

Free energy of formation of zircon and hafnon

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ABSTRACT

The free energy of formation of zircon (ZrSiO_4) from its oxides was determined between 1100 and 1300 K by an electrochemical method, in which values of μ_{O_2} defined by the two assemblages $\text{Fe}_2\text{SiO}_4\text{-Fe-SiO}_2$ (fayalite-iron-quartz) and $\text{Fe}_2\text{SiO}_4\text{-Fe-ZrO}_2\text{-ZrSiO}_4$ were each measured using oxygen concentration cells with calcia-stabilized zirconia solid electrolytes. The difference in μ_{O_2} between these two assemblages corresponds to the reaction $\text{ZrO}_2 + \text{SiO}_2(\text{qz}) = \text{ZrSiO}_4$. The results, when analyzed using calorimetric data for the entropies and high-temperature heat capacities of ZrSiO_4 , ZrO_2 , and $\text{SiO}_2(\text{quartz})$, yields $\Delta_{\text{f,ox}}H_{298\text{K}}^0 = -24.0 \pm 0.2$ kJ/mol for ZrSiO_4 , in good agreement with the calorimetric value of Ellison and Navrotsky (1992). ZrSiO_4 is predicted to decompose to ZrO_2 plus SiO_2 (cristobalite) at 1938 K, assuming a temperature of 1430 K for the martensitic phase transition between the tetragonal and monoclinic forms of ZrO_2 (baddeleyite), with an enthalpy of transition of 8.67 kJ/mol. The same experimental approach was used also to determine the free energy of formation of hafnon (HfSiO_4). The entropy of hafnon ($S_{298\text{K}}^0 = 93.6$ J/mol·K) is similar to that for zircon, but the enthalpy of formation is slightly more exothermic ($\Delta_{\text{f,ox}}H_{298\text{K}}^0 = -25.0 \pm 0.2$ kJ/mol).

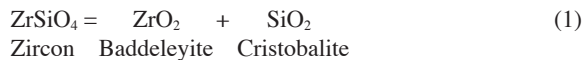
The cells with either $\text{ZrSiO}_4 + \text{ZrO}_2$ or $\text{HfSiO}_4 + \text{HfO}_2$ produce an anomalous excursion in EMF when the temperature of the α - γ transition in Fe metal at 1184 K is traversed; this excursion takes >12 hours to decay back to the equilibrium value. This behavior is presumably related to strain caused by the volume change of the α - γ transition.

The redetermination of the μ_{O_2} of the $\text{Fe}_2\text{SiO}_4\text{-Fe-SiO}_2(\text{qz})$ equilibrium (the quartz-fayalite-iron or QFI oxygen buffer) carried out in the course of this study gave results in reasonable agreement with previous work, but with a different slope vs. temperature, implying a slightly higher value of $S_{298\text{K}}^0$ for Fe_2SiO_4 than the currently accepted calorimetric datum (i.e., 153.5 vs. 151.0 ± 0.2 J/K·mol).

Keywords: Zircon, hafnon, free energy of formation, fayalite, thermodynamic data

INTRODUCTION

Interpreting U-Pb dates obtained from zircon requires knowledge of the stability of this mineral, since it is often not entirely obvious at which stage in the history of the rock the zircon crystallized. However, the thermodynamic properties of zircon remain contentious. In many compilations or databases, the free energy of formation of zircon is still based on calorimetric measurements for entropies and heat capacities (Kelley 1941; Coughlin and King 1950), with the enthalpy of formation deduced from the observation of Curtis and Sowman (1953) that a natural, rather impure, sample of zircon started to decompose, producing ZrO_2 (baddeleyite), at a temperature of 1811 K. This observation was equated with the univariant reaction:



This inference is dubious since the expected cristobalite was not observed. The importance of this is that the thermodynamic data so derived, when combined with the thermodynamic data

for the reaction that defines the activity of silica in upper mantle peridotite:



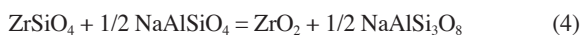
predicts that the reaction:



should proceed to the right at most temperatures and pressures relevant to the crystallization of mafic and ultramafic rocks; accordingly, zircon should not form in the presence of olivine. Yet zircons from olivine-bearing kimberlites often have been used for dating (e.g., Haggerty et al. 1983), as have rare zircons from peridotites and related rocks (e.g., Kinny and Dawson 1992; Gebauer et al. 1992; Grieco et al. 2001; Song et al. 2005). If zircon really were not stable with olivine, the provenance of these zircons could be considered problematic.

A direct experimental reversal of reaction 3 at 1000 K and 1 kb by Schuiling et al. (1976) established that $\text{Mg}_2\text{SiO}_4 + \text{ZrSiO}_4$ was indeed stable at these conditions. Using a series of reactions that define silica activity in the same way as reaction 2 does, Schuiling et al. (1976) bracketed the breakdown of zircon at 1000 K and 1 kb between the reactions:

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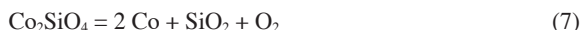


This result places a constraint on the enthalpy of formation of zircon that is inconsistent with the datum of Curtis and Sowman (1953). However, the constraint is not very precise: the width of the bracket corresponds to a free energy of 7.8 kJ/mol, and this does not include the uncertainties in the thermodynamic data for the other phases.

A strategically somewhat similar approach, but one that is capable of much more precision, had been used earlier by Rosen and Muan (1965). They determined the chemical potential of oxygen (μ_{O_2}) at which Co_2SiO_4 (olivine), Co (metal), ZrSiO_4 , and ZrO_2 coexist according to the reaction:



Subtraction of the μ_{O_2} for the reaction:



then gives the free energy of reaction 1. Rosen and Muan (1965) imposed μ_{O_2} using CO-CO₂ gas mixtures and obtained four data in the temperature range 1453 to 1639 K, with an accuracy they estimated as ± 0.4 kJ/mol. Recently, however, Newton et al. (2005) reported a determination of the free energy of formation of zircon at 800 °C and 1.2 GPa from aqueous solubility measurements that is less negative by 1.5 kJ/mol than that found by Rosen and Muan (1965).

The enthalpy of formation of ZrSiO_4 from the oxides was measured directly by Ellison and Navrotsky (1992) at 977 K using oxide-melt solution calorimetry. Their result has an uncertainty of ± 1.9 kJ/mol, which represents a considerable improvement in accuracy over the method of Schuiling et al. (1976), if not over that of Rosen and Muan (1965).

