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UNITED STATES DEPARTMENT OF THE INTERIOR

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CONTENTS

ILLUSTRATIONS

TABLES

TABLES--Continued

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	kcal/mol	kilocalorie per mole
cal	thermochemical calorie	kJ/mol	kilojoule per mole
cal/mol	calorie per mole	K/min	kelvin per minute
cal/(mol•K)	calorie per mole per kelvin	µm	micrometer
g	gram	mol	mole
J	joule	pct	percent
J/(mol•K)	joule per mole per kelvin	ppm	part per million
K	kelvin	wt pct	weight percent
kcal	kilocalorie		

THERMODYNAMIC PROPERTIES OF TWO MANGANESE SILICATES, PYROXMANGITE AND FOWLERITE

By K. O. Bennington,[1] R. R. Brown,[1] H. E. Bell,[2] and R. P. Beyer[2]

ABSTRACT

The thermodynamic properties of two manganese silicates, pyroxmangite and fowlerite (zincian rhodonite), were experimentally determined by the Bureau of Mines. The standard enthalpies of formation were determined by hydrofluoric acid (HF) solution calorimetry, the low-temperature heat capacities by adiabatic calorimetry, and the high-temperature heat capacities by differential scanning calorimetry over the range 322 to 1,372 K. Data for the standard enthalpy of formation (ΔH°_{298}), the derived standard entropy (S°_{298}), and the standard Gibbs energy of formation (ΔGf°_{298}) are as follows:

Pyroxmangite [$(Mn_{0.9554}Ca_{0.0446})(SiO_3)$]--

ΔHf°_{298}	-319.668±0.46 kcal/mol
ΔH°_{298} (from oxides)	-7.215±0.11 kcal/mol
S°_{298}	23.785±0.048 cal/(mol•K)
ΔGf°_{298}	-301.190±7.96 kcal/mol

Fowlerite [$(Mn_{0.703}Zn_{0.0884}Ca_{0.2086})(SiO_3)$]--

ΔHf°_{298}	-329.914±0.419 kcal/mol
ΔH°_{298} (from oxides)	-8.400±0.104 kcal/mol
S°_{298}	21.949±0.059 cal/(mol•K)
ΔGf°_{298}	-310.716±7.99 kcal/mol

These experimentally determined values were combined with data from the literature to calculate the Gibbs energies and equilibrium constants of formation over the temperature range of the measurements. Standard enthalpies, Gibbs energies, and equilibrium constants of formation are given as a function of temperature from both the elements and the constituent oxides.

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[1] Research chemist.

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INTRODUCTION

This investigation of thermodynamic properties of pyroxmangite [$(Mn_{0.9554}Ca_{0.0446})(SiO_3)$] and fowlerite, the zincian rhodonite [$(Mn_{0.703}Zn_{0.0884}Ca_{0.2086})(SiO_3)$], is part of a Bureau of Mines study on natural Mn-containing pyroxenoid minerals. The resulting data contribute toward the understanding of the mineral geochemistry and the slag-metal equilibrium in iron refining.

Deer (6)[3] presents a comprehensive discussion of Mn-containing, single-chain silicate minerals, including pyroxmangite and fowlerite. These minerals readily assimilate Mn, which commonly undergoes a mutual substitution with Ca, Mg, Fe, and less commonly, Zn. Studies by Akimoto (2) of transformations in pure synthetic rhodonite ($MnSiO_3$), with more recent work by Maresch (17), established a relationship between rhodonite and pyroxmangite and confirmed a possibility that Mn^{2+} and Si^{4+} may occupy octahedral sites. A phase study of Mn^{2+}, Mg^{2+} rhodonites-pyroxmangites was made by Ito (10), which confirmed the replacement of Mn^{2+} by Mg^{2+} and argued that Mg^{2+} ions cannot be restricted to a single site but are distributed over several sites in the structure. A synthesis and phase study of Mn^{2+}, Ca^{2+} pyroxenoids was made by Abrecht (1), which showed that at low temperatures a composition richer in calcium silicate ($CaSiO_3$) was required for pyroxmangite and rhodonite structures. X-ray studies by Peruz (23) of a natural pyroxmangite and an iron-rhodonite from an iron slag were made to determine their relation to the mineral rhodonite. In this study, the ion site occupancies were not determined but were chosen for what seemed the most likely location in the minerals used.

The thermodynamic properties of synthetic $MnSiO_3$ were presented by Mah (16). Kelley (13) determined the low-temperature data, which were extrapolated below 52 K; the high-temeperature data were presented by Southard (27), and the enthalpy of formation was determined by King (14). Schwerdtfeger (25) determined some high-temperature experimental data on the Fe-Mn-Si-O system, in which several of these pyroxenoid solid solutions appear. Navrotsky (20) studied synthetic Mn pyroxenoids by molten-salt solution calorimetry. In her enthalpy determinations, she took special precautions to prevent oxidation of manganese oxide (MnO). Application of information on minerals in this system is complicated by cationic substitutions and the fact that pyroxmangite and rhodonite of differing compositions may stably coexist (17).

The thermodynamic properties presented here were determined for two natural manganese silicate minerals, pyroxmangite and the rhodonite variety, fowlerite. The standard enthalpies of formation were determined by HF solution calorimetry. The heat capacities were determined by combined adiabatic and differential scanning calorimetry. Smoothed values of the formation properties were calculated to 1,350 K. These data add to the capability of making interpretations on relative stabilities for these minerals in mixed compositions.

MATERIALS

ACIDS

The acids were reagent-grade products that were used without treatment except for dilution with distilled water to the proper strength.

CALCIUM OXIDE

Reagent-grade calcium carbonate ($CaCO_3$) was roasted overnight at 970° C to provide the calcium oxide (CaO) for each

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

determination. To prevent water vapor assimilation, the preweighed $CaCO_3$ was packed into a formed platinum foil cylinder from which the calcined sample could be very easily and quickly dispensed. The sample was cooled and stored until ready for use in a desiccator over a large dish of newly calcined CaO.

FOWLERITE

The fowlerite $[(Mn_{0.703}Zn_{0.0884}Ca_{0.2086})(SiO_3)]$ used for this study was purchased from Ward's,[4] a commercial collector and supplier. This material was collected at Franklin, NJ, and seemed typical of other specimens from that location. It was crystalline material that was easily crushed, washed, screened, and separated. This mineral was easily dissolved in HF; consequently, fine crushing was not required. The minus 100- plus 200-mesh particle size was used for all measurements. The X-ray diffraction pattern for this zincian rhodonite matched the pattern for rhodonite listed on the powder diffraction file card (PDF) 13-138 (8); however, the relative intensities were different.

MANGANOUS OXIDE

Reagent-grade manganese dioxide (MnO_2) was slowly heated in a stream of H_2 until a temperature of 850° C was reached. It was held at this temperature for several hours, then it was blended, sampled, and analyzed, after which the process was repeated. Final X-ray analysis showed the product to be only face-centered cubic MnO, and the pattern matched that given on PDF card 7-230. No corrections were made for spectrographically detected impurities; the maximum total for Mg and Si is ~100 ppm, and the maximum total for Al, Ca, and Fe is ~400 ppm.

PYROXMANGITE

This mineral specimen of pyroxmangite $[(Mn_{0.9554}Ca_{0.0446})(SiO_3)]$ was purchased from Ward's. It was collected from Butte, MT, and was listed as rhodonite; however, based on optical and X-ray analyses, it has been reclassified as pyroxmangite. The procedure for purifying this mineral was identical to that used for fowlerite, and the same size fraction was used for all measurements. Only pyroxmangite was detected by X-ray, and the pattern matched that given on PDF card 29-895.

SILICA

The silica (SiO_2) used was from an exceedingly clear and single, natural quartz crystal. The crystal was sawed, crushed, ground to pass a 400-mesh screen, and elutriated in distilled water. The size fraction ranging between 10 and 20 µm was retained for the heat-of-solution measurements. This fraction was repeatedly leached with dilute hydrochloric acid (HCl) to remove the Fe introduced from grinding until the solution remained clear; it was then digested with hydrogen peroxide (H_2O_2) and dried. Each sample was heated through the alpha-beta transition immediately before solution measurements were made. No impurities were detected spectrographically, and the X-ray diffraction pattern matched the pattern listed on the PDF card 5-490 for α-quartz.

ZINC OXIDE

The zinc oxide (ZnO) used was a reagent-grade commercial product. A barely detectable trace of Cu was identified spectrographically. Only ZnO was shown to be present by X-ray. The X-ray diffraction pattern matched that on card PDF 5-664.

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[4] Reference to specific equipment or manufacturers does not imply endorsement by the Bureau of Mines.

