Palladium oxide equilibration and the thermodynamic properties of MgAl₂O₄ spinel

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ABSTRACT

The technique of palladium oxide equilibration was used to measure activities of MgO and Al₂O₃ in stoichiometric MgAl₂O₄ spinel at 1150–1400 °C. Activities of MgO range from 0.63 ± 0.03 to 1.00 ± 0.07, and activities of Al₂O₃ range from 0.09 ± 0.01 to 0.05 ± 0.01 (1σ). The activities yield free energies of formation of spinel from the oxides, \( \Delta G^\circ \), ranging from \(-31\) kJ/mol at 1150 °C to \(-39\) kJ/mol at 1400 °C, with a precision of 2–19% (1σ). The derived values of \( \Delta G^\circ \) are consistent with the equilibrium amount of disorder present in the spinel under experimental conditions because the measured activities reflect equilibration at high temperature. Calorimetric heat contents were corrected for the state of order using a Landau formulation for the equilibrium amount of disorder in spinel as a function of temperature. The corrected heat contents, together with the measured \( \Delta G^\circ \), were used to produce a new, self-consistent \( C_p \) function that can account for available experimental data. The modeling results are consistent with previous suggestions that short-range ordering may be important in spinel.

INTRODUCTION

Spinels are constituents of many igneous and metamorphic rocks due to their wide stability in pressure, temperature, and composition space. Partly because of their widespread occurrence, spinels are important petrogenetic indicators and have been used in the calibration of a variety of widely used mineral geothermometers and geobarometers (Buddington and Lindskle, 1964; Sack, 1982; Mattioli et al., 1989; Sack and Ghiorso, 1991). However, our understanding of spinel equilibration is complicated by an incomplete knowledge of the thermodynamic properties of the various end-members.

Deficiencies in the current data base are illustrated by the case of the end-member spinel MgAl₂O₄. Calorimetric measurements of heat capacity and heat content of this mineral (King, 1955; Bonnickson, 1955; Richet and Fiquet, 1991) are insufficient because they do not account for the variable amounts of cation disorder present in MgAl₂O₄. The cation configuration of spinel varies with increasing temperature from a normal distribution, \( \text{Mg}^{2+}\text{(Al}^{3+}\text{)}\text{O}_4 \), with \( \text{Al}^{3+} \) restricted to octahedral sites, toward an inverse distribution, \( \text{Al}^{3+}\text{(Mg}^{2+}\text{Al}^{3+}\text{)}\text{O}_4 \), with \( \text{Al}^{3+} \) substituting into tetrahedral sites (Navrotsky and Kleppa, 1967). Because of kinetic factors, the reconfiguration process is immeasurably slow on the laboratory time scale below \( \sim 700 \) °C, although it occurs on the order of a few hours at 700–900 °C (Fischer, 1967; Peterson et al., 1991). Because the rate slows with decreasing temperature, reordering from high- to low-temperature equilibrium states is often incomplete.

NMR studies of cation occupancy reveal that if spinel is equilibrated at high temperature and then quenched rapidly to below 900–1000 °C, it fails to reorder to the equilibrium state appropriate to the quench temperature but instead retains a residual amount of the disorder present at high temperature (Wood et al., 1986; Millard et al., 1992). This greatly complicates the interpretation of heat-capacity and drop-calorimetric heat-content measurements on MgAl₂O₄. Because synthetic spinels are never perfectly normal, heat capacities measured at low temperature \( (T < 300 \) °C) on synthetic spinel (King, 1955) actually apply to spinel with nonequilibrium disorder. Likewise, heat contents measured on samples quenched from high temperature to below \( \sim 1000 \) °C (Bonnickson, 1955; Richet and Fiquet, 1991) have values lower than the equilibrium values because a reordering contribution is lost (Navrotsky and Kleppa, 1967). Moreover, because spinel can reorder when annealed between 700 and 1000 °C, calorimetric data obtained below 1000 °C are strongly influenced by the thermal history of the starting material.

Researchers have employed a number of methods to extract the equilibrium thermodynamic properties of spinel. For example, Helgeson et al. (1978), Berman (1988), Holland and Powell (1990), and Hallstedt (1992) combined phase-equilibrium data with calorimetric constraints to produce internally consistent sets of thermodynamic data designed to incorporate the equilibrium disorder in the spinel without explicitly quantifying it. However, the accuracy of these models for spinel depends on the quality of the phase-equilibrium and calorimetric data employed and on the validity of the models used to describe the free energies of individual phases in each equilibrium. An alternative method is to estimate the enthalpy and entropy of disordering and then recalculate
the free energy of formation to equilibrium values (Chase et al., 1985), but this procedure is vulnerable to errors in estimating the cation distribution in the spinel and in the model adopted to calculate the entropy. Overall, the derived free energies of formation of MgAl2O4 spinel from the oxides, ΔG°, cited in the literature range over >10 kJ/mol at a particular temperature, a significant discrepancy.

It is desirable in this and similar cases to have an experimental technique for determining thermodynamic properties of materials at high temperature so that the data are independent of any structural or ordering changes that may occur upon quenching. We have developed such a technique, palladium oxide equilibration (Chamberlin et al., 1994), which provides activities of oxide components at high temperature using the equilibrium between a mineral sample and Pd metal alloy at fixed fO2 and temperature. It shares a basic approach with techniques developed by the steel industry for the study of silicate slags in equilibrium with metallic Fe (e.g., Rein and Chipman, 1963, 1965) but is more precise because of the unusual properties of Pd and the application of modern analytical techniques. It also resembles more recent efforts to study the activities of transition-metal oxides by equilibration with an alloy containing the corresponding transition metal (e.g., Dudson and Fraser, 1981; Grove, 1981; Snyder and Carmichael, 1992), but these methods have neither the precision of palladium oxide equilibration nor its ability to measure the activities of less easily reduced oxides such as MgO, Al2O3, and SiO2.

