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STANDARD THERMODYNAMIC PROPERTIES OF ALMANDINE

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ABSTRACT

The standard entropy and high-temperature heat capacity of synthetic almandine, $Fe_3Al_2Si_3O_{12}$, were calculated from experimental high-T, high-P data on the equilibrium: almandine + rutile = ilmenite + sillimanite + quartz (GRAIL reaction). The calculated standard entropy of almandine of 340.28 J/mol agrees almost exactly with the value measured by adiabatic calorimetry. Calculated heat capacity coefficients yield entropy and heat content values in the range 600 – 1200 K, which are considerably larger than those of the major self-consistent datasets. However, the predicted heat content increment from 965 K ($H_{965} - H_{298.15}$ = 306.32 kJ) is in substantial agreement with a drop-calorimetry measurement of 305.52 ± 1.88 kJ, performed in 1972 in this laboratory. The standard enthalpy of formation of almandine was calculated from recent high-pressure experimental data on the reaction: almandine + O_2 = magnetite + kyanite + quartz, buffered at hematite–magnetite oxygen fugacity, making use of the derived heat capacity coefficients of almandine. The resulting value of ΔH°_f, –5266.76 kJ/mol at 298.15 K, is close to those of the self-consistent datasets, but 10 kJ less negative than that given by high-temperature solution calorimetry. The enthalpy of formation of ilmenite, $FeTiO_3$, that is consistent with the present calculations, is 4 kJ more negative than given by acid solution calorimetry, but supports the revision of Anovitz *et al.* (1985) based on reinterpretation of the available measurements of oxygen fugacity on reactions responsible for the formation of ilmenite.

Keywords: almandine, entropy, thermodynamic datasets, equilibria.

SOMMAIRE

Nous avons calculé l'entropie standard et la capacité calorifique à haute température de l'almandine synthétique, $Fe_3Al_2Si_3O_{12}$, à partir de données expérimentales obtenues à pression et à température élevées pour l'équilibre GRAIL: almandine + rutile = ilménite + sillimanite + quartz. L'entropie standard calculée de l'almandine, 340.28 J/mol, concorde presqu'exactement avec la valeur mesurée par calorimétrie adiabatique. Les coefficients calculés de capacité calorifique mènent à des valeurs de l'entropie et de l'enthalpie sur l'intervalle 600–1200 K qui sont considérablement supérieures à celles des banques de données à concordance interne. Toutefois, l'incrément en enthalpie à partir de 965 K ($H_{965} - H_{298.15}$ = 306.32 kJ) concorde avec une mesure réalisée par calorimétrie à la goutte de 305.52 ± 1.88 kJ, effectuée en 1972 dans notre laboratoire. L'enthalpie standard de formation de l'almandine a été calculée à partir de données expérimentales obtenues à pression élevée pour la réaction almandine + O_2 = magnétite + kyanite + quartz, à une fugacité d'oxygène régie par le tampon hématite–magnétite, et avec les coefficients de capacité calorifique que nous avons dérivés pour l'almandine. La valeur qui en résulte, ΔH°_f = –5266.76 kJ/mol à 298.15 K, se rapproche de celle des banques de données courantes, mais se trouve être 10 kJ plus négative que la valeur qui découle de la calorimétrie par solution à température élevée. L'enthalpie de formation de l'ilménite, $FeTiO_3$, qui concorde avec nos calculs est 4 kJ plus négative que la valeur obtenue par calorimétrie par solution dans l'acide. Elle étaye la révision d'Anovitz *et al.* (1985) fondée sur la ré-interprétation des mesures disponibles de la fugacité de l'oxygène pour les réactions menant à la formation de l'ilménite.

(Traduit par la Rédaction)

Mots-clés: almandine, entropie, banque de données thermodynamiques, équilibre.

INTRODUCTION

Almandine-rich garnet is, arguably, the most important mineral for geothermometry and geobarometry of high-grade metamorphic rocks. The most commonly used experimental cation-exchange thermometers involve garnet along with biotite (Ferry & Spear 1978), orthopyroxene (Lee & Ganguly 1988), clinopyroxene (Ellis & Green 1979, Pattison & Newton 1989) and olivine (O'Neill & Wood 1979). Experimentally and calorimetrically calibrated assemblages useful in geobarometry include garnet – ilmenite – rutile – sillimanite – quartz (GRAIL: Bohlen *et al.* 1983a), garnet – orthopyroxene – plagioclase – quartz (GAPES: Newton & Perkins 1982, Eckert *et al.* 1991), garnet – spinel – sillimanite – quartz (Bohlen *et al.* 1986), and garnet –

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Al_2SiO_5 – plagioclase – quartz (GASP: Ghent *et al.* 1979, Newton & Haselton 1981, Koziol & Newton 1989).