MINERAL ANALYSES AND FORMULAS

ANALYSES

The chemical and optical analyses of pyroxmangite and fowlerite presented in tables 1, 2, and 3 were made by the Branch of Analytical Laboratories, U.S. Geological Survey, Menlo Park, CA. The chemical composition and optical properties compare favorably with those listed by Deer (6), with a slightly higher Mn concentration and lower concentrations of Ca and other impurities than are commonly present. For this study of thermodynamic properties, the chemical analysis is considered to be absolutely accurate. Mineral specimens are chosen to be free of discrete separate impurities, and those minor constituents in the analysis are considered to be bonded into the structure. Presentation of information pertaining to substitutions and formula calculations is therefore shown in sufficient detail and completeness for recalculation to a different formula or end member molecule.

FORMULAS

The formulas for pyroxmangite and fowlerite and their formula weights were calculated from the chemical analyses using the anion-based hydrogen-equivalent method. This method for deriving the number of ions per mineral formula consists of calculating the ratios of hydrogen equivalents of the analyzed constituents and normalizing these values to the ideal sum of anions per unit formula. A detailed description for the calculations for this technique is given by Jackson

TABLE 1. - Analysis of pyroxmangite[1]

Composition		Wt pct per equivalent weight	Charge[2]	Extended formula[3]		Substitution site	Adjusted formula[4]	
Oxide	wt pct			Ions	Weight, g		Ions	Weight, g
SiO_2.....	46.66	3.1063	4.0227	1.0057	28.2456	Mn	1.000	28.0855
Al_2O_3....	.76	.0447	.0579	.0193	.5207	Mn		
TiO_2.....	<.01	.0005	.0006	.0002	.0096	Mn		
Fe_2O_3....	.22	.0083	.0108	.0036	.2011	Mn		
FeO......	.23	.0064	.0083	.0041	.2290	Mn		
MgO......	.42	.0208	.0269	.0135	.3281	Mn		
CaO......	1.90	.0678	.0878	.0439	1.7595		.0446	1.7876
MnO......	48.85	1.3773	1.7836	.8918	48.9937		.9554	52.4878
Na_2O.....	<.02	.0006	.0008	.0008	.0184	Ca		
K_2O......	<.02	.0004	.0005	.0005	.0191	Ca		
CO_2......	<.01							
H_2O^+.....	.37							
H_2O^-.....	.17							
O.........			6.000	3.000	47.9982		3.000	47.9982
Total..	99.64	NAp	NAp	NAp	128.323	NAp	NAp	130.359

NAp Not applicable.

[1] Analyst: Sarah T. Neil, chemist, U.S. Geological Survey, Menlo Park, CA.

[2] Equivalents per formula.

[3] Extended formula--$[(Mn_{0.8918}Ca_{0.0439}Mg_{0.0135}Fe^{2+}_{0.0041}Fe^{3+}_{0.0036}Ti_{0.0002}Na_{0.0008}K_{0.0005})(Si_{1.0057}Al_{0.0193})(O_3)]$.

[4] Adjusted formula--$[(Mn_{0.9554}Ca_{0.0446})(SiO_3)]$.

NOTE.--Bound water, H_2O^+, and hygroscopic water, H_2O^-, are calculated out.

TABLE 2. - Analysis of fowlerite[1]

Composition		Wt pct per equivalent weight	Charge[3]	Extended formula[4]		Substitution site	Adjusted formula[5]	
Oxide	wt pct			Ions	Weight, g		Ions	Weight, g
SiO_2....	46.95	3.1256	3.9717	0.9929	27.8861	Si	1.000	28.0855
Al_2O_3...	<.02	.0012	.0015	.0005	.0135	Si		
TiO_2....	<.01	.0050	.0063	.0016	.0766	Si		
P_2O_5....	<.02	.0014	.0018	.0004	.0124			
[2]Fe_2O_3... FeO.....	1.38	.0518	.0658	.0219	1.2230	Si Mn		
Mno.....	34.97	.9859	1.2529	.6264	34.4132			
MgO.....	1.68	.0834	.1060	.0530	1.2882	Mn	.703	38.6214
CaO.....	9.18	.3274	.4160	.2080	8.3366		.2086	8.3607
Na_2O....	.02	.0006	.0007	.0007	.0161	Ca		
K_2O.....	.02	.0004	.0005	.0005	.0195	Ca		
ZnO.....	5.66	.1391	.1768	.0884	5.7796		.0884	5.7796
H_2O^+....	.02							
H_2O^-....	.02							
F.......	<.01							
Cl......	<.05							
O.......			6.000	3.000	47.9982		3.000	47.9982
Total	NAp	NAp	NAp	NAp	127.063	NAp	NAp	128.845

NAp Not applicable.

[1] Analyst: Sarah T. Neil, chemist, U.S. Geological Survey, Menlo Park, CA.

[2] Total Fe reported as ferric. [3] Equivalents per formula.

[4] Extended formula--$[(Mn_{0.6264}Zn_{0.0884}Ca_{0.208}Mg_{0.053}Fe^{3+}_{0.0219}Na_{0.0007}K_{0.0005})(Al_{0.0005}Ti_{0.0016}P_{0.0004}Si_{0.9929})(O_3)]$.

[5] Adjusted formula--$[(Mn_{0.703}Zn_{0.0884}Ca_{0.2086})(SiO_3)]$.

NOTE.--Bound water, H_2O^+, and hygroscopic water, H_2O^-, are calculated out.

TABLE 3. - Optical data for pyroxmangite and fowlerite[1]

	Pyroxmangite (Butte, MT)	Fowlerite (Franklin, NJ)[2]
γ..............	1.746 (2)	1.723 (2)
β..............	1.732 (2)	1.717 (2)
α..............	1.729 (2)	1.712 (2)
$2V_\gamma$............	47 (1)° (dispersion, cannot be measured) 50° calculated	80 (1)° measured, 85° 03' calculated.
r<v............	NAp	Strong.

NAp Not applicable.

[1] Determined by Richard C. Erd, U.S. Geological Survey, Menlo Park, CA.

[2] These indexes seemed somewhat low for a fowlerite (zincian rhodonite), so the powder used for the X-ray diffractometer pattern and the X-ray fluorescence analysis run (which showed considerable Zn) were examined. The crystal used for the optical determination was quite typical and representative of the whole specimen. The birefringence is just about equal to that of quartz.

(11). This procedure was described earlier by Miser (18) and Stevens (28-29), and more recently by Goff (7).

It is necessary to make several assumptions in the construction of these formulas. Following Jackson (11) and Sommerfeld (26), it is assumed that all of the anion positions in the mineral structure are filled and that the charges in the mineral are balanced. Jackson has pointed out that under these assumptions, cation deficiencies may be due to vacant cation positions or analytical error.

The number of atoms of the individual elements in the extended formula was used in computing the formula weight, the total of which provides the gram formula weight of the natural mineral. The grouping of ions into particular positions follows the example of Deer (6). The numbers of ions, even though unrealistic, were carried without rounding to maintain internal consistency.

The number of ions in the extended formula does not provide a practical composition; consequently, it was adjusted by substituting the impurity elements into the most likely sites. The column labeled "Charge" in tables 1 and 2 shows the number of equivalents per formula for each of the cations, and the column marked "Substitution site" indicates the location chosen for the proxying element. For pyroxmangite, the equivalent positions as indicated are added to, then the sum is divided by, the valence of the substitution site ion, Mn or Ca, to provide the maximum number of ions for that position in the adjusted formula. Choices in substitution sites, Mg and excess Si substituted into the Mn position, are based on site occupancy information presented by Akimoto (1) and Ito (10).

The adjusted formula weight for each structural position provides the total adjusted formula weight. The construction necessary to develop the adjusted formula and formula weight requires that corresponding heat corrections be made. The heat-of-solution corrections for cation substitutions were made by determining the net equivalent heat-of-solution difference between the equivalent amounts of the exchanged oxides. The net difference is calculated for each structural site. The thermal change required by the change in the formula weight was applied after the substitution site corrections had been made by scaling the heat-of-solution value to the adjusted formula weight as described by Neuvonen (21). The values for the thermal changes and sequence of application of corrections are given in detail under the reaction descriptions for the minerals.

EXPERIMENTAL DETERMINATIONS

HEATS OF SOLUTION AT 298.15 K

The heat-of-solution values for the minerals pyroxmangite and fowlerite were determined by HF solution calorimetry. The apparatus used has been described in earlier publications (3, 15, 30). The solvent was 948.7 g of 20.1-wt-pct HF to which approximately 0.60 g potassium dichromate ($K_2Cr_2O_7$) was added to ensure oxidation of ferrous iron to ferric. The quantities of all reaction substances were stoichiometric with 0.601 g of α-quartz which, when substituted into reaction 1, table 4 (and table 12, in the section on fowlerite) provides the stoichiometric molar proportions of all succeeding reactions.

