Thermodynamic Properties of Some Metal Oxide-Zirconia Systems

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Summary

Metal oxide-zirconia systems are a potential class of materials for use as structural materials at temperatures above 1900 K. These materials must have no destructive phase changes and low vapor pressures. Both alkaline earth oxide (MgO, CaO, SrO, and BaO)-zirconia and some rare earth oxide (Y$_2$O$_3$, Sc$_2$O$_3$, La$_2$O$_3$, CeO$_2$, Sm$_2$O$_3$, Gd$_2$O$_3$, Yb$_2$O$_3$, Dy$_2$O$_3$, Ho$_2$O$_3$, and Er$_2$O$_3$)-zirconia systems are examined. For each system, the phase diagram is discussed and the vapor pressure for each vapor specie is calculated via a free energy minimization procedure. The available thermodynamic literature on each system is also surveyed. Some of the systems look promising for high temperature structural materials.
I. Introduction

The development of engine materials has been dictated by ever increasing demands for high temperature operation. In a recent report\(^1\) on potential materials for engine applications above 3000 F (1900 K), the various issues involved in selection of such a material were outlined. A primary issue at these high temperatures is surface stability, in particular oxidation resistance. At lower temperatures, metals and non-oxides achieve their oxidation resistance by the formation of a protective oxide film. However at temperatures above 1900 K, it was shown that transport rates are so fast that reasonable environmental durability cannot be achieved with a non-oxide. Therefore it was concluded that oxides showed the most promise for application at temperatures above 1900 K.

The criteria for selecting an oxide include a high melting point, low vapor pressure, and solid phase stability. One of the most interesting refractory oxides is ZrO\(_2\), which has a melting point of 2973 K and a low vapor pressure. The primary difficulty with zirconia are its phase changes:\(^2\)

\[
\begin{align*}
1443 \text{ K} & \quad 2643 \text{ K} \\
\text{Monoclinic} = \text{Tetragonal} = \text{Cubic} & \quad (1) \\
1223 \text{ K} & 
\end{align*}
\]
The first phase change is the most catastrophic. In addition zirconia has limited thermal shock resistance.

The solution to the phase change problem has been to add a second oxide. Depending on the amount of second oxide added, this can work in several ways. A small amount can stabilize a mixture of the monoclinic and tetragonal phase. This is known as partially stabilized zirconia and has generated a great deal of interest. For the temperatures greater than 1900 K, partially stabilized zirconia is of limited interest. A further addition of a second oxide leads to formation of the cubic phase and is termed fully stabilized zirconia. These systems are of interest in the extremely high temperature range. Finally some oxides form compounds with zirconia. These compounds may show the desirable properties of zirconia and eliminate some of the less desirable properties.

The purpose of this report is to discuss the thermodynamic properties of a number of these systems. The primary emphasis will be on fully stabilized cubic zirconia and high melting zirconia-metal oxide compounds. The requirements for fully stabilized zirconia are not completely understood. The second oxide must be cubic and the metal must be of a comparable ionic radius. For these high temperatures the second oxide must be refractory. There is also some evidence that strong interactions between the
zirconia and the second oxide should not occur. The most common stabilizers are the alkaline earth oxides—MgO and CaO. These systems will be discussed in detail. The remaining alkaline earth oxides—SrO and BaO—do not stabilize the cubic phase, but form high melting compounds with zirconia. These will also be discussed. In addition to the alkaline earth metal oxides, many of the rare earth oxides are stabilizers for zirconia. The systems which will be discussed are CeO$_2$-ZrO$_2$, Y$_2$O$_3$-ZrO$_2$, Sc$_2$O$_3$-ZrO$_2$, La$_2$O$_3$-ZrO$_2$, Sm$_2$O$_3$-ZrO$_2$, Gd$_2$O$_3$-ZrO$_2$, Yb$_2$O$_3$-ZrO$_2$, Dy$_2$O$_3$-ZrO$_2$, Ho$_2$O$_3$-ZrO$_2$, and Er$_2$O$_3$-ZrO$_2$. In general these oxide additions do not form compounds with ZrO$_2$, but they do stabilize the cubic phase.

As mentioned, kinetics for temperatures greater than 1900 K are generally quite rapid. Therefore thermodynamics can be used with good reliability to predict the chemical behavior of a particular material at these temperatures. The major concern is volatility. Vapor pressures for each of the various oxide systems are presented. The best thermodynamic data available is used. The appendix includes a discussion of the sources of thermodynamic data and a complete listing of the data used.

There are a number of issues to be considered in these vapor pressure calculations. Consider first pure ZrO$_2$(s). It is known to vaporize as follows\textsuperscript{7,8}:
\[ \text{ZrO}_2(s) = \text{ZrO}_2(g) \]  

(2)

\[ \text{ZrO}_2(s) = \text{ZrO}(g) + \text{O}(g) \]  

(3)

\[ \text{ZrO}_2(s) = \text{Zr}(g) + \text{O}_2(g) \]  

(4)

Subject to the mass balance constraint in a closed system:

\[ 2 \Sigma \text{Zr containing species in the vapor} = \Sigma \text{O containing species in the vapor} \]  

(5)

These four equations can be solved simultaneously or a free energy minimization program such as SOLGASMIX\textsuperscript{9} can be used. It should be noted that in order to obtain equilibrium vapor pressures from SOLGASMIX, one atmosphere of argon was put in as a reactant. The results of such a calculation for pure \text{ZrO}_2 are shown in Figure 1, based on data listed in the appendix. For reactions (3) and (4), where oxygen is released, an overpressure of oxygen will suppress the vaporization process. Figure 2 shows the dramatic effect of one atmosphere of oxygen on suppressing the amount of \text{ZrO}(g) and \text{Zr}(g). However for reaction (2) where no oxygen is released, the oxygen atmosphere has no effect. Thus it is
important to know the dominant vaporization route in assessing an oxide's performance in a particular high temperature environment.

