Palladium oxide equilibration and the thermodynamic properties of MgAl₂O₄ spinel

Laurinda Chamberlin,* John R. Beckett, Edward Stolper

Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, U.S.A.

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, ΔG_f^0, 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 ΔG_f^0 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 ΔG_f^0, 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 Lindsley, 1964; Sack, 1982; Mattioli et al., 1989; Sack and Ghiorso, 1991). However, our understanding of spinel equilibria 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, $Mg^{2+}(Al_2^{3+})O_4$, with Al^{3+} restricted to octahedral sites, toward an inverse distribution, $Al^{3+}(Mg^{2+}Al^{3+})O_4$, with 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 ~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 ~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_f^0, 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 f_{O_2} 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 f_{O_2}, 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 f_{O_2}, and, taking the example of the oxide component Al₂O₃, we can write

$$K\,(T) = \frac{a_{Al_2O_3}^{min}}{(\gamma_{Al}^{Pd} X_{Al}^{Pd,\,min})^2 (f_{O_2})^{\frac{3}{2}}} = \frac{1}{(\gamma_{Al}^{Pd} X_{Al}^{Pd,\,Cor})^2 (f_{O_2})^{\frac{3}{2}}} \quad (1)$$

where K is the equilibrium constant for the oxidation reaction $2Al_{(m)} + \frac{3}{2}O_{2(g)} = Al_2O_{3(Cor)}$, T is the temperature in K, $a_{Al_2O_3}^{min}$ is the activity of Al₂O₃ in the mineral relative to corundum, f_{O_2} is the O₂ fugacity, $X_{Al}^{Pd,min}$ is the mole fraction of Al in Pd in equilibrium with the mineral, $X_{Al}^{Pd,Cor}$ is the mole fraction of Al in Pd in equilibrium with the oxide standard corundum, γ_{Al}^{Pd} is the activity coefficient of Al in Pd, and $a_{Al_2O_3}^{Cor} \equiv 1$. 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

$$a_{Al_2O_3}^{min} = \left(\frac{X_{Al}^{Pd,\,min}}{X_{Al}^{Pd,\,Cor}}\right)^2. \quad (2)$$

Since γ_{Mg}^{Pd} is also virtually constant in the dilute range, we

can write an analogous expression for MgO:

$$a_{MgO}^{min} = \frac{X_{Mg}^{Pd,\,min}}{X_{Mg}^{Pd,\,Per}}. \quad (3)$$

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_{O_2} measurements do not contribute to the uncertainty of the activity determination. These concentrations can be measured precisely, because at experimentally feasible f_{O_2} (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_f^0. 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 [$a_0 = 8.0844(3)$: Navrotsky 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_{O_2}. The pellets were placed in Pd-foil buckets ¼ 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 $MoSi_2$ 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. O_2 fugacity was set using mixtures of H_2 and CO_2 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 f_{O_2} was 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 f_{O_2} 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 f_{O_2} 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 $X_{Al} = 0.01090$.

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 Al_2O_3 relative to periclase and corundum for spinel and the ΔG_f^0 calculated from them using the equilibrium

$$MgO + Al_2O_3 = MgAl_2O_4 \qquad (4)$$

$$\text{Per} \qquad \text{Cor} \qquad \text{Spl}$$

and the relation

$$\Delta G_f^0 = -RT \ln \frac{1}{a_{MgO}^{Spl} a_{Al_2O_3}^{Spl}} \qquad (5)$$

where $a_{MgAl_2O_4}^{Spl} \equiv 1$ for pure end-member spinel with an equilibrium state of order. Table 2 includes the activities and ΔG_f^0 determined for both stoichiometric and periclase-saturated spinel. Figure 1 shows the experimentally determined ΔG_f^0 of spinel as a function of temperature. The ΔG_f^0 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$_4$

T (°C)	$\log_{10} f_{O_2}$	t (h)	$X^{Pd,\,Spl}_{Mg}$	$X^{Pd,\,Per}_{Mg}$	$X^{Pd,\,Spl}_{Al}$	$X^{Pd,\,Cor}_{Al}$
1154	−13.63	260	0.00090(16)	0.00140(14)	0.00066(6)	0.00191(2)
1200	−12.44	240	0.00091(4)	0.00097(3)	0.00029(7)	0.00113(7)
1201	−12.98	264	0.00142(7)	0.00179(7)	0.00071(1)	0.00271(6)
1201*	−13.49	144	—	—	—	—
	−12.91	192	0.00156(9)	0.00171(17)	0.00067(6)	0.00267(7)
1251	−11.79	45	0.00094(8)	0.00136(9)	0.00049(4)	0.00178(10)
1250**	−11.58	144	0.00094(4)	—	0.00026(3)	0.00118(3)
1300†	−11.32	89	0.00202(11)	0.00201(11)	0.00068(1)	0.00291(4)
1305	−11.19	68	0.00148(8)	0.00197(9)	0.00070(7)	0.00248(1)
1351*	−11.02	48	—	—	0.00070(7)	0.00283(9)
	−10.61	48	0.00206(12)	0.00206(12)	0.00070(7)	0.00283(9)
1352	−10.66	43	0.00221(3)	0.00235(4)	0.00085(3)	0.00343(8)
1356**	−10.33	23	0.00151(4)	—	0.00046(3)	0.00213(20)
1397†	−10.20	66	0.00287(13)	0.00267(6)	0.00107(5)	0.00424(7)
1400	−10.17	44	0.00186(7)	0.00294(9)	0.00131(4)	0.00438(7)
1400	−10.17	38	0.00261(5)	0.00281(5)	0.00120(8)	0.00459(5)
1400**	−9.65	45	0.00153(4)	—	0.00044(1)	0.00198(9)

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_{O_2} to ±0.05 log units. $X^{Pd,\,j}_i$ 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_{MgO} assumed to be one.
 † Periclase-saturated spinel.

mal 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 ΔG^0_f within 1σ uncertainty.