Here, I report new measurements based on the idea of Rosen and Muan (1965), but using Fe_2SiO_4 (synthetic fayalite) rather than Co_2SiO_4 , and the experimental method of solid-electrolyte electrochemical cells with solid assemblages as electrodes, rather than gas mixing. The difference in approach is that the gas-mixing method imposes μ_{O_2} , and the resulting phase assemblage is observed on quenching, whereas in the solid electrolyte cells, the phase assemblage is imposed and the resulting μ_{O_2} is measured. The solid electrolyte cells perform best experimentally in a temperature range below that of the gas-mixing method (O'Neill and Pownceby 1993); in this study, results were obtained between 1100 and 1300 K, whereas Rosen and Muan (1965) worked between 1453 and 1639 K. These two temperature ranges are separated by the monoclinic-to-tetragonal phase transition in ZrO_2 ; therefore, a comparison of the present results with the higher temperature data of Rosen and Muan (1965), and also with the thermal decomposition of zircon (reaction 1), requires knowledge of the thermodynamics of this transition, which is not a simple matter because of practical difficulties caused by its martensitic nature. Accordingly, the data for this transition are reviewed and values of enthalpies, entropies, and heat capacities are suggested (Appendix 1). This assessment results in thermodynamic data for ZrSiO_4 and ZrO_2 that are consistent with the present experi-

mental results, the previous work of Rosen and Muan (1965), and the calorimetry of Ellison and Navrotsky (1992).

The analogous reaction with Hf also was studied, and a suggested set of thermodynamic properties for HfSiO_4 and HfO_2 are presented.

EXPERIMENTAL METHODS

Electrochemical cells were prepared and run as described in O'Neill and Pownceby (1993). This experimental arrangement is similar to the one used in a previous study of the QFI equilibrium (O'Neill 1987a), but incorporates a number of small improvements that should increase accuracy. The main improvement is that an increase in the size of the furnace enables a general increase in scale of the experiment, which minimizes thermal gradients and hence thermoelectric contributions to the measured EMFs. The magnitude of the differences in results expected with the experimental improvements may be gauged by noting that the results presented in O'Neill and Pownceby (1993) on the Cu-Cu₂O, Ni-NiO, Co-CoO, Fe-FeO, and W-WO₂ equilibria differ from the earlier measurements of O'Neill (1987b, 1988) by less than 500 J/mol of O₂ (corresponding to less than 1.5 mV in cell EMF).

The electrochemical method measures the difference in the chemical potential of oxygen (μ_{O_2}) between a sample and reference electrode:

$$\mu_{\text{O}_2}(\text{sample}) - \mu_{\text{O}_2}(\text{reference}) = 4FE \quad (8)$$

where F is the Faraday constant (96,485 J/mC) and E is the EMF of the cell in mV. Iron-wüstite (Fe-FeO) was used as the reference electrode in all the cells of this study, values for the μ_{O_2} of which are given in O'Neill and Pownceby (1993).

Sample electrodes of $\text{Fe}_2\text{SiO}_4 + \text{Fe} + \text{SiO}_2$ (qz), and of $\text{Fe}_2\text{SiO}_4 + \text{Fe} + \text{ZrO}_2 + \text{ZrSiO}_4$ (and the Hf equivalent) were prepared as follows. The synthetic fayalite was from the same batch as used in O'Neill (1987a), as was the natural Brazilian quartz. Mixtures of ZrSiO_4 plus ZrO_2 and of HfSiO_4 plus HfO_2 were synthesized in the molar proportions of 2:1 from gels. Solutions containing Zr or Hf were prepared by dissolving zirconyl nitrate and hafnium oxychloride in water acidified by a few drops of nitric acid, in PTFE beakers. Equal volumes of ethanol were added, followed by silica as tetraethyl orthosilicate. The solution was precipitated with concentrated ammonia and the resulting gel evaporated to dryness over a hot plate; the dried material was transferred to a Pt dish and devolatilized over a bunsen burner. The resulting granules were crushed and lightly ground in an agate mortar, and pressed into pellets using a tungsten carbide 1/2 inch core and piston from an old piston-cylinder pressure vessel. The $\text{ZrO}_2 + \text{ZrSiO}_4$ pellet was sintered at 1200 °C for 70 h, the $\text{HfO}_2 + \text{HfSiO}_4$ pellet at 1500 °C for 16 h, in a box furnace. The pellets were removed from the furnace and allowed to cool, then crushed and lightly ground again under acetone.

The above sintering temperatures were selected to be as high as possible (to promote good crystallinity), while being below the monoclinic-tetragonal phase transitions in ZrO_2 and HfO_2 . For ZrO_2 , most thermodynamic compilations give the temperature of the transition as 1478 K (e.g., Robie et al. 1979; Robie and Hemingway 1995; Pankratz 1982; Barin 1995), based on the heat content measurements of Coughlin and King (1950). However, the powder XRD analysis of the sintered starting material showed that the ZrO_2 was a mixture of both the monoclinic and tetragonal forms, with about 10% of the latter. The presence of the tetragonal form implies a lower temperature for the transition. The temperature of the transition is important for the comparison of the present results with previous work, and this topic is reviewed in detail in Appendix 1.

Lattice parameters of starting materials and selected run products were determined by Rietveld analysis of powder XRD patterns obtained on a Seimens D5005 diffractometer using $\text{CoK}\alpha$ radiation, 0.15 mm Soller slits, and a scintillation counter. Samples were mixed with an internal standard of NIST Si ($a_0 = 0.54311946$ nm at 22.5 °C), mounted on a zero-reflection rotating quartz plate (20 rev/min), and data were collected from 15 to 135° 2 θ . In the refinement, the Si lattice parameter was fixed at the recommended value, and the position and sample displacement parameters allowed to vary. Results are reported in Table 1.

In the Hf starting material, only well-crystallized HfSiO_4 and monoclinic HfO_2 were present (Table 1). The same was also true of this material further sintered at 1600 °C for 40 min and quenched by dropping into water. This does not mean that the monoclinic to tetragonal transition in HfO_2 is above this temperature, as the martensitic nature of the transition usually means that it is not quenchable. The preservation of the tetragonal polymorph in the Zr starting material appears to be the exception rather than the rule.

TABLE 1. Lattice parameters (in angstroms) and molar volumes from powder XRD measurements using NIST Si ($a_0 = 5.4311946 \text{ \AA}$) as an internal standard

	ZrO ₂ or HfO ₂ (monoclinic)				ZrSiO ₄ or HfSiO ₄		
	<i>a</i>	<i>b</i>	<i>c</i>	β	<i>a</i>	<i>c</i>	V^0 (cm ³)
Zr starting material*	5.151	5.201	5.313	99.2	21.15	5.982	39.32
Hf starting material	5.120	5.173	5.298	99.2	20.85	5.966	38.81
ZIR 1	5.149	5.204	5.324	99.2	21.20	5.979	39.24
ZIR 2 & 3	5.148	5.204	5.323	99.2	21.20	5.979	39.24

Notes: Patterns refined by the Rietveld method. Accuracy is estimated at better than one unit in the last decimal place given.

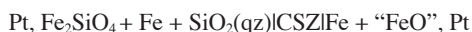
* Plus tetragonal ZrO₂ $a = 3.604 \text{ \AA}$, $c = 5.218 \text{ \AA}$, $V^0 = 20.41 \text{ cm}^3$.

Sample electrodes were constructed from mixtures of one part by weight of synthetic fayalite, two parts metallic Fe powder (Goodfellow, 99.99+%, -500 mesh), and two parts of either SiO₂ (quartz), ZrO₂+ZrSiO₄ or HfO₂+HfSiO₄, mixed by light grinding under acetone in an agate mortar, and pressed into pellets using tungsten carbide die. Each pellet weighed approximately 2 g.