Weighed amounts of solid or liquid substances to be introduced were placed in paraffin-sealed, Teflon (fluorocarbon polymer) tape capsules and dropped at the appropriate time, at 25° C, into the calorimeter, which was operated at 73.7° C. Each measurement resulted from a process of converting the pure reaction substances at 25° C plus the solvent at 73.7° C to a solution product at 73.7° C. Corrections were applied for the heat effects of the paraffin, Teflon, and a gold ballast when used. Electrical calibrations of the calorimeter were made over the temperature range of measurements.

Throughout this report, uncertainties were assigned to measured and derived

TABLE 4. - Reaction scheme for pyroxmangite[1]

Reaction	ΔH, kcal	Uncertainty (±), kcal
(1) $SiO_2(c) + 6HF(sol) \rightarrow H_2SiF_6(sol) + 2H_2O(sol)$	-32.910	0.007
[2](2) $0.9554MnO(c) + 1.9108H^+(sol) \rightarrow 0.9554Mn^{2+}(sol) + 0.9554H_2O(sol)$	-44.402	.042
(3) $0.0446CaO(c) + 0.0892HF(sol) \rightarrow 0.0446CaF_2(p) + 0.0446H_2O(sol)$	-2.492	.002
[2](4) $(Mn_{0.9554}Ca_{0.0446})(SiO_3)(c) + 6.0892HF(sol) + 1.9108H^+(sol) \rightarrow H_2SiF_6(sol) + 0.9554Mn^{2+}(sol) + 0.0446CaF_2(p) + 3H_2O(sol)$	[3]-72.589	.10

$$\Delta H_5 = \Delta H^\circ_{298} = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4$$

$$(5)\ SiO_2(c) + 0.0446CaO(c) + 0.9554MnO(c) \rightarrow (Mn_{0.9554}Ca_{0.0446})(SiO_3)(c)$$

$$\Delta H^\circ_{298}\ (\text{from oxides}) = -7.215 \pm 0.108\ \text{kcal/mol.}$$

---

[1] For reactions 1-4, introduced reactants are at 25° C and reaction products are at 73.7° C.

[2] Mn is oxidized in solution to the same state and is balanced and canceled.

[3] Corrected value.

NOTE.--Symbols c, sol, and p in parentheses denote substances that are crystalline, in solution, or crystalline precipitate, respectively, in all reactions.

values as follows: (1) When several individual heat values were measured for a reaction, the precision uncertainty was taken as $2\sqrt{\Sigma d_i^2/n(n-1)}$, where Σd_i^2 is the sum of the squares of the deviations from the mean value and n is the number of determinations; (2) when the heats of two or more reactions were added, the uncertainty was taken as the square root of the sum of the squares of the uncertainties for the individual reactions. These procedures followed the recommendations of Rossini (24).

All energy units are expressed in terms of the defined calorie (1 cal = 4.1840 J). All weighings were corrected to vacuum, and molecular weights are in accordance with the 1981 table of atomic weights (9). All calibrations are traceable to the National Bureau of Standards (NBS), and sample temperatures are based on the International Practical Temperature Scale of 1968 (IPTS-68) (5). Reactions are written in an abbreviated form sufficient to show the stoichiometry was maintained to permit cancellation of the reaction products. The values and their precision uncertainties are presented for experimentally determined data.

PYROXMANGITE

Standard Enthalpies of Formation

The reaction scheme for the solution calorimetric investigation of pyroxmangite is presented in table 4. The table also lists the mean measured heat values and their precision uncertainties. The experimentally determined heat-of-solution values are listed in table 5 for each reaction. Reaction 1, for the heat of solution of SiO_2, was determined previously under identical conditions, and the values are averaged with the three confirmatory determinations made for this study. Reaction 2, for the heat of solution of MnO in the solution following reaction 1, tended to be erratic. Reaction 3, for the heat of solution of CaO, was determined in the same solution following reaction 2.

Reaction 4 represents the heat of solution of the mineral pyroxmangite in a new charge of acid containing the same amount of $K_2Cr_2O_7$. The mean value of eight determinations is -69.799±0.047 kcal, as shown in table 5. This value is for the

TABLE 5. - Experimental heats of solution for pyroxmangite, kilocalorie per mole

SiO_2, reaction 1	MnO, reaction 2	CaO, reaction 3	Pyroxmangite, reaction 4
-32.904	-46.567	-55.913	-69.793
-32.913	-46.500	-55.877	-69.826
-32.916	-46.562	-55.888	-69.932
-32.908	-46.348	-55.845	-69.791
-32.905	-46.476	-55.916	-69.694
	-46.465	-55.955	-69.790
-32.895	-46.541	-55.781	-69.799
-32.926	-46.393	-55.815	-69.768
-32.917	-46.386		
	-46.480		
	-46.506		
-32.910 ±.007	-46.475 ±.044	-55.874 ±.040	-69.799 ±.047

original mineral with the composition and and gram formula weight represented by the extended formula in table 1. The total water content was calculated out as thermally equivalent to ice; an estimated additional +1.31 kcal/mol was applied to the bound water (H_2O^+) correction only. This resulted in a corrected heat-of-solution value of -70.191 kcal/mol for the extended formula composition and molecular weight of 128.323 g. Neuvonen (21) gives an excellent and detailed discussion of corrections for impurities. The correction for total water was made according to the technique described by Neuvonen. The net correction for total water and for total impurities and substitutions (-1.299 kcal) when calculated with the associated formula weight changes provides the adjusted heat-of-solution value (-72.589±0.10 kcal). The uncertainty for this final value contains an allowance for the corrections procedure.

The final solution after conducting reactions 1 through 3 in sequence in the original charge of acid is identical to the solution obtained after conducting reaction 4 in another charge of acid. The heat-of-solution values were substituted into the reaction scheme and combined according to

$$\Delta H_5 = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4$$

$$= -7.215 \pm 0.108 \text{ kcal},$$

which provides the enthalpy change for reaction 5, the standard enthalpy of formation from the oxides.

The calculation of the standard enthalpy of formation of pyroxmangite requires additional data from the literature. The data for the oxides of Si, Mn, and Ca, all of which have been taken from Pankratz (22), are listed in table 6.

The standard enthalpy of formation for pyroxmangite may be derived from a combination of these reactions and their enthalpies of formation according to the scheme

$$\Delta H_9 = \Delta H_5 + \Delta H_6 + 0.9554\Delta H_7 + 0.0446\Delta H_8,$$

from which it follows that

$$Si(c) + 0.9554Mn(c)$$

$$+ 0.0446Ca(c) + 1.5\ O_2(g)$$

$$\rightarrow (Mn_{0.9554}Ca_{0.0446})(SiO_3)(c),$$

for which

$$\Delta Hf^\circ_{298.15} = -319.668 \pm 0.458 \text{ kcal/mol}.$$

TABLE 6. - Enthalpy of formation of pyroxmangite

Reaction	ΔHf°_{298}, kcal/mol	Uncertainty (±), kcal
(6) $Si(c) + O_2(g) \rightarrow SiO_2(c)$..............................	-217.720	0.34
(7) $Mn(c) + 0.5\ O_2(g) \rightarrow MnO(c)$..........................	-92.07	.30
(8) $Ca(c) + 0.5\ O_2(g) \rightarrow CaO(c)$..........................	-151.79	.30

$$\Delta H_9 = \Delta Hf^\circ_{298} = \Delta H_5 + \Delta H_6 + 0.9554\Delta H_7 + 0.0446\Delta H_8$$

$$(9)\ Si(c) + 0.9554Mn(c) + 0.0446Ca(c) + 1.5\ O_2 \rightarrow (Mn_{0.9554}Ca_{0.0446})(SiO_3)(c)$$

$$\Delta Hf^\circ_{298} = -319.668\pm0.458\ \text{kcal/mol.}$$

Source: Pankratz (22).

These are the values for this composition (and the reactions used in tables 10 and 11 in the following section).

The analysis for this pyroxmangite, table 1, may be calculated to the pure end member composition ($MnSiO_3$) by substituting all of the minor elements including the excess of both Si and Ca into the Mn position. The calculation for water is identical to that previously used; the total net impurity correction is -0.774 kcal. Applying these values to the ideal molecular weight (131.0217 g) provides a corrected heat-of-solution value of -72.538 kcal. Substituting this value into reaction 4, table 4, using 1 mol for reaction 2 for Mn and eliminating reaction 3 for Ca, then according to the scheme for pure $MnSiO_3$,

$$\Delta H_{5A} = \Delta H_1 + \Delta H_2 - \Delta H_4,$$

$$\Delta H^\circ_{298}\ \text{(from oxides)}$$

$$= -6.847\pm0.20\ \text{kcal/mol.}$$

The standard enthalpy of formation of the ideal formula pyroxmangite may be calculated according to the scheme

$$\Delta H_{9A} = \Delta H_{5A} + \Delta H_6 + \Delta H_7 = \Delta Hf^\circ_{298.15}$$

$$= -316.637\pm1.00\ \text{kcal/mol.}$$

The uncertainty has been increased to compensate for possible errors in the substitution procedure.