In spite of its importance to geochemistry, the standard-state thermodynamic parameters of almandine are not yet known as well as for many other rock-forming minerals. One reason for the lag is the difficulty of controlling oxygen fugacity in high-pressure reaction vessels and in the solution calorimeter. Modifications to the apparatus to achieve these conditions have been designed within the last decade (Bohlen 1984, Chatillon-Colinet *et al.* 1983), but the number of experimental studies is not yet large. Tables of self-consistent thermodynamic data of minerals have become available only in the last few years (Holland & Powell 1990, Berman 1988); the parameters tabulated in the datasets, especially for the Fe minerals, are still in a state of revision as key experimental and calorimetric studies appear.

One of the most useful experimental equilibria for retrieval of the standard properties of synthetic almandine is the GRAIL reaction:

A) $Fe_3Al_2Si_3O_{12} + 3TiO_2 = 3FeTiO_3 + Al_2SiO_5 + 2SiO_2$
almandine rutile ilmenite sillimanite quartz

The reaction boundary in terms of pressure and temperature has been worked out with high-precision reversed data (Fig. 1) by Bohlen *et al.* (1983a). Moreover, recent heat capacity measurements of high quality exist for ilmenite (Anovitz *et al.* 1985) and sillimanite (Robie & Hemingway 1984), and earlier reliable thermochemical data exist for the oxides rutile and quartz (Robie *et al.* 1978). The standard entropy and high-temperature heat capacities for almandine are thus obtainable with accuracy from the GRAIL reaction.

The thermal properties of almandine in the major datasets were calculated partly in reference to the experimental GRAIL reaction, but also partly from other experimental reactions of iron-bearing minerals whose properties are not as well known as those of the GRAIL reaction; the tabulated values are, to some extent, compromised by this uncertainty. In the present study, we calculated the heat capacity coefficients of almandine from the experimental GRAIL reaction. A heat content measurement on synthetic almandine at 965 K relative to 298 K by drop calorimetry, performed in this laboratory by Shearer (1972), allows us to discriminate among the sets of heat capacity constants calculated by different authors from the phase equilibria.

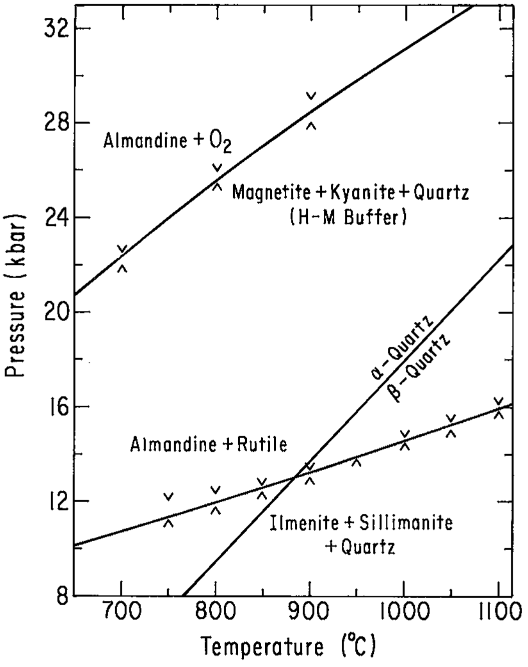

FIG. 1. Experimental data for the GRAIL reaction (Reaction A) of Bohlen *et al.* (1983a) with the present quadratic fit to the midpoints, and data for the almandine oxidation reaction (Reaction B), discussed in the text. The arrow heads mark the nominal (T,P) coordinates of the reversal experiments.

An experimental determination of the high-pressure oxidation reaction of synthetic almandine:

B) $Fe_3Al_2Si_3O_{12} + 1/2\ O_2 = Fe_3O_4 + Al_2SiO_5 + 2SiO_2$
almandine magnetite kyanite quartz

has been carried out with oxygen fugacity controlled by the hematite–magnetite (HM) buffer (Harlov & Newton 1992). These experiments were performed with the 3/4″-diameter piston–cylinder apparatus with the NaCl–graphite assembly, and should thus be of comparable precision to the GRAIL study, though the brackets are not as many or as tight (Fig. 1). Reaction B allows retrieval of the Gibbs free energy of formation of almandine, inasmuch as reliable measurements exist on the the formation properties of magnetite, hematite and quartz (Robie *et al.* 1978) and kyanite (Peterson & Newton 1990). Using our thermal constants of almandine secured from the GRAIL reaction and supported by measurements of heat content, we can get the enthalpy change of reaction B, and hence the enthalpy of formation of almandine. The resulting values of $S°_{298}$ and $\Delta H°_{f,\,298}$ of almandine may be used to critique the values of the self-consistent datasets, none of which incorporate the experimental data of reaction B.

