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Thermodynamic Data on the Amphibole Asbestos Minerals Amosite and Crocidolite

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Enthalpies of formation of two amphibole asbestos minerals were determined by hydrofluoric acid solution calorimetry. The values obtained for formation from the elements at 298.15 K are minus 2,419.24 plus or minus 2.95 Kcal per mole for amosite, and minus 2,433.56 plus or minus 2.99 Kcal per mole for crocidolite. Tables of enthalpies of formation and Gibbs energies of formation are given as a function of temperature both from the elements and the component oxides for amosite and crocidolite.

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CONTENTS

ILLUSTRATIONS

TABLES

TABLES--Continued

THERMODYNAMIC DATA ON THE AMPHIBOLE ASBESTOS MINERALS AMOSITE AND CROCIDOLITE

by

K. O. Bennington,[1] M. J. Ferrante,[1] and J. M. Stuve[1]

ABSTRACT

Thermodynamic properties of two amphibole asbestos minerals were determined by the Bureau of Mines. The enthalpies of formation were determined by the hydrofluoric acid solution calorimetry method. Heat capacity measurements were made with an adiabatic calorimeter over the range of 5 to 315 K. High-temperature enthalpies above 298 K were determined with a copper-block drop calorimeter to 852 K for amosite and to 902 K for crocidolite. Thermodynamic data determined for amosite of the composition $(Fe^{+2}_{5.2766}Mg_{1.5209}Fe^{+3}_{0.12}Mn_{0.0825})(Si_{7.9163}Al_{0.0837}O_{22.0363})(OH)_{1.9637}$ are: $S^\circ_{298.15}$ = 168.8 ± 5 cal/deg-mole; $\Delta Hf^\circ_{298.15}$ (elements) = -2419.24 ± 2.95 kcal/mole; $\Delta Hf_{298.15}$ (oxides) = -30.92 ± 2.47 kcal/mole; and $\Delta Gf^\circ_{298.15}$ = -2260.1 kcal. Corresponding data found for crocidolite of the composition $(Na_{1.9}Ca_{0.1})(Fe^{+3}_{2.024}Fe^{+2}_{2.501}Mg_{0.475})(Si_{7.971}Al_{0.029}O_{22.095})(OH)_{1.905}$ are: $S^\circ_{2.98.15}$ = 161.1 ± 4 cal/deg-mole; $\Delta Hf^\circ_{298.15}$ (elements) = -2433.56 ± 2.99 kcal/mole, $\Delta Hf_{298.15}$ (oxides) = -87.69 ± 1.70 kcal/mole, and $\Delta Gf^\circ_{298.15}$ = -2269.8 kcal.

Calorimetric values from this investigation were combined with other data from the literature to calculate the Gibbs energies of formation and equilibrium constants of formation over the temperature range of the measurements. Tables of enthalpies of formation and Gibbs energies of formation are given as a function of temperature both from the elements and the constituent oxides.

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INTRODUCTION

In keeping with Bureau of Mines goals of minimizing undesirable environmental conflicts, impacts, and occupational hazards associated with mining and mineral processing operations, and in supplying basic information needed for public and private decisionmaking on mineral matters, the thermodynamic properties of two high-iron content amphibole asbestos minerals have been measured. These materials are of interest in the study of slags, in the field of geochemistry, and in industrial processes using recyclable filter materials. Calculations pertaining to silicates with a high iron content have been seriously restricted by the scarcity of such data. The fine-fibrous varieties of these

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minerals were chosen because they are obtainable in greater uniformity and much higher purity than are the more massive or other acicular forms.

Amosite, a fibrous member of the cummingtonite-grunerite series, was found and named in South Africa. The material used for this work is close to grunerite in composition, but with slightly lower iron and higher magnesium contents; it was from the Lydenburg District, Transvaal. Crocidolite is the fibrous form of sodic amphibole and is close to riebeckite in composition but with higher magnesium and lower ferrous iron contents. The material used in this study was from the Prieska District, Griqualand West, South Africa.

Enthalpies of formation were determined by hydrofluoric acid solution calorimetry, low-temperature heat capacity measurements were made with an adiabatic calorimeter, and high-temperature enthalpies above 298 K were determined with a copper-block drop calorimeter. These experimental data were combined with data from the literature to calculate the thermodynamic properties over a wide range of temperatures. Results for the formation reactions are expressed both in terms of the constituent elements and oxides. No similar data have been previously published.

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Acknowledgment is expressed to Edwin Roedder, Geological Survey, Washington, D.C., for providing the clear Brazilian quartz used; to the Denver Rock Analysis Laboratory, Denver, Colo., for the chemical analysis; to G. K. Czamanske at the Experimental Geochemistry and Mineralogy Laboratory at Menlo Park, Calif., for the microprobe analysis; all of the Geological Survey, U.S. Department of the Interior.