Low-Temperature Thermal Properties

The heat capacity of pyroxmangite was measured by adiabatic calorimetry over the temperature range 4.95 to 308 K. Design data and operational details of this calorimeter have been described previously (4).

The pyroxmangite sample for the low-temperature measurements was dried at 383 K overnight before loading into a copper calorimeter vessel. Prior to sealing, the loaded calorimeter was evacuated and backfilled with 1.3×10^{-4} mol He to enhance heat transfer. A pyroxmangite sample of 150.40102 g was used. For series VII and VIII, 2.3×10^{-3} mol He and 119.9634 g sample were used.

The experimental heat capacity values are listed chronologically in table 7 and shown in figures 1, 2, and 3. The smoothed values for heat capacity and related functions were obtained by smoothing the data using the computer program by Justice (12). The results are shown in table 8. The overall uncertainties of the tabulated smooth heat capacities are ±1 pct for 20 to 50 K, ±0.2 pct for 50 to 200 K, and ±0.1 pct for 200 to 300 K.

A second-order transition was observed over the range of approximately 265 to 275 K. The entropy change and enthalpy change over this region were determined graphically to be 0.771 cal/(mol•K) and 0.208 kcal/mol, respectively. A Schottky anomaly was observed, with a maximum near

TABLE 7. - Experimental low-temperature heat capacities of pyroxmangite

T, K	C_p°, cal/(mol·K)
SERIES I	
129.94	11.102
135.90	11.594
SERIES II	
50.88	3.241
53.84	3.515
58.82	4.020
64.25	4.587
70.23	5.225
76.74	5.918
83.93	6.664
91.84	7.483
100.56	8.360
110.45	9.316
120.59	10.256
130.74	11.148
140.97	12.013
150.64	12.787
162.88	13.699
171.71	14.336
180.24	14.928
188.53	15.450
196.57	15.977
204.43	16.429
212.12	16.888
219.64	17.322
227.01	17.717
234.26	18.101
SERIES III	
199.07	16.093
206.84	16.578
214.44	17.007
221.89	17.436
229.22	17.829
236.44	18.268
257.38	19.343
264.40	19.822
SERIES IV	
226.68	17.666
234.03	18.063
241.30	18.454
248.48	18.824
255.56	19.212
262.54	19.641
269.32	20.959
289.44	20.699
296.11	20.932
302.72	21.187
SERIES V	
243.23	18.548
250.47	18.936
255.03	19.158
256.97	19.258
258.91	19.406
260.97	19.579
263.16	19.691
265.22	19.844
267.17	20.033
269.09	20.445
271.11	21.705
273.15	21.481
275.28	20.341
277.42	20.405
279.37	20.303
281.46	20.323
283.54	20.410
285.49	20.521
289.40	20.692
291.35	20.743
293.44	20.826
295.53	20.906
297.61	21.011
299.70	21.129
301.66	21.169
303.76	21.223
305.88	21.277
308.00	21.368
SERIES VI	
13.16	1.485
13.93	1.342
14.62	1.373
15.49	1.330
16.37	1.316
17.24	1.306
18.12	1.298
18.99	1.293
20.47	1.294
22.55	1.321
24.81	1.371
29.30	1.539
32.11	1.688
35.12	1.880
38.38	2.148
41.99	2.409
45.90	2.748
50.18	3.151
54.87	3.615
SERIES VI--Con.	
59.97	4.142
65.61	4.727
71.82	5.387
78.68	6.110
86.26	6.905
253.28	19.161
253.82	19.090
254.35	19.177
254.84	19.281
255.34	19.102
255.83	19.223
256.32	19.574
256.86	19.105
257.37	19.392
257.90	19.535
258.45	19.339
258.97	19.303
259.46	19.553
259.96	19.549
260.48	19.460
261.03	19.374
261.55	19.315
262.04	19.632
262.56	19.621
263.08	19.810
263.57	19.763
264.07	19.672
264.55	19.759
265.04	19.876
265.56	19.992
266.10	19.910
266.60	20.033
267.08	20.180
267.57	20.434
268.07	20.268
268.56	20.312
269.05	20.331
269.53	20.491
270.01	20.820
270.50	21.180
271.01	21.481
271.55	22.141
272.09	22.940
272.60	23.745
273.12	20.751
273.63	19.886
274.12	20.170
274.60	20.038
SERIES VI--Con.	
275.09	20.100
275.57	20.498
276.09	20.159
276.61	20.120
277.13	20.409
277.68	20.374
278.23	20.114
278.75	20.367
279.27	20.661
279.80	20.535
280.29	20.468
280.81	20.529
281.34	20.225
SERIES VII	
4.95	0.781
5.42	.862
5.90	.946
6.42	1.042
6.99	1.122
7.60	1.223
8.26	1.392
9.03	1.504
9.86	1.657
10.79	1.737
11.83	1.740
14.72	1.378
16.36	1.330
18.01	1.329
19.84	1.268
21.75	1.271
SERIES VIII	
5.32	0.847
5.82	.940
6.26	1.015
6.70	1.095
7.15	1.177
7.61	1.239
9.83	1.666
10.16	1.670
10.47	1.717
10.93	1.857
11.44	1.813
11.94	1.739
12.47	1.611
12.99	1.531
13.50	1.496
14.02	1.463

TABLE 8. - Thermodynamic functions of pyroxmangite

T, K	cal/(mol·K)			$H^\circ_T - H^\circ_0$, kcal/mol	T, K	cal/(mol·K)			$H^\circ_T - H^\circ_0$, kcal/mol
	$C_p{}^\circ$	S°	$-(G^\circ - H^\circ_{298})/T$			$C_p{}^\circ$	S°	$-(G^\circ - H^\circ_{298})/T$	
5	0.789	0.615	0.261	0.002	375	23.641	28.906	15.042	5.199
10	1.661	1.432	.640	.008	400	24.380	30.456	15.957	5.799
15	1.365	2.085	1.025	.016	425	25.070	31.955	16.855	6.418
20	1.290	2.461	1.340	.022	450	25.711	33.406	17.734	7.052
25	1.382	2.757	1.594	.029	475	26.307	34.812	18.596	7.703
30	1.579	3.025	1.811	.036	500	26.858	36.176	19.441	8.367
35	1.874	3.289	2.003	.045	525	27.368	37.499	20.270	9.045
40	2.251	3.563	2.181	.055	550	27.838	38.783	21.082	9.735
45	2.682	3.853	2.350	.068	575	28.271	40.030	21.879	10.437
50	3.143	4.159	2.516	.082	600	28.667	41.242	22.661	11.149
55	3.633	4.481	2.679	.099	625	29.029	42.419	23.428	11.870
60	4.156	4.820	2.844	.119	650	29.359	43.565	24.180	12.600
70	5.197	5.538	3.177	.165	675	29.659	44.678	24.919	13.338
80	6.243	6.301	3.519	.223	700	29.930	45.762	25.644	14.083
90	7.282	7.096	3.872	.290	725	30.174	46.817	26.356	14.834
100	8.300	7.916	4.235	.368	750	30.393	47.843	27.055	15.591
110	9.282	8.754	4.608	.456	775	30.588	48.843	27.742	16.353
120	10.219	9.602	4.989	.554	800	30.761	49.817	28.417	17.120
130	11.105	10.455	5.376	.660	825	30.913	50.766	29.080	17.891
140	11.940	11.309	5.770	.776	850	31.046	51.691	29.731	18.666
150	12.729	12.160	6.167	.899	875	31.162	52.592	30.371	19.443
160	13.478	13.005	6.568	1.030	900	31.262	53.472	31.001	20.224
170	14.194	13.844	6.972	1.168	925	31.347	54.329	31.620	21.006
180	14.881	14.675	7.377	1.314	950	31.418	55.166	32.229	21.791
190	15.541	15.497	7.782	1.466	975	31.477	55.983	32.827	22.577
200	16.174	16.311	8.188	1.624	1,000	31.526	56.781	33.416	23.365
210	16.776	17.115	8.594	1.789	1,025	31.565	57.560	33.995	24.153
220	17.342	17.908	9.000	1.960	1,050	31.595	58.321	34.566	24.943
230	17.874	18.691	9.404	2.136	1,075	31.618	59.065	35.127	25.733
240	18.382	19.462	9.807	2.317	1,100	31.635	59.792	35.679	26.524
250	18.900	20.223	10.209	2.504	1,125	31.647	60.503	36.223	27.315
[1]260	19.494	20.976	10.608	2.696	1,150	31.655	61.198	36.758	28.106
[1]265	19.852	21.350	10.807	2.794	1,175	31.659	61.879	37.286	28.898
275	20.185	22.121	11.204	3.002	1,200	31.662	62.546	37.805	29.689
280	20.398	23.487	11.402	3.104	1,225	31.662	63.199	38.316	30.481
290	20.691	23.207	11.797	3.309	1,250	31.663	63.838	38.821	31.272
298.15	21.029	23.785	12.116	3.479	1,275	31.664	64.465	39.317	32.064
300	21.097	23.916	12.189	3.518	1,300	31.666	65.080	39.807	32.855
325	22.002	25.640	13.158	4.057	1,325	31.669	65.683	40.289	33.647
350	22.849	27.302	14.109	4.618	1,350	31.676	66.275	40.765	34.439

[1] Transition temperature.