MEASUREMENTS OF HEAT CONTENT

Synthesis of material

Synthetic almandine was prepared by J.A. Shearer (1972) from finely ground and homogenized mixtures of reagent ferrous oxalate, γ–Al_2O_3 and cristobalite.

About 1 g of starting material was sealed with about 20 mg of H_2O in an Au tube. Crystallization was performed at 900°C and 20 kbar for three hours in the piston-cylinder apparatus. The talc used as pressure medium surrounding the capsule was mixed with Fe metal powder to maintain a low fugacity of oxygen. The product was almandine in clear, faintly pink dodecahedral crystals. Carbonaceous quench material mixed with the almandine was separated with ultrasonic vibration and heavy liquids. The charges were washed, dried and ground to –250 mesh. The resulting separates were without impurities, visible optically or by X-ray diffraction. The unit-cell constant is 11.528 ± 0.001Å. This is, within error, the smallest unit-cell constant obtainable by large-quantity synthesis methods (see Geiger *et al.* 1987), and hence, the almandine contains minimal ferric iron. Mössbauer resonance analysis of the synthetic almandine of Geiger *et al.* (1987), with unit-cell constant of 11.527 ± 0.001 Å, showed that it contained less than 1% of the total iron as ferric iron.

Calorimetric techniques and results

Measurements of heat content were performed by Shearer (1972) in a Ni-block Calvet-type microcalorimeter (Kleppa 1972). Calorimeter temperature was continuously monitored by the Pt – Pt 10% Rh thermopile sensor and periodically checked with an externally introduced National Bureau of Standards Pt–Pt 10% Rh thermocouple. Calorimeter temperature in Shearer's experiments was 965 ± 0.5 K. The laboratory (initial) temperature was maintained at 298 ± 1 K. Approximately 200 mg of almandine was sealed in a thin-walled pure Pt capsule weighing about 50 mg. The heat content of the Pt capsule material was assumed to be identical to that of the certified Pt heat content calibrant used in the laboratory. A small correction was made for heat pick-up during the drop.

Ten drops were performed on the almandine sample, yielding the following ten H_{965}–H_{298} values: 305.56, 306.44, 303.67, 308.74, 303.80, 303.80, 304.51, 307.02, 304.51, 306.98 kJ/mole. The mean heat content is 305.50 ± 1.88 kJ per mole.

DERIVATIONS FROM PHASE-EQUILIBRIUM DATA

Entropy, heat capacity and heat content from GRAIL

A straightforward calculation of the entropy of almandine at one bar and elevated temperatures may be made by applying the Clausius-Clapeyron equation to the experimentally determined reaction curve of Bohlen *et al.* (1983a). First, the midpoints of their tight brackets at seven temperatures were fitted to a quadratic equation by least squares:

$$1)\quad P_{GRAIL}\,(\text{bar}) = 2148 + 5.861T(K) + 0.003051T^2$$

This equation is continuous across the $\alpha - \beta$ quartz transition; any actual change of slope at the transition is nearly imperceptible. The goodness of fit may be seen in Figure 1. Next, the volume change of the reaction was calculated using the compilation of thermal expansion and compressibility coefficients of Holland & Powell (1990), listed in Table 1. These parameters have the advantage of rendering volumes linear with temperature and pressure, but are not significantly different from the parameters of other datasets. The entropy change of the GRAIL reaction, ΔS_{GR}, was calculated from the dP/dT slope and the ΔV at 100 K intervals, and reduced to one bar pressure by the expression:

$$2)\quad \Delta S_{GR}\,(1) = \Delta S_{GR}\,(P) + (P_{GR} - P_{\alpha\beta})\Delta(AV)_\alpha + P_{\alpha\beta}\Delta(AV)_\beta$$

where $P_{\alpha\beta}$ is the pressure of the $\alpha - \beta$ quartz transition at T, $\Delta(AV)_\alpha$ is the difference of the thermal expansion – volume terms between GRAIL products and reactants with α-quartz, and $\Delta(AV)_\beta$ is the corresponding quantity with β-quartz. The maximum correction to ΔS_R brought about by expression 2) is 1.42 J/K.