MATERIALS

Acids

The hydrofluoric and sulfuric acids were reagent-grade products used without treatment except for dilution to the proper strength.

Aluminum Sulfate Dodecahydrate

The $Al_2(SO_4)_3 \cdot 12H_2O$ was prepared by first recrystallizing reagent-grade $Al_2(SO_4)_3 \cdot 18H_2O$, then slowly dehydrating it for several days over the temperature range of 65° to 90° C. Care was taken in adjusting the composition to 12 H_2O of hydration. Analysis by direct ignition showed 18.25 pct Al_2O_3, compared with the theoretical value of 18.26 pct. No significant impurities were detected spectrographically.

Brucite

A natural mineral ($Mg(OH)_2$) was ground and sieved to minus 200-mesh before use. The chemical analysis, after drying at 110° C, was: MgO, 68.78; H_2O, 30.53; CO_2, 0.16; SiO_2, 0.25; Fe_2O_3, 0.17; and Mn_2O_3, 0.17 wt-pct. The total is 100.06 wt-pct.

Calcium Oxide

Reagent-grade calcium carbonate of very high purity was roasted overnight at 970° C to provide the CaO for each determination.

Sodium Sulfate

The Na_2SO_4 was a reagent-grade product, heated at 850° C for 30 hours before use. X-ray examination confirmed that this product was Na_2SO_4 (III).

Ferrous Sulfate Heptahydrate

The $FeSO_4 \cdot 7H_2O$ was a reagent-grade product. On analysis, it was found to have an $Fe:SO_4:H_2O$ ratio of 1.000:0.993:7.04. There was no detectable trace of ferric iron. Compensation for the slight excess of water was made in the calorimetric correction procedure. Samples were weighed, individually double-sealed, and stored in a desiccator until used.

Ferric Oxide

The Fe_2O_3 was a high-purity product that was used without alteration except to dry to constant weight. Only α-Fe_2O_3 was detected by X-ray analysis. No corrections were made for the spectrographically detected amounts ($\sim$400 ppm) of manganese and silicon.

Manganous Oxide

Reagent-grade MnO_2 was slowly heated in a stream of hydrogen 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. No corrections were made for spectrographically detected impurities; the maximum total for Mg and Si is $\sim$100 ppm and for Al, Ca, and Fe the maximum total is $\sim$400 ppm.

Silica

The SiO_2 used was from an exceedingly clear and pure single 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 micrometers was reserved for the heat of solution determinations. It was repeatedly leached with hydrochloric acid until the solution was clear, digested with hydrogen peroxide, dried, and heated through the alpha-beta transition before use.

Amosite and Crocidolite

The natural amphibole asbestos minerals, amosite and crocidolite, were obtained from Wards Natural Science Establishment.[2] In preparation, very pure,

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[2] Reference to specific manufacturers and brands of equipment is made for identification only and does not imply endorsement by the Bureau of Mines.

select material, free of magnetite or other rock fragments, was trimmed, hand-sorted, and crushed in a mortar to separate the fiber bundles which were then separated over a magnet. They were once more hand-sorted under a magnifying glass and checked under a microscope for uniformity. Additional specific sample compaction and drying preparation preceded use for both the low- and high-temperature thermal property investigations.

MINERAL ANALYSES AND FORMULAS

Analyses

The chemical analyses are presented in tables 1-2 for amosite and crocidolite. The agreement between the chemical analyses and the microprobe analyses was excellent. Microprobe analyses indicated that these were exceptionally pure and homogeneous minerals with no evidence of any discrete separate impurities. Chemical analyses were therefore used without alteration except as required for OH^- stoichiometry discussed in the next section.

TABLE 1. - Analysis of amosite

Oxide composition			Ions in extended formula	Formula weight	Substitution site	Site deviations	Adjusted formula	Adjusted formula weight
Major	Minor	Wt-pct						
SiO_2		50.15	7.9088	222.1265		-0.0075	7.9163	222.3372
Al_2O_3		.45	.0837	2.2583			.0837	2.2583
			[1]7.9925					
	TiO_2	.01	.0012	.0575	Fe^{+3}			
Fe_2O_3		1.00	.1188	6.6346			.1200	6.7016
FeO		39.01	5.1448	287.3216		-.0897	5.2766	294.6823
	CaO	.07	.0118	.4729	Fe^{+2}			
	Na_2O	.06	.0180	.4138	Fe^{+2}			4.5324
	K_2O	.06	.0123	.4809	Fe^{+2}			
MnO		.62	.0825	4.5324			.0825	
MgO		6.47	1.5209	36.9655			1.5209	36.9655
			[1]6.9103					
H_2O^+		2.08	2.1878	37.2086	O	+.2241	[2]1.9637	33.3972
	F	.02	.0095	.1805	O			
	Cl	.02	.0057	.2021	O			
			[1]2.2030					
H_2O^-		.15						
O			21.7970	348.7389			22.0363	352.5676
Total formula weight.			-	947.59			-	953.4421

Total charge: 48.