Figure 1 compares the experimentally determined ΔG^0_f with values from six compilations of thermodynam-

TABLE 2. Derived data for MgAl$_2$O$_4$

T (°C)	a_{MgO}	$a_{Al_2O_3}$	ΔG^0_f (J/mol)
1154	0.643(0.131)	0.119(0.022)	−30495(3264)
1200	0.938(0.057)	0.066(0.035)	−34073(6538)
1201	0.793(0.032)	0.069(0.004)	−35609(866)
1201*	0.912(0.104)	0.063(0.011)	−35011(2557)
1251	0.691(0.072)	0.076(0.016)	−37337(2977)
1250**	1.00	0.050(0.012)	−37985(3028)
1300†	1.00(0.074)	0.055(0.002)	−37933(1081)
1305	0.751(0.053)	0.080(0.015)	−36895(2630)
1351*	1.00(0.082)	0.061(0.013)	−37765(3084)
1352	0.940(0.020)	0.061(0.005)	−38624(1146)
1356**	1.00	0.047(0.010)	−41321(2900)
1397†	1.07(0.030)	0.064(0.006)	−37229(1303)
1400	0.633(0.031)	0.089(0.006)	−40011(1161)
1400	0.929(0.024)	0.068(0.009)	−38418(1876)
1400**	1.00	0.050(0.005)	−41633(1396)

Note: numbers in parentheses indicate 1σ errors from propagation of analytical errors based on heterogeneity.
 * Reversal.
 ** Periclase-saturated spinel; a_{MgO} assumed to be one.
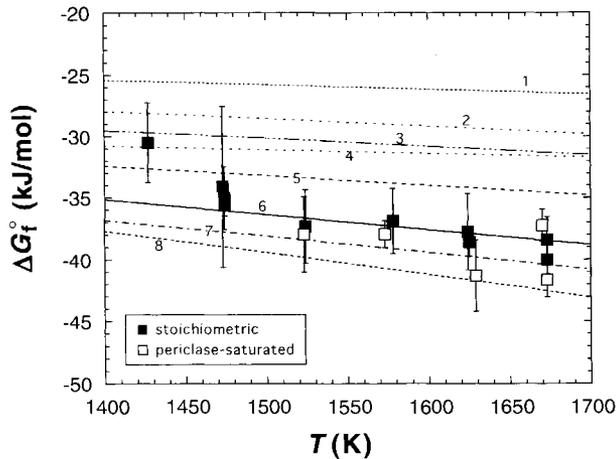 † Periclase-saturated spinel.

ic 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 on 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 by 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 Henrian 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-

Fig. 1. Free energy of formation of spinel from the oxides (ΔG_f^0) vs. temperature (K), showing experimental data (1σ errors from propagation of analytical errors on the basis of heterogeneity) and literature values: 1 = Robie et al. (1978); 2 = Richet and Fiquet (1991); 3 = Helgeson et al. (1978); 4 = Holland and Powell (1990); 5 = Berman (1988); 6 = this study, see Eqs. 14 ff.; 7 = JANAF Tables: Chase et al. (1985); 8 = Hallstedt (1992).
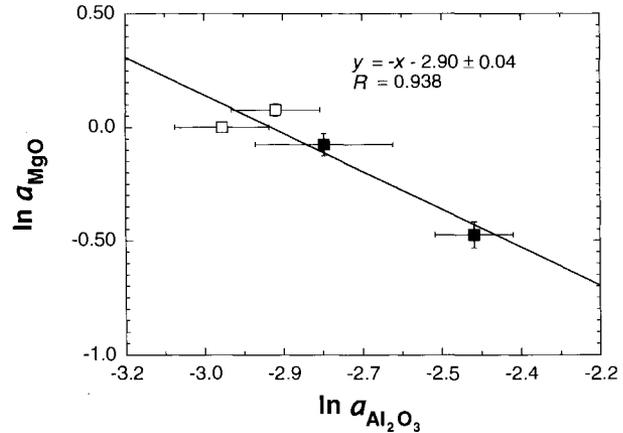

Fig. 2. Values of ln a_{MgO} vs. ln $a_{Al_2O_3}$ for spinel at 1400 °C (1σ error), fitted to a line of slope -1.0. R is the linear correlation coefficient. Symbols as in Fig. 1.

versal 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 ΔG_f^0 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 ΔG_f^0 calculated from Equation 5 agree within 1σ. Stoichiometric spinels in equilibrium with melts in the system CaO-MgO-Al₂O₃-SiO₂-TiO₂ 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-Al₂O₃ that variations in a_{MgO} be coupled with variations in $a_{Al_2O_3}$. Specifically, for spinel,

$$\frac{d\mu_{MgO}^{Spl}}{d\mu_{Al_2O_3}^{Spl}} = \frac{d \ln a_{MgO}^{Spl}}{d \ln a_{Al_2O_3}^{Spl}} = -\frac{X_{Al_2O_3}^{Spl}}{X_{MgO}^{Spl}} \qquad (6)$$

where μ_i^{Spl} is the chemical potential of species i in spinel. For stoichiometric MgAl₂O₄,

$$\frac{d \ln a_{MgO}^{Spl}}{d \ln a_{Al_2O_3}^{Spl}} = -1. \qquad (7)$$

A plot of ln a_{MgO} vs. ln $a_{Al_2O_3}$ in stoichiometric and periclase-saturated spinels at 1400 °C is shown in Figure 2. A best-fit line with a constrained slope of -1.0, as required by the Gibbs-Duhem equation, is shown for comparison and fits the data well.

