High-Temperature Vaporization Behavior of Oxides II. Oxides of Be, Mg, Ca, Sr, Ba, B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, Zn, Cd, and Hg

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R. H. Lamoreaux, D. L. Hildenbrand, and L. Brewer

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High-Temperature Vaporization Behavior of Oxides II. Oxides of Be, Mg, Ca, Sr, Ba, B, Al, Ga, In, Ti, Si, Ge, Sn, Pb, Zn, Cd, and Hg

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In order to assess the high-temperature vaporization behavior and equilibrium gas phase compositions over the condensed oxides of Be, Mg, Ca, Sr, Ba, B, Al, Ga, In, Ti, Si, Ge, Sn, Pb, Zn, Cd, and Hg, the relevant thermodynamic and molecular constant data have been compiled and critically evaluated. Selected values of the Gibbs energy functions of condensed and vapor phases are given in the form of equations valid over wide temperature ranges, along with the standard entropies and enthalpies of formation. These data were used to generate plots of equilibrium partial pressures of vapor species as functions of temperature for representative environmental conditions ranging from reducing to oxidizing. The calculated partial pressures and compositions agree, for the most part, with experimental results obtained under comparable conditions. Maximum vaporization rates have been calculated using the Hertz–Knudsen equation. Literature references are given.

Key words: critically reviewed data; enthalpy increment; enthalpy of formation; entropy; Gibbs energy function; high temperature; oxide; partial pressure; thermodynamic data; vaporization; vaporization rate.

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1. Introduction

1.1. Background

Oxide materials are used or encountered in a wide variety of high-temperature applications where vaporization rates and thermodynamic stabilities are often limiting factors. The efficient design and operation of high-temperature devices and processes requires reliable information about the stability and volatilities of these oxides so that vaporization losses and component lifetimes can be predicted.

Despite continuing research efforts and the use of increasingly sophisticated techniques, there are still many gaps in our knowledge and understanding of the detailed vaporization thermodynamics of metal oxide systems. This puts a premium on critical review of the literature and selection of the necessary thermodynamic data. However, even in cases where most of the requisite data are compiled, the user must resort to a significant amount of additional calculations, sometimes unfamiliar, in order to evaluate vapor composition and vaporization behavior for specific environmental conditions. Thus we perceive a definite need for critically evaluated data, presented in a format that gives users ready access to the detailed vaporization chemistry and equilibrium partial pressures of the various species. To this end, we present graphs of species partial pressures as functions of temperature under representative reducing, neutral, and oxidizing environments. We also give equations for calculating partial pressures and maximum vaporization rates for arbitrary conditions of temperature and oxygen potential.

The present work is the second publication in a program sponsored by the Office of Standard Reference Data of the National Bureau of Standards to provide critically re-
viewed thermodynamic data of oxides, along with overviews of their high-temperature vaporization phenomena. The previous article (Lamoreaux and Hildenbrand, 1984) on alkali metal oxide systems discussed the scope of the program, the relevant literature, methods of data evaluation, and the mathematics of vaporization calculations. This article covers oxide systems of the elements Be, Mg, Ca, Sr, Ba, B, Al, Ga, In, Ti, Si, Ge, Sn, Pb, Zn, Cd, and Hg.

Readers should note that revised JANAF Thermodynamic Tables (Chase et al., 1985), the final CODATA Key Values for Thermodynamics, and the CODATA Thermodynamic Tables (Garvin et al., 1987) have been in preparation in the same time period as the present work and should appear concurrently. The minor differences in selected values of thermodynamic properties are immaterial to the purpose of this paper.

2. Properties of Individual Systems

2.1. Data Evaluation, Units, and Symbols

Molecular constants cited in the text are internuclear distances $r$ in nm, vibrational wavenumbers $\omega$ in cm$^{-1}$, the molecular symmetry number $\sigma$, electronic state quantum weights $g_e$, and excited electronic state term values $T_e$ in cm$^{-1}$. Thermodynamic quantities are expressed in dimensionless units, e.g., $S^*/R$, $G^*/RT$, or in kelvin units, e.g., $\Delta H^*/R$, $\Delta G^*/R$. The symbols $K$ and $kK$, where $1kK = 10^3 K$, are used to represent kelvin units. Values of $R$ used in the present work are 1.987 19 cal/mol K and 8.3144 J/mol K. The standard state pressure was taken as 1 atm ($1.01325 \times 10^5$ Pa), although the unit for computed vaporization partial pressures is the bar ($10^5$ Pa).

The thermodynamic symbols used in the present work are the following: $\Delta H^*_{298}/R$ The standard molar enthalpy of formation at 298.15 K divided by the molar gas constant. Units = kelvins.

$(H^*_{298} - H^*_{0})/R$ The standard molar enthalpy increment between 0 and 298.15 K divided by the molar gas constant. Units = kelvins.

$-(G^*_{T} - H^*_{298})/RT$ The standard molar Gibbs energy function divided by the molar gas constant.

$S^*/R$ The standard molar entropy at $T$ K divided by the molar gas constant.

$T_{trs}, \Delta H_{trs}^*/R$ Solid-phase transition temperature and standard molar enthalpy of transition divided by the molar gas constant.

$T_{fus}, \Delta H_{fus}^*/R$ Melting temperature and standard molar enthalpy of fusion divided by the molar gas constant.

2.2. Thermodynamic Data and Vaporization Equilibria

Selected values of thermochemical properties of the relevant chemical species involved in the high-temperature vaporization equilibria are shown in Tables 1–3. Table 1 lists the reported melting points and enthalpies of fusion of high-temperature oxide phases. Table 2 presents Gibbs energy functions fit to the equation

$$-(G^*_{T} - H^*_{298})/RT = A + BT + CT^2 + DT^3 + ET^4.$$  

(1)

Values of $\Delta H^*_{298}/R$, $S^*/R$, and $(H^*_{298} - H^*_{0})/R$ are presented in Table 3.

After careful review and comparison of the literature, Vols. 2 and 3 of the IVTAN compilation (Glushko et al., 1978, 1979a, 1981, 1983) and recent JANAF (Stull et al., 1971) supplements (Chase et al., 1974, 1975, 1978, 1982, and dated individual issues) were chosen as the primary sources of data for the oxides of Be, Mg, Ca, Sr, Ba, B, Al, Ga, In, Ti, Si, Ge, Sn, and Pb. This choice was due to the uniform coverage of the recent literature and to the thoroughness of the reviews presented; agreement of recent JANAF issues with the IVTAN selected values is excellent. Other literature examined included reviews cited in the first paper (Brewer, 1953; Coughlin, 1954; Kelley, 1960; Schick, 1960; Ackermann and Thorn, 1961; Brewer and Rosenblatt, 1961; Kelley and King, 1961; Olette and Ancy-Moret, 1963; Wicks and Block, 1963; Brewer and Rosenblatt, 1969; Barin and Knacke, 1973; Samsonov et al., 1978) and the 1982 NBS compilation (Wagman et al., 1982). As described below, data from the selected sources were supplemented by our own analyses for a few of the minor gaseous species not