In many cases, the second oxide may have a much higher vapor pressure than ZrO$_2$. This vapor pressure can be calculated using the SOLGASMIX program, with the mass balance now including both metal atoms. Corrections for the lowering of the vapor pressure by the particular solid solution must also be considered. Vapor pressures for a number of alkaline earth--zirconia and rare earth--zirconia systems will be presented in this report. The thermodynamic data used for each of these systems is listed in the appendix. It has been pointed out that in some situations the vaporization of binary oxides is complicated by the presence of binary oxides in the vapor, such as LiBO$_2$(v) over Li$_2$O·B$_2$O$_3$.$^{10}$ In a case like this, the binary oxide cannot be treated as a pseudo-binary system. The vapor pressures of each constituent oxide can no longer be simply calculated from the vapor pressures of the pure oxides and their activities in solution. There is no evidence of this occurring in the various zirconia-metal oxide systems discussed here, but one must be aware of this possibility.

Other factors which can be predicted from thermodynamics include phase changes, reactivity with other gases, and oxide
demixing. As mentioned, the purpose of the second oxide is to eliminate the destructive phase changes present in pure ZrO$_2$. This can be checked with an accurate phase diagram, which unfortunately is not available for all systems. Reactivity with other gases depends on the application, but is likely to include water vapor.

Oxide demixing is not entirely a thermodynamic problem, but should be considered in any discussion of binary oxides at high temperatures.$^{11,12}$ In many applications, such as coatings, the oxide may be under an oxygen potential gradient. Under these conditions, the faster moving metal ion is likely to move to the region of lower oxygen potential. This composition change in the ceramic may lead to a degradation in high temperature properties.

II. Alkaline Earth Oxides-Zirconia Systems

MgO-ZrO$_2$ System

This system has been the subject of numerous studies. Despite these studies, the phase diagram is not firmly established. The most recent phase diagram is shown in
Figure 3. As mentioned, the primary field of interest is the cubic phase field. This phase has a eutectoid at $1679^\circ K$ ($1406^\circ C$) and 13.5 mol/o MgO.

Eutectoid decomposition of the cubic phase is a feature of both MgO and CaO stabilized ZrO$_2$. Clearly this is a factor in cycling cubic ZrO$_2$:

$$c(ss) \rightarrow t(ss) + MgO \quad (6)$$

This phase transformation has been studied in detail$^{14}$ and is fairly slow. It is also further slowed by the addition of SrO.$^{14}$ At still lower temperatures, the tetragonal phase would decompose into the monoclinic phase. Both phase transformations may cause difficulties, particularly the latter.

The liquidus diagram for ZrO$_2$-MgO is shown in Figure 4.$^{15}$ There is a eutectic with the 1:1 mixture at $2100^\circ C$, which is agreed on by several investigators.$^{13,14}$ However there is some question about the existence of an intermediate compound. Most of the phase diagrams do not show an intermediate compound. However MgO·ZrO$_2$ is available commercially.* Several investigators have reported

*Alfa Products, Danvers, MA.
metastable ordered compounds of composition \(2 \text{MgO} \cdot 5 \text{ZrO}_2\) and \(\text{MgO} \cdot 6 \text{ZrO}_2\).\(^{13}\)

One of the major obstacles to the use of this material is the high vapor pressure of MgO—it will preferentially vaporize.\(^{13,16}\) Vaporization studies of MgO indicate that the primary decomposition products are \(\text{Mg}(g)\) and \(\text{O}(g)\), with only a very small amount of \(\text{MgO}(g)\).\(^{17}\) We were unable to find data on how activity of MgO changes in solution. In order to estimate an upper limit, we shall use the value of \(a(\text{MgO})\) along the MgO-rich cubic phase boundary. Since this is in equilibrium with essentially pure MgO, the activity of MgO is essentially unity. Based on this, the vapor pressure for MgO is shown in Figure 5.

**CaO-ZrO\(_2\) System**

This system is similar to the MgO-ZrO\(_2\) system, but has some important differences. A recent phase diagram is shown in Figure 6.\(^{18}\) Unlike the MgO-ZrO\(_2\) system, there is general agreement on the formation of several stable intermediate compounds. At lower temperatures, there is a compound \(\text{CaO} \cdot 4(\text{ZrO}_2)\). There is also a compound \(\text{CaO} \cdot \text{ZrO}_2\), which is stable to its melting point of 2252 K. This compound itself has been considered for use as an ultra high temperature structural material and will be discussed. Like the
MgO-ZrO$_2$ system, the CaO-ZrO$_2$ system forms cubic phase euctectoid and its decomposition must be considered. The CaO-ZrO$_2$ system is quite suitable for electrochemical measurements and there is some information on the activity of CaO in solid ZrO$_2$ solution.$^{19,20}$ These measurements use a cell of the form:

$$O_2, Pt|CaO, CaF_2|CaF_2|ZrO_2-CaO, CaF_2|Pt, O_2$$

(7)

The overall cell reaction is simply:

$$\text{CaO}(a=1) = \text{CaO(solid solution)}$$

(8)

$$\Delta G = -2EF = -RT \ln a(\text{CaO-ss})$$

(9)

Here $\Delta G$ is the Gibbs free energy of formation, $E$ is the measured EMF, $F$ is the Faraday constant, and $R$ is the gas constant. Measurements are carried out between 1200 and 1550 K and the results are shown in Figure 7. These temperatures are somewhat lower than those of interest to us, but nonetheless, the measurements give an indication of the strong negative deviations from Raoult's Law, as shown in the diagram. These indicate a strong interaction between CaO and ZrO$_2$ which is not surprising, given the eventual compound formation. Note the CaO activity is about an order of
magnitude lower than that predicated for Raoult's law behavior or in total about two orders of magnitude lower than for pure CaO. This type of data is very important in evaluating the suitability of ZrO₂ cubic solid solutions for use at very high temperatures.