RESULTS

The Fe₂SiO₄-Fe-SiO₂ (QFI) equilibrium

The results from the cell:



are given in Table 2. In the earlier study (O'Neill 1987a), stable EMFs could not be obtained below 1000 K due to sluggish kinetics, and accordingly, no attempt was made to go below 1025 K. The EMF began to decrease irreversibly at the highest temperature (1291 K), in agreement with the observations of O'Neill (1987a). This is likely due to the onset of sufficient electronic conductivity in the CSZ electrolyte to polarize the Fe₂SiO₄ + Fe + SiO₂(qz) electrode (see O'Neill and Pownceby 1993). Within these temperature limits the cell behaved essentially perfectly. On changing temperature, the EMF of the cell changed to its new value within 20 min, and thereafter remained steady to within ± 0.05 mV for as long as it was left on. The total duration of the experiment was 191 h, including a period of 68 h at the lowest temperature (1025 K).

The results are compared to those of O'Neill (1987a) in Figure 1. The comparison may be viewed in two lights. From a positive perspective, agreement between the new results and the earlier work is good, as most of the new data agree with O'Neill (1987a) to within +400 to -200 J/mol. The magnitude of this disagreement is similar to that between the results of O'Neill and Pownceby (1993) with the earlier work of O'Neill (1987b, 1988) on the simple metal/metal oxide buffers (Cu-Cu₂O, Ni-NiO, Co-CoO, Fe-FeO, and W-WO₂).

The negative aspect of these new results is that they plot on a different slope in μ_{O_2} - T space (Fig. 1). The results of O'Neill (1987a) were in good agreement with the entropy of Fe₂SiO₄ as determined calorimetrically by Robie et al. (1982); accordingly, the different temperature slope of the new data implies disagreement with this calorimetric entropy. The reason is unknown and is regrettable insofar as the new results are obtained from what was felt to be an improvement, albeit only a slight one, of the experimental design. Regression of the difference between the new and the old data, as plotted in Figure 1 assuming an experimental uncertainty of ± 0.3 K in temperature and 0.2 mV in EMF, yields:

$$\Delta[\Delta_r G^\circ(\text{Fe}_2\text{SiO}_4)] = 2917(\pm 247) - 2.507(\pm 0.215) T \text{ J/mol}$$

TABLE 2. Results from the electrochemical cells

<i>T</i> (K)	EMF (mV)	<i>T</i> (K)	EMF (mV)	<i>T</i> (K)	EMF (mV)	<i>T</i> (K)	EMF (mV)
QFI: Pt, Fe ₂ SiO ₄ +SiO ₂ +Fe CSZ FeO+Fe, Pt							
1149	52.6	1108	54.2	1067	55.7	1190	51.3
1169	51.9	1087	54.9	1087	55.1	1211	50.6
1190	51.2	1067	55.5	1108	54.3	1231	49.9
1211	50.5	1046	56.0	1129	53.5	1251	49.1
1190	51.3	1025	57.0	1148	52.8	1271	48.3
1149	52.8	1046	56.4	1169	52.1	1292	47.4
1129	53.5						
ZIR1: Pt, Fe ₂ SiO ₄ +ZrO ₂ +ZrSiO ₄ +Fe CSZ FeO+Fe, Pt							
1108*	16.7	1190†	16.7	1211	17.0	1180	17.3
1129	16.8	1139	17.6	1231	16.8	1176	17.3
1149	16.9	1169	17.4	1251	16.3	1170	17.7
1169	16.9	1191	17.1	1191	17.2	1165†	18.0
ZIR2: Pt, Fe ₂ SiO ₄ +ZrO ₂ +ZrSiO ₄ +Fe CSZ FeO+Fe, Pt							
1129	17.6	1170†	16.7	1170	16.8	1231	16.4
1170	17.4	1129	18.1	1211*	16.6	1251	15.7
1211*	15.7						
ZIR3: Pt, Fe ₂ SiO ₄ +ZrO ₂ +ZrSiO ₄ +Fe CSZ FeO+Fe, Pt							
1190	17.1	1211	16.7	1108	18.0	1211	16.5
1211	17.1	1191	16.8	1129	17.6	1231	16.5
1231	17.1	1169†	17.2	1149	17.2	1251	16.6
1251	16.9	1149	17.4	1169	17.1	1272	16.3
1271	16.5	1129	17.5	1190†	16.6	1292	15.4
1292	15.6						
HAF1: Pt, Fe ₂ SiO ₄ +HfO ₂ +HfSiO ₄ +Fe CSZ FeO+Fe, Pt							
1108	15.1	1190†	14.2	1230	13.8	1251	13.7
1129	14.9	1210	14.0	1251	13.7	1211	13.7
1149	14.8	1230	13.9	1271	13.6	1170†	13.9
1169	14.7	1190	13.8	1292	13.3	1129	15.0

Notes: The data for each cell are listed in the order in which the measurements were made.

* This cell was run for 6 days attempting measurements at <1100 K before a stable EMF was obtained on increasing temperature to 1108 K.

† Anomalous behavior of cell on changing temperature across the $\alpha \leftrightarrow \gamma$ transition in Fe metal.

with an overall uncertainty of ± 58 J/mol (all uncertainties in this paper are reported as ± 1 standard deviation). Taken at face value, this result implies a correction to the entropy of Fe₂SiO₄ from 151.0 ± 0.2 J/mol·K used in O'Neill (1987a), which is from Robie et al. (1982), to 153.5 J/K·mol.

Free energy of formation of zircon (ZrSiO₄)

Results from three cells of the type:



are given in Table 2 and plotted in Figure 2. The cell ZIR3 used the sample electrode pellet recycled from ZIR2, with its surface refreshed by lightly abrading it on emery paper.

Initially, the cells took about 20 h to reach a stable EMF, which was then monitored for a further 14 to 60 h. Stable, reproducible EMFs could not be obtained below 1100 K and, from experience

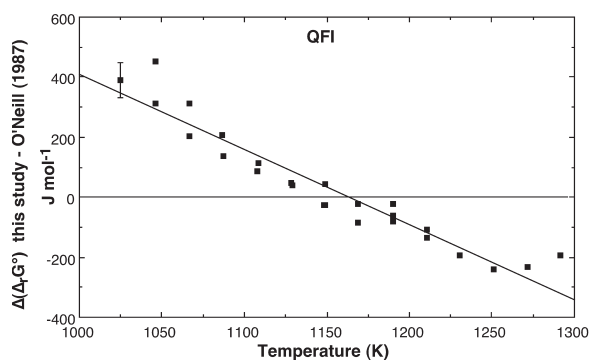


FIGURE 1. Comparison of the results of this study for the cell (Pt, $\text{Fe}_2\text{SiO}_4 + \text{Fe} + \text{SiO}_2(\text{qz}) | \text{CSZ} | \text{Fe} + \text{FeO}$, Pt) with the results of O'Neill (1987a). The error bar attached to the lowest temperature datum corresponds to the estimated uncertainty of ± 0.2 mV in the present results.