<table>
<thead>
<tr>
<th>$T_{fus}$ (K)</th>
<th>$\Delta H_{fus}/R$ (kk)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeO</td>
<td>2851 ± 12</td>
</tr>
<tr>
<td>MgO</td>
<td>3100 ± 25</td>
</tr>
<tr>
<td>CaO</td>
<td>2900 (-50, +300)</td>
</tr>
<tr>
<td>SrO</td>
<td>2970 ± 30</td>
</tr>
<tr>
<td>BaO</td>
<td>2290 ± 30</td>
</tr>
<tr>
<td>B2O3</td>
<td>723 ± 1</td>
</tr>
<tr>
<td>Al2O3</td>
<td>2327 ± 4</td>
</tr>
<tr>
<td>Ga2O3</td>
<td>2080 ± 20</td>
</tr>
<tr>
<td>In2O3</td>
<td>2186 ± 10</td>
</tr>
<tr>
<td>Tl2O</td>
<td>852 ± 10</td>
</tr>
<tr>
<td>Tl2O3</td>
<td>1197 ± 10</td>
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<tr>
<td>SiO2(60)</td>
<td>1726 ± 10</td>
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<tr>
<td>SiO2(900)</td>
<td>1996 ± 5</td>
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<tr>
<td>GeO2</td>
<td>1388 ± 3</td>
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<tr>
<td>SnO</td>
<td>1250 ± 30</td>
</tr>
<tr>
<td>SnO2</td>
<td>1903 ± 10</td>
</tr>
<tr>
<td>PbO</td>
<td>1160 ± 10</td>
</tr>
<tr>
<td>ZnO</td>
<td>2242 ± 25</td>
</tr>
<tr>
<td>CdO</td>
<td>&gt;1500</td>
</tr>
</tbody>
</table>

*See Table 4 for references.*

### Table 2. Gibbs energy function equation parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( A )</th>
<th>( B )</th>
<th>( C )</th>
<th>( D )</th>
<th>( E )</th>
<th>( T ) range, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_2 )</td>
<td>10.988</td>
<td>9.487</td>
<td>-0.383</td>
<td>0.009</td>
<td>0.001</td>
<td>100-1500</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>8.327</td>
<td>6.972</td>
<td>-0.278</td>
<td>0.004</td>
<td>0.001</td>
<td>100-1500</td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>7.723</td>
<td>6.498</td>
<td>-0.235</td>
<td>0.004</td>
<td>0.001</td>
<td>100-1500</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>7.723</td>
<td>6.498</td>
<td>-0.235</td>
<td>0.004</td>
<td>0.001</td>
<td>100-1500</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>7.723</td>
<td>6.498</td>
<td>-0.235</td>
<td>0.004</td>
<td>0.001</td>
<td>100-1500</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>7.723</td>
<td>6.498</td>
<td>-0.235</td>
<td>0.004</td>
<td>0.001</td>
<td>100-1500</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>7.723</td>
<td>6.498</td>
<td>-0.235</td>
<td>0.004</td>
<td>0.001</td>
<td>100-1500</td>
</tr>
<tr>
<td>( \text{N}_2\text{O} )</td>
<td>7.723</td>
<td>6.498</td>
<td>-0.235</td>
<td>0.004</td>
<td>0.001</td>
<td>100-1500</td>
</tr>
<tr>
<td>( \text{SO}_2 )</td>
<td>7.723</td>
<td>6.498</td>
<td>-0.235</td>
<td>0.004</td>
<td>0.001</td>
<td>100-1500</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} )</td>
<td>7.723</td>
<td>6.498</td>
<td>-0.235</td>
<td>0.004</td>
<td>0.001</td>
<td>100-1500</td>
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### Table 3. Gibbs energy function equation parameters (Continued)

<table>
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<tr>
<th>Parameter</th>
<th>( A )</th>
<th>( B )</th>
<th>( C )</th>
<th>( D )</th>
<th>( E )</th>
<th>( T ) range, K</th>
</tr>
</thead>
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<td>0.009</td>
<td>0.001</td>
<td>100-1500</td>
</tr>
<tr>
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<td>6.972</td>
<td>-0.278</td>
<td>0.004</td>
<td>0.001</td>
<td>100-1500</td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>7.723</td>
<td>6.498</td>
<td>-0.235</td>
<td>0.004</td>
<td>0.001</td>
<td>100-1500</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>7.723</td>
<td>6.498</td>
<td>-0.235</td>
<td>0.004</td>
<td>0.001</td>
<td>100-1500</td>
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<tr>
<td>( \text{H}_2\text{O} )</td>
<td>7.723</td>
<td>6.498</td>
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<td>0.004</td>
<td>0.001</td>
<td>100-1500</td>
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<tr>
<td>( \text{CO}_2 )</td>
<td>7.723</td>
<td>6.498</td>
<td>-0.235</td>
<td>0.004</td>
<td>0.001</td>
<td>100-1500</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
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<td>6.498</td>
<td>-0.235</td>
<td>0.004</td>
<td>0.001</td>
<td>100-1500</td>
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<td>6.498</td>
<td>-0.235</td>
<td>0.004</td>
<td>0.001</td>
<td>100-1500</td>
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<tr>
<td>( \text{SO}_2 )</td>
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<td>0.004</td>
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<td>100-1500</td>
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<td>0.004</td>
<td>0.001</td>
<td>100-1500</td>
</tr>
</tbody>
</table>

### Table 2. Gibbs energy function equation parameters (Continued)

#### (G\(^\circ\)-H\(^2\)98a)\(RT = A + BT + CT^2 + DT^3 + ET^4\)

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<tr>
<th>(\Delta G^\circ)</th>
<th>10^8</th>
<th>10^9</th>
<th>10^10</th>
<th>10^11</th>
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<tr>
<td>SnO(_2)</td>
<td>32.251</td>
<td>-17.54</td>
<td>47.34</td>
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<td>SnO(_2)(g)</td>
<td>27.190</td>
<td>8.322</td>
<td>-2.301</td>
<td>0.4159</td>
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<td>SnO(_2)(s)</td>
<td>29.543</td>
<td>7.03</td>
<td>-1.947</td>
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<td>-0.0045</td>
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<td>SnO(_2)(g)</td>
<td>35.752</td>
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<td>1.070</td>
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<td>0.171</td>
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<td>SnO(_2)(s)</td>
<td>44.474</td>
<td>0.177</td>
<td>14.80</td>
<td>-7.026</td>
<td>1.264</td>
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<td>30.1111</td>
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<td>PnO(_2)(g)</td>
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<td>PnO(_2)(s)</td>
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<td>PnO(_2)(s)</td>
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<td>-0.494</td>
<td>0.123</td>
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<tr>
<td>CdO(_2)</td>
<td>25.163</td>
<td>1.166</td>
<td>-1.4237</td>
<td>0.2511</td>
<td>-0.01924</td>
</tr>
<tr>
<td>CdO(_2)(s)</td>
<td>5.195</td>
<td>10.13</td>
<td>-0.409</td>
<td>74.52</td>
<td>-45.76</td>
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<tr>
<td>CdO(_2)(g)</td>
<td>3.011</td>
<td>2.152</td>
<td>-0.823</td>
<td>1.038</td>
<td>299-534-1500</td>
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<tr>
<td>ZnO(_2)(s)</td>
<td>20.748</td>
<td>-5.665</td>
<td>15.305</td>
<td>-12.216</td>
<td>4.055</td>
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<tr>
<td>ZnO(_2)(g)</td>
<td>19.318</td>
<td>2.349</td>
<td>-0.035</td>
<td>0.263</td>
<td>0.064</td>
</tr>
<tr>
<td>ZnO(_2)(s)</td>
<td>29.205</td>
<td>-11.443</td>
<td>31.53</td>
<td>-26.494</td>
<td>9.29</td>
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<tr>
<td>ZnO(_2)(g)</td>
<td>26.046</td>
<td>5.467</td>
<td>-1.6246</td>
<td>0.3157</td>
<td>-0.0286</td>
</tr>
<tr>
<td>HgO(_2)</td>
<td>10.797</td>
<td>-14.507</td>
<td>41.32</td>
<td>-43.32</td>
<td>16.75</td>
</tr>
<tr>
<td>HgO(_2)(g)</td>
<td>21.786</td>
<td>-8.345</td>
<td>19.99</td>
<td>-19.377</td>
<td>0.597</td>
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<tr>
<td>HgO(_2)(s)</td>
<td>19.096</td>
<td>3.195</td>
<td>-0.9736</td>
<td>0.1891</td>
<td>-0.01585</td>
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<tr>
<td>HgO(_2)(g)</td>
<td>10.251</td>
<td>-15.674</td>
<td>42.5</td>
<td>-27.73</td>
<td>12.18</td>
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<tr>
<td>HgO(_2)(s)</td>
<td>21.786</td>
<td>3.237</td>
<td>1.41</td>
<td>-0.8606</td>
<td>0.1332</td>
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</tbody>
</table>