These data also point to the as-yet unsettled differences in the CaO-ZrO₂ phase diagram. They suggest a a temperature independent solubility limit of 17 m/o CaO in ZrO₂ over the temperature range 1200-1500 K. The most recent phase diagram (Figure 6) shows a solubility limit of about 7 m/o CaO below 1413 K and a temperature dependent solubility limit which is about 17 m/o CaO at 1413 K and above. These differences are very likely due to the slow phase changes at these temperatures.

Vapor pressure calculations for both pure CaO and CaZrO₃ are shown in Figures 8 and 9. For CaO, as with MgO, the primary vapor products are the metal atom and oxygen. These figures indicate the compound lowers the vapor pressure of Ca by about two orders of magnitude. This is consistent with the solid solution data in Figure 7, for the solid solution in equilibrium with the compound.
SrO-ZrO$_2$

This system and the BaO-ZrO$_2$ system differ from the two systems previously discussed in that there is limited solid solubility and the cubic phase is not stabilized. The reasons for this are not entirely clear. Some authors have given arguments based on size factors—the strontium and barium atoms have radii too large to enter the zirconia lattice. Other authors have based arguments on thermodynamic factors—the strontium and barium zirconates are so stable that a two phase region of zirconia and zirconate is favorable over a solid solution.

Therefore in this system, the materials of interest are the compounds. These are shown in the phase diagram$^{21}$ in Figure 10. There are several high melting intermediate phases, including SrZrO$_3$, Sr$_4$Zr$_3$O$_{10}$, and Sr$_2$ZrO$_4$. The first of these has a low coefficient of thermal expansion, suggesting good resistance to thermal shock.$^1$

The calculated vapor pressures for the vapor above SrO and SrZrO$_3$ are shown in Figures 11 and 12. As with the other systems discussed, the alkaline earth oxide vaporizes preferentially to the metal atom and atomic and molecular oxygen, with the metal oxide vapor roughly an order of magnitude lower.
It has been reported that this material is quite susceptible to oxide demixing, with a strong separation appearing between the SrO and ZrO$_2$ oxides under the influence of an oxygen potential.$^{22}$ This behavior must be considered when using this material under such conditions. Although not shown on the phase diagram, it has also been reported that SrZrO$_3$ undergoes the following phase transformations$^{23}$:

\[
\begin{align*}
923 \text{ K} & \rightarrow 1003 \text{ K} & 1443 \text{ K} \\
\text{orthorhombic} & \rightarrow \text{tetragonal 1} & \rightarrow \text{tetragonal 2} & \rightarrow \text{cubic}
\end{align*}
\]

These may be limiting factors in the application of SrZrO$_3$ as a structural material.

**BaO-ZrO$_2$**

This system is somewhat similar to the SrO-ZrO$_2$ system in that BaO does not stabilize cubic ZrO$_2$. We could not locate a phase diagram for this binary system. However BaZrO$_3$ is known to be a stable compound and there are several sources of thermodynamic data for the solid as well as vapor pressure measurements.

Figures 13 and 14 show the vapor pressures for the major vapor species over BaO and BaZrO$_3$. Note that the major vapor specie is BaO(g), not the metal atoms and oxygen as in the other systems discussed. This is important, since an oxygen overpressure will not suppress vaporization in this case.
Figure 15 shows the experimental data\textsuperscript{10,24-27} on BaZrO\textsubscript{3}. Note the calculated vapor pressures from the thermodynamic data in the appendix is somewhat lower than the measured \( P(\text{BaO}) \). It may be that the measured BaZrO\textsubscript{3} compounds are a little BaO rich or there may be some inconsistencies in the thermodynamic data. The Odoj and Hilpert\textsuperscript{24-26} data was taken with a Knudsen Cell Mass Spectrometer using a molybdenum cell. There was no evidence of reaction with the cell. The data of Berkowitz-Mattuck\textsuperscript{10} was taken with a Knudsen Cell Mass Spectrometer and a rhenium cell. The rhenium cell is expected to be more inert than the molybdenum cell. The data of Glenn et. al.\textsuperscript{27} is a not equilibrium measurement--it was simply the recession rate of an exposed surface. This was converted to a vapor pressure by the Hertz-Knudsen-Langmuir equation:

\[
J = \frac{P}{(2\pi MRT)^{1/2}}
\]

(11)

Here \( J \) is the flux leaving the surface, \( P \) is the vapor pressure, \( M \) is the molecular weight of the vapor leaving the surface, \( R \) is the gas constant, and \( T \) is the temperature. When the appropriate conversion factors are added, this equation becomes:

\[
P(\text{atm}) = (2.26 \times 10^{-2}) J(\text{mole/cm}^2\text{-sec})(M(\text{gm/mole}))^{1/2}(T(\text{OK}))^{1/2}
\]

(12)

Despite the fact that this is a non-equilibrium measurement, the pressures measured are quite close to the calculated
equilibrium values.