The experimental method, described in detail in Chamberlin et al. (1994), involves equilibrating Pd plus a mineral at the same time as Pd plus an oxide standard. At a given fO2, a small amount of each oxide component reduces to metal and dissolves into the Pd, forming an alloy. Because sample and standard are equilibrated simultaneously, they are at the same temperature and fO2, and, taking the example of the oxide component Al2O3, we can write

\[ K(T) = \frac{\gamma_{\text{Al}}^{\text{Pd, min}}}{(\gamma_{\text{Al}}^{\text{Al}} X_{\text{Al}}^{\text{min}})^2 (f_{\text{O2}}^{\text{Pd}})^{X_{\text{Al}}^{\text{min}}} (f_{\text{O2}}^{\text{Al}})^{X_{\text{Al}}^{\text{min}}}} \]

where \( K \) is the equilibrium constant for the oxidation reaction \( 2\text{Al}(\text{mol}) + \frac{3}{2}\text{O}_2 (\text{at}) = \text{Al}_2\text{O}_3 (\text{cor}) \), \( T \) is the temperature in K, \( a_{\text{min}}^{\text{Pd, Al}} \) is the activity of Al2O3 in the mineral relative to corundum, \( f_{\text{O2}}^{\text{Pd}} \) is the O2 fugacity, \( X_{\text{Al}}^{\text{min}} \) is the mole fraction of Al in Pd in equilibrium with the mineral, \( X_{\text{Al}}^{\text{cor}} \) is the mole fraction of Al in Pd in equilibrium with the oxide standard corundum, \( \gamma_{\text{Al}}^{\text{Pd}} \) is the activity coefficient of Al in Pd, and \( \gamma_{\text{Al}}^{\text{Al}} = 1.0 \). Because the activity coefficient of Al in Pd is essentially constant in the dilute range (up to thousands of parts per million: Chamberlin et al., 1994), Equation 1 simplifies to

\[ a_{\text{Pd, Al}}^{\text{min}} = \left( \frac{X_{\text{Pd}}^{\text{Al, min}}}{X_{\text{Pd}}^{\text{Pd, min}}} \right)^2 \]

Since \( \gamma_{\text{Mg}}^{\text{Pd}} \) is also virtually constant in the dilute range, we can write an analogous expression for MgO:

\[ a_{\text{Pd, Mg}}^{\text{min}} = \frac{X_{\text{Pd}}^{\text{Mg, min}}}{X_{\text{Pd}}^{\text{Pd, min}}} \]

In this treatment, the only measurements involved in the determination of activities are the concentrations of Mg and Al in the Pd, and therefore the uncertainties in \( T \) and \( f_{\text{O2}} \) measurements do not contribute to the uncertainty of the activity determination. These concentrations can be measured precisely, because at experimentally feasible \( f_{\text{O2}} \) (near the iron + wüstite O buffer), Mg and Al dissolve in Pd in amounts easily and accurately measured by electron microprobe (hundreds to thousands of parts per million: Ramsden and French, 1990). Any errors contributed by a particular correction procedure are minimized because activities are determined from concentration ratios. Palladium oxide equilibration can therefore be a precise method for the determination of oxide activities, and from them, ΔG°. This technique is ideal for the study of MgAl2O4 spinel, as all measurements of thermodynamic properties reflect equilibration at the temperature of interest, and therefore structural or ordering changes upon quenching play no role in the results. In this paper, we apply palladium oxide equilibration to the determination of oxide activities for stoichiometric MgAl2O4 spinel and combine the results with calorimetric data and direct measurements of cation disorder to derive thermodynamic properties as a function of temperature for spinel with equilibrium disorder.

**EXPERIMENTAL PROCEDURE**

**Sample preparation**

Powdered stoichiometric MgAl2O4 spinel for these experiments was provided by Glen S. Mattioli of the University of Puerto Rico, Mayagüez. Details of synthesis procedures are given in Mattioli et al. (1987). The spinel was analyzed by X-ray diffraction (XRD), and the lattice parameter, \( a_0 = 8.0855(11) \) Å, is consistent with pure stoichiometric spinel \( [a_0 = 8.0844(3); \text{Navrotovsky et al., 1986}] \). In addition, periclase-saturated spinels, which are essentially stoichiometric in composition (Roy et al., 1953; Alper et al., 1962; Lejus, 1964; Colin, 1968), were synthesized by grinding mixtures of reagent-grade MgO and Al2O3 (JMC Puratronic) for 5 h under ethanol in an agate mortar and sintering for 48 h in air at 1400 °C. XRD analysis of the sintered material confirmed the presence of periclase and spinel. Samples were prepared by pressing powdered starting material into pellets around 99.997% pure Pd wire 3–4 mm in length and 0.25 mm in diameter (Alfa Products). No binder was used because of the tendency of organic binders to leave a C-rich residue in the sample at low \( f_{\text{O2}} \). The pellets were placed in Pd-foil buckets \( \frac{1}{4} \) in. in diameter. The pure oxide standards were prepared by pressing analytical-grade MgO or Al2O3 (JMC Puratronic) around pure Pd wire 3–4 mm long. Before pressing, the initially partially amorphous Al2O3 was converted to corundum (confirmed by XRD)
by heating for about 6 h at 1500 °C in a Pt crucible. The MgO starting material was found by XRD to be crystalline periclase. The Pd + periclase or Pd + corundum pellets were placed in open capsules made from crushable-magnesia or -alumina rods ¼ in. in diameter (Ozark Technical Ceramics).