This wide range in oxide activities for virtually stoichiometric MgAl₂O₄ is easily understood if the molar free energy ($\overline{G}$) curve for spinel is strongly concave upward near stoichiometric spinel. In this case, if the Mg-Al ratio of the spinel is changed slightly from the stoichiometric value, ΔG_f^0 changes very little, but the tangent to the $\overline{G}$ curve at the new Mg-Al ratio differs considerably from that of stoichiometric spinel (Fig. 3). Strong curvature of the free energy surface near stoichiometric spinel is also supported by the MgO-Al₂O₃ phase diagram, which indicates that spinel exhibits very little solid solution toward MgO at temperatures below 1500 °C (although significant alumina solid solution requires a more gentle curvature in the direction of alumina-rich spinels). Above 1500 °C, there is some uncertainty in the literature as to whether the extent of MgO solid solution increases (Lejus, 1964; Shirasuka and Yamaguchi, 1974). If it does, the $\overline{G}$-X curve at higher temperatures must have a more rounded shape in the vicinity of MgAl₂O₄ than in Figure 3, and activities vary less dramatically with small departures from stoichiometry. Thus, in spinel, and probably in any mineral that displays little deviation from stoichiometry, activities of constituent oxides vary widely with only minimal changes in the free energy of formation from the oxides.

Free energies of formation

There are several reasons for the differences between our values of ΔG_f^0 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
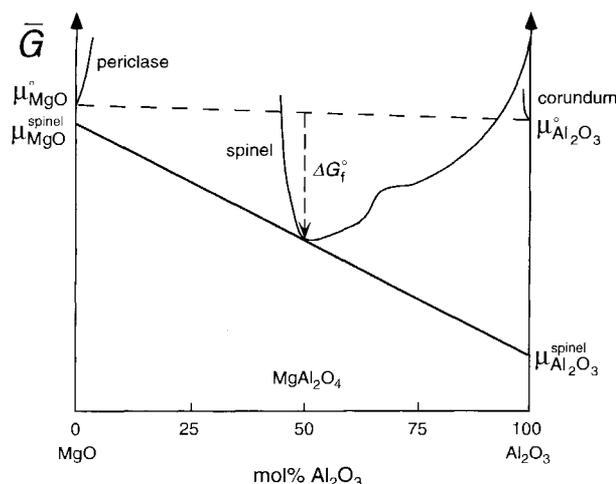
Fig. 3. Schematic representation of molar Gibbs free energy ($\overline{G}$) vs. composition for the system MgO-Al$_2$O$_3$. The extension of the spinel $\overline{G}$ curve to $X_{Al_2O_3} = 1$ indicates the solid solution between MgAl$_2$O$_4$ and γ-Al$_{8/3}$O$_4$ (Lejus, 1964). The $\overline{G}$ curves of periclase and corundum are placed arbitrarily for ease of depiction. Intercepts of tangent lines with vertical axes give the chemical potentials μ_i of MgO and Al$_2$O$_3$, the dashed line between μ^0_{MgO} and $\mu^0_{Al_2O_3}$ is for a mechanical mixture of pure MgO and Al$_2$O$_3$, and the solid line is for stoichiometric spinel. The length of the dashed arrow gives ΔG^0_f of stoichiometric spinel from the oxides.

entropies at high temperature that are lower than the equilibrium values, and because ΔS^0_f of spinel from periclase and corundum is positive, to values of ΔG^0_f 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 ΔG^0_f 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 ΔG^0_f 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 Landa 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 $x = 0.29 + 0.03$ 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 ΔG^0_f.

DISORDER IN SPINEL

A new thermodynamic expression for MgAl$_2$O$_4$

Because our experiments were performed at temperatures well above the onset of rapid disordering, our measured values of ΔG^0_f 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, $H^0_T - H^0_{298}$, 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 $H^0_T - H^0_{298}$ and our experimental values for ΔG^0_f 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 MgAl$_2$O$_4$ applicable over a wide temperature range.