The entropy of almandine was calculated at 100 K intervals from $\Delta S_{GR}(1)$ and the entropy values tabulated by Anovitz *et al.* (1985) for ilmenite to 1000 K and by Robie *et al.* (1978) to higher temperatures for the other GRAIL minerals, modified for sillimanite by Robie & Hemingway (1984). The tabulated values, representing a close approach to measured data, were taken in preference to values calculated from the thermal constants of the Berman (1988) and Holland & Powell (1990) datasets, which have been adjusted, to some extent, for experimental data of reactions other than the GRAIL reaction. Since the entropy data of ilmenite of Anovitz *et al.* (1985) are given only to 1000 K, an additional 500 K extrapolation was made from the C_p expression of Berman (1988), based on the parameterization of Berman & Brown (1985), who claimed that their functional form is better suited to extrapolation than the more conventional forms used by Robie *et al.* (1978) and other authors. The entropies of ilmenite and the other GRAIL minerals at 1000 K are given in Table 1.

The value at 298.15 K of S (almandine) = 340.28 cal/K agrees closely with that derived from the entropy expression given by Bohlen *et al.* (1986), who cited an unpublished paper by Metz and others, and agrees exactly with that given by Metz *et al.* (1983). Since this entropy, and the C_p of 342.80 J/K-mole at the same temperature, derived from the expression of Bohlen *et al.* (1986), are based on adiabatic calorimetry, they should be accurate values. Measured heat capacities of almandine at temperatures to 1000 K are less accurate, since they are based on differential scanning calorimetry.

In the present derivation, calculated entropy increments, S_T–$S_{298.15}$, of almandine at 100 K intervals to 1500 K were fitted by least squares to the four heat

TABLE 1. THERMODYNAMIC DATA FOR ALMANDINE AND ASSOCIATED MINERALS

$$V(T,P) = V + (AV)(T-298) - (BV)P$$

INPUT QUANTITIES

	V^a (1 Bar, 298K) J/Bar	AV^a X10^5 J/Bar-K	BV^a X10^3 J/Bar-kbar	H_{1000}-H_{298}^{b} kJ	S_{1000} J/K	S_{298} J/K	$\Delta H^{\circ}_{f,298}$ kJ
Almandine	11.530	28.3	6.6				
Ilmenite	3.169	9.4	1.8	86.94^{c}	254.51^{c}	108.91^{c}	
Magnetite	4.452	18.3	2.5	147.99^{b}	390.24^{b}	146.14^{b}	-1115.73^{b}
Hematite	3.027	11.6	1.4	100.551^{b}	252.71^{b}	87.40^{b}	-824.64^{b}
α-quartz	2.269	8.0	5.9	44.97^{b}		41.46^{b}	-910.70^{b}
β-quartz	2.367	0	2.6		115.56^{b}		
Sillimanite	4.991	7.2	3.1		294.73^{d,b}	95.79^{d}	
Kyanite	4.414	11.2	1.9	121.68^{b}	283.77^{d,b}	82.30^{d}	-2594.37^{e}
Rutile	1.882	5.0	0.9	46.94^{b}	129.21^{b}	50.29^{b}	-944.75^{b}
O_2				22.71^{b}	243.44^{b}	205.00^{b}	

DERIVED QUANTITIES AND COMPARISONS

	S^{Alm}_{298} J/K	S^{Alm}_{1000} J/K	$(H_{965}$-$H_{298})^{Alm}$ kJ	$\Delta H^{\circ Alm}_{f,298}$ kJ	$\Delta H_{B,1000}$ kJ	$\Delta S_{B,1000}$ J/K
Present	340.28	879.23	305.52±1.88^{f} 306.32^{g}	-5266.76	-240.61	-95.82
Froese (1974)					-244.09	-92.72
Metz *et al.* (1983)	340.16±1.88					
HP (1990)	342.00	870.16	299.47	-5267.85	-233.65	-87.22
Berman (1988)	339.93	867.90	299.48	-5265.50	-236.12	-84.20

Sources: a: Holland & Powell (1990), except for volume of almandine (Geiger *et al.* 1987) and of sillimanite (Navrotsky *et al.* 1973). b: Robie *et al.* (1978). c: Anovitz *et al.* (1985). d: Robie & Hemingway (1984). e: Peterson & Newton (1990). f: Measured. g: Derived from Berman's (1988) Cp formula coefficients (Table 2).

capacity constants of the Holland & Powell (1990) and Berman (1988) formulas, subject to the constraint that C_p at 298.15 K is equal to 342.80 J/mol–K. Resulting heat capacities, entropies and heat contents are given in Table 2. It is seen that the entropy values calculated from GRAIL are replicated closely. The Berman (1988) formula is slightly superior, yielding an average deviation from the GRAIL-derived entropies of only 0.36 J/K. The derived Berman-type coefficients do not conform to the specifications of Berman & Brown (1985) in that the k_1 coefficient is positive, rather than negative. Negative values of k_1 and k_2 are necessary to insure that the C_p values increase indefinitely with temperature. In fact, the derived Berman-type coefficients yield a very broad maximum above 1300 K. It is clear that they cannot be used as extrapolation parameters, though they describe well the GRAIL-derived entropy values of almandine in the range 400–1500 K. The derived Holland–Powell C_p coefficients yield an even more pronounced maximum with increasing temperature, and could be considered less satisfactory for that reason.