*See Table 4 for references.*

---

**High-Temperature Vaporization Behavior of Oxides**

### Table 3. Values of $\Delta H^\circ_{298}^R$, $S^\circ_{298}$, and $H^\circ_{298}$ (Continued)

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta H^\circ_{298}^R$ (KJ/mol)</th>
<th>$S^\circ_{298}$ (J/K mol)</th>
<th>$H^\circ_{298}$ (KJ/mol)</th>
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</thead>
<tbody>
<tr>
<td>Ge(g)</td>
<td>32.7 ± 0.5</td>
<td>20.3180 ± 0.0002</td>
<td>2.7879</td>
</tr>
<tr>
<td>GeO(g)</td>
<td>-11.46 ± 1.</td>
<td>34.21 ± 0.4</td>
<td>1.4712</td>
</tr>
<tr>
<td>GeO(g)</td>
<td>-13.2 ± 0.5</td>
<td>10.316 ± 0.04</td>
<td>1.750</td>
</tr>
<tr>
<td>ln(s)</td>
<td>6.934 ± 0.03</td>
<td>7.9500</td>
<td></td>
</tr>
<tr>
<td>In(g)</td>
<td>28.9 ± 0.1</td>
<td>20.8978 ± 0.0001</td>
<td>0.7455</td>
</tr>
<tr>
<td>InO(g)</td>
<td>20.5 ± 0.3</td>
<td>28.75 ± 0.06</td>
<td>1.081</td>
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<tr>
<td>InO(g)</td>
<td>-5.17 ± 2.4</td>
<td>39.51 ± 0.4</td>
<td>1.5087</td>
</tr>
<tr>
<td>InO(g)</td>
<td>-1.114 ± 0.6</td>
<td>13.00 ± 0.4</td>
<td>2.0807</td>
</tr>
<tr>
<td>Tis(s)</td>
<td>7.734 ± 0.02</td>
<td>8.2127</td>
<td></td>
</tr>
<tr>
<td>Tis(g)</td>
<td>21.7 ± 0.2</td>
<td>21.7522 ± 0.0001</td>
<td>0.74538</td>
</tr>
<tr>
<td>TiO(g)</td>
<td>23.6 ± 5.5</td>
<td>29.76 ± 1.</td>
<td>1.0904</td>
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<tr>
<td>TiO(g)</td>
<td>-20.1 ± 0.2</td>
<td>17.56 ± 1.</td>
<td>1.816</td>
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<tr>
<td>TiO(g)</td>
<td>3.7 ± 1.4</td>
<td>37.85 ± 0.6</td>
<td>1.554</td>
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<tr>
<td>TiO(g)</td>
<td>-6.5 ± 0.5</td>
<td>28.244 ± 1.</td>
<td>2.4295</td>
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<tr>
<td>Sn(s)</td>
<td>5.42 ± 1.</td>
<td>20.1903 ± 0.0001</td>
<td>0.9081</td>
</tr>
<tr>
<td>SnO(g)</td>
<td>-11.0 ± 0.6</td>
<td>25.4723 ± 0.0002</td>
<td>1.0482</td>
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<tr>
<td>SnO(g)</td>
<td>-105.3 ± 0.1</td>
<td>4.99 ± 0.02</td>
<td>0.8319</td>
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<tr>
<td>SnO(g)</td>
<td>-3.7 ± 0.1</td>
<td>27.496 ± 0.1</td>
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<tr>
<td>SnO(g)</td>
<td>67.9 ± 2.3</td>
<td>27.262 ± 0.1</td>
<td>1.1141</td>
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<td>SnO(g)</td>
<td>-43.2 ± 2.2</td>
<td>27.3 ± 2.</td>
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<tr>
<td>SnO(g)</td>
<td>74. ± 2.3</td>
<td>22.3 ± 0.5</td>
<td>1.6783</td>
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<tr>
<td>Ge(s)</td>
<td>3.74 ± 0.2</td>
<td>5.5756</td>
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<tr>
<td>Ge(s)</td>
<td>44.7 ± 0.4</td>
<td>20.1941 ± 0.0004</td>
<td>0.8990</td>
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<tr>
<td>GeO(g)</td>
<td>-4.8 ± 0.5</td>
<td>25.915 ± 0.0005</td>
<td>1.0562</td>
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<tr>
<td>GeO(g)</td>
<td>-69.7 ± 0.1</td>
<td>4.775 ± 0.02</td>
<td>0.8996</td>
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<tr>
<td>GeO(g)</td>
<td>-13. ± 2.3</td>
<td>29.0 ± 0.1</td>
<td>1.354</td>
</tr>
<tr>
<td>GeO(g)</td>
<td>58. ± 2.3</td>
<td>20.506 ± 0.0001</td>
<td>1.3983</td>
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<tr>
<td>GeO(g)</td>
<td>-53.2 ± 2.2</td>
<td>37.6 ± 2.</td>
<td>1.900</td>
</tr>
<tr>
<td>GeO(g)</td>
<td>-59.6 ± 2.2</td>
<td>50.2 ± 2.5</td>
<td>3.259</td>
</tr>
<tr>
<td>Sn(s)</td>
<td>6.156 ± 0.01</td>
<td>7.9065</td>
<td></td>
</tr>
<tr>
<td>SnO(g)</td>
<td>26.23 ± 0.1</td>
<td>20.2517 ± 0.0004</td>
<td>0.7475</td>
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<tr>
<td>SnO(g)</td>
<td>-33.78 ± 0.2</td>
<td>4.775 ± 0.03</td>
<td>1.0507</td>
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<tr>
<td>SnO(g)</td>
<td>1.8 ± 0.8</td>
<td>27.904 ± 0.0005</td>
<td>1.6683</td>
</tr>
<tr>
<td>SnO(g)</td>
<td>-69.47 ± 0.2</td>
<td>5.895 ± 0.01</td>
<td>1.0094</td>
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<tr>
<td>SnO(g)</td>
<td>-5.3 ± 2.</td>
<td>30.248 ± 0.5</td>
<td>1.4185</td>
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<tr>
<td>SnO(g)</td>
<td>49.8 ± 1.1</td>
<td>31.325 ± 0.1</td>
<td>1.235</td>
</tr>
<tr>
<td>SnO(g)</td>
<td>-29.2 ± 2.3</td>
<td>37.3 ± 2.</td>
<td></td>
</tr>
<tr>
<td>SnO(g)</td>
<td>-61.3 ± 2.3</td>
<td>45.6 ± 2.</td>
<td></td>
</tr>
<tr>
<td>SnO(g)</td>
<td>-95.3 ± 2.3</td>
<td>54.4 ± 4.</td>
<td></td>
</tr>
<tr>
<td>Po(g)</td>
<td>7.794 ± 0.03</td>
<td>8.2033</td>
<td></td>
</tr>
<tr>
<td>Po(g)</td>
<td>23.48 ± 0.1</td>
<td>21.0801 ± 0.0001</td>
<td>0.74538</td>
</tr>
<tr>
<td>PoO(g)</td>
<td>-20.29 ± 0.06</td>
<td>8.15 ± 0.12</td>
<td>1.1095</td>
</tr>
<tr>
<td>PoO(g)</td>
<td>8.2 ± 1.2</td>
<td>26.857 ± 0.0003</td>
<td>1.0778</td>
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<tr>
<td>PoO(g)</td>
<td>0.8 ± 0.6</td>
<td>31.39 ± 0.1</td>
<td>1.4735</td>
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<tr>
<td>PoO(g)</td>
<td>-33.1 ± 0.3</td>
<td>8.635 ± 0.02</td>
<td>1.3184</td>
</tr>
<tr>
<td>PoO(g)</td>
<td>35.9 ± 0.3</td>
<td>32.383 ± 0.1</td>
<td>1.270</td>
</tr>
<tr>
<td>Po2O5(g)</td>
<td>-15.3 ± 3.3</td>
<td>37.3 ± 3.</td>
<td></td>
</tr>
<tr>
<td>Po2O5(g)</td>
<td>-59.1 ± 0.4</td>
<td>18.27 ± 0.25</td>
<td>2.5113</td>
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<tr>
<td>Po2O5(g)</td>
<td>-38. ± 4.5</td>
<td>47.5 ± 4.</td>
<td></td>
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<td>P2O5(g)</td>
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<td>25.49 ± 0.3</td>
<td>3.6309</td>
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<td>P2O5(g)</td>
<td>-68. ± 6.2</td>
<td>54.2 ± 5.</td>
<td></td>
</tr>
<tr>
<td>P2O5(g)</td>
<td>-93. ± 6.2</td>
<td>58.8 ± 6.</td>
<td></td>
</tr>
<tr>
<td>P2O5(g)</td>
<td>-119. ± 6.2</td>
<td>67.8 ± 6.</td>
<td></td>
</tr>
</tbody>
</table>
included in the major compilations. In all cases, the thermodynamic values selected reproduce, within experimental uncertainty, the vapor pressure measurements considered reliable.