Normalizing factor: 9.4753.

Adjusted formula:

$[(Fe^{+3}_{0.1200}Fe^{+2}_{5.2766}Mg_{1.5209}Mn_{0.0825})(Si_{7.9163}Al_{0.0837}O_{22.0363})(OH)_{1.9637}]$.

[1] Total ions in extended formula.

[2] Determined from reaction scheme, table 3.

TABLE 2. - Analysis of crocidolite

Oxide composition			Ions in extended formula	Formula weight	Substitution site	Site deviations	Adjusted formula	Adjusted formula weight
Major	Minor	Wt-pct						
SiO_2		51.38	7.9037	221.9833		-0.0673	7.9710	223.8735
Al_2O_3		.16	.0290	.7825			.0290	.7825
			[1]7.9327					
Fe_2O_3		17.49	2.0245	113.0622			2.0245	113.0622
	MnO	.08	.0102	.5604	Fe^{+2}			
FeO		19.19	2.4687	137.8695		-.0220	2.5009	139.6678
	TiO_2	.02	.0023	.1102	Mg			
MgO		2.06	.4723	11.4792			.4746	11.5351
			[1]4.9785					
CaO		.61	.1003	4.0200			.1003	4.0200
Na_2O		6.24	1.8615	42.7955		-.0280	1.8997	43.6737
	K_2O	.05	.0102	.3988	Na			
			[1]1.9720					
H_2O^+		2.18	2.2367	38.0402	O	+.3317	[2]1.905	32.3989
	F-	.01	.0048	.0912	O			
			[1]2.2415					
H_2O^-		.33						
O			21.7585	348.1229			22.095	353.5067
Total formula weight.			-	919.316			-	922.520

Total charge: 48.

Normalizing factor: 9.2425.

Adjusted formula:

$$[(Na_{1.9}Ca_{0.100})(Fe^{+3}_{2.024}Fe^{+2}_{2.501}Mg_{0.475})(Si_{7.971}Al_{0.029}O_{22.095})(OH)_{1.905})]$$

[1] Total ions in extended formula.

[2] Determined from reaction scheme, table 5.

Formulas

The mineral formulas for amosite and crocidolite were derived from the chemical analyses using the anion-based hydrogen equivalent method. By this method, the cation equivalents were adjusted to equal the total number of anion equivalents in the formula. The technique was described by Miser and Stevens (23),[3] Stevens (28-29), and has more recently been applied to amphiboles by Jackson, Stevens, and Bowen (15) and Goff and Czamanske (11). The extended formulas, the complete uncorrected formulas for the mineral analyses, were constructed using 24 oxygen anions, or charge equal to 48, per formula. These may also be described as the number of gram equivalents of the cation required to make up a molecule containing 24 oxygen anions. The limitations and merits of methods using 23 oxygen anions per formula for amphiboles were discussed by Borg (4), who pointed out that analytical errors, particularly for bound water (H_2O^+) may be disguised by a fortuitous fit to the ideal formula when the 23-oxygen calculation is used.

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

The number of gram atoms of the individual elements in the extended formulas were used in computing the formula weights. The total provides the gram formula weight of the natural mineral. Addition of the ions in any structural position does not provide the even numbered totals required for a stoichiometric mineral. The grouping of ions into particular positions follows the example of Deer, Howie, and Zussman (7). The apparent deviation from ideality may be caused by analytical error or vacant cation positions as discussed by Sommerfeld (27) and Jackson. It was necessary to make several assumptions in the construction of these formulas, namely, that all of the charges in the mineral balance, that the chemical analysis is absolutely accurate and, following Jackson and Sommerfeld, that all of the anion positions are filled.

The number of ions in the extended formula does not provide a practical composition, and to adjust it to an ideal end member molecule is inappropriate. The composition was therefore readjusted. This was done by substituting some of the minor elements into the most likely major element sites. The deviations in each structural position represent the difference between the ideal stoichiometry and the sum of ions substituted per structural site. The substitution sites are chose for the major ion site that may be brought nearest to a whole number in the adjusted formula. The assumption is made that the deficiencies are caused by vacant sites.