The entropy and heat content near 1000 K predicted by the above equations are significantly higher than given by the Holland & Powell (1990) and the Berman (1988) datasets (Table 1), which adopt high-temperature heat capacity measurements of Metz *et al.* (unpubl. data) based on differential scanning calorimetry. In view of the fact that the probable uncertainties of this method near its upper limit of 1000 K are 2% relative, the derived and measured heat capacities could be considered in agreement.

The present measured heat content of 305.52 ± 1.88 kJ at 965 K provides a definitive test of the several sets of almandine thermal constants in favor of the present set in Table 2. The 965 K heat content yielded by the present Berman-type C_p coefficients is 306.32 kJ, and that yielded by the present Holland–Powell-type coefficients is 306.22 kJ. These values are discrepant by

TABLE 2. FITTED HEAT CAPACITY (Cp, J/K) COEFFICIENTS, ENTROPY (S, J/K) AND HEAT CONTENT (H_T–H_{298}, kJ) OF ALMANDINE, AND ENTROPY DERIVED DIRECTLY FROM GRAIL

	BERMAN			HOLLAND-POWELL			GRAIL
T(K)	Cp	S	H_T-H_{298}	Cp	S	H_T-H_{298}	S_{der}
400	398.82	448.52	37.705	400.07	449.36	37.988	448.23
500	442.88	542.62	79.944	439.86	543.17	80.102	543.67
600	470.83	626.01	125.740	467.60	625.97	125.561	625.80
700	488.11	700.03	173.755	486.72	699.56	173.340	699.36
800	498.77	765.92	223.142	499.57	765.46	222.70	765.17
900	505.30	825.08	273.374	507.69	824.83	273.098	825.63
1000	509.23	878.56	324.120	512.16	878.56	324.119	879.23
1100	511.45	927.22	375.166	513.84	927.47	375.440	927.43
1200	512.54	971.78	426.372	513.17	972.19	426.807	971.65
1300	512.83	1012.82	477.647	510.66	1013.16	478.012	1012.40
1400	512.67	1050.81	528.926	506.60	1050.85	528.887	1050.73
1500	512.12	1086.17	580.167	501.24	1085.66	579.289	1086.29

Berman formula: $Cp = k_0 + k_1/\sqrt{T} + k_2/T^2 + k_3/T^3$

$k_0 = 415.121$ $k_1 = 4835.49$ $k_2 = -70.4617 \times 10^6$ $k_3 = 11.6691 \times 10^9$

Holland and Powell formula: $Cp = a + bT + c/T^2 + d/\sqrt{T}$

$a = 1108.87$ $b = -.172611$ $c = 6.58799 \times 10^6$ $d = -1.36188 \times 10^4$

several kJ from the values yielded by the two datasets (Table 1).

Enthalpy of formation from almandine–hematite equilibrium

The standard free energy of formation of almandine, $\Delta G°_f$, and the corresponding enthalpy of formation, $\Delta H°_f$, can be calculated in a straightforward manner from the experimental data of reaction B, since the formation properties of the other participating minerals have been measured with considerable accuracy. Reaction B and the hematite–magnetite buffer reaction can be combined to yield the reaction:

$$B^1)\quad \underset{\text{hematite}}{3Fe_2O_3} + \underset{\text{almandine}}{Fe_3Al_2Si_3O_{12}} = \underset{\text{magnetite}}{3Fe_3O_4} + \underset{\text{kyanite}}{Al_2SiO_5} + \underset{\text{quartz}}{2SiO_2}$$

The equation of equilibrium is:

$$3)\quad \Delta G_{B^1}(T,P) = 0 = \Delta G°(T,1) + \int_1^P \Delta V_{B^1} dP$$

where ΔG_{B^1} is the Gibbs free energy change of reaction B^1, and ΔV_{B^1} is the volume change.