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

$$^{[4]}Mg^{2+} + {}^{[6]}Al^{3+} = {}^{[4]}Al^{3+} + {}^{[6]}Mg^{2+} \qquad (8)$$
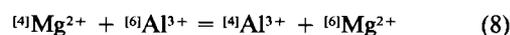
is associated with an enthalpy of disordering, ΔH_D, given by

$$\Delta H_D (T) = H^0_{x=x'}(T) - H^0_{x=x}(T) \qquad (9)$$

where x is the fraction of tetrahedral sites occupied by Al^{3+}, $H^0_{x=x'}(T)$ is the enthalpy of spinel with disorder x' at temperature T, and $H^0_{x=x}(T)$ 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 $MgAl_2O_4$ 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

$$1.908Q^5 + 0.0023(T - 395)Q - 1 = 0 \qquad (10)$$

where Q is an order parameter equal to $-\frac{3}{2}x + 1$, defined such that $Q = 0$ for a completely random spinel ($x = \frac{2}{3}$). The free energy of ordering in joules per mole between completely disordered $MgAl_2O_4$ spinel and $MgAl_2O_4$ with an equilibrium state of order is (Carpenter et al., 1994)

$$G^{ord} = (-8575 \pm 5048)Q + (9.85 \pm 5.81)(T - 395)Q^2$$
$$+ (2727 \pm 1605)Q^6. \qquad (11)$$

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

$$H^{ord} = (-8575 \pm 5048)Q - (3895 \pm 2293)Q^2$$
$$+ (2727 \pm 1605)Q^6. \qquad (12)$$

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 $\partial G^{ord}/\partial Q = 0$), 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 $C_{P,x} = (\partial H/\partial T)_{P,x}$ 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 $Q = -\frac{3}{2}x + 1$ to $Q = -\frac{3}{2}x' + 1$) can be obtained from

$$\Delta H_D = H^{ord}_{Q=-3/2x'+1} - H^{ord}_{Q=-3/2x+1}. \qquad (13)$$

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 ~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 Cr^{3+} 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 ΔH_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 ΔH_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 ~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 ΔH_D for ordering between $x =$ equilibrium and $x = 0.25$ (ΔH_{D1}; Fig. 4b) and add the ΔH_D for ordering between $x = 0.06$ and $x = 0.25$ (ΔH_{D2}; Fig. 4b), which amounts to adding ΔH_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 ΔH_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 Takéuchi, 1983; Peterson et al., 1991), but we cannot include the transition in our treatment because its energetics have not been quantified.
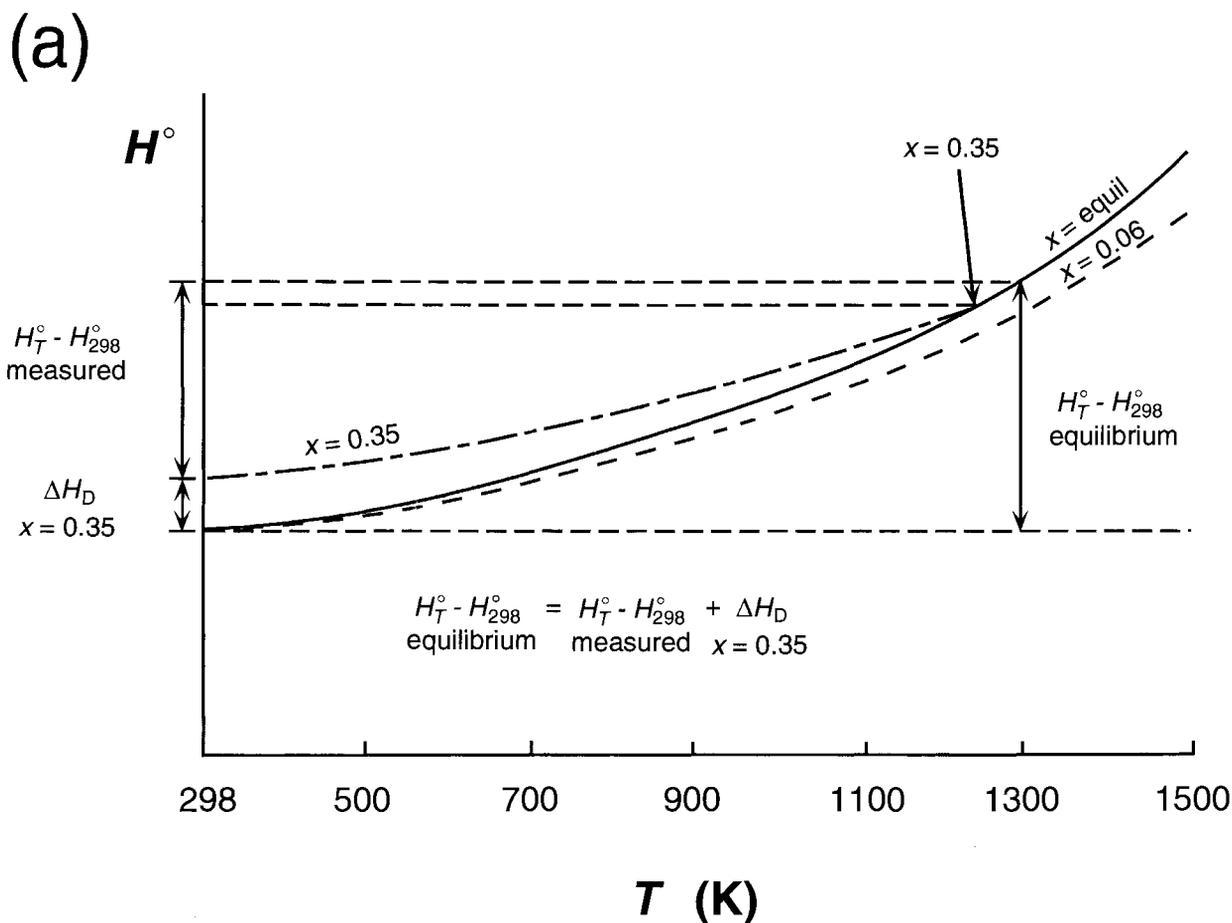
(a)

$$H^\circ_T - H^\circ_{298} \text{ equilibrium} = H^\circ_T - H^\circ_{298} \text{ measured} + \Delta H_D \; x = 0.35$$