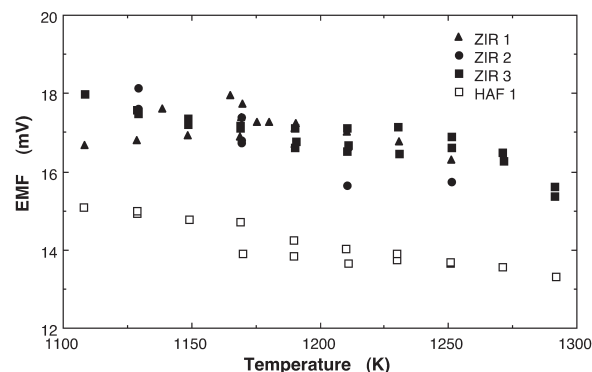


FIGURE 2. Results from the cells: Pt, $\text{Fe}_2\text{SiO}_4 + \text{Fe} + \text{ZrSiO}_4 + \text{ZrO}_2 | \text{CSZ} | \text{Fe} + \text{FeO}$, Pt and Pt, $\text{Fe}_2\text{SiO}_4 + \text{Fe} + \text{HfSiO}_4 + \text{HfO}_2 | \text{CSZ} | \text{Fe} + \text{FeO}$, Pt. The data are given in Table 2.

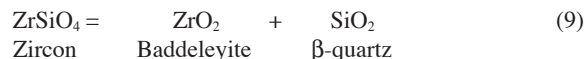
with the QFI vs. Fe + FeO cells (see also O'Neill 1987a), the temperature was not taken above 1300 K. Between 1100 and 1300 K, the three cells gave consistent results. On changing temperature, the cell EMFs usually changed smoothly to their new values within an hour, except when the temperature change traversed the α - γ transition in Fe metal at 1184 K. Then a remarkable phenomenon occurred: If the transition was crossed on increasing temperature, the EMF of the cell decreased smoothly by about 4 or 5 mV in the first half-hour, before increasing to the new equilibrium EMF over a period of 12 to 24 h; the reverse happened on decreasing temperature, with the EMF of the cell first increasing, also by 4 or 5 mV, before decreasing. Exactly the same phenomenon occurred in the Hf cell. The data taken after this anomalous behavior are identified in Table 2. There appears to be some hysteresis in at what temperature the phenomenon occurs. Usually it was observed between 1170 and 1190 K, but it occurred between 1170 and 1165 K when stepping down in smaller intervals of temperature at the end of the run with cell ZIR1.

It would appear that the decrease in volume of Fe across the α - γ transition (the volume change is -0.5% , from the lattice constant vs. temperature measurements of Kohlhaas et al. 1967) causes strain in the Fe_2SiO_4 - ZrO_2 - ZrSiO_4 assemblage and its Hf analog that affects its free energy, which is then seen in the μ_{O_2}

monitored by the cell. This strain then takes more than 12 h to decay away, presumably by recrystallization. If this explanation is credible, it raises the interesting question of whether erroneous results from electrochemical cells on kinetically unfavorable reactions (of which there are many examples in the literature) may be due to strain that does *not* decay away by recrystallization.

Parts of the sample pellets from ZIR1 and ZIR2/3 were cut off after the runs, and the Fe_2SiO_4 and Fe metal removed by dissolution in hot, concentrated HCl. The resulting powder was then examined by XRD, which showed that the tetragonal ZrO_2 present in the starting material had disappeared. The lattice parameters of ZrO_2 (monoclinic) and ZrSiO_4 are given in Table 1, and are only marginally different from the lattice parameters of the starting materials. This similarity indicates that deviations from the assumed ideal stoichiometry are small. Rosen and Muan (1965) established by optical examination and powder XRD that the extent of solubility of CoO in tetragonal ZrO_2 and of Co_2SiO_4 in ZrSiO_4 (and vice versa) was less than 2% at 1673 K. Because of the lower temperatures of this study, it is likely that the extent of the equivalent substitutions is even less, assuming FeO behaves similarly to CoO. In their optimization of the ZrO_2 -MgO system, Du and Jin (1991) reviewed the experimental data pertaining to the substitution of MgO in ZrO_2 ; they concluded that about 0.5 to 1.0 mol% MgO dissolved in tetragonal ZrO_2 , and that dissolution of MgO into monoclinic ZrO_2 , the form of interest here, is even lower. It therefore seems safe to assume that both the ZrO_2 and ZrSiO_4 , as well as the Fe_2SiO_4 , have activities that differ negligibly from the pure stoichiometric phases.

Subtraction of the results for the Fe_2SiO_4 -Fe-SiO₂ (qz) equilibrium (using the results from O'Neill 1987a) from those for Fe_2SiO_4 -Fe-ZrSiO₄-ZrO₂ gives the free energy of the reaction:



These data were then assessed using the third-law method and the calorimetric data for entropies and heat capacities summarized in Table 3. The results of this assessment are presented in Figure 3. Regression of these data gives:

$$\Delta_{f,\text{ox}} H_{298\text{K}}^0 = -23.95 \text{ kJ/mol} \quad (10)$$

with an uncertainty estimated from the scatter in the data (± 0.15 kJ/mol) and from the uncertainty in μ_{O_2} for the Fe_2SiO_4 -Fe-SiO₂ (qz) assemblage (± 0.14 kJ/mol, O'Neill 1987a) of ± 0.2 kJ/mol (all uncertainties are reported as 1 standard deviation).

This result is in excellent agreement with the solution calorimetry of Ellison and Navrotsky (1992), who obtained $\Delta_{f,\text{ox}} H_{(977\text{K})}^0 = -27.9 \pm 1.9$ kJ/mol, which translates to -25.1 kJ/mol at 298 K (Fig. 3).

Because calorimetric data have been used to obtain the enthalpy of formation of zircon, the quandary raised by the discrepancy of the new results for the μ_{O_2} of the QFI equilibrium (reported in Table 2) with the earlier work of O'Neill (1987a), and hence also with the calorimetric entropy of Fe_2SiO_4 (Robie et al. 1982), has an almost negligible impact. If the new data had been used, the value of $\Delta_{f,\text{ox}} H_{298\text{K}}^0$ would change only to -24.02 kJ/mol (i.e., a difference of -0.07 kJ/mol), with the agreement

TABLE 3. Thermodynamic data: heat capacity equations were obtained by weighted least squares fitting of the original calorimetric data

Substance	T range (K)	Reference T (K)	S° (T _{ref}) J/K-mol	H°(T _{ref})-H°(298.15)	C _p = A + BT + CT ² + DT ^{-1/2}			
					A	B(×10 ³)	C(×10 ⁻⁶)	D
SiO ₂ (qz)*	847–1676	900	109.05	38730	65.28	5.529	1.8463	–
SiO ₂ (crs)*	532–1834	900	110.93	37990	66.93	4.843	2.5419	–
ZrO ₂ (mono)†	298–1430	298.15	49.79	–	103.48	-4.547	-0.4162	-713.6
ZrO ₂ (tet)‡	1430–2400	1430	165.79§	90920§	78.56	–	–	–
ZrSiO ₄	298–2200	298.15	84.03	–	232.4	-14.405	–	-2238.2
HfO ₂ #	298–1800	298.15	59.33	–	85.85	5.427	-0.7410	-330.1
HfSiO ₄ **	298–1800	298.15	93.57	–	214.8	-4.430	-0.3245	-1854.7

Notes: Where necessary, reported temperatures were corrected to ITS-90. To ensure that the high temperature data join smoothly to the low temperature data, the heat capacities from adiabatic calorimetry above 250 K were included in the fit.