In general the alkaline-stabilized zirconia cubic solutions compounds have some severe limitations for applications above 1900 K. The major problem is likely to be preferential volatilization of the alkaline earth oxides. Other difficulties include phase changes and possible oxide demixing. The materials with the least limitations are SrZrO$_3$ and CaZrO$_3$.

III. Rare Earth Oxide-Zirconia Systems

The rare earth oxide-zirconia systems may be more promising. In general they have lower vapor pressures and some exhibit very high melting points. The Russian group of Belov and Semenov$^{28-32}$ have looked extensively at these binary oxide systems.

Consider first the the pure rare earth oxides. These vaporize as follows:

$$M_2O_3(s) = 2 MO(g) + O(g) \quad (13)$$

This is with the exception of Yb, which decomposes as:

$$Yb_2O_3(s) = 2 Yb(g) + 3 O(g) \quad (14)$$
In their initial survey, Belov and Semenov\textsuperscript{28} list the various rare earth oxides and their vapor pressures relative to Lu$_2$O$_3$. Their data is given in Table I. They also point out that the zirconia systems with Gd$_2$O$_3$, Dy$_2$O$_3$, Yb$_2$O$_3$, Ho$_2$O$_3$, Er$_2$O$_3$, and Y$_2$O$_3$ exhibit liquidus maxima. They studied the volatilization of each of these and the Lu$_2$O$_3$-ZrO$_2$ system in the temperature range 2773-2823 K. Only the Yb$_2$O$_3$-ZrO$_2$ and Gd$_2$O$_3$-ZrO$_2$ systems decompose, preferentially losing the stabilizing oxide.

Belov and Semenov have examined a range of rare earth oxide-zirconia stabilized systems and found the following general behavior. These systems first undergo a period of incongruent vaporization, during which the oxides lose oxygen and go from ZrO$_2$(M$_2$O$_3$) to ZrO$_2$-x(M$_2$O$_3$-y). The oxygen pressure created tends to suppress decomposition vaporization reactions, such as 3, 4, 13 and 14. After this a period of congruent vaporization begins.

The activities of the two oxide components can be determined from the congruent vaporization stage. Typically the activity of a component in solution is given by:

$$a(i) = \frac{P(i)}{P^0(i)}$$  \hspace{1cm} (15)

Here $P(i)$ is the vapor pressure of the component in solution.
and $P^0(i)$ is the vapor pressure of the pure component. In the case of a rare-earth oxide-zirconia system, the activity of zirconia can be calculated as:

$$a(\text{ZrO}_2) = \frac{P(\text{ZrO}_2)}{P^0(\text{ZrO}_2)}$$

(16)

However the mass spectrometer intensity of the ZrO$_2^+$ ion may not always be easy to determine as a function of composition. Therefore it is desirable to use the other ions to determine activities of the components.

Belov$^{32}$ points out that use of the other ions is more complex because they are dissociation products. He proposes a calculation method based on the intensity of the Mo$^+$ ion from M$_2$O$_3$, as a function of composition. The two primary vaporization routes for ZrO$_2$ and M$_2$O$_3$ are given by equations (3) and (13). The equilibrium constants give the following relations:

$$a(\text{ZrO}_2) = \frac{P(\text{ZrO}) P(\text{O-tot})}{P^0(\text{ZrO}) P^0(\text{O-tot})}$$

(17)

$$a(\text{M}_2\text{O}_3) = \frac{P(\text{MO})^2 P(\text{O-tot})}{P^0(\text{MO})^2 P^0(\text{O-tot})}$$

(18)

Note that $P(\text{O-tot})$ is the amount of O from both ZrO$_2$ decomposition, $P(\text{O-ZrO}_2)$, and M$_2$O$_3$ decomposition, $P(\text{O-M}_2\text{O}_3)$. The actual calculation is iterative. The first step involves
setting $P(\text{ZrO}) = 0$ and taking $P(\text{O-tot}) = P(\text{O-M}_2\text{O}_3)$. This is in equation (18) to calculate the value of $a(\text{M}_2\text{O}_3)$. Then the Gibbs-Duhem equation is used to calculate $a(\text{ZrO}_2)$. This value is put into equation (17) to calculate $P(\text{ZrO})$ and $P(\text{O-ZrO}_2)$. The new $P(\text{O-tot})$ becomes $P(\text{O-M}_2\text{O}_3) + P(\text{O-ZrO}_2)$ and the second iteration begins. This continues until the iterations converge. This is an important and useful technique for obtaining activities in these complex oxide systems.

In the following discussion of rare earth oxide-zirconia stabilized materials, a number of systems will be discussed. Their vapor pressures and solid solution behavior will be discussed.

$\text{Y}_2\text{O}_3\text{-ZrO}_2$

This is the most common of the rare earth stabilized zirconia systems. A recent phase diagram \textsuperscript{33} is shown in Figure 16. Note that the cubic phase field does not extend to lower temperatures, but undergoes a eutectoid decomposition, similar to that of the MgO and CaO stabilized zirconia. This phase change is slow and has only been recently detected.

Figure 17 is an activity-composition diagram determined by mass spectrometry \textsuperscript{30} for this system. This data was
obtained by the two calculation methods described in the preceding discussion. Note the negative deviations from Raoult's Law, indicating attractive interactions. However interactions are stronger in the CaO-ZrO$_2$ system (Figure 7), in which compound formation is eventually observed.