In reviewing the available tabulations of thermodynamic functions for gaseous atoms, it was discovered that heat capacity, Gibbs energy function, entropy, and enthalpy increment values for many elements are in error because they are based on only the observed electronic levels, e.g., as listed by Moore (1949, 1952, 1958), and do not include unobserved low-lying levels, which can contribute significantly. Although this problem was not severe for the elements covered in this paper, it should be noted that the equations for Gibbs energy functions given for gaseous atoms in Table 2 are consistent with new calculations that take into account more recent spectroscopic data and estimates of missing low-lying electronic levels (Brewer, 1983). The equations given for \(- (G^0_T - H^0_{298}) / T\) represent the tabulated values within typical limits of \(\pm 0.01\) over their applicable temperature ranges. The equations were derived by fitting tabular data and are not direct integrations of heat capacity equations. Because of the nature of the polynomial fits, values derived by differentiating these equations do not represent thermodynamic properties, e.g., heat capacities, accurately.

Data sources for each of the selected values are in any case summarized in Table 4, and more complete discussions of data sources are given below, when necessary.

The calculated partial pressures of major gaseous species in equilibrium with stable condensed oxide phases are shown below as plots of \(\log P\) vs 1/T for several representative vaporization conditions. The particular conditions are 0.2 bar O\(_2\), representing oxidizing conditions, congruent vaporization, representing neutral vaporization, and either 10\(^{-12}\) bar O\(_2\) or the O\(_2\) pressure of the metal–metal oxide equilibria, representing reducing conditions. The metal–metal oxide equilibrium O\(_2\) pressure was chosen when it exceeded 10\(^{-15}\) bar. The maximum vaporization rates calculated by the Hertz–Knudsen equation are also shown in plots below.
The only high-temperature solid phase is the oxide, BeO. Under neutral and reducing conditions, vaporization takes place primarily by decomposition to Be atoms and oxygen species. BeO, BeO₂, Be₂O₃, BeO₃, and Be₂O₅ are the principal vapor species under oxidizing conditions. Partial pressures of major vapor species and calculated maximum vaporization rates are shown in Figs. 1–4.

Be₂O₅(g), Be₂O₆(g) enthalpy of formation was calculated by the third-law method using the mass spectrometric data of Chupka, Berkowitz, and Giese (1959) and of Iheard and Hildenbrand (1964).

a. Be–O System

b. Mg–O System

The only high-temperature solid phase is the oxide, MgO. In neutral and reducing atmospheres, vaporization takes place by dissociation to give gaseous oxygen species and Mg(g); the MgO(g) partial pressure is comparable to that of Mg(g) in oxidizing atmospheres. Partial pressures of major vapor species and calculated maximum vaporization rates are shown in Figs. 5–8. As can be seen from the graphs, MgO is especially volatile at high temperatures under reducing conditions. This has important practical consequences in pointing out the instability and limited usefulness of magnesia-based refractories in hydrogen-containing or otherwise...

<table>
<thead>
<tr>
<th>Table 4. (continued)</th>
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<tbody>
<tr>
<td>$\Delta f H^*_{298}$</td>
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<td>----------------------</td>
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References to Table 4

2. Stull et al., 1971.
5. Chase et al., 1978.
17. Stull et al., 1971, 31 December 1979 unbound supplement. JANAF issued two sets of supplements on Al–O species dated 1979; the later set, with references to literature as late as 1982, is cited.

*References without parentheses are in essential agreement; those in parentheses differ from the chosen value by a significant portion of the stated uncertainty. The sources of the selected data are in boldface.

See text.
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Fig. 1. BeO vaporization in $10^{-15}$ bar O$_2$.

Fig. 2. BeO congruent vaporization.

Fig. 3. BeO vaporization in 0.2 bar O$_2$.

Fig. 4. BeO maximum vaporization rates. A—$10^{-15}$ bar O$_2$; B—congruent vaporization; C—0.2 bar O$_2$.

Fig. 5. MgO vaporization in $10^{-15}$ bar O$_2$.

Fig. 6. MgO congruent vaporization.

reducing atmospheres. The same is true of several of the other alkaline earth oxides.

c. Ca–O System

The only high-temperature solid phase is the oxide, CaO. The equilibrium oxygen pressure of the peroxide, CaO$_2$, exceeds 0.2 bar at temperatures above about 300 K (Vannerberg, 1962). Vaporization takes place primarily by dissociation to Ca(g) and oxygen under neutral and reducing conditions; CaO(g) is the primary vapor phase product in oxidizing atmospheres. Partial pressures of major vapor species and calculated maximum vaporization rates are shown in Figs. 9–12.

d. Sr–O System

SrO(s) is the stable high-temperature condensed phase under neutral and reducing conditions. SrO$_2$(s) is stable in oxidizing atmospheres at lower temperatures; the O$_2$ pressure over SrO$_2$(s) reaches 0.2 bar at about 800 K (Vannerberg, 1962). Vaporization takes place primarily by dissociation to Sr(g), SrO(g), and oxygen species under neutral and oxidizing conditions, while sublimation to SrO(g) dominates in oxidizing atmospheres. The calculated neutral vapor composition is consistent with the observation of Kaufman et al. (1965) from electric deflection experiments that the vapor at 2500 K contains about 5 mol % molecular SrO. Partial pressures of major vapor species and calculated maximum vaporization rates are shown in Figs. 13–16.