**Experimental methods**

Experiments were conducted in a 1-atm home-built furnace with MoSi₂ heating elements. Temperature was controlled to within 1–2 °C by a Eurotherm 812 Controller-Programmer and measured with a Type S thermocouple calibrated at the melting point of Au. Stated temperatures are estimated to be accurate to ±3 °C. O₂ fugacity was set using mixtures of H₂ and CO₂ and measured with an yttria-doped zirconia solid-electrolyte O sensor (Ceramic Oxide Fabricators Pty., Australia). The sensor was calibrated at the iron + wüstite O buffer at 1200 and 1400 °C by measuring changes in the resistance of pure Fe wire as f₀₂ varied. Drift of the emf of the sensor during an experiment was typically 1 mV or less.

The samples and standards were suspended from Ir hanging wire and placed adjacent to each other in the 1-atm gas-mixing furnace. Experiments were conducted at 1150–1400 °C at 50 °C intervals. The f₀₂ was typically an order of magnitude or two below iron + wüstite. Experiments at T > 1250 °C were conducted for 1–3 d, and those at lower temperatures were conducted for 10 d. The results on stoichiometric spinel were reversed at 1200 and 1350 °C by approaching equilibrium from the high-concentration side by first equilibrating the Pd wires with spinel, periclase, and corundum at an f₀₂ half an order of magnitude lower than those of the final equilibrations. Experiments were terminated by drop quenching into deionized water at 25 °C. The pellets were removed from their containers, mounted in epoxy, and rough-polished to expose a lengthwise cross section through the Pd wire. The Pd was then fine-polished with diamond paste using an automatic polisher.

**Analytical techniques**

Analysis of the Pd alloys was performed on a JEOL 733 Superprobe operated at an accelerating potential of 15 keV, a takeoff angle of 40°, and a beam current of 100 nA. Pure Mg, Al, and Pd metal served as standards, and ZAF correction procedures were used to determine concentrations (Armstrong, 1988). Three points were analyzed across each Pd wire to determine heterogeneity. Each point in this profile was analyzed for at least 120 s, and all analysis points were chosen to be at least 20 μm away from the edge of the wire to avoid secondary fluorescence from the surrounding oxide. For the trace constituents Mg and Al, the k ratio for each analysis point was determined by averaging the k ratios measured by two to three spectrometers per point. The uncertainty in the k ratio for each sample wire was taken to be equal to the standard deviation over all analysis points. This standard deviation based on heterogeneity was similar in magnitude to the standard deviation of the mean based on counting statistics from the six to nine independent analyses per wire. Arithmetic corrections to the Mg and Al concentrations due to structure in the Pd background near the Mg and Al peaks were made by analyzing Puratronic Pd wire (JM Specialty Products) and subtracting from each sample analysis the false Mg and Al concentrations determined in the pure Pd wire. Previously analyzed binary Pd-Mg and Pd-Al alloys were reanalyzed during each microprobe session as a check on reproducibility of analysis; on the basis of the results of four sessions, the reproducibility with respect to mole fractions was found to be within 3% for Mg at X_Mg = 0.00720 and 1% for Al at X_AI = 0.01090.

Postexperiment analyses were performed on the presumably stoichiometric spinels to determine their Mg-Al ratios. These analyses were performed at 15 keV, a 40° takeoff angle, a 30-s counting time, and a 1-nA beam current to restrict the sampling volume to about 1 μm. Standardization was done on a stoichiometric Union Carbide MgAl₂O₄ laser crystal, and concentrations were determined through ZAF correction procedures (Armstrong, 1988). Analysis points on the stoichiometric spinel ranged from within 5 μm of the Pd to 1 mm or more away. Because the difference between accelerating potential and peak location is virtually identical for Mg and Al, signal loss due to porosity of the powdered spinel pellets is the same for both elements, and Mg-Al ratios can be determined to better than ±1% (J. Armstrong, P. Carpenter, 1990, personal communication).

**RESULTS**

Experimental conditions and analyses of Pd alloys are given in Table 1. Postexperiment analysis of selected pure spinels, including reversal experiments, show that with one exception they are stoichiometric to within a mole percent. Analysis of a pellet from a failed experiment at 1150 °C for 2 d shows a slight depletion in MgO (Mg to Al ranges down to 0.486). Table 2 shows the derived activities of MgO and Al₂O₃ relative to periclase and corundum for spinel and the ΔGₚ calculated from them using the equilibrium

\[
\text{MgO} + \text{Al}_2\text{O}_3 = \text{MgAl}_2\text{O}_4
\]

and the relation

\[
\Delta G_p^o = -RT \ln \frac{1}{a_{\text{MgO}}a_{\text{Al}_2\text{O}_3}}
\]

where \(a_{\text{MgO}}a_{\text{Al}_2\text{O}_3} = 1\) for pure end-member spinel with an equilibrium state of order. Table 2 includes the activities and ΔGₚ for both stoichiometric and periclase-saturated spinel. Figure 1 shows the experimentally determined ΔGₚ of spinel as a function of temperature. The ΔGₚ values determined in the periclase-saturated spinel are within 1σ uncertainty of those determined for the stoichiometric mineral, as expected given the mini-
TABLE 1. Experimental data for MgAl$_2$O$_4$