Figures 18 shows the calculated vapor pressures above pure Y$_2$O$_3$ as well as some data points for the vapor pressure of YO(g)$^{34}$ above Y$_2$O$_3$. These show good agreement with the calculated values. Figure 19 shows the calculated vapor pressures above Y$_2$O$_3$·2(ZrO$_2$). Note that the vapor pressures of YO(g) and Y(g) are lowered by less then an order of magnitude, which is consistent with Figure 17.

Some recent evidence$^{35}$ indicates that the Y$_2$O$_3$ in this material reacts with water. This is an important point which merits further investigation for structural applications of this material.

Sc$_2$O$_3$-ZrO$_2$

This system is of interest due the low density of Sc$_2$O$_3$. Figure 20 shows a phase diagram$^{36}$. There are some low temperature phase changes and the location of the liquidus is still in question. However there is a large cubic phase field.
Semenov\textsuperscript{37} and Belov et. al.\textsuperscript{38-39} have investigated the vaporization behavior of pure Sc\textsubscript{2}O\textsubscript{3} and Sc\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2} solid solutions. For the solid solutions, they observe the following near ideal behavior:

\[ P(\text{ScO-sol}) = P^\circ(\text{ScO})[x(\text{Sc}_{2}\text{O}_3)] \]  \hspace{1cm} (15)

From this relation and the iterative calculation method described above, they calculate an activity-composition diagram is shown in Figure 21. Note the similarity to that for Y\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2}. Both exhibit negative deviations from Raoult's Law, indicating attractive forces.

Figure 22 is a plot of the calculated vapor pressures above pure Sc\textsubscript{2}O\textsubscript{3} and the experimental data of Semenov\textsuperscript{37}, which is in good agreement. In the Sc\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2} solution, one would expect limited vapor pressure lowering consistent with Figure 21 and similar to the Y\textsubscript{2}O\textsubscript{3}·2(ZrO\textsubscript{2}) case. It should be noted that the vapor pressure in the solid solution is sufficiently high that Belov et. al.\textsuperscript{38} observe after 100 minutes at 2580\textdegree K, all the Sc\textsubscript{2}O\textsubscript{3} has vaporized from their sample of 50 m/o Sc\textsubscript{2}O\textsubscript{3} - 50 m/o ZrO\textsubscript{2}.
**La$_2$O$_3$-ZrO$_2$**

The phase diagram for this system\textsuperscript{40} is shown in Figure 23. While the cubic phase undergoes a eutectoid decomposition at about 2248 K, there is a pyrochlore phase which seems to be stable over a wide range of temperatures. Figures 24 and 25 show the vapor pressure above La$_2$O$_3$ and La$_2$O$_3$·2(ZrO$_2$), respectively. La$_2$O$_3$ has one of the higher vapor pressures of the rare earth oxides (Table I), which would be a limitation of applications of this system. Consistent with the other systems, relatively little vapor pressure lowering is expected in the solid solution (Figure 25).

It is well known that La$_2$O$_3$ is quite hygroscopic. This may be also be a limitation in the application of the solid solution.

**CeO$_2$-ZrO$_2$**

There is currently interest in the partially stabilized zirconia of this system.\textsuperscript{41} However, as shown in the phase diagram (Figure 26), there is not a fully stabilized composition down to low temperatures for this system. The catastrophic monoclinic to tetragonal phase transformation
limits this material's use as a high temperature structural material.

Vapor pressure calculations for pure Ce$_2$O$_3$ and Ce$_2$Zr$_2$O$_{7-x}$ are shown in Figures 27 and 28. This system also has a rather high vapor pressure, which also limits its application. Note that in Figure 28, the vapor pressure of ZrO and Zr is actually higher than their vapor pressure above pure ZrO$_2$. This is an interesting consequence of vaporization of Ce$_2$O$_3$ as CeO$_2$(g) and CeO(g). In the solid solution, Ce$_2$O$_3$·2(ZrO$_2$), when both these species are formed, very little O(g) is generated. In fact, since the species are not formed in equal amounts, some oxygen must come from ZrO$_2$. There is no suppression of the vaporization/decomposition processes (i.e. reactions (3) and (4)) and the vapor pressures of ZrO and Zr go up. These vapor pressures are not simply related to the activity of ZrO$_2$, which must remain one or less in solution.

Sm$_2$O$_3$-ZrO$_2$ and Gd$_2$O$_3$-ZrO$_2$

The phase diagrams for these two systems appear similar. The phase diagram for the Sm$_2$O$_3$-ZrO$_2$ system is shown in Figure 29. There is a large cubic phase field and also a miscibility gap and temperatures less than 2000 K.
The vapor pressures for Sm$_2$O$_3$ are shown in Figure 30. The heat of formation of the solid solution Sm$_2$O$_3$$\cdot$2(ZrO$_2$) has been measured$^{42}$. However, when put into the free energy minimization program, it was found that the solid solution decomposed to the constituent oxides at about 1500 K. This indicates either an inconsistency in the data or the phase diagram. Nonetheless Sm$_2$O$_3$ does have a fairly low vapor pressure and stabilizes the cubic phase of ZrO$_2$.

The phase diagram for the Gd$_2$O$_3$-ZrO$_2$ system$^{44}$ is shown in Figure 31. Note the large cubic phase field. The vapor pressures for above pure Gd$_2$O$_3$ are shown in Figure 32. The same situation for the free energy minimization as in Sm$_2$O$_3$$\cdot$2(ZrO$_2$) was found, also indicating an inconsistency in the data or the phase diagram. Although Gd$_2$O$_3$ is one of the lower vapor pressure rare earth oxides, Belov and Semenov$^{28}$ have found that on heating in the range 2773-2823 K, Gd$_2$O$_3$ completely vaporizes from a solid solution with ZrO$_2$.