The integral term can be evaluated as:

$$4)\quad \int_1^{P_{B^1}} \Delta V_{B^1} dP = (P_{B^1} - P_{\alpha\beta})\Delta V_{B^1,\alpha} + P_{\alpha\beta}\Delta V_{B^1,\beta}$$

where P_{B^1} is the equilibrium pressure of B^1, $\Delta V_{B^1,\alpha}$ is the volume change of the reaction with α-quartz, evaluated at T and $(P_{B^1} + P_{\alpha\beta})/2$, and $\Delta V_{B^1,\beta}$ is the volume change with β-quartz, evaluated at T and $P_{\alpha\beta}/2$. Because of the constant thermal expansion and compression coefficients (Table 1), expression 4) is exact.

Taking the equilibrium pressure of reaction B at 1000 K to be 23.4 ± 0.2 kbar, $\Delta G°_{B^1}(1,T)$ comes out to be –40.63 kJ. With the aid of the almandine entropy previously derived at 1000 K (879.23 J/K) and the other data of Table 1, the standard enthalpy of reaction B^1 at 1000 K comes out to be:

$$5)\quad \Delta H°_{B^1} = \Delta G°_{B^1} + 1000\,\Delta S°_{B^1} = 7.62\text{ kJ}$$

This gives the enthalpy of formation of almandine at 298 K as:

$$6)\quad \Delta H°_f(\mathrm{Alm}) = \Delta H°_f(\mathrm{Mag}) + \Delta H°_f(\mathrm{Ky}) + 2\Delta H°_f(\mathrm{Qtz}) - \Delta H°_{B^1} = -5266.83\text{ kJ}$$

using the thermal constants in Table 1.

The $\Delta H°_f$ derived from the experimentally studied almandine oxidation reaction lies midway between the dataset values (Table 1), and would seem to be in substantial agreement with them. This agreement is more of a reality for the Berman (1988) dataset, which tabulates enthalpy of formation values close to the calorimetrically measured values. However, the formation properties of magnetite, hematite and kyanite given in the Holland & Powell (1990) dataset are quite different from the Robie *et al.* (1978) and Peterson & Newton (1990) values used here; if the Holland and Powell (1990) values are used in the present derivation, the derived ΔH°_{f}(almandine) value comes out to –5274.5 kJ.

The above derivation procedure was repeated at 1100 K (P_{B^1} = 26.3 kbar) and 1200 K (29.1 kbar), giving ΔH°_{f}(almandine) = –5266.71 kJ and –5266.72 kJ, respectively. The similarity of the three values of ΔH°_{f} indicates the thermodynamic consistency of the experimental determination of reaction B. The average of the three determinations is given in Table 1.

It would be very difficult to give a rigorous account of the uncertainty in the derived ΔH°_{f} of almandine. An approximate estimate is given by:

$$\sigma_{\mathrm{H}}(\mathrm{Alm}) = \sqrt{[\sigma^2(\mathrm{P}\Delta V_{\mathrm{B}^1}) + 3\sigma_H^2(\mathrm{Hem}) + 3\sigma_H^2(\mathrm{Mag}) + 3\sigma_H^2(\mathrm{Qtz}) + \sigma_H^2(\mathrm{Crn}) + \sigma_H^2(\mathrm{Ky})]},$$

where the first term under the square root represents the uncertainty in the pressure of reaction B^1, and σ_H for hematite (Hem), magnetite (Mag), quartz (Qtz) and corundum (Crn) are given by Robie *et al.* (1978) as, respectively, 1.255, 2.092, 1.000, and 1.300 kJ for formation from the elements. An additional small uncertainty of ± 0.15 kJ/mole for formation of kyanite from the oxides is based on the experimental determination of the formation reaction by Peterson & Newton (1990). The calculated uncertainty, ± 4.77 kJ/mole, does not take into account errors in the heat capacities or volumes.

DISCUSSION AND APPLICATIONS

This paper presents evidence that the high-temperature heat capacity and entropy of almandine are larger than previously considered. At 1000 K, the Gibbs free energy of formation is about 2–4 kJ more negative than given by the major datasets, and dP/dT slopes of many equilibria like reaction A are smaller than those yielded by the datasets.