* C_p from Richet et al. (1982). Δ_rH°_{298 K}(qz-crs) = 3.44 kJ/mol, to give T_v = 1350 K (O'Neill 1987b).

† Tojo et al. (1999), Coughlin and King (1950), and Chekhovskoi et al. (1979).

‡ Chekhovskoi et al. (1979).

§ Includes Δ_vH°=8.67 kJ/mol and Δ_vS°= 6.06 J/mol-K at T_v = 1430 K.

|| Kelley (1941), and Coughlin and King (1950).

Todd (1953) and Orr (1953).

** From HfSiO₄ = ZrSiO₄ - ZrO₂(mono) + HfO₂.

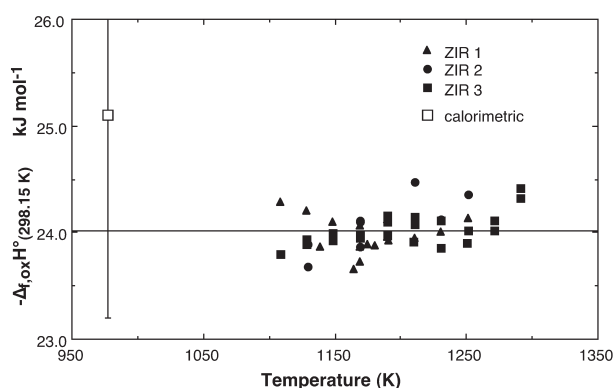


FIGURE 3. Third law analysis to recover the enthalpy of the reaction ($\text{ZrO}_2 + \text{SiO}_2(\text{qz}) = \text{ZrSiO}_4$) from the present experiments. The calorimetric datum is from the heat of solution measurements of Ellison and Navrotsky (1992) at 977 K, using molten $2\text{PbO}\cdot\text{B}_2\text{O}_3$ as the solvent.

with the calorimetric data according to the third-law assessment becoming slightly poorer.

The value of $\Delta_{f,\text{ox}}H_{298\text{K}}^0$ from the present work was then combined with the heat capacity and entropy data to generate smoothed values of the free energy of reaction 9 to give:

$$\Delta_{f,\text{ox}}G^0(\pm 200) = -26780 + 11.434 T \quad (860 \leq T \leq 1350 \text{ K}) \quad (12)$$

The free energy of the equivalent high-temperature reaction between zircon, tetragonal ZrO_2 , and the cristobalite form of SiO_2 (reaction 1) was obtained in a similar way using the calorimetric data in Table 3:

$$\Delta_{f,\text{ox}}G^0(\pm 200) = -39090 + 20.173 T \quad (1430 \leq T \leq 2000 \text{ K}) \quad (13)$$

These free energies are plotted as a function of temperature in Figure 4. There is good agreement with the earlier results of Rosen and Muan (1965), given their estimated uncertainty of ± 0.4 kJ/mol. The slight tendency of the results of Rosen and Muan (1965) to diverge from the calculated line at higher temperatures may be due to increasing substitution of CoO in the tetragonal ZrO_2 of their experiments with increasing temperature. This sub-

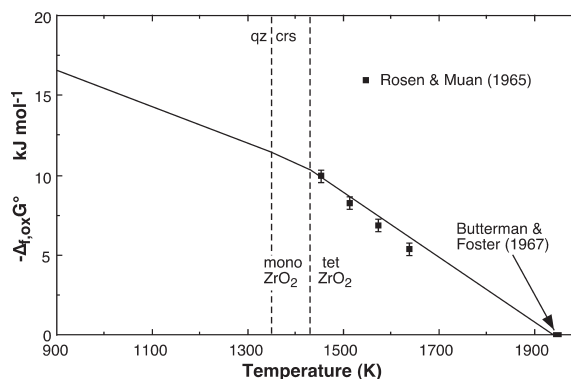


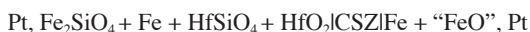
FIGURE 4. The free energy of formation of zircon from the oxides ($\Delta_{f,\text{ox}}G^0$) from the present results and calorimetric data (solid line), compared to the earlier measurements of Rosen and Muan (1965), and the decomposition to ZrO_2 and SiO_2 (cristobalite) at 1940 K as observed by Buttermann and Foster (1967). The transition temperatures of β -quartz to cristobalite at 1350 K (from O'Neill 1987b) and of monoclinic ZrO_2 (baddelyite) to the tetragonal form at 1430 K (see Appendix 1) are indicated by the vertical dashed lines.

stitution is limited to less than 2% by the observations of Rosen and Muan (1965), but from $\Delta(\Delta G^\circ) = nRT \ln(X)$, the free energy change involved could amount to 0.55 kJ/mol for $X = 0.98$ if n is two (i.e., for mixing on two sublattices, Co^{2+} and Zr^{4+} on a cation sublattice, and O^{2-} and vacancies on an anion sublattice).

Another novel means of measuring the free energy of formation of zircon recently has been reported by Newton et al. (2005). These investigators determined the solubility of SiO_2 in H_2O in equilibrium with $\text{ZrSiO}_4 + \text{ZrO}_2$ at 800 °C and 1.2 GPa. By comparing this solubility with that in equilibrium with pure SiO_2 (quartz), and invoking a model for activity-composition relations in H_2O - SiO_2 fluids, they obtained a value of $\Delta_{f,\text{ox}}G^0$ for zircon at 800 °C, 1.2 GPa of -18.5 ± 0.6 kJ/mol. Using $\int_0^{1.2\text{GPa}} \Delta V(T,P) dP = 6.7$ kJ/mol, calculated with the equation of state recommended by Holland and Powell (1998) together with the data tabulated in that reference, gives $\Delta_{f,\text{ox}}G^0 = -11.8$ kJ/mol at 800 °C and 1 bar, which is 2.7 kJ/mol less negative than the value obtained in this study.

Free energy of formation of hafnon (HfSiO₄)

The results from the cell with the configuration:



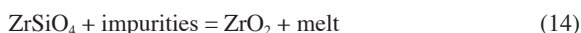
are reported in Table 2 and plotted as a function of temperature in Figure 2. The data fall on a line parallel to those from the Zr runs, but displaced to ~2.5 mV lower, meaning that hafnon is ~1 kJ/mol more stable than zircon relative to its component oxides. The parallelism of the two sets of data also means that the entropy of formation of hafnon from the oxides is similar to zircon, and this has been used to estimate the entropy of hafnon at 298.15 K and its high-temperature heat capacity (Table 3). With these estimates, the third-law analysis of the data gives $\Delta_{\text{r,ox}} H_{298\text{K}}^0 = -24.98$ kJ/mol, with an uncertainty similar to that for the Zr reaction, ± 0.2 kJ/mol. This value is in agreement with a value of -22.3 ± 4.7 kJ/mol measured by drop solution calorimetry (quoted in Table 1 of Navrotsky and Ushakov 2005).

