

## Heat capacity and thermodynamic properties of andradite garnet, $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ , between 10 and 1000 K and revised values for $\Delta_f G_m^\circ$ (298.15 K) of hedenbergite and wollastonite

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**Abstract**—The heat capacity of synthetic andradite garnet ( $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ ) was measured between 9.6 and 365.5 K by cryogenic adiabatic calorimetry and from 340 to 990 K by differential scanning calorimetry. At 298.15 K  $C_{p,m}^\circ$  and  $S_m^\circ$  are  $351.9 \pm 0.7$  and  $316.4 \pm 2.0$  J/(mol·K), respectively.

Andradite has a  $\lambda$ -peak in  $C_{p,m}^\circ$  with a maximum at  $11.7 \pm 0.2$  K which is presumably associated with the antiferromagnetic ordering of the magnetic moments of the  $\text{Fe}^{3+}$  ions. The Gibbs free energy of formation,  $\Delta_f G_m^\circ$  (298.15 K) of andradite is  $-5414.8 \pm 5.5$  kJ/mol, and was obtained by combining our entropy and heat capacity data with the known breakdown of andradite to pseudowollastonite and hematite at  $\approx 1410$  to 1438 K. From a reexamination of the calcite + quartz = wollastonite equilibrium data we obtained  $\Delta_f H_m^\circ$  (298.15 K) =  $-1634.5 \pm 1.8$  kJ/mol for wollastonite.

Between 300 and 1000 K the molar heat capacity of andradite can be represented by the equation

$$C_{p,m}^\circ = 809.24 - 7.025 \times 10^{-2} T - 7.403 \times 10^3 T^{-0.5} - 6.789 \times 10^5 T^{-2}.$$

We have also used our thermochemical data for andradite to estimate the Gibbs free energy of formation of hedenbergite ( $\text{CaFeSi}_2\text{O}_6$ ) for which we obtained  $\Delta_f G_m^\circ$  (298.15 K) =  $-2674.3 \pm 5.8$  kJ/mol.

### INTRODUCTION

ANDRADITE, hedenbergite, and ilvaite are the common Ca-Fe silicates of calcic skarns. The coexistence of andradite and hedenbergite (with quartz) is restricted to only a narrow range in  $f_{\text{O}_2}$ -temperature space (LIU, 1974) and is therefore useful for delineating the conditions of formation of the Fe-calcic skarns which are frequently major sources for tungsten, copper and zinc ore bodies (EINAUDI *et al.*, 1981).

The currently available values for the thermodynamic properties of andradite (KISILEVA *et al.*, 1972; TAYLOR and LIU, 1978; BIRD and HELGESON, 1980) are unsatisfactory. For example,  $\Delta_f G_m^\circ$  (298.15 K) given by TAYLOR and LIU (1978) differs from that recommended by BIRD and HELGESON (1980) by 17.1 kJ/mol. Obviously, accurate heat capacity and entropy data for andradite are essential if one hopes to extract meaningful values for  $\Delta_f G_m^\circ$  (298.15 K) from the several existing phase equilibrium studies.

In order to reduce this uncertainty in  $\Delta_f G_m^\circ$  (298.15 K) we have measured the heat capacity of synthetic andradite garnet ( $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ ) between 9.6 and 990 K to obtain accurate values of  $C_{p,m}^\circ$  and  $S_m^\circ$  as a function of temperature. We have combined our  $C_{p,m}^\circ$  and entropy data for andradite with existing phase equilibrium studies to extract values of  $\Delta_f G_m^\circ$  (298.15 K) and  $\Delta_f H_m^\circ$  (298.15 K) for andradite and for hedenbergite ( $\text{CaFeSi}_2\text{O}_6$ ).

### SAMPLE PREPARATION

Reagent grade  $\text{CaCO}_3$ ,  $\text{Fe}_2\text{O}_3$  and acid cleaned Lisbon, Maryland, quartz were combined in andradite stoichiometry

and mixed under methanol for about one hour with an agate mortar and pestle. The large quantity of starting material prepared (>40 g) required preparation in several batches. These batches were not remixed with each other, but were combined in a single container at the end. The oxide mix was fired at 1073 K for 1 day.