Sr$_2$O(g) thermodynamic data—although Sr$_2$O is not a major species and is not listed in the IVTAN or JANAF compilations, the results of Drowart et al. (1964) indicate that it should be included for completeness. Therefore, their estimated molecular constants were adopted and used to evaluate thermodynamic functions: $\langleSr–O–Sr = 180^\circ$, $r(Sr–O) = 0.192$ nm, vibrational fundamentals of 256, 233 (doubly degenerate), and 888 cm$^{-1}$, an electronic ground state degeneracy of 3, and no excited electronic states. The enthalpy of formation of Sr$_2$O(g) was derived from a third-
HIGH-TEMPERATURE VAPORIZATION BEHAVIOR OF OXIDES

Fig. 11. CaO vaporization in 0.2 bar $O_2$.

Fig. 12. CaO maximum vaporization rates. A—$10^{-15}$ bar $O_2$; B—congruent vaporization; C—0.2 bar $O_2$.

Fig. 13. SrO vaporization in $10^{-15}$ bar $O_2$.

Fig. 14. SrO congruent vaporization.

Fig. 15. SrO vaporization in 0.2 bar $O_2$.

Fig. 16. SrO maximum vaporization rates. A—$10^{-12}$ bar $O_2$; B—congruent vaporization; C—0.2 bar $O_2$.

law treatment of the equilibrium data of Drowart et al. (1964) using these calculated functions. As can be seen in the graphs, Sr$_2$O is a minor feature of the vaporization chemistry under each of the environmental conditions.

CaO$_2$(s) thermodynamic data—the enthalpy of formation was recalculated by (Garvin et al., 1987) from the experimental data cited by Glushko et al. (1979b).

e. Ba–O System

BaO(s) is the condensed phase stable at high temperatures under neutral and reducing conditions. In oxidizing atmospheres BaO$_2$(s) is stable at low temperatures; the O$_2$ pressure over BaO$_2$(s) reaches 0.2 bar at about 1000 K (Vannerberg, 1962; Kedrovskii et al., 1967).

The calculated vaporization equilibria shown in Figs. 17–19 indicate that BaO(g) is the principal product for vaporization under oxidizing and neutral conditions, but that Ba(g) becomes important at high temperatures under reducing conditions. It should be pointed out that our calculated neutral vapor composition differs appreciably from the reported results of four separate mass spectrometric studies (Inghram et al., 1955; Newbury et al., 1968; Semenov et al., 1972; Hilpert and Gerads, 1975) in that the latter indicate almost comparable BaO and Ba partial pressures at 1500 to 1800 K. Recent mass spectrometric investigation in our own laboratory (Lamoreaux and Hildenbrand, 1983), however, show that under neutral conditions the ratio $p$(BaO)/$p$(Ba) > 100, so that, as suspected, some reduction of BaO was occurring in the earlier work. The calculated maximum vaporization rate is shown in Fig. 20.

Here again, the major compilations do not include data for the species BaO$_2$ and Ba$_2$O, but they are included here for completeness since they have been observed; molecular constants were selected as noted below. The enthalpies of formation for these species were chosen so as to be consistent with the neutral composition inferred from our mass spectra at low ionizing energy.

Ba$_2$O(g) thermodynamic data—the Gibbs energy functions were calculated using the approximate molecular
HIGH-TEMPERATURE VAPORIZATION BEHAVIOR OF OXIDES

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constants of Kudin (1981): r(Ba–O) = 0.231 nm, \( \angle \text{Ba–O–Ba} = 180^\circ \), electronic ground state degeneracy = 3, no excited electronic states, and vibrational fundamentals of 500, 280(2), and 720 cm\(^{-1} \).

\( \text{Ba}_2\text{O}_3 \) thermodynamic data—the Gibbs energy functions were calculated using the matrix isolation spectroscopy results of Ault and Andrews (1975) for the planar rhombic molecule with a derived O–Ba–O angle of 102° and observed vibrational fundamentals at 402 and 501 cm\(^{-1} \), and the estimated molecular constants of Kudin (1981): r(Ba–O) = 0.21 nm, vibrational fundamentals 470, 330, 270, and 200 cm\(^{-1} \), electronic ground state degeneracy = 1, and no excited electronic states.

f. B–O System

The stable solid phase is \( \text{B}_2\text{O}_3 \), with a melting point of 723 K. Vaporization takes place primarily by evolution of \( \text{B}_2\text{O}_3 \)(g), except that \( \text{B}_2\text{O}_2 \)(g) becomes important at high temperatures under reducing conditions and \( \text{BO}_2 \)(g) is important at low temperatures under oxidizing conditions. The calculated vaporization equilibria and vaporization rates are shown in Figs. 21–24. Partial pressures under reducing conditions were calculated for an \( \text{O}_2 \) partial pressure of \( 10^{-13} \) bar up to 1923 K, where the calculated \( \text{O}_2 \) pressure of the B–\( \text{B}_2\text{O}_3 \) equilibrium reaches this value, and for the \( \text{O}_2 \) pressure of the B–\( \text{B}_2\text{O}_3 \) equilibrium at higher temperatures. If liquid \( \text{B}_2\text{O}_3 \) is the only condensed phase present, its composition will change during vaporization unless \( \text{B}_2\text{O}_3 \)(g) evolution dominates; if the liquid composition is changing, the partial pressures indicated are thus strictly applicable only at the start of vaporization.

g. Al–O System

\( \text{Al}_2\text{O}_3 \) is the stable solid phase in this system. The major gaseous aluminum species are \( \text{Al} \), \( \text{AlO} \), and \( \text{Al}_2\text{O} \), depending on conditions. Some earlier reviews selected data that indicated a much higher thermodynamic stability for \( \text{AlO}_2 \)(g), such that this species dominated the vaporization chemistry under oxidizing conditions. We agree with the recent

\[ \text{Fig. 21. B}_2\text{O}_3 \text{ vaporization in } 10^{-13} \text{ bar O}_2 \text{ below } 1923 \text{ K and vaporization of B–B}_2\text{O}_3 \text{ mixture above } 1923 \text{ K.} \]

\[ \text{Fig. 22. B}_2\text{O}_3 \text{ congruent vaporization.} \]

\[ \text{Fig. 23. B}_2\text{O}_3 \text{ vaporization in } 0.2 \text{ bar O}_2. \]

\[ \text{Fig. 24. B}_2\text{O}_3 \text{ maximum vaporization rates. A—}10^{-13} \text{ bar O}_2 \text{ B—congruent vaporization; C—}0.2 \text{ bar O}_2. \]

IVTAN (Glushko et al., 1981) and JANAF table (Stull et al., 1971, December 31, 1979 unbound supplement) publications that assign a significantly lower stability to AlO$_2$ (g), based primarily on the studies of Ho and Burns (1980). The calculated vaporization equilibria and maximum vaporization rates are shown in Figs. 25-28. Vaporization under reducing conditions was calculated for an O$_2$ pressure of 10$^{-15}$ bar of O$_2$ up to 2230 K, where the calculated O$_2$ pressure of the Al-Al$_2$O$_3$ equilibrium reaches 10$^{-15}$ bar, and for the O$_2$ pressure of the Al-Al$_2$O$_3$ equilibrium above this temperature.