The surplus OH^-, which was determined by calculation, could not appear in the original calculation because the total charge was established as 48. The total of oxygen and the anions (OH^-, F^-, and Cl^-) is 24; however, the distribution of charge between the amount of oxygen and the anions would not permit the reaction schemes to balance. The reaction schemes must balance exactly, regardless of all substitutions; consequently, the total redistribution was applied to the OH^- group with the amount of OH^- required by the reaction schemes, Cl^- and F^-, having been substituted into the oxygen position with the excess OH^-. This correction procedure is justified on the evidence that the minerals actually contained hygroscopic water that appears as bound water in the analysis. The excess water was demonstrated during the high-temperature enthalpy determinations described in a following section.

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 and impurities were made by treating the minor element as substituted into the most likely major element sites as previously described. The difference in energy between the quantity of the major element that has been displaced by an equal quantity of the proxying element was computed from the respective heat of solution values of their oxides determined under similar conditions. The correction applied was the net energy difference for the specific number of ions in a particular structure position. This procedure was previously proposed by Bennington (3), and further discussed by Sommerfeld.

The excess OH^- is probably due to analytical error as discussed by Borg. This excess was therefore recalculated as H_2O^+, then it was added to the hydroscopic water (H_2O^-). The heat correction applied for total excess water (H_2O^-) is treated as though it were thermally equivalent to ice.

The thermal correction required by the change in gram formula weight was applied by scaling the heat of solution value for the natural mineral to the adjusted gram formula weight. This was done assuming that the vacancy sites are uniformly distributed, that the added ions are completely bonded in the structure, and that the heat of solution of the natural mineral is more suitable than a thermal adjustment based on the separate heats of solution of the deficient or excess oxides.

The values for the thermal corrections and sequence of application of the corrections are given in detail under the reactions descriptions for each mineral, reaction 9 for amosite and reaction 33 for crocidolite. The heat of solution values were determined and calculated for the formula weights of the natural minerals, and the corrections were then applied.

The fractions of mole numbers appearing in tables 1-2 were selectively rounded to facilitate the exact balancing required in the reaction schemes, tables 3 and 5, for amosite and crocidolite. This could be done with constituents in the crocidolite formula with less distortion than in the amosite formula, partly because the values for silicon and oxygen required no rounding. An example is reaction 30, in the scheme for crocidolite, which shows the value for sodium ion rounded from 1.8997 to 1.9 moles, which is derived from 0.95 mole of sodium sulfate. Internal consistency was rigorously maintained by a minimum of rounding, even though the fractions of moles were unrealistic.

EXPERIMENTAL DETERMINATIONS

Heats of Formation at 298.15 K

The heats of formation of amosite and crocidolite were determined by hydrofluoric acid solution calorimetry. The apparatus used has been described in earlier publications (19, 32). The solvent was 948.7 g of 20.1 wt-pct hydrofluoric acid which contained the necessary amount of potassium dichromate ($K_2Cr_2O_9$), which was determined separately, to oxidize ferrous ion. The quantities of all reacting substances were stoichiometric with 0.742 g of alpha-quartz. Determinations of heats of solution were approximately 2 hours long.

Weighed amounts of solid or liquid substances to be dissolved were placed in paraffin-sealed, Teflon 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 the process of converting the pure reacting substance 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 the reaction measurements.

The precision uncertainty assigned to the mean of solution heat values is twice the standard deviation of the mean. When two or more separate heat values are combined, the uncertainty is taken as the square root of the sum of the squares of the individual uncertainties.

All energy units are expressed in terms of the defined calories (1 cal = 4.1840 joules). All weighings were corrected to vacuum, molecular weights are in accordance with the 1971 table of atomic weights (14), and final values are rounded to 10 calories.

The reaction scheme for the solution calorimetric investigation of amosite is given in table 3. The symbols c, l, p, and sol are used to denote substances that are crystalline, liquid, precipitated, and in solution. The reactions are written in an abbreviated form sufficient to show that stoichiometry was maintained in such a way as to permit cancellation of the reaction products. The table also contains the average measured heat values and their precision uncertainties.

Reaction 1, the heat of solution of silica, was conducted in a charge of new acid. Six measurements of this heat gave -32.876, -32.914, -32.901, -32.952, -32.883, and -32.881 kcal/mole of SiO_2. The mean is -32.901 ±0.023 kcal/mole.

Reaction 2, the heat of solution of $Al_2(SO_4)_3 \cdot 12H_2O$ was determined in the solution resulting from reaction 1. The following measurements were made for the heat of this reaction: -17.197, -17.269, -17.388, -17.312, and -17.330 kcal/mole. The mean is -17.299±0.064 kcal/mole.

Reaction 3, the heat of solution of Fe_2O_3, was measured in the solution resulting from reaction 2. Six measurements of this heat gave -42.042, -42.011, -42.045, -41.959, -42.049, and -41.961 kcal/mole. The mean is -42.011±0.34 kcal/mole.