Yb$_2$O$_3$-ZrO$_2$, Dy$_2$O$_3$-ZrO$_2$, Ho$_2$O$_3$-ZrO$_2$, and Er$_2$O$_3$-ZrO$_2$

These systems all show similar phase diagrams, which exhibit large cubic phase fields and liquidus maxima. These diagrams$^{45-48}$ are shown in Figures 33, 35, 37, and 39. Note that in each case the liquidus maxima is at a composition of
0.15 to 0.20 M$_2$O$_3$-ZrO$_2$ and a temperature near 2800 K. The phase diagrams are very likely all somewhat tentative, but they do show a lack of phase changes for these compositions.

As mentioned previously, Yb$_2$O$_3$ is one of the few rare earth oxides which decomposes to the metal and oxygen. Its vapor pressure is shown in Figure 34. Data for the solid oxide solution was not available. Belov and Semenov$^{28}$ have noted that in the temperature range 2773 K to 2823 K, Yb$_2$O$_3$ tends to completely vaporize from the solid solution.

The vapor pressures above Dy$_2$O$_3$, Ho$_2$O$_3$, and Er$_2$O$_3$ are shown in Figures 36, 38, and 40. Solid solution data was not available. However systems which exhibit liquidus maxima show significant interactions$^{49}$ and hence these systems should show a corresponding vapor pressure lowering. Belov and Semenov$^{28}$ have shown that each of these systems at 2, 3, 10, and 50 m/o do not decompose at temperatures of 2773-2823 K. They have also suggested the Lu$_2$O$_3$-ZrO$_2$ system, since Lu$_2$O$_3$ has the lowest vapor pressure of the rare earth oxides, as shown in Table I. However a phase diagram could not be located for the Lu$_2$O$_3$-ZrO$_2$ system. Clearly more work is needed on these important systems.
V. Conclusions

The thermodynamic properties of a number of oxide-zirconia systems have been examined. Particular emphasis has been on phase changes and volatility.

The alkaline earth oxide systems have been examined. Magnesia and calcia stabilize zirconia, strontia and baria do not stabilize zirconia but form compounds. Clearly the MgO-ZrO₂ and BaO-ZrO₂ systems show too much volatility to be useful. The CaO-ZrO₂ and SrO-ZrO₂ systems may show some limited application.

The rare earth oxide-zirconia systems generally have lower vapor pressures. The Y₂O₃-ZrO₂, Sc₂O₃-ZrO₂, La₂O₃-ZrO₂, Ce₂O₃-ZrO₂, Sm₂O₃-ZrO₂, Gd₂O₃-ZrO₂, Dy₂O₃-ZrO₂, Ho₂O₃-ZrO₂, and Er₂O₃-ZrO₂ systems were examined. The La₂O₃-ZrO₂ system has a high vapor pressure and is hygroscopic. The Ce₂O₃-ZrO₂ system has a very high vapor pressure and does not really have a fully stabilized cubic structure to lower temperatures. The Sm₂O₃-ZrO₂ and Gd₂O₃-ZrO₂ system may have some phase changes--more work needs to be done. Previous investigations have suggested that the Sc₂O₃-ZrO₂, Yb₂O₃-ZrO₂, and Gd₂O₃-ZrO₂ systems may have a volatility problem--more work in the temperature range of interest is needed. The Y₂O₃-ZrO₂, Dy₂O₃-ZrO₂, Ho₂O₃-ZrO₂, and Er₂O₃-ZrO₂ systems all look quite promising.
They have low vapor pressures and current evidence suggests no serious phase changes. Other more exotic rare earth systems may also show promise.

The purpose of this review has been to bring together all the available thermodynamic data on some metal oxide-zirconia systems. A good deal of this data is from obscure and difficult to locate sources. From this data a number of systems appear promising for use as structural materials in the temperatures above 1900 K. However this review also points towards the need for more data—in particular more phase change information, further vapor pressure measurements, and in general upper temperature limits for the application of each material.

Acknowledgement

Special thanks are due to Dr. Ajay Misra for his assistance in the use of the SOLGASMIX computer program.
Table I. Relative vapor pressures of some rare earth oxides, according to Belov and Semenov\textsuperscript{28}

<table>
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<th>Oxide</th>
<th>Evaporation Rate at 2500 K $\frac{W(M_2O_3)}{W(Lu_2O_3)}$</th>
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<td>Gd$_2$O$_3$</td>
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<td>Dy$_2$O$_3$</td>
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<tr>
<td>Yb$_2$O$_3$</td>
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<td>Lu$_2$O$_3$</td>
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REFERENCES


38. Belov, A.N. et. al.: Evaporation and Thermodynamic Properties of Sc₂O₃ and of ZrO₂-Sc₂O₃ Binary Solid Solutions


42. op. cit. Reference 40, p. 139.


44. op. cit. Reference 40, p. 129.
45. op. cit. Reference 40, p. 143.

46. op. cit. Reference 40, p. 125.

47. op. cit. Reference 40, p. 131.


Figure 1. - Vapor pressures above ZrO$_2$.

Figure 2. - Vapor pressures above ZrO$_2$ + 1 atm. O$_2$.

Figure 3. - ZrO$_2$-MgO phase diagram. Reprinted by permission of the American Ceramic Society.