This evaluation of almandine stability is not unprecedented. Froese (1973) calculated Gibbs free energies of reactions among almandine, ferroan cordierite, magnetite, hercynite, sillimanite and quartz, based on experimental work at 2 kbar of Hsu (1968), Rutherford (1970), Rutherford & Eugster (1967), and Richardson (1968). The assemblages were investigated with quartz – magnetite – fayalite and Ni–NiO buffers and involved hercynite – magnetite solid solutions. With the aid of an empirical activity model for magnetite, Froese (1973) derived the Gibbs free energy for reaction B with sillimanite instead of kyanite:

7) $\Delta G^{\circ}_{\mathrm{B}} = -232.3 + 0.0816\ \mathrm{T\ kJ}$

with a standard state of the solids at 2 kbar. This expression applies to temperatures in the neighborhood of 1000 K. Making a –6.54 kJ correction for the enthalpy change of sillimanite to kyanite, based on the Berman (1988) data, and a corresponding correction to entropy of –11.13 J/K, and correcting the standard state of the solids from 2 kbar to one bar, the preceding expression is modified to:

8) $\Delta G^{\circ}_{\mathrm{B}} = -240.72 + 0.09272\ \mathrm{T} = \Delta H^{\circ}_{\mathrm{B}} - \mathrm{T}\Delta S^{\circ}_{\mathrm{B}}$

The agreement of these estimates of $\Delta H^{\circ}_{\mathrm{B}}$ and $\Delta S^{\circ}_{\mathrm{B}}$ with those derived from the considerations of this paper is quite remarkable, as shown in Table 1.

The single study available of almandine by solution calorimetry (Chatillon-Colinet *et al.* 1983) was based on the reaction:

C) $3/2\ \mathrm{Fe_2SiO_4} + 3/2\ \mathrm{SiO_2} + \mathrm{Al_2O_3} = \mathrm{Fe_3Al_2Si_3O_{12}}$
fayalite quartz corundum almandine

The solution measurements were made in a eutectic (Li, Na) borate melt at 1023 K. The somewhat higher calorimeter temperature than for solution studies with lead borate is necessary because of the higher viscosity of the alkali borate. Two values of ΔH_{C} at 1023 K were yielded, –15.98 ± 3.43 kJ/mol and –24.77 ± 3.60 kJ/mol, using two different samples of synthetic fayalite. No reasons for the large discrepancy were apparent. These values translate, with the aid of the fayalite data of Robie *et al.* (1978), to a $\Delta H^{\circ}_{f,298}$ of –5276.2 kJ and –5285.0 kJ. The agreement with the present derivation is poor, even for the less negative value. A possible problem with the calorimetry was that the fugacity of oxygen was controlled at the tarnish point of a Ni foil in the sample holder area of the calorimeter, which conditions may have allowed for a small amount of oxidation of the fayalite.

Woodland & Wood (1989) measured the oxygen fugacity electrochemically at 1073 – 1173K in a solid electrolyte cell at one bar of a mixture of synthetic almandine, Fe metal, sillimanite and quartz. This mineral assemblage gave a reversible oxygen fugacity $\log f(\mathrm{O_2})$ of –2.23 + 2400/T in their temperature range, values very near the Fe–FeO buffer. These data yield ΔH°_{f}(almandine) = –5267.8 kJ at 298 K, using thermal constants from Berman (1988). The ΔH°_{f} of Woodland & Wood is in apparent agreement with the present value. The agreement is fortuitous, however; use of the present C_{p} function for almandine would have resulted in a considerably different ΔH°_{f}. A possible problem with the solid-state emf technique is the difficulty of actually performing a reversible reaction involving $\mathrm{SiO_2}$ and $\mathrm{Al_2O_3}$ in mineral mixes at these low temperatures and at one bar pressure. It seems possible that the results of Woodland & Wood were actually influenced by surface reactions of the Fe metal, without participation of the quartz or sillimanite. The solid-state emf method has not yet proven itself as a tool for measuring ΔG of heterogeneous reactions among silicates.

Although our ΔH°_f of almandine is close to the dataset values, the properties of almandine derived in this paper are not generally consistent with the other mineral data of either dataset, because the C_p coefficients in this paper are significantly different from those of the datasets. The somewhat higher heat capacity and entropy of almandine predicted here are actually more consistent with some well-constrained experimental equilibria. Next to GRAIL, the most thoroughly studied experimental reaction is that involving anorthite, fayalite and garnet:

$$\text{D)}\quad \underset{\text{garnet solid solution}}{2Fe_3Al_2Si_3O_{12} + Ca_3Al_2Si_3O_{12}} = \underset{\text{anorthite}}{3CaAl_2Si_2O_8} + \underset{\text{fayalite}}{3Fe_2SiO_4}$$