Reaction 4, the heat of solution of ferrous sulfate heptahydrate was measured in the solution resulting from reaction 3. Potassium dichromate was added to the original acid solution, in approximately 10 pct excess, to insure the rapid oxidation of ferrous iron. Nine measurements were made for the heat of this reaction which gave the following values corrected for the very slight excess of water: -20.124, -20.151, -20.141, -20.159, -20.065, -20.085, -20.139, -20.079, and -20.144. The mean is -20.121±0.023 kcal/mole.

Reaction 5, the heat of solution of brucite, was performed in the solution resulting from reaction 4. Six measurements of the heat of this reaction corrected for impurities gave: -18.466, -18.430, -18.337, -18.592, -18.703, -18.327 kcal/mole. The mean is -18.479±0.12 kcal/mole.

Reaction 6 represents the heat of solution of MnO in the solution resulting from reaction 5. Six determinations provided -48.082, -47.311, -48.069, -47.449, -47.749, and -47.389 kcal/mole. The mean is -47.675±0.281 kcal/mole.

Reaction 7 is a dilution reaction required to maintain stoichiometry and represents the solution of 5.23975 moles of water in the solution resulting from reaction 6. Six measurements of this heat yielded: 0.824, 0.824, 0.824, 0.824, 0.826, and 0.823 kcal/mole. The mean is 0.824±0.0008 kcal/mole.

TABLE 3. - Reaction scheme for amosite

Reaction	ΔH, kcal	Uncer-tainty, ± kcal
(1) $7.9163SiO_{2(c,25^\circ)} + 47.4978HF_{(sol,73.7^\circ)} = 7.9163H_2SiF_{6(sol,73.7^\circ)}$ $15.8326H_2O_{(sol,73.7^\circ)}$	-260.454	0.182
(2) $0.04185Al_2(SO_4)_3 \cdot 12H_2O_{(c,25^\circ)} = 0.0837Al^{+3}_{(sol,73.7^\circ)} + 0.12555SO_4^{-2}{}_{(sol,73.7^\circ)}$ $+ 0.5022H_2O_{(sol,73.7^\circ)}$	-0.724	.003
(3) $0.06Fe_2O_{3(c,25^\circ)} + 0.36H^+_{(sol,73.7^\circ)} = 0.12Fe^{+3}{}_{(sol,73.7^\circ)} + 0.18H_2O_{(sol,73.7^\circ)}$	-2.521	.002
(4) $5.2766FeSO_4 \cdot 7H_2O_{(c,25^\circ)} = 5.2766Fe^{+3}{}_{(sol,73.7^\circ)} + 5.2766SO_4^{-2}{}_{(sol,73.7^\circ)}$ $+ 36.9362H_2O_{(sol,73.7^\circ)}$	-106.170	.121
(5) $1.5209Mg(OH)_{2(c,73.7^\circ)} + 3.0418HF_{(sol,73.7^\circ)} = 1.5209MgF_{2(p,73.7^\circ)}$ $+ 3.0418H_2O_{(sol,73.7^\circ)}$	-28.105	.182
(6) $0.0825MnO_{(c,25^\circ)} + 0.165\ H^+_{(sol,73.7^\circ)} = 0.0825Mn^{+2}{}_{(sol,73.7^\circ)} + 0.0825H_2O_{(sol,73.7^\circ)}$	-3.933	.023
(7) $5.23975H_2O_{(l,25^\circ)} = 5.23975H_2O_{(sol,73.7^\circ)}$	4.317	.004
(8) $5.40215H_2SO_4 \cdot 7H_2O_{(l,25^\circ)} = 10.8043H^+_{(sol,73.7^\circ)} + 5.40215SO_4^{-2}{}_{(sol,73.7^\circ)}$ $+ 37.81505H_2O_{(sol,73.7^\circ)}$	33.699	.036
(9) $[(Fe^{+2}_{5.2766}Mg_{1.5209}Fe^{+3}_{0.12}Mn_{0.0825})(Si_{7.9163}Al_{0.0837}O_{22.0363})(OH)_{1.9637}]_{(c,25^\circ)}$ $+ 50.5396HF_{(sol,73.7^\circ)} + 11.3293H^+_{(sol,73.7^\circ)} = 7.9163H_2SiF_{6(sol,73.7^\circ)}$ $+ 0.0837Al^{+3}{}_{(sol,73.7^\circ)} + 0.12Fe^{+3}{}_{(sol,73.7^\circ)} + 5.2766Fe^{+3}{}_{(sol,73.7^\circ)}$ $+ 1.5209MgF_{2(p,73.7^\circ)} + 0.0825Mn^{+2}{}_{(sol,73.7^\circ)} + 24H_2O_{(sol,73.7^\circ)}$	-607.21	1.35

$$\Delta H_{10} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7 - \Delta H_8 - \Delta H_9$$