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$\log_{10} f_0$</th>
<th>t (h)</th>
<th>$X_{\text{pd}}^{\text{ext}}$</th>
<th>$X_{\text{pd}}^{\text{ext}}$</th>
<th>$X_{\text{pd}}^{\text{ext}}$</th>
<th>$X_{\text{pd}}^{\text{ext}}$</th>
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<tr>
<td>1154</td>
<td>-13.63</td>
<td>250</td>
<td>0.0090(16)</td>
<td>0.00140(14)</td>
<td>0.00069(5)</td>
<td>0.00191(2)</td>
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<tr>
<td>1200</td>
<td>-12.44</td>
<td>240</td>
<td>0.0098(1)</td>
<td>0.00097(3)</td>
<td>0.00029(7)</td>
<td>0.00113(7)</td>
</tr>
<tr>
<td>1201</td>
<td>-12.98</td>
<td>264</td>
<td>0.00012(7)</td>
<td>0.00019(7)</td>
<td>0.00071(1)</td>
<td>0.00271(6)</td>
</tr>
<tr>
<td>1201*</td>
<td>-13.49</td>
<td>144</td>
<td></td>
<td>0.00017(17)</td>
<td>0.00067(6)</td>
<td>0.00267(7)</td>
</tr>
<tr>
<td>1251</td>
<td>-11.79</td>
<td>45</td>
<td>0.0094(8)</td>
<td>0.00038(9)</td>
<td>0.00049(4)</td>
<td>0.00178(10)</td>
</tr>
<tr>
<td>1250**</td>
<td>-11.58</td>
<td>144</td>
<td>0.0099(4)</td>
<td>0.00028(3)</td>
<td>0.00118(3)</td>
<td></td>
</tr>
<tr>
<td>1300†</td>
<td>-11.32</td>
<td>89</td>
<td>0.00202(11)</td>
<td>0.00020(11)</td>
<td>0.00068(1)</td>
<td>0.00291(4)</td>
</tr>
<tr>
<td>1305</td>
<td>-11.19</td>
<td>88</td>
<td>0.00148(8)</td>
<td>0.00197(9)</td>
<td>0.00118(3)</td>
<td></td>
</tr>
<tr>
<td>1351*</td>
<td>-11.02</td>
<td>48</td>
<td>0.00206(12)</td>
<td>0.00026(12)</td>
<td>0.00070(7)</td>
<td>0.00248(1)</td>
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<tr>
<td>1352</td>
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<td>43</td>
<td>0.00221(3)</td>
<td>0.00235(4)</td>
<td>0.00089(3)</td>
<td>0.00343(8)</td>
</tr>
<tr>
<td>1356**</td>
<td>-10.33</td>
<td>23</td>
<td>0.00151(4)</td>
<td>0.00048(3)</td>
<td>0.00213(20)</td>
<td></td>
</tr>
<tr>
<td>1397†</td>
<td>-10.20</td>
<td>66</td>
<td>0.00287(13)</td>
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<td>0.00107(5)</td>
<td>0.00424(7)</td>
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<tr>
<td>1400</td>
<td>-10.17</td>
<td>44</td>
<td>0.00186(7)</td>
<td>0.00294(5)</td>
<td>0.00131(4)</td>
<td>0.00435(7)</td>
</tr>
<tr>
<td>1400</td>
<td>-10.17</td>
<td>38</td>
<td>0.00261(5)</td>
<td>0.00281(9)</td>
<td>0.00120(8)</td>
<td>0.00459(5)</td>
</tr>
<tr>
<td>1400**</td>
<td>-9.65</td>
<td>45</td>
<td>0.00153(4)</td>
<td>0.00044(1)</td>
<td>0.00198(9)</td>
<td></td>
</tr>
</tbody>
</table>

Note: numbers in parentheses indicate 1σ errors in the last digits based on heterogeneity. Temperatures are estimated to be accurate to ±3 °C and $f_0$ to ±0.05 log units. $X_{\text{pd}}^{\text{ext}}$ defined as mole fraction of solute i dissolved in Pd alloy in equilibrium with phase j.

* Reversal. First row refers to conditions of initial equilibration, the second to conditions of final equilibration.
** Periclase-saturated spinel; $a_{\text{MgO}}$ assumed to be one.
† Periclase-saturated spinel.

mical MgO solid solution implied by the MgO-Al$_2$O$_3$ phase diagram below 1500 °C (Roy et al., 1953; Alper et al., 1962; Lejus, 1964; Colin, 1968). The offset of the 1154 °C (1427 K) point (Fig. 1) from the trend of the others and the above analysis of the 1150 °C spinel suggests that incomplete diffusive rehomogenization of the spinel near the palladium-spinel interface during experiments may become a problem at $T < 1200$ °C (see the section on sources of experimental error). However, a close approach to equilibrium in the pure spinel experiments at $T \geq 1200$ °C is demonstrated by the other spinel analyses and by the reversal experiments, which reproduce the $\Delta G_f$ within 1σ uncertainty.

Figure 1 compares the experimentally determined $\Delta G_f$ with values from six compilations of thermodynamic data for minerals. The figure reveals that our experimental data for stoichiometric spinel are in good agreement with Chase et al. (1985) but are for the most part distinct at the 1σ level from the other compilations and at the 2σ level from the calorimetric values (Robie et al., 1978). The variation of our free energies with temperature implies an entropy of formation from the oxides of the order of 11–13 J/(mol·K) in this temperature range (see Eq. 14), a value comparable with that in Chase et al. (1985) [12–13 J/(mol·K)] but less than that in Hallstedt (1992) [~16 J/(mol·K)] and substantially larger than those of the four other data sets [2.5–8 J/(mol·K)].