The most comprehensive reversed data are those of Bohlen *et al.* (1983b), shown in Figure 2. Assuming ideal solution of Fe and Ca in garnet, the Berman (1988) and Holland & Powell (1990) datasets give a dP/dT slope close to 11 bar/K, considerably steeper than the experimental slope of 7.2 bar/K (Fig. 2). However, using the present high-temperature entropy of almandine, along with the entropies and volumes of the other minerals given by the Berman (1988) dataset, the calculated slope is 7.8 bar/K at 1100 K, and with the Holland & Powell (1990) dataset, it is 7.2 bar/K. It is concluded that the present high-temperature heat capacity and entropy functions of almandine give a better account of the experimental slope of reaction D than do those of either dataset. The equilibrium curves predicted by the two datasets are able to intersect a portion of the array of experimental data by virtue of their steep dP/dT slopes, but this partial agreement is achieved by adjustment of the thermodynamic properties of the other minerals in the reaction, which properties are greatly discrepant between the two datasets [for instance, Holland & Powell (1990) used ΔH°_f of anorthite of −4232.74 kJ, in contrast with Berman's (1988) value of −4228.73 kJ]. It is probable that the properties of other minerals in both datasets would be improved by incorporation of the experimental data of reaction B used in this paper and consideration of the measured heat content of almandine at 965 K. Relatively small adjustments in the thermody-

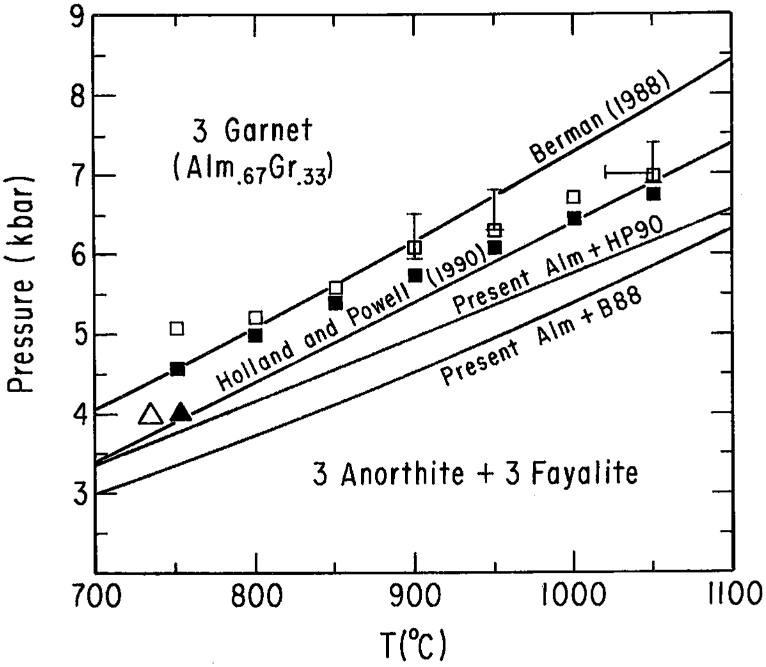

FIG. 2. Experimental and calculated P–T curves of Reaction D (see text). Square symbols: reversals of Bohlen *et al.* (1983b). Triangles: reversals of Grafchikov & Fonarev (1986). Brackets: reversal intervals of Perkins & Vielzeuf (1992). Thin lines: calculated curves are shown using the Berman (1988) dataset ("B 88"), the Holland & Powell (1990) dataset ("HP 90"), and the present properties of almandine derived together with data for the other minerals of Reaction D from the Berman (1988) and the Holland & Powell (1990) datasets. Ideal solution of Fe and Ca in garnet is assumed in all calculations.

namic properties of the other minerals in reaction D, along with adjustment of the $\Delta H°_f$ of almandine within the 4.77 kJ uncertainty of the present estimate, would allow agreement with the absolute position of the calculated position of reaction D as well as with its dP/dT slope.

Anovitz & Essene (1987) were able to fit the flat experimental dP/dT of reaction D by assuming a large excess entropy of mixing in almandine-grossular solid solution. However, phase-equilibrium measurements of the free energy of mixing on this join (Koziol 1990), together with measurements of the excess enthalpy of mixing by solution calorimetry (Geiger *et al.* 1987), provide no evidence for nonideal mixing.

A consequence of the present deductions is that the $\Delta H°_f$ of ilmenite must be about 4 kJ less negative than the value tabulated by Robie *et al.* (1978). This is in accord with the deduction of Anovitz *et al.* (1985). They reinterpreted available measurements of oxygen pressure of the reaction of Fe, quartz and rutile to ilmenite and revised $\Delta G°_f$(ilmenite) to a value of −1153.9 kJ/mol, 5 kJ less negative than given by earlier interpretations. Our derived properties of almandine require $\Delta H°_f$ (ilmenite) to be −1232.85 kJ/mol at 298K, in order to reproduce the high-pressure GRAIL curve. This value is midway between the values tabulated by Berman (1988) and Holland & Powell (1990) (respectively, −1231.95 kJ and −1233.26 kJ): both datasets accept the Anovitz *et al.* (1985) revisions.

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