(10) $7.9163SiO_{2(c,25^\circ)} + 0.04185Al_2(SO_4)_3 \cdot 12H_2O_{(c,25^\circ)} + 0.06Fe_2O_{3(c,25^\circ)}$
$+ 5.2766FeSO_4 \cdot 7H_2O_{(c,25^\circ)} + 1.5209Mg(OH)_{2(c,25^\circ)} + 0.0825MnO_{(c,25^\circ)}$
$+ 5.23975H_2O_{(l,25^\circ)} = [(Fe^{+2}_{5.2766}Mg_{1.5209}Fe^{+3}_{0.12}Mn_{0.0825})$
$(Si_{7.9163}Al_{0.0837}O_{22.0363})(OH)_{1.9367}]_{(c,25^\circ)} + 5.40215H_2SO_4 \cdot 7H_2O_{(l,25^\circ)}$
$\Delta H_{10} = +175.921 = +175.921 \pm 1.38$ kcal

Reaction 8 represents the heat of solution of sulfuric acid in a new charge of acid which contained the same amount of potassium dichromate as used in reaction 4. Six determinations of this heat provided 6.230, 6.242, 6.239, 6.228, 6.243, and 6.249 kcal/mole. The mean is 6.238 ±0.0066 kcal/mole.

Reaction 9 represents the heat of solution of the mineral amosite in the solution resulting from reaction 8. Six determinations of this heat yielded: -602.86, -601.76, -603.15, -601.89, -603.29, and -603.28 kcal/mole. The mean is -602.71 ±0.57 kcal/mole. This value is for the original mineral with the gram formula weight and composition represented by the extended formula, table 1. The thermal correction for hygroscopic (H_2O^-) water (0.40 kcal), the correction for the weight percentage of water, and the total net corrections for impurity substitutions (-1.41 kcal) were made, then values were corrected to the adjusted gram formula weight. A final value of -607.21 ±1.35 kcal/mole was obtained. This uncertainty contains an additional allowance for the uncertainties involved in the impurities correction procedure.

The final solution, after conducting reactions 1 through 7 consecutively, is identical with the solution resulting from the combination of reactions 8 and 9. The reactions and their heats may therefore be combined as indicated in table 3 to obtain the resulting reaction 10, the overall calorimetric reaction, with an enthalpy change of 175.921 ±1.38 kcal.

To derive the standard enthalpy of formation of amosite, the heats of formation of alpha-quartz (SiO_2), ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), magnesium hydroxide or brucite ($Mg(OH)_2$), water, a 7.9298 molal solution of sulfuric acid ($H_2SO_4 \cdot 7H_2O$), ferric oxide (Fe_2O_3), manganous oxide (MnO), and aluminous sulfate dodecahydrate compensated for the heat of formation of water ($Al_2(SO_4)_3 \cdot 12H_2O$) at 25° C are required as represented by equations 11-15 and 18-20. The sources for the values of these reactions are as follows: Alpha-quartz, from Wise, Margrave, Feder, and Hubbard (38); ferrous sulfate heptahydrate, from Adami and Kelly (1), recalculated in accordance with the value from reaction 15; magnesium hydroxide, from King (20); water, sulfuric acid and ferric oxide from Wagman (35-36); and aluminum sulfate dodecahydrate, from Ko, Stuve, and Brown (21).

The enthalpy of formation of amosite for reaction 22 of this specific composition from its constituent elements is derived from these reactions and heats presented in table 4 according to the scheme

$$\Delta H_{22} = \Delta H_{10} + 7.9163\Delta H_{11} + 5.2766\Delta H_{12} + 1.5209\Delta H_{13} + 5.23975\Delta H_{14} \\ - 5.40215\Delta H_{15} + 0.06\Delta H_{18} + 0.0825\Delta H_{19} + 0.04185\ \Delta H_{20}.$$

This combination of reactions and heats yields

$$\Delta Hf^\circ_{298.15}\ \text{(elements)} = -2419.237 \pm 2.95\ \text{kcal}.$$