Thick-walled silver capsules containing 500–750 mg of oxide mix and 20–100 mg of water were run at  $1023 \pm 10$  K and  $2000 \pm 100$  bars for 2–3 days in conventional cold-seal bombs. The oxygen fugacity of the “René” bombs was probably near Ni-NiO. The products from each run were examined both in oil and by x-ray diffraction. The run products were generally very fine-grained and were largely isotropic. The only additional crystalline phase observed in the x-ray diffraction results was wollastonite. These wollastonite bearing charges were rerun for two days. It was not possible to completely eliminate the wollastonite. Based upon microscopic observation, scanning electron microscope studies, and x-ray diffractometry we estimate the amount of wollastonite as  $\approx 2$  percent. It is possible that the excess of wollastonite in the run products resulted from small losses of hematite in the preparation procedure. The hematite used was exceedingly fine grained ( $< 1 \mu$ ) and tended to stick to all surfaces with which it came into contact. All the satisfactory charges, comprising about 80 runs in total, were combined in the final sample.

Least squares refinements of the cell dimensions of seven samples ranged from 1.20614(5) to 1.20370(5) nm; however, the two lowest (and by far the least precise) determinations had systematic irregularities in their peak positions and were therefore not included in the average value of 1.2060(6) nm. The uncertainty in this average is 2 e.s.d. This result compares well with the value of 1.2058(1) nm given by NOVAK and GIBBS (1971), that of LIU (1974) 1.2064(4), of GUSTAFSON (1974) 1.2058(6), and that of SUWA *et al.* (1976) 1.2059(3) nm. Our value leads to a molar volume of  $132.04 \pm 0.05$  cm<sup>3</sup>. The calorimetric sample corrected for buoyancy had a mass of 34.507 g. The formula weight used in our calculations was 508.183 g/mol.



Table 2. Experimental molar heat capacities of synthetic andradite between 340 and 990 K measured by differential scanning calorimetry.

Temp kelvins	$C_p^o$ J/(mol·K)	Temp kelvins	$C_p^o$ J/(mol·K)
340.3	379.0	408.8	408.7
350.1	383.8	418.6	412.5
359.9	388.4	428.4	416.1
369.6	392.2	438.2	420.9
379.4	396.6	447.9	424.5
389.2	401.0	457.7	427.9
399.0	404.5	467.5	432.0
408.8	409.0	477.3	434.2
418.6	412.6	487.1	436.6
428.4	416.1	495.9	440.2
438.2	419.4	507.9	444.1
447.9	424.4	517.8	448.1
457.7	427.6	527.8	451.0
467.5	431.4	537.8	453.2
477.3	434.9	547.7	455.8
487.1	435.3	557.7	458.5
495.9	439.0	567.7	461.5
340.3	380.1	596.6	464.0
350.1	385.6	606.2	480.1
359.9	389.3	616.2	479.8
369.6	393.4	626.2	473.4
379.4	396.5	636.2	486.2
389.2	401.1	646.2	496.4
399.0	404.9	656.2	502.3
		666.2	501.5

Therefore a significant amount of short range order must be retained by the spins to well above the Néel temperature.

In order to compare the vibrational part of the heat capacity of andradite to that arising from the magnetic spin system we have calculated the heat capacity for a Debye solid using a Debye temperature ( $\theta_D$ ) of 721 K which we calculated from the elastic constant data of BASS (1986) using the procedure of ROBIE and EDWARDS (1966). This calculated vibrational heat capacity, ( $C_{lat}$ ), should be a good approximation up to about 15 K, *i.e.*  $T < \theta_D/50$ . At 15 K for example  $C_{lat} = 0.35$  J/(mol·K) *versus* a measured value of 8.2 J/(mol·K) (lattice plus magnetic heat capacity), that is the magnetic part of the heat capacity is 96 percent of the total at 15 K.

#### $\Delta_f G_m^o$ OF ANDRADITE

The most direct route for determining  $\Delta_f G_m^o$  of andradite is by using its observed thermal break down to pseudowollastonite and hematite at one bar pressure. HUCKENHOLZ and YODER (1971) give 1410 K (1137°C) for this temperature whereas SUWA *et al.* (1976) give 1438 K (1165°C). At the breakdown temperature the Gibbs free energy of formation of andradite is equal to the sum of the Gibbs free energies of 3 pseudowollastonite plus hematite. In calculating  $\Delta_f G_m^o$  (298.15 K) for andradite we have accepted the values for  $Fe_2O_3$  tabulated by ROBIE *et al.* (1979). Because of the rather large difference in the values for  $\Delta_f H_m^o$  (298.15 K) for wollastonite between the tables of ROBIE *et al.* (1979) and those of HELGESON *et al.* (1978) and inasmuch as the multiple regression analysis

by HAAS *et al.* (1981) did not include phase equilibria in which  $CO_2$  was a component, we have made a third-law analysis of the equilibrium data for the reaction