**h. Ga--O System**

The stable solid phase is Ga$_2$O$_3$. The calculated vaporization equilibria and maximum vaporization rates are shown in Figs. 29-32. Vaporization under reducing conditions was calculated for an O$_2$ pressure of 10$^{-15}$ bar up to 1446 K, where the O$_2$ pressure of the Ga--Ga$_2$O$_3$ equilibrium reaches this value, and for the O$_2$ pressure of the Ga--Ga$_2$O$_3$ equilibrium at higher temperatures.

**i. In--O System**

The stable solid phase is In$_2$O$_3$. The calculated vaporization partial pressures and maximum vaporization rates are shown in Figs. 33-36. Partial pressures under reducing conditions were calculated for an O$_2$ pressure of 10$^{-12}$ bar up to 1239 K, where the O$_2$ pressure of the In--In$_2$O$_3$ equilibrium reaches this value, and for the O$_2$ pressure of the In--In$_2$O$_3$ equilibrium at higher temperatures.

**j. Tl--O System**

The stable solid oxide phase under neutral and reducing conditions, and in 0.2 atm of O$_2$ above about 1060 K, is Tl$_2$O. Tl$_2$O is the stable phase at lower temperatures under oxidizing conditions. Calculated partial pressures and maximum rates for vaporization processes are shown in Figs. 37-40. Partial pressures over Tl$_2$O under reducing conditions were calculated for an O$_2$ pressure of 10$^{-15}$ bar up to 731 K, where the O$_2$ partial pressure of the Tl--Tl$_2$O equilibrium

**Fig. 25.** Al$_2$O$_3$ vaporization in 10$^{-15}$ bar O$_2$ below 2230 K and vaporization of Al--Al$_2$O$_3$ mixture above 2230 K.

**Fig. 26.** Al$_2$O$_3$ vaporization in 0.2 bar O$_2$.

**Fig. 27.** Al$_2$O$_3$ vaporization in 0.2 bar O$_2$.

**Fig. 28.** Al$_2$O$_3$ maximum vaporization rates. A—10$^{-15}$ bar O$_2$; B—congruent vaporization; C—0.2 bar O$_2$.
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Fig. 29. Ga$_2$O$_3$ vaporization in 10$^{-15}$ bar O$_2$ below 1446 K and vaporization of Ga–Ga$_2$O$_3$ mixture above 1446 K.

Fig. 30. Ga$_2$O$_3$ congruent vaporization.

Fig. 31. Ga$_2$O$_3$ vaporization in 0.2 bar O$_2$.

Fig. 32. Ga$_2$O$_3$ maximum vaporization rates. A—10$^{-15}$ bar O$_2$; B—congruent vaporization; C—0.2 bar O$_2$.

Fig. 33. In$_2$O$_3$ vaporization in 10$^{-15}$ bar O$_2$ below 1239 K and vaporization of In–In$_2$O$_3$ mixture above 1239 K.

Fig. 34. In$_2$O$_3$ congruent vaporization.

Fig. 35. In$_2$O$_3$ vaporization in 0.2 bar O$_2$.

Fig. 36. In$_2$O$_3$ maximum vaporization rates. A—10$^{-15}$ bar O$_2$; B—In-In$_2$O$_3$; C—congruent vaporization; D—0.2 bar O$_2$.

Fig. 37. Tl$_2$O vaporization in 10$^{-15}$ bar O$_2$ below 731 K and vaporization of Tl-Tl$_2$O mixture above 731 K.

Fig. 38. Tl$_2$O congruent vaporization.

Fig. 39. Tl$_2$O vaporization below 1060 K and TlO vaporization above 1060 K in 0.2 bar O$_2$.

Fig. 40. Maximum vaporization rates of thallium oxides. A—Tl$_2$O in 10$^{-15}$ bar O$_2$; B—Tl-Tl$_2$O equilibrium vaporization; C—Tl$_2$O congruent vaporization; D—Tl$_2$O vaporization in 0.2 bar O$_2$; E—Tl$_2$O vaporization in 0.2 bar O$_2$. 

reaches this value, and for the $O_2$ pressure of the $Tl-Tl_2O$ equilibrium at higher temperatures. Partial pressures for vaporization in 0.2 bar of $O_2$ were calculated for $Tl_2O_3$ up to 1060 K, and for $Tl_2O$ at higher temperatures.

k. Si-O System

Calculated partial pressures for vaporization of $SiO_2$ are shown in Figs. 41-44. $SiO(g)$ is the principal silicon-containing vaporization product under neutral and reducing conditions, while $SiO_2(g)$ is favored under oxidizing conditions below about 2500 K.

$SiO_2$ (quartz, cristobalite, liquid) thermodynamic data—the CODATA (Cox, 1978) value of the enthalpy of formation of quartz was accepted. Other data were taken from the recent article of Richet et al. (1982), which reviewed the available literature.

$SiO_2(g)$ thermodynamic data—Gibbs energy functions were calculated using the molecular constants of Khanna et al. (1981) for a planar $Si-O-Si$ molecule with the terminal atoms lying on opposite sides of the central $O-Si$ bond axis: $\angle Si-O-Si = O-Si-O = 109.5^\circ$, $r(Si-O, terminal) = 0.174$ nm, $r(Si-O, central) = 0.151$ nm, ground electronic state degeneracy = 1, and no excited electronic states. The vibrational fundamentals as measured by infrared and Raman matrix isolation spectroscopy were 1222, 804, 766, 252, and 79 cm$^{-1}$; the remaining fundamental at 180 cm$^{-1}$ was calculated by force constant calculations (Khanna et al., 1981). The Gibbs energy functions calculated using these constants are 2.8 K greater than those calculated using the data of Anderson and Ogden (1969) for a molecule with $D_{3h}$ symmetry. The enthalpy of formation was then calculated by the third-law method from the mass spectrometric data of Porter et al. (1955) and of Zmbov et al. (1973).

l. Ge-O System

The stable condensed phase below 1308 K is tetragonal $GeO_2$; the hexagonal crystal structure is stable from 1308 K to the melting temperature, 1388 K (Glushko et al., 1979a). Calculated partial pressures for vaporization of $GeO_2$ are shown in Figs. 45-48. $GeO$ is the major germanium-contain-
ing vapor species under most conditions, with the polymeric species GeO\textsubscript{2} and Ge\textsubscript{2}O\textsubscript{3} becoming important at higher temperatures under reducing conditions.

\textbf{GeO\textsubscript{2}} \textit{(g)} thermodynamic data—Gibbs energy functions were calculated using the molecular data of Ogden and Ricks (1970) which were estimated except for the observed vibrational fundamentals at 601 and 666 cm\textsuperscript{-1}: D\textsubscript{2h} symmetry, symmetry number = 4, $r$(Ge–O) = 0.187 nm, $\angle$O–Ge–O = 83°. The electronic ground state degeneracy was taken as unity, no excited electronic states were considered, and the remaining vibrational fundamentals of 120, 500, 450, and 80 cm\textsuperscript{-1} were estimated by analogy with the alkali metal M\textsubscript{2}O\textsubscript{2} species (Lamoreaux and Hildenbrand, 1984). The enthalpy of vaporization was chosen to yield calculated vaporization equilibria consistent with the mass spectrometric data of Drowart \textit{et al.} (1965).