DISCUSSION

**Sources of experimental error**

In addition to purely analytical sources of error, there are a variety of other possible contributions to error in the determination of oxide activities and free energies for palladium oxide equilibration. A full discussion of these contributions was given by Chamberlin et al. (1994). Basically, the method is critically dependent on the validity of Henry's law for Mg and Al in Pd. Although there is evidence for higher order dependence of the activity coefficients of Mg and Al at high concentrations (Schaller, 1978; R. Mendybaev, unpublished data), it should not be a factor in our results because the Mg and Al levels achieved in our experiments lie in the concentration range demonstrated to exhibit Henriean behavior. Also, we can assume that in the dilute range, there are no interactions between Mg and Al in the Pd alloy that influence activity coefficients. This assumption is supported by experiments on periclase- and corundum-saturated spinels, where the activity of the oxide with which the spinel was saturated was determined to be 1.0 within the uncertainty (this study; Chamberlin, 1994). Furthermore, we have used postexperiment microanalysis of the spinel and re-
universal experiments to show that any depletion in MgO of the thin layer of the spinel next to the Pd caused by the different solubilities of Mg and Al in the Pd is compensated during the experiment by diffusive rehomogenization of the spinel. The reproducibility and internal consistency of our results in Figure 1 and the success of the reversals suggest not only that our results closely approach equilibrium, but that sources of error other than those involved in the chemical analysis of the Pd alloys are minor, and that the error bars on $\Delta G_f$ from propagation of uncertainties in the analysis of the Pd alloys are realistic.

**Activities**

Table 2 reveals that the activity of MgO in spinel varies from about 0.6 in some of the stoichiometric spinels to 1 in the MgO-saturated spinels, even though the spinels appear to have the same Mg-Al ratios and the values of $\Delta G_f$ calculated from Equation 5 agree within 1σ. Stoichiometric spinels in equilibrium with melts in the system CaO-MgO-Al$_2$O$_3$-SiO$_2$-TiO$_2$ have $a_{MgO}$ as low as 0.2 (Chamberlin et al., 1994). This variation in activity is consistent with the Gibbs-Duhem equation, which requires in the binary system MgO-Al$_2$O$_3$ that variations in $a_{MgO}$ be coupled with variations in $a_{Al_2O_3}$. Specifically, for spinel,

$$\frac{d \mu_{MgO}^{\text{spinel}}}{d \mu_{Al_2O_3}^{\text{spinel}}} = \frac{d \ln a_{MgO}^{\text{spinel}}}{d \ln a_{Al_2O_3}^{\text{spinel}}} = -\frac{X_{MgO}}{X_{Al_2O_3}} \tag{6}$$

where $\mu_{i}^{\text{spinel}}$ is the chemical potential of species $i$ in spinel. For stoichiometric MgAl$_2$O$_4$,

$$\frac{d \ln a_{MgO}^{\text{spinel}}}{d \ln a_{Al_2O_3}^{\text{spinel}}} = -1. \tag{7}$$

**Free energies of formation**

There are several reasons for the differences between our values of $\Delta G_f$ and those of the other workers shown in Figure 1. Values given by Robie et al. (1978) were derived from the calorimetric work of Bonnickson (1955) and King (1955), with no correction for the amount of Mg-Al disorder in the spinel. Such calculations lead to...
entropies at high temperature that are lower than the equilibrium values, and because \( \Delta S^\circ \) of spinel from periclase and corundum is positive, to values of \( \Delta G^\circ \) that are too high. If the effect of ordering on enthalpy were negligible, the addition of 8.2 J/(mol·K) of residual disorder to the entropy of Robie et al. (1978) would bring their values of \( \Delta G^\circ \) into agreement with our data. However, a somewhat greater amount of residual disorder would be needed if there is an ordering effect on enthalpy. The thermodynamic data bases of Helgeson et al. (1978), Berman (1988), and Holland and Powell (1990) were all obtained by optimization of phase-equilibrium and calorimetric data. Values of \( \Delta G^\circ \) in these studies are based mostly on experiments in which the spinel obtained an equilibrium amount of disorder at high temperature, and it is evident in Figure 1 that their values agree more closely with ours than do those of Robie et al. (1978). The discrepancies between their results and ours can probably be attributed to uncertainties in the phase-equilibrium and calorimetric data used to constrain the fits. In particular, many of the equilibria used in these studies to derive the thermodynamic properties of spinel also involve pyrope and aluminous enstatite, two phases whose thermodynamic properties are poorly known (Cohen, 1985; Téqui et al., 1991).

The agreement of our data with values given by Chase et al. (1985) is surprising and probably fortuitous. The JANAF compilation relies on the heat-capacity equation of Landau and Naumova (1979) and includes a zero-point entropy correction of 8.2 J/(mol·K) based on a disorder estimate of 15% from Navrotsky and Kleppa (1967). NMR and neutron diffraction studies indicate that the residual disorder of spinels quenched from high temperature is actually variable and >15% (up to \( x = 0.39 \pm 0.04 \) at 900 °C: Wood et al., 1986; \( x = 0.35 \pm 0.02 \) at 1000 °C: Peterson et al., 1991; or \( x = 0.29 \pm 0.03 \) at 1000 °C: Millard et al., 1992, where \( x \) is the fraction of tetrahedral sites occupied by \( Al^{3+} \), so the basis for the JANAF correction is almost certainly invalid. It appears that Chase et al. (1985), using questionable assumptions, have nevertheless obtained what we believe are the correct values for \( \Delta G^\circ \).

**DISORDER IN SPINEL**

**A new thermodynamic expression for MgAl2O4**

Because our experiments were performed at temperatures well above the onset of rapid disordering, our measured values of \( \Delta G^\circ \) represent spinel with an equilibrium state of order. However, as explained in the introduction, the calorimetric heat contents and heat capacities do not. The equilibrium value of the heat content, \( H^\circ - \Delta H^\circ_{298} \), is equal to the difference between the enthalpy of spinel with equilibrium order at temperature \( T \) and the enthalpy of spinel with equilibrium order at the reference temperature, 298 K. However, because of incomplete reordering during a drop-calorimetric experiment, an enthalpy contribution is lost, and the measured heat contents are less than the equilibrium values. With some knowledge of the ordering state of spinel as a function of temperature and time, it should be possible to correct the calorimetric data to approximate equilibrium disorder. We can then simultaneously fit the corrected values for \( H^\circ - \Delta H^\circ_{298} \) and our experimental values for \( \Delta G^\circ \) using the empirical expression for the heat capacity at constant pressure, \( C_p \), of Berman and Brown (1985) to derive a corrected thermodynamic expression for MgAl2O4 applicable over a wide temperature range.