to provide an independent value of  $\Delta_f H_m^o$  (298.1 K) for wollastonite and hopefully to resolve this discrepancy. In making this calculation we have used the values of ROBIE *et al.* (1979) for  $CaCO_3$ ,  $SiO_2$ , and  $CO_2$ , and those of KRUPKA *et al.* (1985a,b) for wollastonite. Values for the Gibbs free energies of  $CO_2$  at high pressures and temperatures were taken from the tables of BOTTINGA and RICHET (1981). The results of this analysis are shown in Fig. 2 for the data of HARKER and TUTTLE (1956), HASELTON *et al.* (1978), JACOBS and KERRICK (1979), and ZIEGENBEIN and JOHANNES (1982). We also show on this graph values for  $\Delta_f H^o$  (298.15 K) for reaction (1) calculated from the calo-

Table 3. Molar thermodynamic properties for  $Ca_3Fe_2Si_3O_{12}$ , andradite. Formula weight 508.183 g/mol.

Temp.	Heat capacity	Entropy	Enthalpy function	Gibbs energy function
T Kelvin	$C_p^o$	$S_T^o - S_0^o$	$(H_T^o - H_0^o)/T$ J/(mol·K)	$-(G_T^o - H_0^o)/T$
5	0.5	0.14	0.100	0.04
10	28.9	4.35	3.780	0.57
15	8.22	13.90	9.990	3.91
20	4.74	15.60	8.950	6.44
25	4.71	16.62	8.080	8.54
30	6.16	17.59	7.620	9.97
35	9.25	18.75	7.610	11.14
40	13.51	20.25	8.071	12.18
45	18.52	22.12	8.945	13.18
50	24.64	24.38	10.20	14.18
60	39.12	30.12	13.78	16.34
70	55.76	37.38	18.57	18.81
80	73.64	45.98	24.33	21.66
90	91.98	55.71	30.82	24.89
100	110.4	66.36	37.86	28.50
110	128.7	77.74	45.29	32.45
120	146.4	89.71	52.98	36.72
130	163.6	102.1	60.84	41.27
140	180.0	114.8	68.76	46.07
150	195.4	127.8	76.70	51.09
160	210.1	140.9	84.58	56.29
170	224.1	154.0	92.38	61.65
180	237.6	167.2	100.1	67.15
190	250.3	180.4	107.6	72.76
200	262.3	193.6	115.1	78.47
210	273.5	206.6	122.4	84.27
220	284.2	219.6	129.5	90.12
230	294.3	232.5	136.4	96.03
240	304.0	245.2	143.2	102.0
250	313.0	257.8	149.8	108.0
260	321.6	270.2	156.3	114.0
270	330.0	282.5	162.5	120.0
280	338.2	294.7	168.7	126.0
290	346.0	306.7	174.7	132.0
300	353.2	318.5	180.5	138.0
310	359.9	330.2	186.2	144.1
320	366.6	341.8	191.7	150.1
330	373.2	353.1	197.1	156.0
340	379.6	364.4	202.4	162.0
350	385.9	375.5	207.5	167.9
273.15	332.6	286.4	164.5	121.9
298.15	351.9	316.4	179.4	136.9

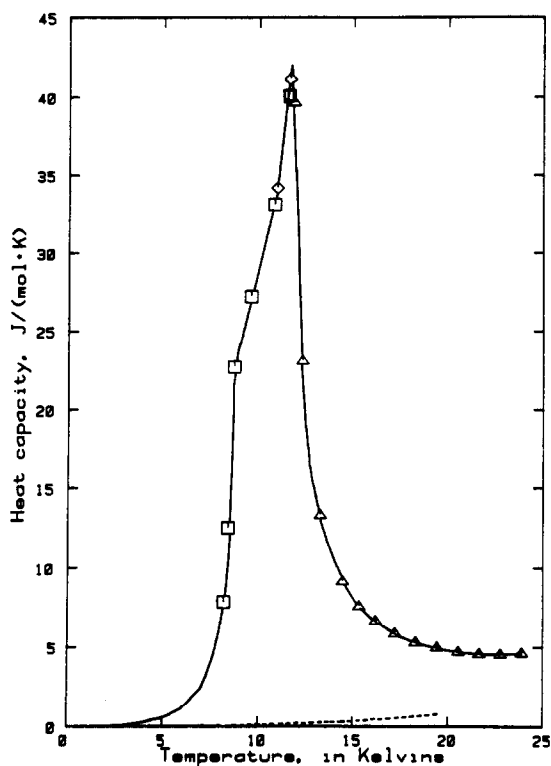


FIG. 1. Heat capacity of synthetic andradite in the neighborhood of the paramagnetic to antiferromagnetic transition. The Néel temperature is  $11.7 \pm 0.2$  K. Series 4, squares; series 5, diamonds; series 7, triangles. The dashed line is the calculated lattice heat capacity based on a Debye temperature of 721 K.