\textbf{Ge\textsubscript{2}O\textsubscript{3}} \textit{(g)} thermodynamic data—Gibbs energy functions were calculated using the molecular data of Ogden and Ricks (1970), which were estimated except for doubly degenerate vibrational fundamentals at 824 and 438 cm\textsuperscript{-1}: D\textsubscript{3h} symmetry, symmetry number = 6, $r$(Ge–O) = 0.185 nm, $\angle$O–Ge–O = 100°, $\angle$Ge–O–Ge = 140°. The electronic ground state degeneracy was taken to be 1, no excited electronic states were considered, and the remaining vibrational fundamentals were estimated by analogy to Be\textsubscript{3}O\textsubscript{3}: 159(2), 70(2), 150, 70(2), and 90 cm\textsuperscript{-1}. The enthalpy of formation was chosen to yield calculated vaporization equilibria in agreement with the mass spectrometric studies of Drowart \textit{et al.} (1965).

\textbf{m. Sn–O System}

The stable condensed phase is SnO\textsubscript{2}. Calculated partial pressures for vaporization of SnO\textsubscript{2} are shown in Figs. 49–52. SnO\textsubscript{2}(g) is the principal tin-containing vaporization species, with the polymeric species Sn\textsubscript{2}O\textsubscript{4}, Sn\textsubscript{3}O\textsubscript{4}, and Sn\textsubscript{4}O\textsubscript{4} becoming important at higher temperatures under reducing conditions.

\textbf{SnO\textsubscript{2}} \textit{(g)} thermodynamic data—because the existing spectroscopic data are insufficient to adequately determine...
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Fig. 49. SnO₂ vaporization in 10⁻¹⁵ bar O₂ below 1163 K and vaporization of Sn-SnO₂ mixture above 1163 K.

Fig. 50. SnO₂ congruent vaporization.

Fig. 51. SnO₂ vaporization in 0.2 bar O₂.

Fig. 52. SnO₂ maximum vaporization rates. A—10⁻¹⁵ bar O₂; B—Sn-SnO₂ equilibrium; C—congruent vaporization; D—0.2 bar O₂.

The molecular constants of Sn₃O₅(g), the estimated S₉²₉₈/R value of Colin et al. (1965) was used along with the estimated value C₉/R = 2.3 g-at. derived by analogy to other gaseous compounds to calculate the Gibbs energy functions shown in Table 2. The enthalpy of formation was selected to yield calculated equilibria in agreement with the results of Colin et al.; the thermodynamic data presented in Tables 2 and 3 are consistent with observed partial pressures over the temperature range of the mass spectrometer studies.

Sn₅O₃(g) thermodynamic data—the data were derived as for Sn₂O₃(g), except that the value of C₉/R was estimated as 2.5/g-at.

Sn₆O₆(g) thermodynamic data—the data were derived as for Sn₃O₅(g).

n. Pb–O System

The stable condensed oxide phase under neutral and reducing conditions, and in 0.2 atm of O₂ at temperatures above about 800 K, is PbO. Calculated partial pressures for vaporization of PbO are shown in Figs. 53–56. The predominant vapor phase species under neutral and oxidizing conditions are PbO and its polymers Pb₂O₂, Pb₃O₃, Pb₄O₄, Pb₅O₅, and Pb₆O₆; under reducing conditions the predominant vapor species is atomic lead.

Pb₂O₂, Pb₃O₃, Pb₄O₄, Pb₅O₅, and Pb₆O₆ thermodynamic data—Drowart, Colin, and Exsteen (1965) and Kazenas, Chizhikov, and Tsvetkov (1968) analyzed the vapors over PbO by mass spectroscopy. The thermodynamic properties of the gaseous PbO polymers given in Tables 2 and 3 were derived from the results of Drowart and co-workers, who made measurements to 1200 K and observed all five of these species. Kazenas et al. made measurements at temperatures up to 950 K and did not observe the pentamer or hexamer. The enthalpies of formation and entropies at 298 K selected by Drowart et al. were accepted for the dimer, trimer, and tetramer; the Gibbs energy functions for these species were derived by assuming that C₉/R = 3.0/g-at. at all temperatures above 298 K. Although this heat capacity
value seems somewhat large, calculations using the resulting thermodynamic properties are in excellent agreement with Drowart's gas phase equilibria over the temperature range of measurements. Equilibrium data are available for PbO \(_2\) and Pb\(_6\)O\(_6\) at only one temperature, 1200 K. The entropy at 298 K for these two species was estimated by extrapolating the values for the monomeric through tetrameric species, and the estimated value \(C_R^* = 3.0\) was used to calculate values of the Gibbs energy functions. The gas phase equilibria at 1200 K were then used to derive values of the enthalpies of formation.

**o. Zn–O System**

The stable solid phase is ZnO. Vaporization takes place predominantly by dissociation into gaseous Zn and O\(_2\), and a much smaller amount of ZnO\(_g\). Figures 57–60 show calculated partial pressures for vaporization of ZnO. The Gibbs energy function of gaseous ZnO \(_g\) was calculated using the estimated internuclear distance of Brewer and Rosenb-
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\( r(Zn-O) = 0.174 \text{ nm} \) and the value of the vibrational fundamental, 810 cm\(^{-1}\), from the matrix-isolation study of Prochaska and Andrews (1980). The selected value of \( \Delta_H^{298}/R \) for ZnO(g), 10.9 ± 1 kK, was derived using the mass spectrometric relative intensity measurements of Grade et al. (1982) for the vaporization of ZnO(s), and is in reasonable accord with the selected value of Pedley and Marshall (1983), 13.1 ± 5 kK.

p. Cd-O System

The stable solid phase is CdO. Vaporization takes place predominantly by dissociation into gaseous Cd and O\(_2\) and a much smaller amount of CdO(g). Figures 61–64 show calculated partial pressures for vaporization of CdO. The Gibbs energy function of CdO(g) was calculated using the estimated internuclear distance of Brewer and Rosenblatt (1969) for the nondegenerate electronic ground state, \( r(Cd-O) = 0.185 \text{ nm} \). The vibrational fundamental, 719 cm\(^{-1}\), was taken from the matrix-isolation study of Prochaska and Andrews (1980). The selected value of \( \Delta_H^{298}/R \) for CdO(g), 15.6 ± 1 kK, was derived from the mass spectrometric relative intensity measurements of Grade and Hirschwald (1982) for the vaporization of CdO(s), and is in good accord with the selected value of Pedley and Marshall (1983), 15.1 ± 10 kK, and the lower limit found by Behrens and Mason (1981), 13.7 kK.

q. Hg-O System

The stable solid phase is HgO. Vaporization takes place primarily by dissociation into gaseous Hg and O\(_2\) and a smaller amount of HgO(g). Figures 65–68 showed calculated partial pressures for vaporization of HgO. The Gibbs energy function of HgO(g) was calculated using the estimated internuclear distance of Brewer and Rosenblatt (1969), 0.195 nm, for the nondegenerate electronic ground state and the vibrational fundamental, 676 cm\(^{-1}\), of Butler et al. (1979) determined by matrix-isolation spectroscopy. The calculated values of \(- (G_T - H_{298}^f)/RT\) are about 0.1 greater...
Fig. 62. CdO congruent vaporization.