The disordering reaction for Mg and Al on the tetrahedral and octahedral sites,

\[
\]

is associated with an enthalpy of disordering, \( \Delta H_D \), given by

\[
\Delta H_D (T) = H^0_{x \rightarrow x'} (T) - H^0_{x \rightarrow x} (T)
\]

where \( x \) is the fraction of tetrahedral sites occupied by \( Al^{3+} \), \( H^0_{x \rightarrow x'} (T) \) is the enthalpy of spinel with disorder \( x' \) at temperature \( T \), and \( H^0_{x \rightarrow x} (T) \) is the enthalpy of spinel with disorder \( x \) at \( T \). Given an appropriate expression for enthalpy as a function of order, we can use Equation 9 to correct the calorimetric enthalpy measurements for the missing disordering contribution. Carpenter et al. (1994) used Landau theory to obtain an expression for the free energy of ordering based on a fit to the in situ neutron diffraction measurements of Mg-Al order vs. temperature by Peterson et al. (1991) and the enthalpy-of-ordering
measurements of Navrotsky (1986). Landau theory has the advantage of being able to account quantitatively for excess entropy contributions, which Wood et al. (1986) and Carpenter et al. (1994) inferred may significantly lower the entropy of MgAl₂O₄ from purely random-configurational values (values calculated based on the assumption that all microstates have equal probability). The problem may also be addressed by means of a regular solution model; the implications of this approach are discussed following the Landau calibration.

The equilibrium relationship between Mg-Al order and temperature given by Carpenter et al. (1994) is

\[ 1.908Q^4 + 0.0023(T - 395)Q - 1 = 0 \]  (10)

where \( Q \) is an order parameter equal to \( -\frac{1}{2}x + 1 \), defined such that \( Q = 0 \) for a completely random spinel (\( x = \frac{1}{2} \)). The free energy of ordering in joules per mole between completely disordered MgAl₂O₄ spinel and MgAl₂O₄ with an equilibrium state of order is (Carpenter et al., 1994)

\[ G_{\text{ord}} = (-8575 \pm 5048)Q + (9.85 \pm 5.81)(T - 395)Q^2 + (2727 \pm 1605)Q^3. \]  (11)

From this expression, with \( G = H - TS \), the enthalpy of ordering is given by

\[ H_{\text{ord}} = (-8575 \pm 5048)Q - (3895 \pm 2293)Q^2 + (2727 \pm 1605)Q^3. \]  (12)

According to Equation 10, \( Q \) depends on \( T \), a reflection of the heat capacity of ordering. This relationship holds, however, only at equilibrium (i.e., where \( \frac{dG_{\text{ord}}}{dQ} = 0 \)), and we assume in using Equation 12 that the difference in enthalpy between two ordering states (values of \( Q \) or \( x \)) is the same at any temperature. This in turn implies that any spinel with a constant state of order has the same heat capacity, that is, that \( C_p,x = \frac{\delta H}{\delta T} \bigg|_{p,x} \) is independent of \( x \) at a given temperature. This assumption is supported by the measurements of Richet and Fiquet (1991), which indicate that \( C_p,x \) is the same within uncertainty for spinels with different states of order. Using Equations 9 and 12, the enthalpy of disordering from \( x \) to \( x' \) (or from \( Q = -\frac{1}{2}x + 1 \) to \( Q = -\frac{1}{2}x' + 1 \)) can be obtained from

\[ \Delta H_D = H_{\text{ord}}^0 - \frac{1}{2}x + 1 - H_{\text{ord}}^0 - \frac{1}{2}x' + 1. \]  (13)

Given an effective temperature at which reordering stopped in a calorimetric measurement, we can use Equation 10 to estimate the residual disorder quenched into the spinel and Equations 12 and 13 to correct the calorimetric heat contents of Bonnickson (1955) (which are equivalent within interlaboratory uncertainty to those of Richet and Fiquet, 1991) for the missing disordering contribution.

According to the NMR measurements of Millard et al. (1992), all samples quenched rapidly from \( T > 1000 \) °C retain a state of disorder appropriate to \( \sim 1000 \) °C. The NMR work of Wood et al. (1986) implied that disordering levels off at 900 °C rather than 1000 °C, but given the procedural errors in this study (Peterson et al., 1991; Millard et al., 1992), we prefer to use the results of Millard et al. (1992). Likewise, we do not use the ESR work of Schmocker and Waldner (1976) or Schmocker et al. (1972) because the spinels were natural (hence impure), and ESR is more sensitive to the local environment of the impurity Cr³⁺ than to the overall degree of disorder (S. Kim, 1994, personal communication). Assuming that the disorder measured in situ at 1000 °C by Peterson et al. (1991), \( x = 0.35 \), is characteristic of all spinels quenched from \( T > 1000 \) °C, we add a \( \Delta H_D \) for ordering between \( x = 0.06 \) (or \( Q = 0.91 \), the equilibrium value at 298 K according to Eq. 10) and \( x = 0.35 \) (\( Q = 0.475 \)) to the calorimetric heat contents obtained for \( T > 1000 \) °C (Fig. 4a). Because spinel can reorder to the equilibrium state upon annealing between 700 and 1000 °C, spinel in this temperature range probably reorders at least partially to its equilibrium state in the calorimeter before being dropped. We therefore add a \( \Delta H_D \) appropriate to the equilibrium disorder for the temperature of the experiment.