T (K)

Fig. 4. Schematic representation of enthalpy of spinel vs. temperature. **(a)** Above about 1273 K, spinel cools along the x_{equil} curve, where it has the equilibrium amount of disorder at each temperature. When temperature drops below 1273 K, disorder is frozen in at $x = 0.35$, and spinel cools along the curve corresponding to $x = 0.35$. The actual heat content $H^\circ_T - H^\circ_{298}$ at 1273 K is equal to the measured heat content plus the disordering enthalpy ΔH_D between $x = 0.06$ and $x = 0.35$. **(b)** Spinel heated to 973 K $< T < 1273$ K in the calorimeter can anneal to x_{equil}, but it cannot reorder below 973 K. Therefore, below 973 K, the disorder is frozen at $x = 0.25$, and spinel cools along the curve $x = 0.25$. The actual heat content at $T < 973$ K is equal to the measured heat content minus the disordering enthalpy ΔH_{D1} between $x =$ equil and $x = 0.25$ plus the disordering enthalpy ΔH_{D2} between $x = 0.06$ and $x = 0.25$.

In order to fit our ΔG°_f values, we also need equilibrium values for enthalpy of formation and absolute entropy at some particular temperature. Solution calorimetric measurement of ΔH°_f from the oxides at 970 K gives $\Delta H^\circ_f(970)$ = -22510 ± 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 ΔH°_f of spinel is therefore constrained to this value at 970 K in our fitting procedure. We do not use the ΔH°_f 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°_{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°_{298} to 80.58 J/(mol·K).

We fitted the corrected $H^\circ_T - H^\circ_{298}$ values and our experimentally determined ΔG°_f for stoichiometric spinel simultaneously by weighted ($1/\sigma^2$) linear least-squares methods (Mathematica, Wolfram Research). We obtained ($\chi^2 = 6$)
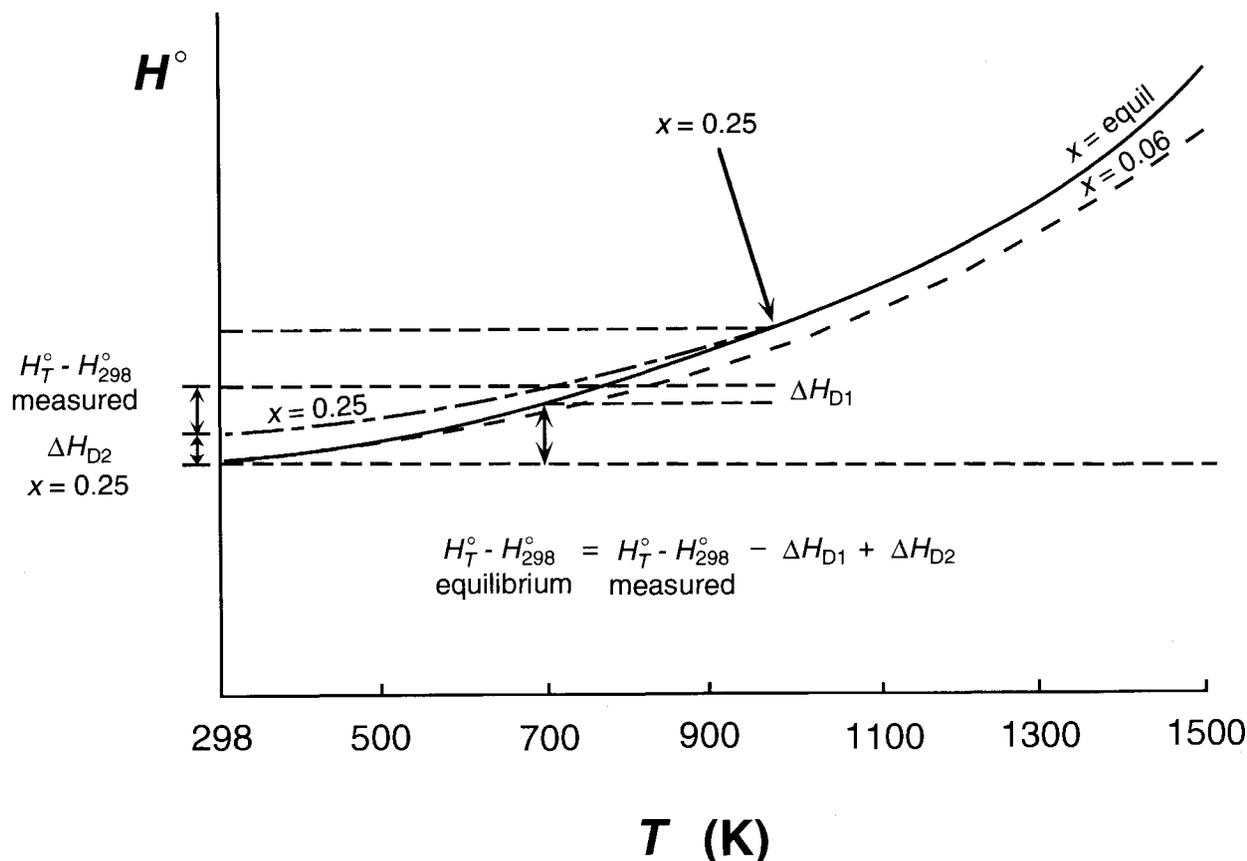
(b)