11 K. The entropy and enthalpy were determined graphically to be 2.326 cal/(mol•K) and 19.862 cal/mol, respectively, from 0 to 18 K.

High-Temperature Thermal Determinations

The heat capacity of pyroxmangite was measured over the temperature range 323 to 1,372 K with a differential scanning calorimeter (DSC). The DSC was a Mettler Corp. model TA2000C, with a nominal operating range from 298 to 1,473 K.

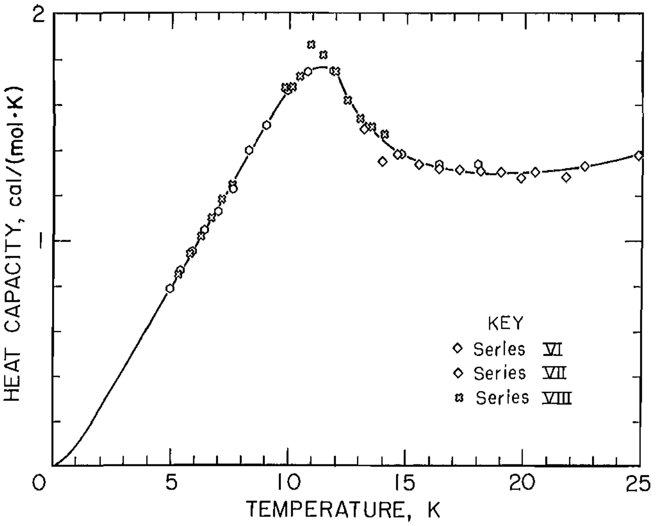

FIGURE 1.—Heat capacities of pyroxmangite measured with the adiabatic calorimeter, Schottky anomaly region (0 to 25 K), showing smoothed curve.

Two separate samples of pyroxmangite of 0.12023 and 0.1109 g were measured. A platinum crucible of 0.47047 g was used with both samples. The full capsule and an empty reference capsule were placed in the DSC. The DSC was then evacuated, filled with Ar, and operated at a scan rate of 10 K/min in 50-K steps from 322 to 1,372 K. The collected data were analyzed according to the "enthalpy method," as described by Mraw (19). The accuracy of the DSC was determined by measuring the heat capacity of magnesia (MgO) and comparing the measured values with accepted values from Pankratz (22). The accuracies of the heat capacities are estimated to be ±3 pct from 298 to 700 K and ±1 pct from 700 to 1,473 K for these data relative to the calibration compound; however, the uncertainty for these data is ~1.5 pct from 700 to 1,473 K.

The experimental heat capacities, shown in table 9 and figure 4, were smoothed in the same manner as described above and joined smoothly to the low-temperature values. The smoothed values along with the related functions are shown in table 8. The standard formation data for pyroxmangite are presented in tables 10 and 11.

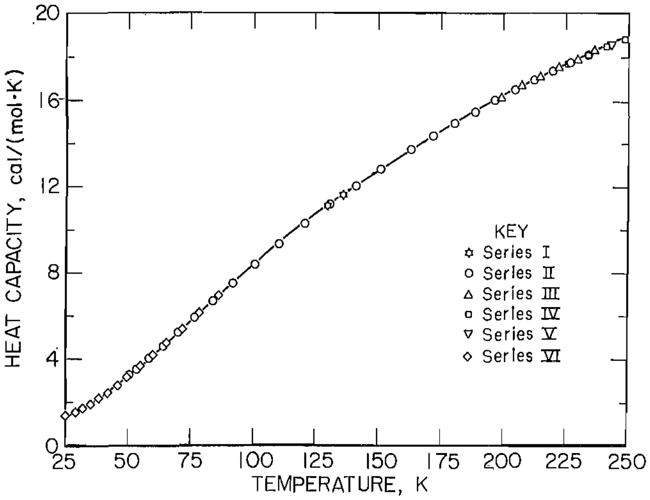

FIGURE 2.—Heat capacities of pyroxmangite measured with the adiabatic calorimeter (25 to 250 K), showing smoothed curve in the transition region.

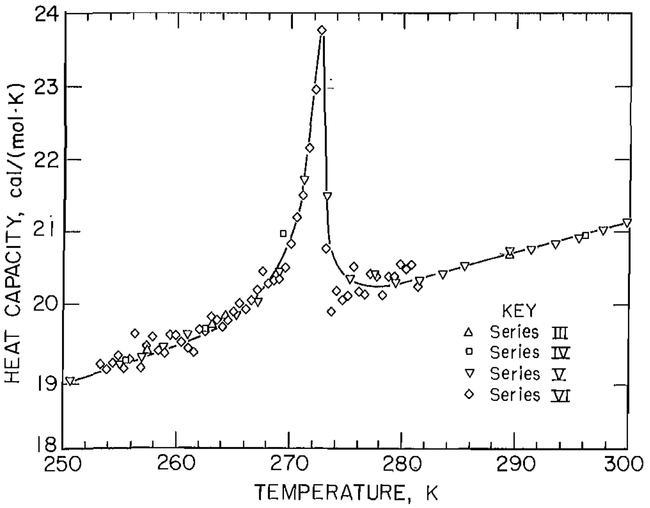

FIGURE 3.—Heat capacities of pyroxmangite measured with the adiabatic calorimeter, lambda transition region (250 to 300 K), showing smoothed curve.

TABLE 9. - Experimental high-temperature heat capacities of pyroxmangite

T, K	C_p°, cal/(mol·K)	T, K	C_p°, cal/(mol·K)	T, K	C_p°, cal/(mol·K)
347.15	24.528	697.15	30.075	1,047.15	31.656
397.15	25.317	747.15	30.757	1,097.15	31.711
447.15	25.728	797.15	30.879	1,147.15	31.612
497.15	26.814	847.15	30.886	1,197.15	31.586
547.15	27.701	897.15	31.311	1,247.15	31.583
597.15	28.640	947.15	31.268	1,297.15	31.594
647.15	29.170	997.15	31.761	1,347.15	31.609

TABLE 10. - Standard formation data for pyroxmangite, reaction [(0.9954Mn(c) + 0.0446Ca(c,ℓ) + Si(c) + 1.5 O_2(g) = $Mn_{0.9554}Ca_{0.0446}SiO_3$(c)]

T, K	cal/(mol·K)			kcal/mol			Log Kf
	C_p°	S°	$-(G° - H°_{298})/T$	$H° - H°_{298}$	ΔHf°	ΔGf°	
298.15	21.029	23.785	23.785	0	-319.668	-301.190	220.776
300	21.097	23.915	23.785	.039	-319.669	-301.075	219.330
400	25.202	30.606	24.671	2.374	-319.557	-294.890	161.118
500	27.511	36.500	26.460	5.020	-319.249	-288.752	126.212
600	28.987	41.654	28.572	7.849	-318.864	-282.690	102.969
700	30.116	46.210	30.773	10.806	-318.445	-276.698	86.388
[1]720	30.302	47.061	31.214	11.410	-318.358	-275.506	83.627
720	30.302	47.061	31.214	11.410	-318.368	-275.506	83.627
800	31.048	50.295	32.962	13.866	-318.011	-270.764	73.968
900	31.729	53.994	35.097	17.007	-317.559	-264.885	64.322
[2]980	31.979	56.710	36.752	19.559	-317.202	-260.207	58.028
980	31.979	56.710	36.752	19.559	-317.711	-260.210	58.029
1,000	32.042	57.357	37.158	20.199	-317.627	-259.039	56.612
1,100	31.938	60.409	39.134	23.402	-317.230	-253.198	50.305
[3]1,112	31.894	60.755	39.366	23.785	-317.186	-252.500	49.625
1,112	31.894	60.755	39.366	23.785	-317.277	-252.499	49.625
1,200	31.575	63.173	41.025	26.578	-316.970	-247.394	45.056
1,300	31.456	65.692	42.827	29.724	-316.673	-241.611	40.618
1,350	31.772	66.884	43.697	31.303	-316.531	-238.713	38.644

[1] Transition point for Ca. [2] Transition point for Mn. [3] Melting point for Ca.