DISCUSSION

Thermal decomposition of ZrSiO₄ to ZrO₂(tetragonal) and SiO₂(cristobalite)

Equation 13 predicts that the decomposition of zircon to tetragonal ZrO₂ plus cristobalite (reaction 1) should occur at 1938 K. The uncertainty depends greatly on the calorimetric data, particularly the data for the monoclinic to tetragonal transition in ZrO₂ (Appendix 1), compared to which the uncertainties in the present results are trivial. Nevertheless, agreement with the experimentally observed decomposition temperature would be a valuable indication of the internal consistency of the data for both ZrSiO₄ and ZrO₂.

Curtis and Sowman (1953) reported what they believed to be the thermal decomposition of zircon to its component oxides started at 1811 K. This datum was used by the compilers of the JANAF tables (Stull et al. 1965) to deduce the enthalpy of formation of zircon, and these tables have stood staunchly by this estimate through subsequent editions (e.g., Chase 1998). However, it seems apparent from their description of their experiments that what Curtis and Sowman (1953) observed was not reaction 1, but rather partial melting induced by the impurities in their sample, according to the reaction:



This would explain why only a small extent of reaction was observed at 1811 K despite reaction 1 being univariant, and why cristobalite was not observed as a reaction product. It seems reasonable to expect that impurity induced partial melting would occur at about this temperature, given that the sample used by Curtis and Sowman contained a considerable amount of impurities (1.1 wt% Al₂O₃ is quoted, and the presence of excess SiO₂ was not sought in the analysis), and that the eutectic in the pure ZrO₂-SiO₂ system is at 1960 K, as determined by Butterman and Foster (1967).

The more convincing study of Butterman and Foster (1967) determined the temperature of decomposition as 1949 ± 7 K, in excellent agreement with the present results. The weakness of

the Butterman and Foster (1967) study is that again cristobalite was not identified positively. Their results have recently been confirmed by Kamaev et al. (2005) by DTA, who report a decomposition temperature of 1947 ± 7 K, but also without positive identification of the form of silica.

In their high-temperature neutron diffraction study of synthetic ZrSiO₄, Mursic et al. (1992) reported "a previously unknown displacive structural change in the vicinity of 1100 K," (p. 584) and onset of the decomposition of the zircon at 1750 K. Again ZrO₂ was identified in the breakdown product, but not cristobalite. Instead, Mursic et al. observed "no traces of a third phase," (p. 586) but an increase in diffuse background scattering. The extent of the reaction also was quite low, the sample at 1900 K still consisting mostly of ZrSiO₄. The zircon sample used by Mursic et al. (1992) was obtained commercially, and no details on its synthesis conditions were given. Because of its generally refractory nature, zircon is often synthesized using an alkali (Li or Na) tungstate, molybdate, or borate flux to obtain well-crystallized material. Melting of residual flux (e.g., present in the sample as melt inclusions) near 1100 K might result in liquid-phase sintering causing the sample position to change (the melting points of Li- or Na-tungstates, molybdates or borates are mostly in the range 1000 to 1200 K). Perhaps this was responsible for the putative phase transition, which is manifested in the neutron diffraction data only by discontinuities in the scale factor and the lattice parameters vs. temperature. No other evidence exists for anomalous properties in synthetic zircon in this temperature range, although metamict natural zircons might be expected to begin recrystallizing at about this temperature. At higher temperatures, incongruent dissolution of the ZrSiO₄ into the flux would result in the appearance of ZrO₂, as observed; the diffuse background scattering could be from SiO₂-rich melt.

In assessing the observations of Mursic et al. (1992) and of Curtis and Sowman (1953), it is important to remember that the reaction of zircon to ZrO₂ plus cristobalite is univariant, and should occur at a unique temperature at ambient pressure. Although overstepping of such a reaction due to a nucleation barrier might be expected, the persistence of coexisting products and reactants to well over a hundred degrees above the equilibrium temperature seems unlikely, especially given the high temperatures involved.

Hafnon is slightly more stable relative to its oxide components (monoclinic HfO₂ and SiO₂) than zircon, and the phase transformation in HfO₂ from the monoclinic to the tetragonal form takes place at higher temperatures than in ZrO₂. Both these factors mean that the analogous decomposition of hafnon would take place at higher temperatures, and probably above the melting point of cristobalite, making it metastable relative to incongruent melting.

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REFERENCES CITED

- Barin, I. (1995) Thermochemical Data of Pure Substances (3rd ed.), 816 p. VCH Publishers, Weinheim.