rimetric measurements of  $\Delta_f H_m^\circ$  (298.15 K) for wollastonite of TORGESON and SAHAMA (1948), CHARLU *et al.* (1978), and KISELEVA *et al.* (1979) using ancillary data for  $\Delta_f H^\circ$  (298.15 K) for the reaction



from ROBIE *et al.* (1979). The results of HARKER and TUTTLE (1956) from which HELGESON *et al.* (1978) extracted their  $\Delta_f G_m^\circ$  and  $\Delta_f H_m^\circ$  values for wollastonite are clearly aberrant. HASELTON *et al.* (1978) data points are all at temperatures for which the stable form of  $\text{CaCO}_3$  is calcite V, (MIRWALD, 1976). We have excluded HARKER and TUTTLE's (1956) results, and have averaged the remaining values to obtain  $\Delta_f H^\circ$  (298.15 K) =  $90.05 \pm 0.55$  kJ. Combining this result with the values for  $\Delta_f H_m^\circ$  (298.15 K) for  $\text{CaCO}_3$ ,  $\text{SiO}_2$ , and  $\text{CO}_2$  leads to  $\Delta_f H_m^\circ$  (298.15 K) and  $\Delta_f G_m^\circ$  (298.15 K) for wollastonite of  $-1634.5 \pm 1.8$  and  $-1549.1 \pm 1.8$  kJ/mol, respectively, which agrees very well with the values derived by ROBIE *et al.* (1979) and by HAAS *et al.* (1981) but is 3.5 kJ more negative than the value recommended by HELGESON *et al.* (1978).

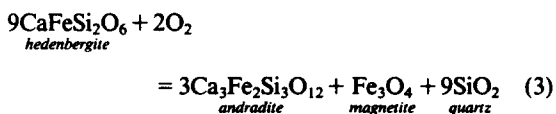
Using the temperature given by SUWA *et al.* (1976) for the andradite breakdown, 1438 K, together with the wollastonite values derived above after correcting for the transition to pseudowollastonite ( $\approx 0.15$  kJ) us-

ing the values of HAAS *et al.* (1981) and hematite values from ROBIE *et al.* (1979) we get  $\Delta_f G_m^\circ$  (1438 K) =  $-4134.5 \pm 5.5$  kJ/mol for andradite. Combining this value with our heat capacity and entropy and values for the elements from ROBIE *et al.* (1979) yields  $\Delta_f G_m^\circ$  (298.15 K) =  $-5415.4 \pm 5.5$  and  $\Delta_f H_m^\circ$  (298.15 K) =  $-5758.4 \pm 5.5$  kJ/mol. These values differ significantly from those given by TAYLOR and LIU (1978), HELGESON *et al.* (1978), and KISELEVA *et al.* (1972). From HUCKENHOLZ and YODER's (1971) temperature for the upper stability of andradite, 1410 K, we calculate  $\Delta_f G_m^\circ$  (298.15 K) =  $-5414.2 \pm 5.5$  and  $\Delta_f H_m^\circ$  (298.15 K) =  $-5758.2 \pm 5.5$  kJ/mol for andradite. If however we use the results of GUSTAFSON (1974) for the equilibrium



we calculate  $-5427.0$  or  $-5426.4$  kJ/mol for  $\Delta_f G_m^\circ$  (298.15 K) depending upon whether the QFM or Ni-NiO buffer was used. There seems to be no way that the entropy value for andradite can be altered that would bring the results of the decomposition studies into agreement with GUSTAFSON's (1974) result. Furthermore Gustafson's data imply that andradite would be stable at temperatures much higher than where it has been observed to decompose. We have therefore accepted  $-5414.8 \pm 5.5$  kJ/mol for  $\Delta_f G_m^\circ$  (298.15 K) for andradite.