Fig. 63. CdO vaporization in 0.2 bar O₂.

Fig. 64. CdO maximum vaporization rates. A—10⁻¹⁵ bar O₂; B—congruent vaporization; C—0.2 bar O₂.

Fig. 65. HgO vaporization in 10⁻¹⁵ bar O₂ below 361 K and vaporization of Hg–HgO mixture above 361 K.

Fig. 66. HgO congruent vaporization.

Fig. 67. HgO vaporization in 0.2 bar O₂.

than those of JANAF (Stull et al., 1971) from 298 to 2000 K. The selected value of $\Delta H_{298}^{\circ}/R$ for HgO(g), $11.2 \pm 1$ kK, was derived from the mass spectrometric ion intensity ratio measurements of Grade and Hirschwald (1982). JANAF (Stull et al., 1971), and Pankratz (1982) had selected the estimated value 5 $\pm$ 8 kK.

3. High-Temperature Equilibria and Reaction Rates

Calculations using the selected thermochemical data were discussed in the previous paper (Lamoreaux and Hildenbrand, 1984). The basic equations are presented here so that species partial pressures and maximum vaporization rates can be calculated for specific temperatures and oxidation conditions.

3.1. Mathematics of Vaporization Calculations

For many vaporization conditions one or two vapor species are predominant, and calculation of the chemical equilibrium from thermodynamic data is straightforward. Calculations can be more complicated when several species are present in significant quantities. The following procedure is a general method for calculating the equilibrium pressures of vapor species in equilibrium with a condensed phase of known composition.

The chemical species present at equilibrium in the vaporization of a condensed binary oxide can be described mathematically as being formed by linear combination of the vaporizing oxide $M_bO_x$ and oxygen $O_2$ according to the general reaction for the production of species $i$,

$$d(i) = x(i)/b$$

and

$$e(i) = [by(i) - cx(i)]/2b.$$  

We define the Gibbs energy of species $i$ at temperature $T$ as

$$G_{\text{eq}}^+(i)/RT = (G_{\text{eq}}^+(i)/RT - \Delta iH_{298}^{\circ}(i)/RT).$$

The Gibbs energy change for the reaction producing species $i$ from $M_bO_x$ (s or l) and $O_2(g)$, $\Delta G_{\text{eq}}^+(i)$, is given by

$$\Delta G_{\text{eq}}^+(i)/RT = \frac{G_{\text{eq}}^+(i)/RT - d(i)}{RT} \times G_{\text{eq}}^+(M_bO_x(s \text{ or } l))/RT,$$

and the equilibrium constant for producing gas species $i$ is

$$K(i) = \exp[-\Delta G_{\text{eq}}^+(i)/RT].$$

where the pressures $p(i)$ are considered low enough that they are equal to fugacities, and $a(1)$ is the activity of $M_bO_x$. If $M_bO_x$ is a pure condensed phase, its activity is unity, and

$$p(i) = k(i)p(O_2)^{e(i)}$$

for the gas species. If the oxygen pressure is known, the pressure of each species $i$ can be calculated from this equation.

For congruent vaporization, the vapor composition is the same as the condensed phase, and

$$\sum [p(i)x(i)] = b,$$

$$\sum [p(i)y(i)] = c.$$  

This leads to the expression

$$\sum \{K(i)p(O_2)^{e(i)}[cx(i) - by(i)]\} = 0,$$

where summation is over the gaseous species present. In practice, this equation is solved for $p(O_2)$ by graphical interpolation or by numerical methods. The value found for $p(O_2)$ is then used in Eq. (8) to find the other partial pressures.

For the above calculations to correspond to equilibrium vaporization, they must be used for vaporization of the condensed oxide phases or phases stable under the particular vaporization conditions. Where more than one oxide phase is a possibility, the stable phase or phases must be determined. Two condensed oxide phases of fixed composition at a given temperature are related by the equilibrium

$\text{Oxide}(1) = \text{Oxide}(2) + fO_2(g).$  

Oxide(1) is assumed to have the greater oxygen activity. The equilibrium constant for this reaction is

$$K_{eq} = a(2)p(O_2)^{f}/a(1).$$

If both condensed phases are at equilibrium, their activities are unity, and the pressure of $O_2$ is given by the equation

$$p_{eq}(O_2) = K_{eq}^{1/f}.$$  

Oxide (1) is the stable phase for $O_2$ pressures greater than $P_{eq}(O_2)$, and oxide (2) is stable for $O_2$ pressures less than $P_{eq}(O_2)$ at the given temperature.
3.2. Vaporization Rate Calculations

Maximum vaporization rates are calculated using the Hertz–Knudsen equation of classical kinetic theory, which applies to free vaporization from an uncontaminated surface at low pressures. For gas species i evolving from the surface, the maximum vaporization rate \(dn(i)/dt\) in mol cm\(^{-2}\) s\(^{-1}\) is

\[
\frac{dn(i)}{dt} = \frac{p(i)}{[2\pi M(i)RT]^{1/2}},
\]

where \(M(i)\) and \(p(i)\) are the gram molecular weight and equilibrium partial pressure of vapor species i, and \(R\) and \(T\) are the molar gas constant and absolute temperature. Since 1 bar is \(10^5\) dyn cm\(^{-2}\) and \(R\) is 8.3144 \times 10^6\ erg mol\(^{-1}\) deg\(^{-1}\), for pressures in bar, this is equivalent to

\[
\frac{dn(i)}{dt} = 43.8 \left(\frac{p(i)}{[M(i)T]^{1/2}}\right) \text{ mol cm}^{-2} \text{s}^{-1}.
\]

Calculation of maximum vaporization rates is more difficult for incongruent than for congruent processes. In general, solid-phase activities during the vaporization process are not known, and calculated maximum vaporization rates of oxides that deviate from their original stoichiometry should be considered indicative rather than exact (Beruto et al., 1981). In the present work, maximum vaporization rates have been calculated for incongruent, as well as congruent vaporization. Only initial vaporization rates, for which no condensed phase composition changes have taken place, are considered. Vaporization rates are expressed in terms of the mass of originally present oxide \(M_0\) lost as measured by the volatility of metal atoms. The total mass loss thus calculated is

\[
\frac{dm}{dt} = 44.3 \left(\frac{M(M_0)}{b}\right) \sum \left(\frac{p(i)x(i)}{[M(i)T]^{1/2}}\right),
\]

where \(dm/dt\) is the mass loss rate in g cm\(^{-2}\) s\(^{-1}\), \(M_0\) is the formula of the condensed oxide, and \(x(i)\) and \(M(i)\) are the number of gram atoms of metal per mole and gram molecular weight of gas species i.

Although actual vaporization rates may be lower because of kinetic factors, the calculated maximum vaporization rate is useful as a rough guide to material loss rates. Recent references on maximum vaporization rates include works by Turkdogan (1980) and Beruto et al. (1981).

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5. References

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Stull, D. R. et al. (Eds.), JANAF Thermochemical Tables, 2nd ed. NSRDS-NBS 37 (U.S. GPO, Washington, DC, 1971). Individual table supplements to this reference are identified by the data of their issue. The published collections of supplementary tables are referenced separately. JANAF data not contained in the 1971 compendium or the collected supplements (Chase et al., 1974, 1975, 1978, 1982) are referenced as dated supplements to the 1971 work.