Correction of heat contents below 700 °C is more problematic. It is not known whether Bonnickson (1955) conducted heat-content measurements between 421 and 1805 K at progressively higher or lower temperatures. If we assume that he began his experiments at 1805 K and moved to progressively lower temperatures, because of repeated drops of the same sample, the synthetic spinel would then have eventually gained a state of order appropriate to \( \sim 700 \) °C. Because of slow reaction rates, the spinel would not have reordered any further in the calorimeter during experiments at \( T < 700 \) °C (Fischer, 1967), and we can therefore correct all the low-temperature values by assuming that measurements were carried out on spinel with the equilibrium degree of disorder appropriate to 700 °C (\( Q = 0.625 \) or \( x = 0.25 \), see Eq. 10). To correct these values, we subtract the \( \Delta H_D \) for ordering between \( x = \) equilibrium and \( x = 0.25 \) (\( \Delta H_{D1} \), Fig. 4b) and add the \( \Delta H_D \) for ordering between \( x = 0.06 \) and \( x = 0.25 \) (\( \Delta H_{D2} \); Fig. 4b), which amounts to adding \( \Delta H_D \) for ordering between \( x = 0.06 \) and \( x = \) equilibrium (Fig. 4b).

Table 3 lists the calorimetrically measured heat contents and our corrected values. If we assume instead that Bonnickson began his experiments at 421 K and moved to progressively higher temperatures, then the low-temperature experiments would have been performed on spinel with \( x = 0.35 \) (the value characteristic of spinels quenched from the synthesis temperature of his starting material, 1480–1500 °C). However, under our assumptions, the values of \( \Delta H_D \) we would add to the measured heat contents would still be those for ordering between \( x = 0.06 \) and \( x = \) equilibrium. Our approach to correcting the low-temperature thermodynamic data is somewhat oversimplified, as it neglects a possible second-order transition that may occur in spinel near 700 °C (Suzuki and Kumazawa, 1980; Weeks and Sonder, 1980; Yamanaka and Takeuchi, 1983; Peterson et al., 1991), but we cannot include the transition in our treatment because its energetics have not been quantified.
In order to fit our $\Delta G^\circ$ values, we also need equilibrium values for enthalpy of formation and absolute entropy at some particular temperature. Solution calorimetric measurement of $\Delta H^\circ$ from the oxides at 970 K gives $\Delta H^\circ(970) = -22510 \pm 783$ J/mol (Charlu et al., 1975). We assume that this value applies to spinel with equilibrium disorder, as the spinel was heated at 700 °C for several hours prior to measuring the enthalpy of solution. The $\Delta H^\circ$ of spinel is therefore constrained to this value at 970 K in our fitting procedure. We do not use the $\Delta H^\circ$ of Shearer and Kleppa (1973) because of the probability of error due to incomplete solution of periclase in that study (Charlu et al., 1975). Entropy at 298 K ($S^\circ_{298}$) can be determined given the assumption (cf. Eq. 12) that the difference in enthalpy between two specific states of order is independent of temperature, which means that $C_{P,x}$ is independent of $x$ at a given temperature. King (1955) measured $C_P$ at temperatures between 51 and 298.16 K, fitted the values as a function of $T$, and integrated $C_P/T$ to obtain $S^\circ_{298} = 80.58 \pm 0.42$ J/(mol·K), assuming zero entropy at 0 K. Although the spinel studied by King was synthesized at 1480–1500 °C and thus probably had $x \sim 0.35$, the value of 80.58 J/(mol·K) would be correct for a spinel with $x = 0.06$ at 298 K, given that $C_{P,x}$ is independent of $x$. We therefore constrain $S^\circ_{298}$ to 80.58 J/(mol·K).

We fitted the corrected $H^\circ_T - H^\circ_{298}$ values and our experimentally determined $\Delta G^\circ$ for stoichiometric spinel simultaneously by weighted ($1/\sigma^2$) linear least-squares methods (Mathematica, Wolfram Research). We obtained ($\chi^2 = 6$)
and $\Delta H_0(298) = -25.621 \pm 4.548$ kJ/mol (from the oxides) or $-2302.811 \pm 5.776$ kJ/mol (from the elements). To test our assumption that $C_{p,x}$ is independent of $x$ at a given temperature, we refitted the data with no constraint on the value of $S_{298}$. For this case, the predicted values of $H^0_T - H^0_{298}$ and $\Delta G^0$ agree with those from the constrained fit to within $\sim200$ J/mol, and the fit value for $S_{298}$ [81.1 $\pm$ 2.75 J/(mol·K)] is identical within uncertainty to the calorimetric value of King (1955). The assumption that $C_{p,x}$ is independent of the state of order is therefore reasonable. The values of $\Delta G^0$ and $H^0_T - H^0_{298}$ predicted by the fit associated with Equation 14 are shown in Figure 1 and Table 3. It is notable that a Landau approach reproduces the available experimental data within the uncertainty, consistent with the idea that the configurational entropy is significantly nonrandom in spinel, perhaps because of short-range ordering. This is also compatible with the evidence for negative excess entropy found in spinel solid solutions on the join MgAl2O4-Al2O3/Al2O3 (Navrotsky et al., 1986).