TABLE 4. - Enthalpy of formation of amosite

Reaction	$\Delta H_{298.15}$kcal/mole	Reference
(11) $Si(c) + O_2(g) = SiO_2(c)$	-217.720±0.34	38
(12) $Fe(c) + S(rh) + 1\text{-}1/2\ O_2(g) + 7H_2(g) = FeSO_4\cdot 7H_2O(c)$	-720.47 ± .14	1
(13) $Mg(c) + O_2(g) + H_2(g) = Mg(OH)_2(c)$	-221.100± .200	20
(14) $1/2\ O_2(g) + H_2(g) = H_2O(l)$	-68.315± .010	35
(15) $S(rh) + 5\text{-}1/2\ O_2(g) + 8H_2(g) = H_2SO_4\cdot 7H_2O(l)$	-687.633± .170	35
(16) $Fe(c) + 1/2\ O_2(g) = FeO(c)$	-65.00 ± .30	36
(17) $Mg(c) + 1/2\ O_2(g) = MgO(c)$	-143.7 ± .10	30
(18) $2Fe(c) + 1\text{-}1/2\ O_2(g) = Fe_2O_3(c)$	-197.0 ± .30	36
(19) $Mn(c) + 1/2\ O_2(g) = MnO(c)$	-92.07 ± .30	36
(20) $2Al(c) + 3S(rh) + 12\ O_2(g) + 24H_2(g) = Al_2(SO_4)_3\cdot 12H_2O(c)$	-1701.51 ± .126	21
(21) $2Al(c) + 1\text{-}1/2\ O_2(g) = Al_2O_3(c)$	-400.5 ± .3	30

$$\Delta H_{22} = \Delta H_{10} + 7.9163\Delta H_{11} + 5.2766\Delta H_{12} + 1.5209\Delta H_{13} + 5.23975\Delta H_{14} - 5.40215\Delta H_{15} + 0.06\Delta H_{18} + 0.0825\Delta H_{19} + 0.04185\Delta H_{20}$$

(22) $5.2766Fe(c) + 1.5209Mg(c) + 12Fe(c) + 0.0825Mn(c) + 7.9163Si(c) + 0.0837Al(c) + 12\ O_2(g) + 0.98185H_2(g) = [(Fe^{+2}_{5.2766}Mg_{1.5209}Fe^{+3}_{0.12}Mn_{0.0825})(Si_{7.9163}Al_{0.0837}O_{22.0363})(OH)_{1.9637}](c)$

$\Delta H_{22} = -2419.24 \pm 2.95$ kcal

$$\Delta H_{23} = \Delta H_{10} + 0.04185\Delta H_{20} + 5.2766\Delta H_{12} + 1.5209\Delta H_{13} + 4.2579\Delta H_{14} - 5.40215\Delta H_{15} - 0.04185\Delta H_{21} - 1.5209\Delta H_{17} - 5.2766\Delta H_{16}$$

(23) $5.2766FeO(c) + 1.5209MgO(c) + 0.06Fe_2O_3(c) + 0.0825MnO(c) + 7.9163SiO_2(c) + 0.04185Al_2O_3(c) + 0.98185H_2O(l) = [(Fe^{+2}_{5.2766}Mg_{1.5209}Fe^{+3}_{0.12}Mn_{0.0825})(Si_{7.9163}Al_{0.0837}O_{22.0363})(OH_{1.9637})](c)$

$\Delta H_{23} = -30.916 \pm 2.47$ kcal

To derive the heat of formation of amosite from its constituent oxides, the heats of formation of ferrous oxide (FeO), magnesium oxide (MgO), and alumina (Al_2O_3) are required, in addition to the data already quoted as represented by equations 16-17 and 21. Data for reaction 16 were from Wagman and 17 and 21 were taken from Stull and Prophet (30). The uncertainty for the value for reaction 16 was assigned. Combination of the reactions and heats according to the relationship

$$\Delta H_{23} = H_{10} + 5.2766\Delta H_{12} + 1.5209\Delta H_{13} + 4.2579\Delta H_{14} - 5.40215\Delta H_{15} - 5.2766\Delta H_{16} - 1.5209\Delta H_{17} + 0.04185\Delta H_{20} - 0.04185\Delta H_{21}$$

provides $\Delta Hf_{298.15}$ (oxides) = -30.916 ±2.47 kcal for reaction 23.

The reaction scheme for the solution calorimetric investigation of crocidolite is presented in table 5. Reactions 24-28 and 31, the heats of solution of silica, $Al_2(SO_4)_3 \cdot 12H_2O$, Fe_2O_3, $Fe(SO_4) \cdot 7H_2O$, $Mg(OH)_2$, and water, are essentially the same and were run under the same conditions as reactions 1-5 and 7, respectively, and the values are adopted directly.

Reaction 29, the heat of solution of CaO, was measured previously in this laboratory and the value of $\Delta H_{soln.}$ = -55.492 ±0.062 kcal/mole is adopted directly.

Reaction 30, the heat of solution of sodium sulfate III, was conducted in the solution resulting from reaction 29, which contained the stoichiometric amounts of materials for the preceding reactions. Six measurements of this heat gave 1.065, 1.099, 1.044, 1.064, 1.045, and 1.067 kcal/mole. The mean is 1.064 ±0.017 kcal/mole.