Figure 4. - ZrO$_2$-MgO liquidus curve. Reprinted by permission of the American Ceramic Society.
Figure 5. - Vapor pressures above MgO.

Figure 6. - ZrO₂-CaO phase diagram. Reprinted by permission of the American Ceramic Society.

Figure 7. - Activity-Composition diagram for ZrO₂-CaO. Reprinted by permission of the Royal Society of Chemistry.

Figure 8. - Vapor pressures above CaO.
SrO–ZrO$_2$

**Figure 9.** Vapor pressures above CaZrO$_3$.

**Figure 10.** Phase diagram for ZrO$_2$–SrO. Reprinted by permission of the American Ceramic Society.

**Figure 11.** Vapor pressures above SrO.

**Figure 12.** Vapor pressures above SrZrO$_3$. 
Figure 13. - Vapor pressures above BaO.

Figure 14. - Vapor pressures above BaZrO₃.

Figure 15. - Measured P(BaO) above BaZrO₃.

Figure 16. - Phase diagram for ZrO₂-Y₂O₃. Reprinted by permission of the American Ceramic Society.
Figure 17. - Activity-composition diagram for ZrO$_2$-$\text{Y}_2\text{O}_3$. Reprinted by permission of the British Library. Line 1 shows the experimental data for $a$(ZrO$_2$). Line 2 shows the $a$(Y$_2$O$_3$) values from the Gibbs-Duhem integration. Line 3 shows the $a$(Y$_2$O$_3$) obtained by comparing the values for the solid solution to the pure compound and applying the appropriate equilibrium equation.

Figures 18 and 19. - Vapor pressures above Y$_2$O$_3$. Calculated vapor pressures of Waish et al. 34

Figure 20. - Phase diagram for ZrO$_2$-Sc$_2$O$_3$. Reprinted by permission of the American Ceramic Society.


**ZrO$_2$–Sc$_2$O$_3$**

Figure 21. Activity–composition diagram for ZrO$_2$–Sc$_2$O$_3$. Reprinted by permission of the British Library. Lines 1 and 2 were calculated by the approximation method. Point 3 is a (ZrO$_2$) measured by comparing the solid solution to the pure compound.

La$_2$O$_3$–ZrO$_2$

Figure 23. Phase diagram for ZrO$_2$–La$_2$O$_3$. Reprinted by permission of the American Ceramic Society.

Figure 22. Vapor pressures above Sc$_2$O$_3$.

Figure 24. Vapor pressures above La$_2$O$_3$. 
Figure 25. - Vapor pressures above La$_2$O$_3$ (ZrO$_2$).

Figure 26. - Phase diagram for ZrO$_2$-CeO$_2$Reprinted by permission of the American Ceramic Society.

Figure 27. - Vapor pressures above Ce$_2$O$_3$.

Figure 28. - Vapor pressures above Ce$_2$O$_3$ (ZrO$_2$).
Sm$_2$O$_3$–ZrO$_2$

![Phase diagram for ZrO$_2$-Sm$_2$O$_3$](image)

Figure 29. - Phase diagram for ZrO$_2$-Sm$_2$O$_3$. Reprinted by permission of the American Ceramic Society.

Gd$_2$O$_3$–ZrO$_2$

![Phase diagram for ZrO$_2$-Gd$_2$O$_3$](image)

Figure 31. - Phase diagram for ZrO$_2$-Gd$_2$O$_3$. Reprinted by permission of the American Ceramic Society.

Figure 30. - Vapor pressures above Sm$_2$O$_3$.

Figure 32. - Vapor pressures above Gd$_2$O$_3$.
**Yb₂O₃-ZrO₂**

Figure 33.- Phase diagram for ZrO₂-Yb₂O₃.⁴⁵ Reprinted by permission of the American Ceramic Society.

**Dy₂O₃-ZrO₂**

Figure 35.- Phase diagram for ZrO₂-Dy₂O₃.⁴⁶ Reprinted by permission of the American Ceramic Society.

Figure 34.- Vapor pressures above Yb₂O₃.

Figure 36.- Vapor pressures above Dy₂O₃.
**Ho₂O₃-ZrO₂**

![Phase Diagram](image1.png)

Figure 37. ZrO₂-Ho₂O₃ phase diagram. Reprinted by permission of the American Ceramic Society.

**Er₂O₃-ZrO₂**

![Phase Diagram](image2.png)

Figure 39. ZrO₂-Er₂O₃ phase diagram. Reprinted by permission of the American Ceramic Society.

**Vapor Pressures**

![Pressure vs Temperature](image3.png)

Figure 38. Vapor pressures above Ho₂O₃.

![Pressure vs Temperature](image4.png)

Figure 40. Vapor pressures above Er₂O₃.
APPENDIX. THERMODYNAMIC DATA

Thermodynamic data for the more common oxides is quite plentiful; for the less common oxides it is sparse. Where possible, the best thermodynamic data was used. The most desirable information for each system is the \( \Delta H(298) \), \( S(298) \), heat capacity and heat of any phase changes. This data is listed in Table AI.