- Butterman, W.C. and Foster W.R. (1967) Zircon stability and the ZrO_2 - SiO_2 phase diagram. *American Mineralogist*, 52, 880–885.
- Chase, M.W., Jr. (1989) NIST-JANAF thermochemical tables (4th ed.). *Journal of Physics and Chemical Reference Data*, Monograph 9, 1–1951.
- Chekhovskoi, V.Y., Zhukova, I.A., and Tarasov, V.D. (1979) Enthalpy and heat capacity of zirconium dioxide in the high-temperature region 1100–2500 K. *High Temperature*, 17, 637–640.
- Coughlin, J.P. and King, E.G. (1950) High-temperature heat contents of some zirconium-containing substances. *Journal of the American Chemical Society*, 72, 2262–2265.
- Curtis, C.E. and Sowman, H.G. (1953) Investigation of the thermal dissociation, reassociation, and synthesis of zircon. *Journal of the American Ceramic Society*, 36, 190–198.
- Dallwitz, W.H., Green, D.H., and Thompson, J.E. (1966) Clinostatite in a volcanic rock from the Cape Vogel area, Papua. *Journal of Petrology*, 7, 375–403.
- Du, Y. and Jin, Z. (1991) Optimization and calculation of the ZrO_2 - MgO system. *CALPHAD*, 15, 59–68.
- Ellison, A.J.G. and Navrotsky, A. (1992) Enthalpy of formation of zircon. *Journal of the American Ceramic Society*, 75, 1430–1433.
- Garvie, R.C. and Goss, M.F. (1986) Intrinsic size dependence of the phase transformation temperature in zirconia microcrystals. *Journal of Materials Science*, 21, 1253–1257.
- Gebauer, D., Grünfelder, M., Titon, G., Trommsdorf, V., and Schmid, S. (1992) The geodynamic evolution of garnet-peridotites, garnet pyroxenites and eclogites of Alpe Arami and Cima di Gagnone (central Alps) from early Proterozoic to Oligocene. *Schweizerische Mineralogische und Petrographische Mitteilungen*, 72, 107–111.
- Grieco, G., Ferrario, A., Von Quadt, A., Koeppl, V., and Mathez, E.A. (2001) The zircon-bearing chromitites of the phlogopite peridotite of Finero (Ivrea zone, Southern Alps): Evidence and geochronology of a metasomatized mantle slab. *Journal of Petrology*, 42, 89–101.
- Haggerty, S.E., Raber, E., and Naeser, C.W. (1983) Fission-track dating of kimberlitic zircons. *Earth and Planetary Science Letters*, 63, 41–50.
- Holland, T.J.B. and Powell, R. (1998) An internally consistent thermodynamic data set for phases of petrological interest. *Journal of Metamorphic Geology*, 16, 309–343.
- Kamaev, D.N., Archugov, S.A., and Mikhailov, G.G. (2005) Study and thermodynamic analysis of the ZrO_2 - SiO_2 system. *Russian Journal of Applied Chemistry*, 78, 200–203.
- Kelley, K.K. (1941) The specific heat at low temperatures of ferrous silicate, manganese silicate and zirconium silicate. *Journal of the American Chemical Society*, 63, 2750–2752.
- — — (1944) Specific heat of zirconium dioxide at low temperatures. *Industrial and Engineering Chemistry*, 36, 377.
- Kinny, P.D. and Dawson, J.B. (1992) A Mantle Metasomatic Injection Event Linked To Late Cretaceous Kimberlite Magmatism. *Nature*, 360, 726–728.
- Kohlhaas, R., Dünner, P., and Schmitz-Pranghe, N. (1967). Über die Temperaturabhängigkeit der Gitterparameter von Eisen, Kobalt und Nickel im Bereich hoher Temperaturen. *Zeitschrift für Angewandte Physik*, 23, 245–249.
- Mitsuhashi, T. and Fujiki, Y. (1973) Phase transformation of monoclinic ZrO_2 single crystals. *Journal of the American Ceramic Society*, 56, 493.
- Mursic, Z., Vogt, T., and Frey, F. (1992) High-temperature neutron powder diffraction study of $ZrSiO_4$ up to 1900 K. *Acta Crystallographica*, B48, 584–590.
- Navrotsky, A. and Ushakov, S.V. (2005) Thermodynamics of oxide systems relevant to alternative gate dielectrics. In A.A. Demkov and A. Navrotsky, Eds., *Materials Fundamentals of Gate Dielectrics*, p. 57–108. Springer, Dordrecht.
- Newton, R.C., Manning, C.E., Hanchar, J.M., and Finch, R.J. (2005) Gibbs free energy of formation of zircon from measurement of solubility in H_2O . *Journal of the American Ceramic Society*, 88, 1854–1858.
- O'Neill, H.St.C. (1987a) Quartz-fayalite-iron and quartz-fayalite-magnetite equilibria and the free energy of formation of fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4). *American Mineralogist*, 72, 67–75.
- — — (1987b) Free energies of formation of NiO , CoO , Ni_2SiO_4 , and Co_2SiO_4 . *American Mineralogist*, 72, 280–291.
- — — (1988) Systems Fe-O and Cu-O: thermodynamic data for the equilibria Fe - FeO , Fe - Fe_2O_3 , FeO - Fe_2O_3 , Fe_2O_3 - Fe_3O_4 , Fe_3O_4 - FeO , Fe_3O_4 - Fe_2O_3 , Cu - Cu_2O , and Cu_2O - CuO from emf measurements. *American Mineralogist*, 73, 470–486.
- O'Neill, H.St.C. and Powncely, M.I. (1993) Thermodynamic data from redox reactions at high temperatures. I. An experimental and theoretical assessment of the electrochemical method using stabilized zirconia electrolytes, with revised values for the Fe - FeO , Co - CoO , Ni - NiO , and Cu - Cu_2O oxygen buffers, and new data for the W - WO_2 buffer. *Contributions to Mineralogy and Petrology*, 114, 296–314.
- Ono, A. (1972) Syntheses of monoclinic and tetragonal ZrO_2 at high temperatures. *Mineralogical Journal*, 6, 442–447.
- Orr, R.L. (1953) High-temperature heat contents of hafnium dioxide and hafnium tetrachloride. *Journal of the American Chemical Society*, 75, 1231–1232.
- Pankratz, L.B. (1982) *Thermodynamic Properties of Elements and Oxides*, 509 p. United States Bureau of Mines, Washington, D.C.
- Richet, P., Bottinga, Y., Denielou, L., Petit, J.P., and Tequi, C. (1982) Thermodynamic properties of quartz, cristobalite and amorphous SiO_2 —drop calorimetry measurements between 1000 and 1800 K and a review from 0 to 2000 K. *Geochimica et Cosmochimica Acta*, 46, 2639–2658.
- Robie, R.A. and Hemingway, B.S. (1995) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin, 2131, 461 p.
- Robie, R.A., Hemingway, B.S., and Fisher, J.R. (1979) Thermodynamic properties of minerals and related substances at 298.15 K and 1 Bar (10^5 Pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin, 1452, 456 p.
- Robie, R.A., Finch, C.B., and Hemingway, B.S. (1982) Heat capacity and entropy of fayalite (Fe_2SiO_4) between 5.1 and 383 K: comparison of calorimetric and equilibrium values for the QFM buffer reaction. *American Mineralogist*, 67, 463–469.
- Rosen, E. and Muan, A. (1965) Stability of zircon in the temperature range 1180 to 1366 °C. *Journal of the American Ceramic Society*, 48, 603–604.
- Schuijling, R.D., Vergouwen, L., and van der Rijst, H. (1976) Gibbs energies of formation of zircon ($ZrSiO_4$), thorite ($ThSiO_4$), and phenacite (Be_2SiO_4). *American Mineralogist*, 61, 166–168.
- Smyth, J.R. (1974) Experimental study of the polymorphism of enstatite. *American Mineralogist*, 59, 345–352.
- Song, S.G., Zhang, L.F., Niu, Y.L., Su, L., Jian, P., and Liu, D.Y. (2005) Geochronology of diamond-bearing zircons from garnet peridotite in the North Qaidam UHPM belt, Northern Tibetan Plateau: A record of complex histories from oceanic lithosphere subduction to continental collision. *Earth and Planetary Science Letters*, 234, 99–118.
- Stull, D.R. (1965) *JANAF Tables of Thermochemical Data*, 945 p. Dow Chemical Company, Midland, Michigan.
- Subbarao, E.C., Maiti, H.S., and Srivastava, K.K. (1974) Martensitic transformation in zirconia. *Physica Status Solidi A—Applied Research*, 21, 9–40.
- Todd, S.S. (1953) Heat capacities at low temperatures and entropies at 298.16 K, of hafnium dioxide and hafnium tetrachloride. *Journal of the American Chemical Society*, 75, 3035–3036.
- Tojo, T., Atake, T., Mori, T., and Yamamura, H. (1999). Heat capacity and thermodynamic functions of zirconia and yttria-stabilized zirconia. *Journal of Chemical Thermodynamics*, 31, 831–845.
- Wolten, G.M. (1963) Diffusionless phase transformations in zirconia and hafnia. *Journal of the American Ceramic Society*, 46, 418–422.

