Composition of the Gas Phase over Al\textsubscript{2}O\textsubscript{3} and the Enthalpies of Atomization of AlO, Al\textsubscript{2}O, and Al\textsubscript{2}O\textsubscript{2}

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Abstract—The Al, O, AlO, Al\textsubscript{2}O, Al\textsubscript{2}O\textsubscript{2}, WO\textsubscript{3}, and WO\textsubscript{2} partial pressures in the vapor over Al\textsubscript{2}O\textsubscript{3} in a tungsten Knudsen effusion cell between 2300 and 2600 K were derived from Al\textsuperscript{+}, O\textsuperscript{+}, AlO\textsuperscript{+}, Al\textsubscript{2}O\textsuperscript{+}, Al\textsubscript{2}O\textsubscript{2}\textsuperscript{+}, WO\textsubscript{3}\textsuperscript{+}, and WO\textsubscript{2}\textsuperscript{+} ion intensities. The mass spectrometer was calibrated against the equilibrium constant of the WO\textsubscript{2}(g) = WO\textsubscript{3}(g) + O(g) reaction. Refined values of the ionization cross sections of AlO and Al\textsubscript{2}O\textsubscript{2} were used in the partial pressure calculations. The enthalpies of atomization of aluminum suboxides were determined to be $\Delta_{\text{at}} H^\circ (\text{AlO}, \text{g}, 0) = 510.7 \pm 3.3$ kJ mol\textsuperscript{-1}, $\Delta_{\text{at}} H^\circ (\text{Al}_2\text{O}_2, \text{g}, 0) = 1067.2 \pm 6.9$ kJ mol\textsuperscript{-1}, and $\Delta_{\text{at}} H^\circ (\text{Al}_2\text{O}_3, \text{g}, 0) = 1556.7 \pm 9.9$ kJ mol\textsuperscript{-1}.

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Numerous mass spectrometric studies of the vapor resulting from evaporation of Al\textsubscript{2}O\textsubscript{3} and Al + Al\textsubscript{2}O\textsubscript{3} mixtures [1–12] demonstrated that the gas phase contains aluminum and oxygen atoms and the aluminum suboxides AlO, Al\textsubscript{2}O, and Al\textsubscript{2}O\textsubscript{2}. When a tungsten or molybdenum Knudsen cell was used, WO\textsubscript{3} or MoO\textsubscript{3} ($x = 1–3$) appeared in the gas phase owing to the partial oxidation of the structural material of the cell. Discussion of the abnormally high AlO\textsubscript{2} partial pressure [11, 13] measured by Faber et al. [6] in Al\textsubscript{2}O\textsubscript{3} evaporation from an alundum Knudsen cell ended after it was proved theoretically [14] and experimentally [12] that only very small amounts of AlO\textsubscript{2} can be present in the gas phase.

The experimental data reported in [1–12], obtained by Knudsen evaporation [1–3, 5–8, 11] and by evaporation from an open surface [4, 9, 10, 12], and the results of the effusion measurements in which partial pressures were calculated from the weight lost by the sample [15–18] were systematized by Gurvich et al. [19] in their description of the thermodynamic properties of aluminum suboxides. It was noted that the AlO dissociation energy derived from the data reported in [3, 4, 6, 8, 10, 11] is in satisfactory agreement with chemiluminescence and fluorescence data and with the absorption spectrum of the AlO molecule. The error in the recommended value of the dissociation energy is $\pm 5$ kJ mol\textsuperscript{-1}. The enthalpies of atomization of Al\textsubscript{2}O and Al\textsubscript{2}O\textsubscript{2} were determined with larger errors of $\pm 25$ and $\pm 50$ kJ mol\textsuperscript{-1}, respectively. Gurvich et al. [19] were quite right to note that one of the sources of these large errors is the uncertainty in the ionization cross sections used in the conversion of mass spectrometric ion intensities into absolute values of partial pressure. An attempt to minimize this uncertainty was made by Milushin et al. [20], who derived the thermodynamic properties of AlO, Al\textsubscript{2}O, and Al\textsubscript{2}O\textsubscript{2} from data for isomolecular reactions, for which the additivity scheme of ionization cross section calculation [21] was assumed to introduce the smallest error into equilibrium constants.

In this work, we calculated partial pressures from earlier measurements of the ion currents of the components emitted by Al\textsubscript{2}O\textsubscript{3} heated in a tungsten effusion cell at 2300–2600 K [11]. To do this, we used not only the ionization cross sections that had been widely used in such measurements for a long time [22], but also recent ionization cross section data for the oxygen atom [23], aluminum atom [24], AlO [25], and Al\textsubscript{2}O [25]. This was particularly appropriate because the latter report contains ionization cross section data for tungsten oxides [25]. In our earlier study [11], the sensitivity constant of the mass spectrometer was determined using the equilibrium constant of the reaction WO\textsubscript{3}(g) = WO\textsubscript{2}(g) + O(g).