TABLE 11. - Standard formation data for pyroxmangite from the oxides, reaction [SiO_2(c) + 0.0446CaO(c) + 0.9554MnO(c) = ($Mn_{0.9554}Ca_{0.0446}$)(SiO_3)(c)]

T, K	kcal/mol		Log Kf	T, K	kcal/mol		Log Kf
	ΔHf°	ΔGf°			ΔHf°	ΔGf°	
298.15	-7.215	-7.139	5.233	847	-6.780	-7.353	1.897
300	-7.215	-7.139	5.201	900	-6.659	-7.394	1.795
400	-7.154	-7.120	3.890	1,000	-6.417	-7.487	1.636
500	-7.012	-7.126	3.115	1,100	-6.195	-7.606	1.511
600	-6.852	-7.163	2.609	1,200	-6.030	-7.742	1.410
700	-6.699	-7.228	2.257	1,300	-5.924	-7.889	1.326
800	-6.583	-7.312	1.998	1,350	-5.877	-7.966	1.290
[1]847	-6.605	-7.353	1.897				

[1] Transition point for SiO_2.

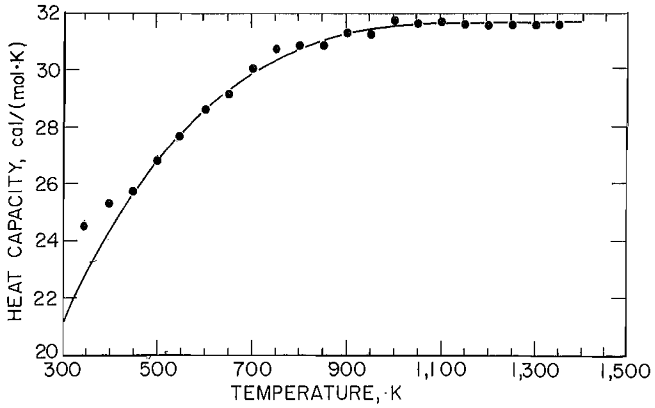

FIGURE 4.—Heat capacities of pyroxmangite measured with the differential scanning calorimeter (300 to 1,400 K), showing smoothed curve.

FOWLERITE (ZINCIAN RHODONITE)

Standard Enthalpies of Formation

The reaction scheme for the solution calorimetric determination of the enthalpy of formation of the zincian rhodonite, fowlerite, is presented in table 12. The difference in stoichiometry made it desirable to redetermine MnO, reaction 10, and the results are listed in table 13. The heat of solution of ZnO, reaction 11, was determined in the same solution following reaction 10, and the results are listed in table 13. Reaction 12, the heat of solution of CaO, is identical to reaction 3 on a per-mole basis, and the

TABLE 12. - Reaction scheme for fowlerite[1]

Reaction	ΔH, kcal	Uncertainty (±), kcal
(1) $SiO_2(c) + 6HF(sol) \rightarrow H_2SiF_6(sol) + 2H_2O(sol)$.......	-32.910	0.007
[2](10) $0.703MnO(c) + 1.406H^+(sol) \rightarrow 0.703Mn^{2+}(sol)$ $+ 0.703H_2O(sol)$..................................	-32.419	.027
(11) $0.0884ZnO(c) + 0.1768H^+(sol) \rightarrow 0.0884Zn^{2+}(sol)$ $+ 0.0884H_2O(sol)$.................................	-1.997	.003
(12) $0.2086CaO(c) + 0.4172HF(sol) \rightarrow 0.2086CaF_2(p)$ $+ 0.2086H_2O(sol)$.................................	-11.655	.008
[2](13) $(Mn_{0.703}Zn_{0.0884}Ca_{0.2086})(SiO_3)(c) + 6.4172HF(sol)$ $+ 1.5828H^+(sol) \rightarrow H_2SiF_6(sol) + 0.703Mn^{2+}(sol)$ $+ 0.0884Zn^{2+}(sol) + 0.2086CaF_2(p) + 3H_2O(sol)$....	[3]-70.581	.100

$$\Delta H_{14} = \Delta H^\circ_{298} = \Delta H_1 + \Delta H_{10} + \Delta H_{11} + \Delta H_{12} - \Delta H_{13}$$

(14) $SiO_2(c) + 0.703MnO(c) + 0.0884ZnO(c) + 0.2086CaO(c) \rightarrow (Mn_{0.703}Zn_{0.0884}Ca_{0.2086})(SiO_3)(c)$

$$\Delta H^\circ_{298} = -8.400 \pm 0.104 \text{ kcal/mol.}$$

---

[1] For reactions 1, and 10-13, introduced reactants are at 25° C and solvent and reaction products are at 73.7° C.

[2] Mn is oxidized in solution to the same state and is balanced and canceled.

[3] Corrected value.

NOTE.--Symbols c, sol, and p in parentheses denote substances that are crystalline, in solution, or crystalline precipitate, respectively, in all reactions.

TABLE 13. - Experimental heats of solution for fowlerite, kilocalories per mole

MnO, reaction 10	ZnO, reaction 11	Fowlerite, reaction 13	MnO, reaction 10	ZnO, reaction 11	Fowlerite, reaction 13
-46.086	-22.617	-68.618	-46.078	-22.565	-68.541
-46.061	-22.635	-68.496	-46.081	-22.632	
-46.156	-22.548	-68.533	-46.116	-22.592	-68.554
-46.180	-22.621	-68.513	±.038	±.034	±.044
-46.169	-22.523	-68.625			

value was adopted directly. Reaction 13 was conducted in a new charge of acid containing an equal amount of $K_2Cr_2O_7$. The heat of solution for the mineral fowlerite, reaction 13, was determined for the original mineral with the extended formula and formula weight shown in table 2. The heat of solution of the natural mineral (-68.554±0.044 kcal/mol) is listed in table 13. This value, corrected for total water (21), becomes -68.582 kcal. The total net correction for impurities is -1.024 kcal, which, when applied and calculated to the adjusted formula weight (128.845 g), gives an adjusted heat of solution of -70.581 ±0.100 kcal/mol. The uncertainty has been increased to compensate for potential errors in the corrections procedure. This final value has been substituted into the reaction scheme, table 12, for reaction 13.

These heat-of-solution values along with the reactions presented in table 12 may be combined as indicated according to the scheme

$$\Delta H_{14} = \Delta H_1 + \Delta H_{10} + \Delta H_{11} + \Delta H_{12} - \Delta H_{13}$$

to obtain ΔH_{14} for the overall calorimetric reaction:

$$SiO_2(c) + 0.2086CaO(c) + 0.703MnO(c) + 0.0884ZnO(c) \rightarrow (Mn_{0.703}Zn_{0.0884}Ca_{0.2086})(SiO_3)(c),$$

which is also the standard enthalpy of formation from the oxides for which

$$\Delta H^\circ_{298} = -8.400\pm0.104 \text{ kcal.}$$

To derive the standard enthalpy of formation of this fowlerite, the enthalpy of formation of ZnO, reaction 15, is required in addition to those presented in table 6:

$$Zn(c) + 0.5\ O_2(c) \rightarrow ZnO(c),$$

$$\Delta H_{15} = -83.762\pm0.30 \text{ kcal/mol.}$$

The value for reaction 15 is also taken from Pankratz (22). The standard enthalpy of formation may be derived according to the scheme

$$\Delta H_{16} = \Delta H_{14} + \Delta H_6 + 0.703\Delta H_7 + 0.0884\Delta H_{15} + 0.2086\Delta H_8$$

and the reaction

$$Si(c) + 0.2086Ca(c) + 0.703Mn(c) + 0.0884Zn(c) + 1.5\ O_2 \rightarrow (Mn_{0.703}Zn_{0.0884}Ca_{0.2086})(SiO_3)(c),$$

for which

$$\Delta Hf^\circ_{298.15} = -329.914\pm0.419 \text{ kcal/mol.}$$

Low-Temperature Thermal Properties

The fowlerite sample for the low-temperature measurements was dried at 383 K overnight before loading into a copper calorimeter vessel. Prior to sealing, the loaded calorimeter was evacuated and backfilled with 2×10^{-3} mol He to enhance heat transfer. A fowlerite sample of 146.6258 g was used. Runs 3 and 4 were made with 2.36×10^{-3} mol He and 114.6054 g sample.

