getters” (in the form of Ti, Zr or Hf sheets) inside the multiple effusion cell furnace and the vacuum chamber. These have been added to the furnace as shown in figure 2 but additional heated sheets are probably required outside the furnace, particularly around the field aperture and also inside the ion source chamber. Obviously there is a limit to reducing \( p(O_2) \) as the Al₂O₃ effusion-cell must remain stable. It is also important to notice that this behavior is likely to occur in other metal-oxygen systems that contain very stable oxides, for example Y-O, Zr-O, Ti-O.

While this investigation has focused on the heterogeneous growth of Al₂O₃, there is no reason to assume that corresponding homogeneous reactions are not also occurring within the molecular beam between the orifice and the ion source. Homogenous reactions between Al(g) and Al₂O(g) in the molecular beam and O₂(g) or O(g) in the vacuum chamber could result in the formation of AlO, Al₂O₃, Al₂O₇ and Al₂O₃ molecules unrelated to the sample being studied within the effusion cell. Reducing \( p(O_2) \) inside the vacuum chamber will help to limit these reactions and further improve thermodynamic measurements in the Al-O system.

5. Conclusions

In an effort to better determine the thermodynamic properties of vapor species in the Al-O system the problem of Al₂O₃ condensation and orifice clogging was reconsidered. Motzfeldt’s theory for Al₂O₃ condensation was reviewed and serious questions were raised about its validity. This theory was based on the apparent increase in \( p(Al₂O)/p(Al) \) with effusion orifice area and this was attributed to “hindered” vaporization of Al(g) from Al₂O₃(s). This study tested this assumption by monitoring \( p(Al₂O)/p(Al) \) over 8 hours at 1550±3 K while the effusion orifice clogged due to the growth of Al₂O₃ crystals. A consistent
$p(Al_2O_3)/p(Al)$ ratio was observed during this period while the measured partial pressures of $Al_2O_3$ and $Al(g)$ both dropped about 41%. This disagrees with the previous explanation for $Al_2O_3$ condensation. A much simpler explanation was proposed based on the large difference in $p(O_2)$ between the inside of the effusion cell (defined by the $Al(l) + Al_2O_3(s)$ equilibrium) and the furnace environment. As the $Al$ and $Al_2O_3$ molecules leave the effusion-cell they enter an environment with a greatly increased $p(O_2)$ and $Al_2O_3$ condensation occurs by heterogeneous growth by the reaction of impinging $Al(g)$ or $Al_2O_3(g)$ molecules with absorbed $O$ on a $Al_2O_3$-surface. According to this theory $Al_2O_3$ condensation occurs at all temperatures while studying $Al(l) + Al_2O_3(s)$ but it only occurs at an observable rate at temperatures above 1500 K when the fluxes of $Al(g)$ and $Al_2O_3(g)$ are high. To obtain more accurate thermodynamic data in the $Al-O$ system it was proposed to either: 1) limit measurements to below about 1450K with the highest temperature measurement taken first, or 2) reduce the $p(O_2)$ inside the furnace to levels that approach the dissociation pressure in equilibrium with $Al(l) + Al_2O_3(s)$. A combination of both is currently being tried.

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References

Figure Captions

**Figure 1.** $\text{Al}_2\text{O}_3$ effusion-cells: internal cell-body dimensions 10 mm diameter by 8.6 mm tall, orifice dimensions 1.0 mm diameter by 3.5 mm long. The orifice is offset by 2 mm from cell centerline while the hole in the bottom is part of blackbody source (2.5 mm in diameter by 13.5 mm long) used for temperature measurement.

**Figure 2.** Schematic cross section of vapor source furnace with the insert showing detail of the areas where $\text{Al}_2\text{O}_3$ condensation was observed. 1) effusion-cell; 2) Mo envelop for 3 effusion-cells; 3) W-foil (25 $\mu$m thick) heating element; 4) Ta heat shields; 5) blackbody source; 6) Ta light shield; 7) Mo heat shield support; 8) additional Hf-foil (~150 $\mu$m thick) “oxygen getter”.

**Figure 3.** SEM image of $\text{Al}_2\text{O}_3$ condensation and growth observed on the outer edge of the effusion orifice after 8 hours at 1550$\pm$3 K.

**Figure 4.** Measured ion-intensities of $\text{Au}^+$ versus time at 1550$\pm$3 K.

**Figure 5.** Measured ion intensities of $\text{Al}^+$, $\text{Al}_2\text{O}_3^+$ and $F = p(\text{Al}_2\text{O}_3)/p(\text{Al})$ versus time at 1550$\pm$3 K as the orifice closed due to $\text{Al}_2\text{O}_3$ condensation.
Figure 1. Al₂O₃ effusion-cells: internal cell-body dimensions 10 mm diameter by 8.6 mm tall, orifice dimensions 1.0 mm diameter by 3.5 mm long. The orifice is offset by 2 mm from cell centerline while the hole in the bottom is part of blackbody source (2.5 mm in diameter by 13.5 mm long) used for temperature measurement.

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Figure 5. Measured ion intensities of $\text{Al}^+$, $\text{Al}_2\text{O}^+$ and $\mathcal{R} = p(\text{Al}_2\text{O})/p(\text{Al}) \propto R(\text{Al}_2\text{O}^+)/R(\text{Al}^+)$ verses time at 1550±3K as the orifice closed due to $\text{Al}_2\text{O}_3$ condensation.