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APPENDIX I. THERMODYNAMIC PROPERTIES OF ZrO_2 AND ITS MONOCLINIC TO TETRAGONAL PHASE TRANSITION

ZrO_2 has a monoclinic crystal structure in the temperature range covered by the solid-electrolyte experiments of this study, but it transforms to a tetragonal structure at slightly higher temperatures. An interesting aspect of this phase transition is that it is martensitic (Wolten 1963; Subbarao et al. 1974; Garvie and Goss 1986). Such transitions are fairly common in metals, but are rarer in non-metallic phases. Another well-known example of geological interest is the protoenstatite to clinoenstatite inversion that causes the twinning seen in the low-Ca clinopyroxene of boninites (Dallwitz et al. 1966; Smyth 1974).

The defining feature of a martensitic phase transition is that the transition takes place by the cooperative movement of large numbers of atoms by a shear mechanism. The rearrangement is diffusionless, as the atoms move less than an interatomic distance. In what may be thought of as the idealized case, the transition starts on pre-existing planar defects, of the type present in all real crystals, that form a local geometry similar to the transformed phase. The transition therefore requires no nucleation and hence no activation energy, and is known as “athermal.” This is in contrast to phase transitions that require nucleation, and hence an activation energy, which are designated “isothermal.” In practice, many martensitic transitions, although being approximately athermal, appear also to have an isothermal component.

The kinetics of an athermal transition are extremely fast, approaching the speed of sound in the crystal. Consequently, the high-temperature form of an athermal transition cannot be retained at room temperature by quenching, at least as a pure phase.

In many cases, martensitic transformations are accompanied by an increase in strain energy and/or surface energy between the transformed and untransformed parts of the crystal, which puts a stop to further transformation at that particular temperature. Thus, on heating a crystal of the low-temperature form above the transition temperature, a certain fraction transforms almost instantaneously to the high-temperature form, but then no further reaction occurs, and an increase in temperature is required to increase the fraction of the high-temperature polymorph. The result is that the two polymorphs coexist over a finite temperature interval. The reverse happens on cooling, such that a mixture of both polymorphs is commonly obtained on material quenched from above the transition temperature. ZrO_2 is a good example of this phenomenon, and this effect is seen in this study in the ZrO_2 starting material, which contained both the tetragonal (high-temperature) and the monoclinic (low-temperature) forms. The mineral name "baddeleyite" properly refers to the monoclinic form.

Martensitic phase transitions usually exhibit thermal hysteresis as regards the extent of the transition at a given temperature between heating and cooling cycles, and this hysteresis is quite large in ZrO_2 , in most samples on the order of several hundred kelvins. Because of the role that defects and strain and surface energies play in promoting or retarding the transition, details such as the temperature at which the transition begins, and the width of the thermal hysteresis loop, depend on the grain size and thermal history of the sample, as well as any deviations from the ideal chemical composition (e.g., impurities or nonstoichiometry).

The martensitic nature of the transition is of importance here because it raises problems in extracting its thermodynamic properties (i.e., the temperature, enthalpy, and entropy of transition) from the usual calorimetric measurements. The thermodynamic transition temperature can be defined as the temperature at which the free energies of the two polymorphs, each in their pure form, would be equal. Because the "pure form" is specified, this definition excludes the strain and surface energies, etc., that accompany the transition in practice. As the above discussion should have made clear, the thermodynamic transition temperature cannot be found from straightforward heating or cooling experiments. The problem was discussed by Garvie and Goss (1986), who presented a simple theory that accounts for the variation in temperature of the transition in terms of the surface energy (hence size) of the crystal domains undergoing the transition. Garvie and Goss (1986) further suggested that two previous studies could be used to deduce the thermodynamic transition temperature. In one, Ono (1972) grew single crystals of ZrO_2 from a borax flux at different temperatures. Above 1438 ± 10 K, the crystals had a tetragonal crystal habit, and below 1413 ± 10 K a monoclinic habit, implying that the thermodynamic transition temperature lies between these limits. In the second study, Mitsuhashi and Fujiki (1973) determined the temperature of the transition on heating of a population of 65 "pristine" small single crystals of monoclinic ZrO_2 . Here "pristine" means that the crystals were prepared in the monoclinic stability field and had not previously been transformed to the tetragonal structure. They would thus be free of such defects as are caused by previous transformations. Mitsuhashi and Fujiki (1973) found that each individual crystal transformed completely over a narrow temperature interval (0.1 K), but the population as a whole

exhibited an approximately normal distribution of transition temperatures, with a mean of 1447 K and a standard deviation of 7 K. Garvie and Goss (1986) adopted this mean temperature as the thermodynamic transition temperature, but it seems to me that the minimum observed temperature is more appropriate, as some overstepping of the transition due to its slightly isothermal character is to be expected. This minimum temperature observed for the transition was 1433 ± 3 K. Here, I adopt $T_{tr} = 1430$ K; this temperature also lies in the middle of the bracket reported by Ono (1972), and is not too discrepant from the 1418 ± 10 K value that he himself recommended from an additional observation that a small amount of the tetragonal form appeared when he heated his samples to 1423 K.

In interpreting measurements of heat content by drop calorimetry from temperatures well above the transition temperature, all the ZrO_2 is assumed to be tetragonal at the temperature T before the drop. If back-transformation to the monoclinic form is complete after the drop, then:

$$H_T - H_{298} = \int_{298}^{T_{tr}} C_p(\text{mono})dT + \int_{T_{tr}}^T C_p(\text{tet})dT + \Delta_{tr}H^0 \quad (A1)$$

Heat content measurements have been reported by Coughlin and King (1950) and by Chekhovskoi et al. (1979). There is excellent agreement between the two studies at temperatures below the transition, but above the transition, the measurements of Chekhovskoi et al. (1979) are about 3–4% higher than those of Coughlin and King (1950). A possible explanation is that the sample used by the latter investigators failed to revert fully to the monoclinic form on quenching (as in the starting material of this study). Consequently the data of Chekhovskoi et al. (1979) are preferred for the tetragonal form (10 data from 1574 to 2414 K). Although it is by no means certain that the material of this latter study did transform fully to the monoclinic (low-temperature) form during the calorimetric drop, the reported transition temperature of 1423 K is sufficiently close to the thermodynamic transition temperature deduced here (i.e., 1430 K) to suggest that the material used by Chekhovskoi et al. (1979) transformed, somewhat unusually, without much hysteresis, implying further that the degree of transformation may have been complete. Future high-temperature calorimetry on the martensitic transition in ZrO_2 should ascertain the extent of the phase transformation directly on each and every sample that passes through the transition (e.g., by XRD). It is necessary for each sample to be examined because the fraction of transformed material may depend on its history, including previous journeys through the transition. Material that only partially reverts to the low-temperature form (e.g., like the starting material of this study) would give an apparent value of $\Delta_{tr}H^0$ that is too small.

For the monoclinic polymorph, both sets of data were used: 27 data from 397 to 1459 K from Coughlin and King (1950), 4 data from 1157 to 1350 K from Chekhovskoi et al. (1979), together with 24 data from 250 to 300 K from the heat-capacity measurements by adiabatic calorimetry of Tojo et al. (1999). These latter data are in good agreement with the earlier study of Kelley (1944), but the measurements of Tojo et al. (1999) extend to lower temperature (13 vs. 52 K), and their value for the entropy of ZrO_2 has therefore been adopted. The thermodynamic data for ZrO_2 derived from the above assessment are given in Table 3.