The heat capacity of fowlerite was measured by adiabatic calorimetry over the range 4.95 to 302.9 K.

A Schottky anomaly was observed, with a maximum at about 8 K. The lowest temperature data were found to fit well to a function of form

$$C_p = AT^3 + BT + D\left(\frac{E}{T}\right)^2 \exp\left(-\frac{E}{T}\right).$$

Constants A and B were determined by regression over the temperature range 28.67 to 51.34 K (well above the anomalous region). The anomalous heat capacity component was as much as five times the cubic-linear component. Constants D and E were determined by a least squares fit to the eight lowest temperature data points using the constants A and B previously evaluated. Hence, the constants A, B, D, and E for the previous equation used in extrapolating from 5 to 0 K were 1.143×10^{-5} cal/(mol•K^4), 0.024975 cal/(mol•K^2), 1.204 cal/(mol•K), and 11.056 K, respectively.

Above 5 K, the data were smoothed using the previously mentioned polynomial curve-fitting computer program by Justice (12).

The experimental low-temperature heat capacities of fowlerite are presented in table 14 and figures 5 and 6. The overall uncertainties of the heat capacity values from the adibatic calorimeter were ±1 pct for 18 to 50 K, ±0.2 pct for 50 to 200 K, and ±0.1 pct for 200 to 300 K.

High-Temperature Thermal Determinations

The high-temperature heat capacity was measured with a DSC (previously described) over the range 322 to 1,372 K.

A 0.09256-g sample of fowlerite was used in a platinum capsule. Measurements for both the full and empty capsules, along with measurements on an alumina (Al_2O_3) reference sample, were made in the DSC. The DSC was operated with Ar at a scan rate of 10 K/min in 50-K steps from 322 to 1,372 K. The data were analyzed according to the "enthalpy method," as described by Mraw (19). The accuracy of the heat capacity values was determined by measuring MgO and comparing the measured values to accepted values from Pankratz (22). The uncertainties of the heat capacity values are ±3 pct from 298 to 700 K and ±1 pct from 700 to 1,473 K. The experimental high-temperature heat capacities are presented in table 15 and figure 7.

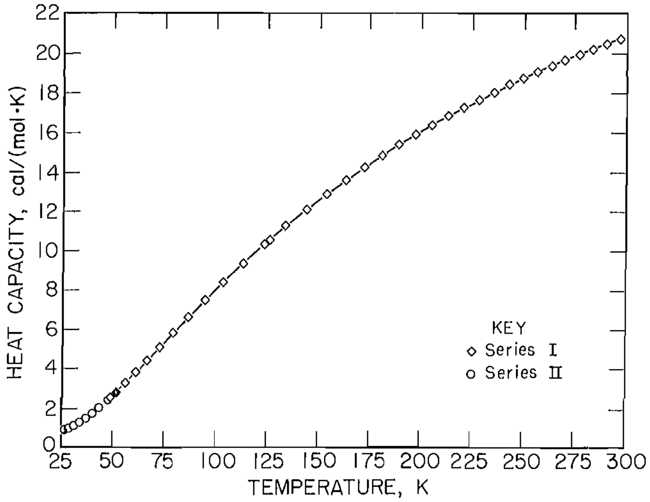

FIGURE 6.—Heat capacities of fowlerite measured with the adiabatic calorimeter (25 to 300 K), showing smoothed curve.

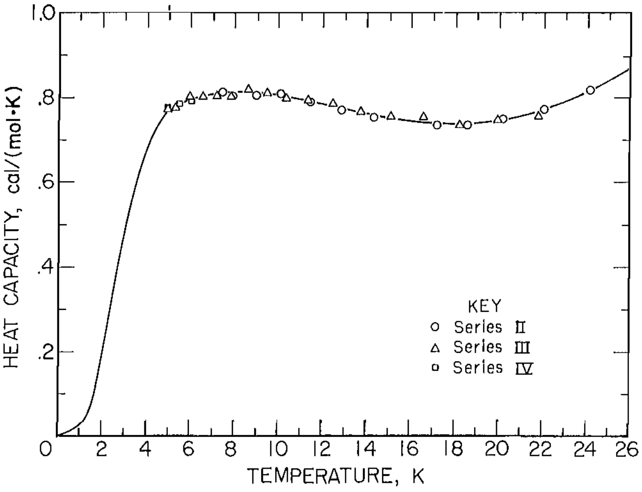

FIGURE 5.—Heat capacities of fowlerite measured with the adiabatic calorimeter, Schottky anomaly region (0 to 25 K), showing smoothed curve.

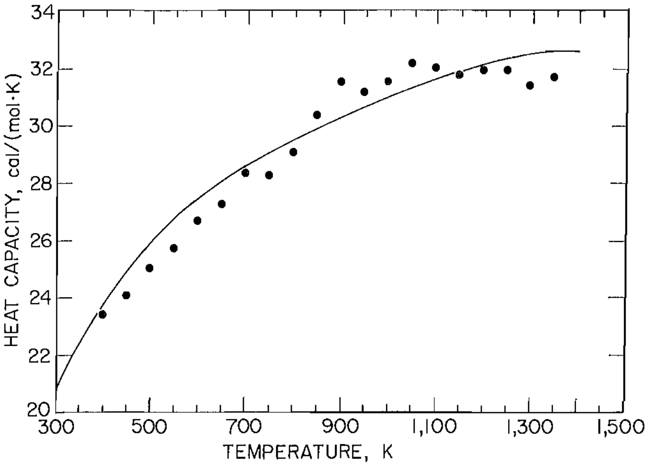

FIGURE 7.—Heat capacities of fowlerite measured with the differential scanning calorimeter (300 to 1,400 K), showing smoothed curve.

TABLE 14. - Experimental low-temperature heat capacities of fowlerite

T, K	C_p°, cal/(mol•K)	T, K	C_p°, cal/(mol•K)	T, K	C_p°, cal/(mol•K)
SERIES I		SERIES I--Con.		SERIES II--Con.	
48.28	2.496	249.64	18.704	36.79	1.486
51.17	2.782	256.57	19.035	39.96	1.735
55.79	3.257	263.43	19.328	43.41	2.028
60.79	3.798	269.79	19.612	47.20	2.382
66.39	4.406	276.51	19.883	51.34	2.797
72.46	5.083	283.19	20.155	SERIES III	
79.09	5.807	289.81	20.423	4.95	0.773
86.42	6.603	296.38	20.673	5.28	.775
94.51	7.460	302.90	20.928	5.93	.800
103.45	8.371	SERIES II		6.51	.802
112.93	9.306	7.40	0.814	7.13	.804
123.42	10.290	7.90	.083	7.81	.803
126.12	10.542	8.93	.805	8.56	.818
133.84	11.219	10.09	.809	9.40	.808
143.83	12.056	11.40	.788	10.32	.796
153.60	12.833	12.84	.770	11.33	.792
162.99	13.542	14.30	.752	12.45	.783
171.98	14.180	15.75	.739	13.70	.765
180.66	14.781	17.19	.732	15.07	.753
189.08	15.329	18.58	.733	16.55	.752
197.28	15.837	20.18	.748	18.20	.732
205.27	16.308	22.07	.772	19.93	.744
212.91	16.783	24.13	.817	21.79	.754
220.56	17.201	26.33	.887	SERIES IV	
228.04	17.630	28.67	.981	4.94	0.775
235.40	18.007	31.17	1.113	5.48	.785
242.59	18.392	33.87	1.280	6.00	.792

TABLE 15. - Experimental high-temperature heat capacities of fowlerite

T, K	C_p°, cal/(mol•K)	T, K	C_p°, cal/(mol•K)	T, K	C_p°, cal/(mol•K)
397.15	23.422	747.15	28.266	1,097.15	32.006
447.15	24.073	797.15	29.078	1,147.15	31.740
497.15	25.048	847.15	30.335	1,197.15	31.942
547.15	25.739	897.15	31.514	1,247.15	31.929
597.15	26.698	947.15	31.162	1,297.15	31.399
647.15	27.268	997.15	31.530	1,347.15	31.688
697.15	28.344	1,047.15	32.147		

The tabulated values for the heat capacity and related functions were obtained by smoothing the data using the previously mentioned computer program of Justice (12). The results are shown in table 16. All the experimental heat capacities are shown in figures 5-7.