An alternative approach to modeling the thermodynamic properties of spinel is to correct the calorimetric data using a regular-solution model, which assumes that entropy is purely randomly configurational and therefore does not account for effects such as short-range ordering. Here,

$$\Delta H_D = \Delta H_D^{ideal} + \Delta H_D^{excess} = x \Delta H^{mi} + \omega x(1-x)$$

where $\Delta H_D^{ideal}$ is the ideal and $\Delta H_D^{excess}$ the nonideal contribution to the enthalpy of Mg-Al disordering, $\Delta H^{mit}$ is the temperature-independent enthalpy of interchanging 1 mole of Mg and Al on the octahedral and tetrahedral sites, and $\omega$ is a temperature-independent Margules parameter. Sack and Ghiorso (1991) fitted the neutron diffraction data of Peterson et al. (1991) to obtain for the relationship between order and temperature.
TABLE 3. Measured and corrected $H^\circ_f - H^\circ_{so}$ for spinel (J/mol)

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>Meas.</th>
<th>$x^\ast$</th>
<th>$\Delta\tilde{H}_d^\ddagger$</th>
<th>Corr. $\ddagger$</th>
<th>Fit (Eq. 14)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>0.0</td>
<td>0.059</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>421.0</td>
<td>16.025</td>
<td>0.087</td>
<td>254</td>
<td>16.279</td>
<td>17.027</td>
</tr>
<tr>
<td>485.7</td>
<td>25.397</td>
<td>0.10</td>
<td>446</td>
<td>25.843</td>
<td>28.764</td>
</tr>
<tr>
<td>584.5</td>
<td>40.836</td>
<td>0.13</td>
<td>795</td>
<td>41.531</td>
<td>42.368</td>
</tr>
<tr>
<td>767.4</td>
<td>70.584</td>
<td>0.19</td>
<td>1667</td>
<td>72.251</td>
<td>72.989</td>
</tr>
<tr>
<td>814.4</td>
<td>78.324</td>
<td>0.20</td>
<td>1890</td>
<td>80.214</td>
<td>81.140</td>
</tr>
<tr>
<td>900.0</td>
<td>94.433</td>
<td>0.23</td>
<td>2466</td>
<td>96.899</td>
<td>97.825</td>
</tr>
<tr>
<td>1020.9</td>
<td>113.330</td>
<td>0.27</td>
<td>3120</td>
<td>117.050</td>
<td>117.982</td>
</tr>
<tr>
<td>1108.9</td>
<td>130.332</td>
<td>0.30</td>
<td>3661</td>
<td>133.963</td>
<td>134.292</td>
</tr>
<tr>
<td>1212.2</td>
<td>149.327</td>
<td>0.34</td>
<td>4321</td>
<td>153.648</td>
<td>153.304</td>
</tr>
<tr>
<td>1325.5</td>
<td>170.331</td>
<td>0.35</td>
<td>4559</td>
<td>174.890</td>
<td>174.650</td>
</tr>
<tr>
<td>1388.4</td>
<td>182.548</td>
<td>0.35</td>
<td>4559</td>
<td>187.107</td>
<td>186.818</td>
</tr>
<tr>
<td>1508.2</td>
<td>205.267</td>
<td>0.35</td>
<td>4559</td>
<td>209.826</td>
<td>209.619</td>
</tr>
<tr>
<td>1610.1</td>
<td>224.221</td>
<td>0.35</td>
<td>4559</td>
<td>228.780</td>
<td>229.379</td>
</tr>
<tr>
<td>1695.0</td>
<td>241.710</td>
<td>0.35</td>
<td>4559</td>
<td>246.269</td>
<td>245.966</td>
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<tr>
<td>1805.5</td>
<td>262.295</td>
<td>0.35</td>
<td>4559</td>
<td>266.854</td>
<td>267.709</td>
</tr>
</tbody>
</table>

* Bonnickson (1955).
** Fraction of tetrahedral sites occupied by $Al^\ddagger$ based on Eq. 10 (see text); experimental errors of Peterson et al. (1991) range from 0.01 to 0.02.
† Disordering enthalpy (Eq. 13).
‡ Measured plus $\Delta H_d$. 

Further observations on disorder

On the basis of the calorimetric data and their NMR measurements of the Mg-Al disorder in spinel, Wood et al. (1986) also postulated the existence of substantial short-range order in spinel. They noted that if calorimetrically derived entropies of spinel (Bonnickson, 1955) are corrected by adding the random-configurational entropy term

$$\Delta S_C = -R(x \ln x + (1 - x)\ln(1 - x) + x \ln(x/2) + (2 - x)\ln[1 - (x/2)])$$

(18)

to correct for frozen-in disorder, then there is a substantial mismatch between the calculated and observed pressure-temperature positions of the equilibrium involving pyrope, forsterite, enstatite, and spinel at 18–30 kbar and 900–1600 °C that indicates that the corrected entropies are too high. Although their conclusions are partly a consequence of overestimating the degree of disorder in spinel (Peterson et al., 1991; Millard et al., 1992), they are supported by the work of Carpenter et al. (1994), who inferred from applying Landau theory that the entropy of spinel was less than randomly configurational, and by our success in describing the known thermodynamic data on spinel with a Landau enthalpy-of-ordering expression. Although we cannot rule out mitigating effects due to an apparent second-order transition near 700 °C, the inability of a regular-solution model to describe the same data base without requiring $C_{p,s}$ to vary between different constant states of order also suggests that nonrandom configurational effects are important in the spinel lattice. HRTEM investigations have not yielded independent evidence of short-range order in spinel (Navrotsky et al., 1986), but it may exist at a scale not detectable by this method. We note finally with respect to this equilibrium that our more precise values for $\Delta G^\circ_f$ of spinel may be used to refine the poorly known thermodynamic properties of pyrope and aluminous enstatite.

Fiske and Stebbins (1989) have suggested that a second type of disorder may be present in MgAl₂O₄ at high temperature. Their NMR work on natural single crystals shows that annealing at 800 °C of samples quenched from high temperature causes the diminution and disappearance of certain satellite transition peaks, a process that they link either to changes in structure or to disordering on sites other than the normally occupied octahedral and tetrahedral ones. The presence of a second type of disorder would certainly complicate efforts to correct for equilibrium disorder, as this disordering has not been characterized, and we cannot include its effects. Because of this, we assumed in our treatment of the data that either it is not an energetically significant process or it is adequately accounted for by the calorimetry or Landau corrections.

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