The purpose of this work is to refine the partial pressures of the components of the gas phase over Al\textsubscript{2}O\textsubscript{3}; to obtain more reliable values of the enthalpies of atomization of AlO(g), Al\textsubscript{2}O(g), and Al\textsubscript{2}O\textsubscript{2}(g); and to find the most suitable computational scheme for the ionization cross sections of O, Al, AlO, Al\textsubscript{2}O, Al\textsubscript{2}O\textsubscript{2}, WO\textsubscript{3}, and WO\textsubscript{2}.

Calculation of ionization cross sections. In our previous study [11], the partial pressures of vapor components were calculated using the familiar equation relating the partial pressure of component $i$ in the effu-
The only exception is \( \sigma(Al) \) values, which were calculated in [25] and is accepted here to be 1.25, as was recommended in [27].

As can be seen from Table 1, it was calculated that \( \sigma(AlO) < \sigma(Al) \) [25]. This relationship (which depends quantitatively on whether the DM formalism or the MAR formalism is used as the computational model) is in conflict with the additivity calculations of ionization cross section [21]. At the same time, this relationship was suggested in a much earlier work by Drowart [28], who believed that use of the \( \sigma(AlO)/\sigma(Al) \approx 0.7 \) ratio would improve the fit between the enthalpy of atomization of AIO derived from mass spectrometric partial pressure data [8] and the same enthalpy determined by other methods. It is likely that some of the earlier mass spectrometric partial pressures of vapor components can be reconciled with the corresponding recommended values by applying appropriate corrections to ionization cross sections.

Array 1 of \( \sigma_i \) values (Table 1) was derived from the atomic cross sections \( \sigma(O), \sigma(Al), \) and \( \sigma(W) \) calculated by Mann [22]. In the calculation of the ionization cross sections of some molecules, we took into account a number of experimental facts [27, 29–31] in the following way.

Mann [22] reported the ionizing electron energy values \( E_{\text{max}} \) and the corresponding maximum values of ionization cross sections (\( \sigma_{\text{max}} \)). In the calculation of the ionization cross sections for the electron energies used in our experiments (\( E \)), it was assumed that \( \sigma \) is a linear function of \( E \) between its threshold value (\( \sigma_{\text{th}} = 0 \)) and its maximum value. Hence,

\[
\sigma = \sigma_{\text{max}} \left( \frac{E - IP}{E_{\text{max}} - IP} \right),
\]

where \( IP \) is the ionization potential.

The values of \( \sigma(Al_2O), \sigma(WO_2), \) and \( \sigma(WO_3) \) were calculated as

\[
\sigma_i = 0.75 [\sigma(M) + n \sigma(O)],
\]

where \( M = Al \) or \( W \) and \( m \) and \( n \) are the corresponding stoichiometric coefficients.

Since \( \sigma_{\text{max}} \) for \( O, Al, \) and \( W \) were determined for \( E_{\text{max}} = 61, 31, \) and 32 eV, respectively [22], we initially calculated \( \sigma(O) \) for 31 and 32 eV via Eq. (2) and then calculated the corresponding \( \sigma_i \) values via Eq. (3). These were converted, using Eq. (2), to the values corresponding to the ionizing electron energies at which the \( Al_2O^+, WO_2^+, \) and \( WO_3^+ \) ion currents were measured in [11].

As is demonstrated in Table 1 (arrays 2, 3), \( \sigma(Al_2O)/\sigma(Al) \approx 0.14 \) or \( \approx 0.61 \). Both values are smaller than the value suggested by Drowart [28]. We found it possible to use the relationship \( \sigma(AlO) = \sigma(Al)/3 \) in our calculations. The validity of this assumption will be proved below. In all of the three \( \sigma(Al_2O_3) = 1.25 \sigma(AlO) \) arrays, we set \( \sigma(Al_2O_3) = 1.25 \sigma(AlO) \) based on the data reported by Drowart et al. [27], which are recommended for estimating the ionization.

### Table 1. Ionization cross sections (Å²) at energies 5 eV above the ionization threshold

<table>
<thead>
<tr>
<th>Array</th>
<th>O</th>
<th>Al</th>
<th>AlO</th>
<th>Al₂O</th>
<th>Al₂O₂</th>
<th>WO₂</th>
<th>WO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.115</td>
<td>1.235</td>
<td>0.385</td>
<td>2.106</td>
<td>0.616</td>
<td>1.729</td>
<td>2.000</td>
</tr>
<tr>
<td>2</td>
<td>0.186</td>
<td>6.88</td>
<td>0.95</td>
<td>4.00</td>
<td>1.19</td>
<td>1.15</td>
<td>0.70</td>
</tr>
<tr>
<td>3</td>
<td>0.186</td>
<td>6.88</td>
<td>4.18</td>
<td>12.90</td>
<td>5.22</td>
<td>2.55</td>
<td>2.23</td>
</tr>
</tbody>
</table>

Notes: * Data from [25] (DM formalism).

** Data from [25] (MAR formalism).