Fig. 4—*Continued*

$$C_P = (244.672 \pm 4.709) - (2003.98 \pm 114.12) T^{-\frac{1}{2}}$$
$$(14)$$

and $\Delta H_f^0(298) = -25.621 \pm 4.548$ kJ/mol (from the oxides) or -2302.811 ± 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}^0. For this case, the predicted values of $H_T^0 - H_{298}^0$ and ΔG_f^0 agree with those from the constrained fit to within ~200 J/mol, and the fit value for S_{298}^0 [81.1 ± 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 ΔG_f^0 and $H_T^0 - H_{298}^0$ 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 MgAl$_2$O$_4$-Al$_{8/3}$O$_4$ (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,

$$\Delta H_D = \Delta H_D^{ideal} + \Delta H_D^{excess} = x\Delta H^{int} + \omega x(1-x) \quad (15)$$

where ΔH_D^{ideal} is the ideal and ΔH_D^{excess} the nonideal contribution to the enthalpy of Mg-Al disordering, ΔH^{int} is the temperature-independent enthalpy of interchanging 1 mole of Mg and Al on the octahedral and tetrahedral sites, and ω 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 $H_T^0 - H_{298}^0$ for spinel (J/mol)

T (K)	Meas.*	x^{**}	ΔH_D†	Corr.‡	Fit (Eq. 14)
298.15	0.0	0.059	0.0	0.0	0.0
421.0	16025	0.087	254	16279	17027
485.7	25397	0.10	446	25843	26764
584.5	40836	0.13	795	41631	42369
767.4	70584	0.19	1667	72251	72989
814.4	78324	0.20	1890	80214	81140
909.0	94433	0.23	2466	96899	97825
1020.9	113930	0.27	3120	117050	117982
1109.9	130332	0.30	3661	133993	134292
1212.2	149327	0.34	4321	153648	153304
1325.5	170331	0.35	4559	174890	174650
1388.4	182548	0.35	4559	187107	186618
1508.2	205267	0.35	4559	209826	209619
1610.1	224221	0.35	4559	228780	229379
1695.0	241710	0.35	4559	246269	245966
1805.5	262295	0.35	4559	266854	267709

* Bonnickson (1955).
** Fraction of tetrahedral sites occupied by Al^{3+} 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 ΔH_D.

$$-18.41 = RT \ln \frac{x^2}{(1-x)(2-x)}$$
$$+ \; 15.06(1 - 2x) \qquad (16)$$

which in turn yields (cf. O'Neill and Navrotsky, 1983)

$$\Delta H_D = 33.47x - 15.06x^2. \qquad (17)$$

Equation 17 results in enthalpy corrections at high temperature that are about twice the magnitude of those given by Equation 13 and hence in a larger corrected heat-capacity dependence on temperature. This forces a downward adjustment of S_{298}^0 by ~ 6 J/(mol·K) relative to King's (1955) calorimetrically derived value to accommodate the available enthalpy and free energy data, well outside the uncertainty in King's determination. This large adjustment in S_{298}^0 could be rationalized if $C_{P,x}$ were a function of the state of order at a given temperature, but such a $C_{P,x}$ dependence on order has been neither demonstrated nor quantified.

The regular solution model may also be made to predict the S_{298}^0 of King (1955) if the second-order transition near 700 °C is held to be energetically significant. In order to obtain a rough estimate of the energetics required, we can treat the transition as a first-order decrease in enthalpy and entropy at 700 °C and assume no effect on the state of order in spinel. This allows us to make the same straightforward ΔH_D corrections as before, while simply decreasing the enthalpy and entropy below 700 °C by some fixed amount. We find that an enthalpy of transition of about 1660 J/mol and an entropy of transition of about 1.7 J/(mol·K) allow us to obtain $S_{298}^0 = 80.25$ J/(mol·K). This approach is speculative, however, since neither the nature nor the energetics of this transition has actually been constrained. Overall, we prefer the Landau approach, which is able to account more straightforwardly for the experimental data.

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 $C_{P,x}$ 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 ΔG_f^0 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 MgAl$_2$O$_4$ 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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REFERENCES CITED

Alper, A.M., McNally, R.N., Ribbe, P.H., and Doman, R.C. (1962) The system MgO-MgAl₂O₄. Journal of the American Ceramic Society, 45, 263–268.

Armstrong, J.T. (1988) Quantitative analysis of silicate and oxide minerals: Comparison of Monte Carlo, ZAF, and $\phi(\rho z)$ procedure. In D.E. Newbury, Ed., Microbeam analysis, p. 239–246, San Francisco Press, San Francisco, California.

Berman, R.G. (1988) Internally-consistent thermodynamic data for minerals in the system Na₂O-K₂O-CaO-MgO-FeO-Fe₂O₃-Al₂O₃-SiO₂-TiO₂-H₂O-CO₂. Journal of Petrology, 29, 445–522.