We now use this value for  $\Delta_f G_m^\circ$  together with the existing equilibrium studies of the andradite-hedenbergite reaction to calculate  $\Delta_f G_m^\circ$  (298.15 K) of hedenbergite. The reaction



has been investigated by KURSHAKOVA (191), GUSTAFSON (1974) and most recently by BURTON *et al.* (1982). We have used our andradite values together with the data for magnetite and quartz from ROBIE *et al.* (1979) and heat capacity and entropy data for hedenbergite of HASELTON *et al.* (1987) in combination with the equilibrium results of BURTON *et al.* (1982) to calculate  $\Delta_f G_m^\circ$  (298.15 K) =  $-2674.3 \pm 5.8$  and  $\Delta_f H_m^\circ$  (298.15 K) =  $-2837.6 \pm 5.8$  kJ/mol for hedenbergite. Our value for  $\Delta_f H_m^\circ$  (298.15 K) is 11.5 kJ less negative than the value measured by BENNINGTON *et al.* (1984),  $-2849.1 \pm 3.6$  kJ by HF(aq) calorimetry on a natural Mn-bearing hedenbergite. HELGESON *et al.* (1978) give  $-2838.8$  kJ/mol which is in excellent agreement with our result, whereas the estimate by NAVROTSKY and COONS (1976) leads to  $-2850.4$  kJ/mol.

KURSHAKOVA and AVETISYAN (1974) have studied the reaction



between 573 and 1023 K at  $P_{\text{total}} = P_{\text{H}_2\text{O}} = 1000$  and 2000 atm. They give values for  $\Delta_f G_m^\circ$  (298.15 K) of

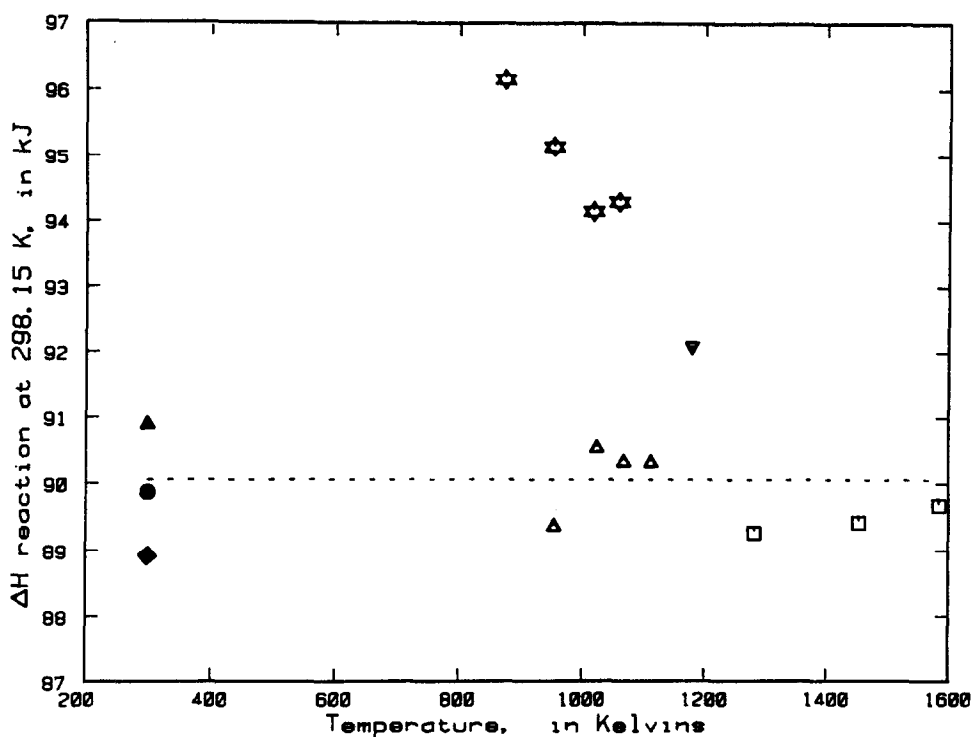


FIG. 2. Enthalpy change for the reaction  $\text{CaCO}_3 + \text{SiO}_2 = \text{CaSiO}_3 + \text{CO}_2$  at 298.15 K calculated from the data of HARKER and TUTTLE (1956), stars; HASELTON *et al.* (1978), squares; ZIEGENBEIN and JOHANNES (1982), triangles; JACOBS and KERRICK (1979), inverted triangle; TORGESON and SAHAMA (1948), solid circle; CHARLU *et al.* (1978), solid diamond; KISELEVA *et al.* (1979), solid triangle. The dashed line is the average value adopted as discussed in the text.

hedenbergite calculated from their data that are 18.9 kJ more negative than our values at 600 K and less negative than our values by 0.5 kJ at 1300 K. At  $\approx 1285$  K KURSHAKOVA and AVETISYAN's (1974) values is the same as ours. Their  $\Delta_r S_m^\circ$  versus temperature data corresponds to a  $\Delta_r S_m^\circ$  of  $-560$  J/(mol · K) at 1000 K, whereas the calorimetric measurements yield  $\Delta_r S_m^\circ$  (1000 K) =  $-529.2 \pm 0.6$  J/(mol · K).

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