TABLE 16. - Thermodynamic functions of fowlerite

T, K	cal/(mol·K)			$H^\circ_T - H^\circ_0$, kcal/mol
	C_p°	S°	$-(G^\circ - H^\circ_{298})/T$	
5	0.773	0.547	0.194	0.002
10	.803	1.102	.524	.006
15	.749	1.418	.774	.010
20	.743	1.630	.963	.013
25	.840	1.805	1.114	.017
30	1.048	1.974	1.243	.022
35	1.355	2.158	1.360	.028
40	1.739	2.363	1.473	.036
45	2.179	2.593	1.584	.045
50	2.661	2.847	1.698	.057
60	3.713	3.424	1.936	.089
70	4.806	4.078	2.194	.132
80	5.904	4.792	2.474	.185
90	6.982	5.549	2.773	.250
100	8.027	6.340	3.090	.325
110	9.028	7.152	3.422	.410
120	9.981	7.979	3.768	.505
130	10.884	8.814	4.124	.610
140	11.739	9.652	4.488	.723
150	12.548	10.489	4.861	.844
160	13.314	11.324	5.239	.974
170	14.040	12.153	5.621	1.110
180	14.730	12.975	6.007	1.254
190	15.388	13.789	6.395	1.405
200	16.014	14.595	6.785	1.562
210	16.611	15.391	7.176	1.725
220	17.180	16.177	7.567	1.894
230	17.722	16.952	7.958	2.069
240	18.236	17.718	8.349	2.248
250	18.724	18.472	8.739	2.433
260	19.185	19.215	9.128	2.623
270	19.622	19.948	9.515	2.817
273.15	19.754	20.176	9.636	2.879
280	20.035	20.669	9.900	3.015
290	20.429	21.379	10.284	3.218
298.15	20.738	21.949	10.595	3.385
300	20.798	22.078	10.665	3.424
325	21.638	23.776	11.609	3.954
350	22.419	25.408	12.537	4.505
375	23.138	26.980	13.448	5.075
400	23.798	28.495	14.341	5.661
425	24.405	29.956	15.217	6.264
450	24.962	31.367	16.075	6.881
475	25.473	32.730	16.916	7.512
500	25.994	34.049	17.740	8.155
550	26.774	36.562	19.338	9.473
600	27.480	38.923	20.873	10.830
650	28.086	41.147	22.347	12.219
700	28.613	43.248	23.766	13.637
750	29.079	45.238	25.132	15.080
800	29.501	47.128	26.448	16.544
850	29.890	48.929	27.718	18.029
900	30.255	50.648	28.944	19.553
950	30.603	52.293	30.130	21.054
1,000	30.938	53.871	31.278	22.593
1,100	31.566	56.850	33.469	25.719
1,200	32.105	59.620	35.534	28.903
1,300	32.477	62.206	37.488	32.134
1,350	32.562	63.434	38.426	33.761

STANDARD ENTHALPIES AND GIBBS ENERGIES OF FORMATION

The experimentally determined thermal data for pyroxmangite and fowlerite, the enthalpies of formation, the low-temperature heat capacities, and the high-temperature thermal data may be combined with the necessary data for the constituent elements and oxides for the calculation of the enthalpies, the Gibbs energies of formation, and other relevant properties as a function of temperature. The thermodynamic property changes for the formation of pyroxmangite and fowlerite from the elements and oxides are presented in tables 10 and 11, and 17 and 18, respectively. These two minerals are shown to be stable throughout the range of the data.

TABLE 17. - Standard formation data for fowlerite, reaction $[(0.703Mn(c,\ell) + 0.0884Zn(c,\ell,g) + 0.2086Ca(c,\ell,g) + Si(c,\ell) + 1.5\ O_2(g) = Mn_{0.703}Zn_{0.0884}Ca_{0.2086}SiO_3(c)]$

T, K	cal/(mol•K)			kcal/mol			Log Kf
	$C_p°$	S°	$-(G° - H°_{298})/T$	$H° - H°_{298}$	ΔHf°	ΔGf°	
298.15	20.738	21.949	21.949	0	-329.914	-310.716	227.755
300.00	20.808	22.078	21.948	.039	-329.911	-310.592	226.263
400.00	23.332	28.442	22.799	2.257	-329.907	-304.153	166.179
500.00	24.994	33.835	24.481	4.677	-329.811	-297.721	130.132
600.00	26.454	38.522	26.439	7.250	-329.665	-291.317	106.111
[1]692.73	27.848	42.421	28.321	9.767	-329.484	-285.407	90.042
692.73	27.848	42.421	28.321	9.767	-329.639	-285.407	90.042
700.00	27.957	42.712	28.469	9.970	-329.622	-284.943	88.962
[2]720.00	28.258	43.504	28.876	10.532	-329.576	-283.667	86.103
720.00	28.258	43.504	28.876	10.532	-329.622	-283.666	86.103
800.00	29.462	46.544	30.493	12.841	-329.396	-278.572	76.101
900.00	30.770	50.093	32.475	15.856	-329.055	-272.236	66.107
[3]980.00	31.470	52.747	34.023	18.350	-328.756	-267.191	59.585
980.00	31.470	52.747	34.023	18.350	-329.130	-267.192	59.586
1,000.00	31.645	53.385	34.404	18.981	-329.055	-265.931	58.118
1,100.00	31.945	56.419	36.269	22.165	-328.683	-259.637	51.584
[4]1,112.00	31.921	56.765	36.488	22.548	-328.641	-258.885	50.880
1,112.00	31.921	56.765	36.488	22.548	-329.067	-258.884	50.880
[5]1,180.00	31.787	58.659	37.712	24.718	-328.782	-254.607	47.156
1,180.00	31.787	58.659	37.712	24.718	-331.218	-254.607	47.156
1,200.00	31.747	59.193	38.066	25.353	-331.135	-253.309	46.133
1,300.00	31.473	61.722	39.790	28.511	-330.752	-246.843	41.498
1,350.00	31.566	62.910	40.624	30.086	-330.576	-243.606	39.437

[1] Melting point for Zn.
[2] Transition point for Ca.
[3] Transition point for Mn.
[4] Melting point for Ca.
[5] Boiling point for Zn.

TABLE 18. - Standard formation data for fowlerite from the oxides, reaction [$SiO_2(c) + 0.2086CaO(c) + 0.703MnO(c) + 0.0884ZnO(c) = (Mn_{0.703}Zn_{0.0884}Ca_{0.2086})(SiO_3)(c)$]

T, K	kcal/mol		Log Kf
	ΔHf°	ΔGf°	
298.15	-8.400	-8.128	5.958
300	-8.397	-8.126	5.920
400	-8.442	-8.031	4.388
500	-8.520	-7.918	3.461
600	-8.613	-7.789	2.837
700	-8.694	-7.645	2.387
800	-8.763	-7.491	2.046
[1]847	-8.851	-7.412	1.912
847	-9.026	-7.412	1.912
900	-8.961	-7.313	1.776
1,000	-8.781	-7.138	1.560
1,100	-8.571	-6.985	1.388
1,200	-8.383	-6.849	1.247
1,300	-8.253	-6.728	1.131
1,350	-8.203	-6.670	1.080

[1] Transition point for SiO_2.

DISCUSSION

No thermodynamic data on natural pyroxene or pyroxenoid Mn minerals were found in the literature. The thermodynamic properties of synthetic rhodonite have been determined (14), and comparative studies have been made (20, 25). Navrotsky experimentally determined the heat of transition for $MnSiO_3$ (rhodonite) → $MnSiO_3$ (pyroxmangite) of $\Delta H^\circ_{986} = +0.060 \pm 0.33$ kcal/mol. No other data were found in the literature for pyroxmangite.

For the minerals pyroxmangite and fowlerite, tables 1 and 2, Mg^{2+} ion impurity has been substituted into the Mn^{2+} position in order to approach the ideal formula as closely as possible, rather than to calculate it proxying for Ca^{2+}, another impurity. If, however, Mg in the pyroxmangite analysis, table 1, is added to the Ca position, the difference is shown to be 287 calories, by the following procedure. The total weight thermal correction for this substitution becomes -1.185 kcal, the formula weight becomes 130.160 g, and the heat of solution of the mineral of composition $(Mn_{0.942}Ca_{0.058})(SiO_3)$ becomes -72.478 ± 0.10 kcal/mol. Using this value in the reaction scheme (table 4) and the corresponding coefficients for reactions 2 and 3, and calculating according to the indicated scheme,

$$\Delta H^\circ_{298.15} \text{ (from oxides)}$$

$$= -7.452 \pm 0.108 \text{ kcal/mol.}$$

For the study reported here, the oxidizing agent, $K_2Cr_2O_7$, was added in excess as determined by titration. The action of the oxidizing agent tended to override the slow and irregular reaction caused by dissolved oxygen and ensured the rapid oxidation to a fairly consistent and reproducible state. This procedure was considered especially necessary for these natural specimens. Differences between these and the reported values from the literature are probably caused by the relative proportions of impurities substituting in the composition or to variations in the oxidation state of Mn.

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