Berman, R.G., and Brown, T.H. (1985) Heat capacity of minerals in the system Na₂O-K₂O-CaO-MgO-FeO-Fe₂O₃-Al₂O₃-SiO₂-TiO₂-H₂O-CO₂: Representation, estimation, and high temperature extrapolation. Contributions to Mineralogy and Petrology, 89, 168–183.

Bonnickson, K.R. (1955) High temperature heat contents of aluminates of calcium and magnesium. Journal of Physical Chemistry, 59, 220–221.

Buddington, A.F., and Lindsley, D.H. (1964) Iron-titanium oxide minerals and synthetic equivalents. Journal of Petrology, 5, 310–357.

Carpenter, M.A., Powell, R., and Salje, E.K.H. (1994) Thermodynamics of nonconvergent cation ordering in minerals: II. Spinels and the orthopyroxene solid solution. American Mineralogist, 79, 1068–1083.

Chamberlin, L. (1994) Pd-oxide equilibration: A new experimental method for the direct determination of oxide activities in melts and minerals, 224 p. Ph.D. thesis, California Institute of Technology, Pasadena, California.

Chamberlin, L., Beckett, J.R., and Stolper, E. (1994) Pd-oxide equilibration: A new experimental method for the direct determination of oxide activities in melts and minerals. Contributions to Mineralogy and Petrology, 116, 169–181.

Charlu, T.V., Newton, R.C., and Kleppa, O.J. (1975) Enthalpies of formation at 970 K of compounds in the system MgO-Al₂O₃-SiO₂ from high temperature solution calorimetry. Geochimica et Cosmochimica Acta, 39, 1487–1497.

Chase, M.W., Jr., Davies, C.A., Downey, J.R., Jr., Frurip, D.J., McDonald, R.A., and Syverud, A.N. (1985) The JANAF thermochemical tables (3rd edition), 1856 p. Journal of Physical Chemistry Reference Data, 14, Supplement 1.

Cohen, R.E. (1985) Thermodynamics of aluminous pyroxenes: Effects of short-range order, 340 p. Ph.D. thesis, Harvard University, Cambridge, Massachusetts.

Colin, F. (1968) Des phases formées au cours de la réduction de certains oxydes mixtes nAl₂O₃·MO. Revue Internationale des Hautes Températures et des Réfractaires, 5, 269.

Dudson, P.J., and Fraser, D.G. (1981) Nickel oxide activities in silicate melts in the system CaO-MgO-Al₂O₃-SiO₂-NiO. Progress in Experimental Petrology, 5, 247–251.

Fischer, P. (1967) Neutronenbeugungsuntersuchung der Strukturen von MgAl₂O₄- und ZnAl₂O₄-Spinellen, in Abhängigkeit von der Vorgeschichte. Zeitschrift für Kristallographie, 124, 275–302.

Fiske, P.S., and Stebbins, J.F. (1989) Evidence for multiple mechanisms of disorder in MgAl₂O₃ spinel: An ²⁷Al NMR study. Eos, 70, 1375.

Grove, T.L. (1981) Use of Fe-Pt alloys to eliminate iron loss problem in 1 atmosphere gas mixing experiments: Theoretical and practical considerations. Contributions to Mineralogy and Petrology, 78, 298–304.

Hallstedt, B. (1992) Thermodynamic assessment of the system MgO-Al₂O₃. Journal of the American Ceramic Society, 75, 1497–1507.

Helgeson, H.C., Delany, J.M., Nesbitt, H.W., and Bird, D.K. (1978) Summary and critique of the thermodynamic properties of rock-forming minerals. American Journal of Science, 278A, 229 p.

Holland, T.B.J., and Powell, R. (1990) An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations: The system K₂O-Na₂O-CaO-MgO-MnO-FeO-Fe₂O₃-Al₂O₃-TiO₂-SiO₂-C-H₂-O₂. Journal of Metamorphic Geology, 8, 89–124.

King, E.G. (1955) Heat capacities at low temperatures and entropies at 298.16 °K of crystalline calcium and magnesium aluminates. Journal of Physical Chemistry, 59, 218–219.

Landa, Ya.A., and Naumova, I.A. (1979) Determination of enthalpies and heat capacities of magnesian spinels in the interval 1400–2200 K. Ogneupory, 9, 9–11 (in Russian).

Lejus, A. (1964) Sur la formation a haute température de spinelles non stœichiométriques et de phases dérivées; dans plusieurs systèmes d'oxydes a base d'alumine et dans le système alumine-nitrure d'aluminium. Revue des Hautes Températures et des Réfractaires, 1, 53–95.

Mattioli, G.S., Wood, B.J., and Carmichael, I.S.E. (1987) Ternary-spinel volumes in the system MgAl₂O₄-Fe₃O₄-γFe₈/₃O₄: Implications for the effect of P on intrinsic f_{O_2} measurements of mantle-xenolith spinels. American Mineralogist, 72, 468–480.

Mattioli, G.S., Baker, M.B., Rutter, M.J., and Stolper, E.M. (1989) Upper mantle oxygen fugacity and its relationship to metasomatism. Journal of Geology, 97, 521–536.

Millard, R.L., Peterson, R.C., and Hunter, B.K. (1992) Temperature dependence of cation disorder in MgAl₂O₄ spinel using ²⁷Al and ¹⁷O magic-angle spinning NMR. American Mineralogist, 77, 44–52.