The data for the zirconium-oxygen and alkaline earth metal-oxygen systems was taken from the JANAF tables.\(^1\) Heat capacities were fitted to an equation of the form:

\[
C_p = A + B \times 10^{-3}T + C \times 10^5/T^2 + D \times 10^{-6}T^2
\]  \hspace{1cm} (1)

The data for the alkaline earth zirconate systems were taken from other sources and is listed in Table AII. This includes both estimated and measured data. Where possible measured data were used in the final calculations, as shown in Table AI. As mentioned in the text, the CaO-ZrO\(_2\) system forms a solid solution. The electrochemical data\(^{17,18}\) is for the reaction of the saturated solid solution with CaO to form CaZrO\(_3\). For this reason the electrochemical data cannot be directly compared to the calorimetric data. However in the case of SrZrO\(_3\) and BaZrO\(_3\), the two types of measurements can
be directly compared and show good agreement, as indicated in the Table AII.

Thermodynamic data for the rare earth-oxygen systems was more difficult to locate. Most of the data for the rare earth metals and condensed phase oxides was taken from the tables by Pankratz.9 Most of these oxides vaporize to the monoxide. Data for some of the rare earth monoxides of Y and Sc was taken from the tables of Ruzinov.10 Data for the volatile oxides of the other rare earth monoxide was available as the free energy of formation from the original sources.14,16 The heats of formation of the solid oxide solutions of the composition M2O3·2(ZrO2) were taken from the calorimetric data of Korneev et. al.11 Entropies were estimated to be 47.8 cal/mole-°K, after Barin and Knacke13 and heat capacities were estimated by summing the contribution from M2O3 and 2(ZrO2)20.

For each of the systems, the data was combined to obtain free energy of formation from the elements in their standard states. The free energy was obtained in the following form:

\[ G = AG/T + BG + CG*T + DG*T^{-2} + EG*T^3 + FG*T*LOG(T) \] (2)

This free energy was then put into the SOLGASMIX-PV computer program to calculate the vapor pressures for each system.
APPENDIX. REFERENCES


### ZrO₂

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<th>Compound</th>
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<th>S (298), cal/K mol</th>
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<th>Temperatures</th>
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### MgO

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### TABLE A-I. - Continued.

#### CaO

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### Sc-O

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### La-Zr-O

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<td>La(γ)</td>
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Note: ΔH° = -7 360 - 10.8T
ΔS° = -131 350 + 7.0T

ΔS°(g) = 5 953 - 47 688
### TABLE A-I. - Continued.

#### Gd-O

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<th>S (298), cal/K mol</th>
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<th>Temperatures</th>
<th>Comments</th>
<th>Source</th>
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<td>A</td>
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<td>C</td>
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\( \Delta G = -11.675T + 28.781 \)

#### Yb-O

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\( \Delta(\alpha-\beta) = 0.150 \)

\( \Delta(\alpha-\beta) = 0.418 \)

\( \Delta(\beta-L) = 1.830 \)

\( \Delta(\alpha-L) = 2.403 \)
TABLE A-I. - Concluded.

Dy-O

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<td>3.490</td>
<td>4.450</td>
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Ho-O

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Er-O

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<th>$C_p$</th>
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<th>Comments</th>
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### Table A-II.

**Thermodynamic Data for CaZrO₃**

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<tr>
<td>L'vova and Feodos'ev (6)</td>
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<td>Bomb calorimetry</td>
</tr>
<tr>
<td>Parker (3)</td>
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<td>Value of L'vova and Feodos'ev corrected with recent ΔHₚ(ZrO₂)</td>
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<td>22.4</td>
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<tr>
<td>King and Weller (7)</td>
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<td>23.9±0.2</td>
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<td>Calorimetry</td>
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<td>Mezaki et al. (5)</td>
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<td>Barin and Knacke (12)</td>
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**Thermodynamic Data for SrZrO₃**

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<th>Comments</th>
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<tr>
<td>L'vova and Feodos'ev (6)</td>
<td>-418.3</td>
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<td></td>
<td>Bomb calorimetry</td>
</tr>
<tr>
<td>Parker (3)</td>
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<td>Levitskii et al. (8)</td>
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<td>Calorimetry</td>
</tr>
<tr>
<td>King and Weller (7)</td>
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<td>27.5±0.2</td>
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<td>Electrochemical cell</td>
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<td>S-estimated</td>
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<td>Barin and Knacke (12)</td>
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<td>Levitskii et al. (8)</td>
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<td>$\alpha 25.63 + 6.24 \times 10^{-3}T - 2.82 \times 10^{5}/T^2$</td>
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<tr>
<td>King and Weller (7)</td>
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<td>$\beta 27.77 - 0.18 \times 10^{-3}T$</td>
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<tr>
<td>Levitskii (17)</td>
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<td>29.0±0.3</td>
<td>$\gamma 24.75 + 4.42 \times 10^{-3}T$</td>
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<tr>
<td>Barin and Knacke (12)</td>
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<td>$29.35 + 2.1 \times 10^{-3}T - 5.25 \times 10^{5}/T^2$</td>
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<tr>
<td>Kubachewski (15)</td>
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<td>26.5±2.0</td>
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<td>Electrochemical cell</td>
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16. Abstract

Metal oxide-zirconia systems are a potential class of materials for use as structural materials at temperatures above 1900 K. These materials must have no destructive phase changes and low vapor pressures. Both alkaline earth oxide (MgO, CaO, SrO, and BaO)-zirconia and some rare earth oxide (Y_2O_3, Sc_2O_3, La_2O_3, CeO_2, Sm_2O_3, Gd_2O_3, Yb_2O_3, Dy_2O_3, Ho_2O_3, and Er_2O_3)-zirconia system are examined. For each system, the phase diagram is discussed and the vapor pressure for each vapor specie is calculated via a free energy minimization procedure. The available thermodynamic literature on each system is also surveyed. Some of the systems look promising for high temperature structural materials.