Navrotsky, A. (1986) Cation-distribution energetics and heats of mixing in MgFe₂O₄-MgAl₂O₄, ZnFe₂O₄-ZnAl₂O₄, and NiAl₂O₄-ZnAl₂O₄ spinels: Study by high-temperature calorimetry. American Mineralogist, 71, 1160–1169.

Navrotsky, A., and Kleppa, O.J. (1967) The thermodynamics of cation distribution in simple spinels. Journal of Inorganic and Nuclear Chemistry, 29, 2701–2714.

Navrotsky, A., Wechsler, B.A., Geisinger, K., and Seifert, F. (1986) Thermochemistry of MgAl₂O₄-Al₈/₃O₄ defect spinels. Journal of the American Ceramic Society, 69, 418–422.

O'Neill, H.St.C., and Navrotsky, A. (1983) Simple spinels: Crystallographic parameters, cation radii, lattice energies, and cation distribution. American Mineralogist, 68, 181–194.

Peterson, R.C., Lager, G.A., and Hitterman, R.L. (1991) A time-of-flight neutron powder diffraction study of MgAl₂O₄ at temperatures up to 1273 K. American Mineralogist, 76, 1455–1458.

Ramsden, A.R., and French, D.H. (1990) Routine trace-element capabilities of electron-microprobe analysis in mineralogical investigations: An empirical evaluation of performance using spectrochemical standard glasses. Canadian Mineralogist, 28, 171–180.

Rein, R.H., and Chipman, J. (1963) The distribution of silicon between Fe-Si-C alloys and SiO₂-CaO-MgO-Al₂O₃ slags. Transactions of the Metallurgical Society of AIME, 227, 1193–1203.

———(1965) Activities in the liquid solution SiO₂-CaO-MgO-Al₂O₃ at 1600 °C. Transactions of the Metallurgical Society of AIME, 233, 415–425.

Richet, P., and Fiquet, G. (1991) High-temperature heat capacity and premelting of minerals in the system MgO-CaO-Al₂O₃-SiO₂. Journal of Geophysical Research, 96, 445–456.

Robie, R.A., Hemingway, B.R., and Fisher, J.R. (1978) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10⁵ Pascals) pressure and at higher temperatures. U.S. Geological Society Bulletin, 1452, 1–456.

Roy, D.M., Roy, R., and Osborn, E.F. (1953) The system MgO-Al₂O₃-H₂O and influences of carbonate and nitrate ions on the phase equilibria. American Journal of Science, 251, 337–361.

Sack, R. (1982) Spinels as petrogenetic indicators: Activity-composition relations at low pressure. Contributions to Mineralogy and Petrology, 78, 169–186.

Sack, R.O., and Ghiorso, M.S. (1991) Chromian spinels as petrogenetic indicators: Thermodynamics and petrological applications. American Mineralogist, 76, 827–847.

Schaller, H.-J. (1978) Der Einfluß der Lage der Fermi-Energie auf das Mischungsverhalten von Palladium/Aluminium-Legierungen. Berichte der Bunsen Gesellschaft für Physikalische Chemie, 82, 365–371.

Schmocker, U., and Waldner, F. (1976) The inversion parameter with

respect to space group of MgAl$_2$O$_4$ spinels. Journal of Physics C: Solid State Physics, 9, L235–L237.

Schmocker, U., Boesch, H.R., and Waldner, F. (1972) A direct determination of cation disorder in MgAl$_2$O$_4$ spinel by ESR. Physics Letters, 40A, 237–238.

Shearer, J.A., and Kleppa, O.J. (1973) The enthalpies of formation of MgAl$_2$O$_4$, MgSiO$_3$, Mg$_2$SiO$_4$, and Al$_2$SiO$_5$ by oxide melt solution calorimetry. Journal of Inorganic and Nuclear Chemistry, 35, 1073–1078.

Shirasuka, K., and Yamaguchi, G. (1974) Precise measurement of the crystal data and the solid solution range of the defective spinel MgO-nAl$_2$O$_3$. Yogyo Kyokaishi, 82, 650–653.

Snyder, D.A., and Carmichael, I.S.E. (1992) Olivine-liquid equilibria and the chemical activities of FeO, NiO, Fe$_2$O$_3$, and MgO in natural basic melts. Geochimica et Cosmochimica Acta, 56, 303–318.

Suzuki, I., and Kumazawa, M. (1980) Anomalous thermal expansion in spinel MgAl$_2$O$_4$: A possibility for a second order phase transition? Physics and Chemistry of Minerals, 5, 279–284.

Téqui, C., Robie, R.A., Hemingway, B.S., de Neuville, D.R., and Richet, P. (1991) Melting and thermodynamic properties of pyrope (Mg$_3$Al$_2$Si$_3$O$_{12}$). Geochimica et Cosmochimica Acta, 55, 1005–1010.

Weeks, R.A., and Sonder, E. (1980) Electrical conductivity of pure and Fe-doped magnesium-aluminum spinel. Journal of the American Ceramic Society, 63, 92–95.

Wood, B.J., Kirkpatrick, R.J., and Montez, B. (1986) Order-disorder phenomena in MgAl$_2$O$_4$ spinel. American Mineralogist, 71, 999–1006.

Yamanaka, T., and Takéuchi, Y. (1983) Order-disorder transition in MgAl$_2$O$_4$ spinel at high temperatures up to 1700 °C. Zeitschrift für Kristallographie, 165, 65–78.