Reaction 32, the heat of solution of sulfuric acid, is identical to reaction 8; however, the stoichiometry requires a much smaller sample and sulfate tends to act erratically. This reaction was therefore repeated in a new charge of acid containing the same amount of $K_2Cr_2O_7$ that was added for reaction 1. Six measurements gave 6.263, 6.237, 6.277, 6.265, 6.246, and 6.207 kcal/mole. The mean is 6.249 ±0.020 kcal/mole.

Reaction 33, the heat of solution of the mineral crocidolite, was determined in the acid solution resulting from reaction 32. Seven determinations provided -470.951, -470.766, -472.107, -470.486, -470.496, -471.195, and -470.850. The mean is -470.940 ±0.44 kcal/mole. This value is for the natural mineral represented by the extended formula and gram formula weight shown in table 2. The thermal correction for adsorbed water (H_2O; 0.65 kcal), the weight percentage correction for this excess water, and the total net corrections for impurity substitutions (-0.027 kcal) were made, then values were corrected to the adjusted gram formula weight. A final value of -475.63 ±0.88 kcal/mole was obtained. This uncertainty includes an allowance for the uncertainty involved in the impurities correction procedure.

TABLE 5. - Reaction scheme for crocidolite

Reaction	$\Delta H_{298.15}$, kcal	Uncertainty, ± kcal
(24) $7.971SiO_{2(c,25^\circ)} + 47.826HF_{(sol,73.7^\circ)} = 7.971H_2SiF_{6(sol,73.7)} + 15.942H_2O_{(sol,73.7^\circ)}$	-262.254	0.183
(25) $0.0145Al_2(SO_4)_3 \cdot 12H_2O_{(c,25^\circ)} = 0.029Al^{+3}_{(sol,73.7^\circ)} + 0.0435SO_4^{-2}{}_{(sol,73.7^\circ)}$ $+ 0.174H_2O_{(sol,73.7^\circ)}$	-0.251	.001
(26) $1.012Fe_2O_{3(c,25^\circ)} + 6.072H^+_{(sol,73.7^\circ)} = 2.024Fe^{+3}_{(sol,73.7^\circ)} + 3.036H_2O_{(sol,73.7^\circ)}$	-42.515	.034
(27) $2.501FeSO_4 \cdot 7H_2O_{(c,25^\circ)} = 2.501Fe^{+3}_{(sol,73.7^\circ)} + 2.501SO_4^{-2}{}_{(sol,73.7^\circ)}$ $+ 17.507H_2O_{(sol,73.7^\circ)}$	-50.323	.057
(28) $0.475Mg(OH)_{2(c,25^\circ)} + 0.95Hf_{(sol,73.7^\circ)} = 0.475MgF_{2(p,73.7^\circ)} + 0.95H_2O_{(sol,73.7^\circ)}$	-8.7775	.057
(29) $0.100CaO_{(c,25^\circ)} + 0.2HF_{(sol,73.7^\circ)} = 0.100CaF_{2(p,73.7^\circ)} + 0.1H_2O_{(sol,73.7^\circ)}$	-5.5492	.006
(30) $0.95Na_2SO_{4(c,25^\circ)} = 1.9Na^+_{(sol,73.7^\circ)} + 0.95SO_4^{-2}{}_{(sol,73.7^\circ)}$	1.011	.015
(31) $10.7525H_2O_{(l,25^\circ)} = 10.7525H_2O_{(sol,73.7^\circ)}$	8.860	.009
(32) $3.4945H_2SO_4 \cdot 7H_2O_{(l,25^\circ)} = 6.989H^+_{(sol,73.7^\circ)} + 3.4945SO_4^{-2}{}_{(sol,73.7^\circ)}$ $+ 24.4615H_2O_{(sol,73.7^\circ)}$	21.837	.070
(33) $[(Na_{1.9}Ca_{0.1})(Fe^{+3}_{2.024}Fe^{+2}_{2.501}Mg_{0.475})(Si_{7.971}Al_{0.029}O_{22.095})(OH)_{1.905}]_{(c,25^\circ)}$ $+ 48.976HF_{(sol,73.7^\circ)} + 13.061H^+_{(sol,73.7^\circ)} = 1.9Na^+_{(sol,73.7^\circ)} + 0.1CaF_{2(p,73.7^\circ)}$ $+ 2.024Fe^{+3}_{(sol,73.7^\circ)} + 2.501Fe^{+3}_{(sol,73.7^\circ)} + 0.475MgF_{2(p,73.7^\circ)}$ $+ 7.971H_2SiF_{6(sol,73.7^\circ)} + 0.029Al^{+3}_{(sol,73.7^\circ)} + 24H_2O_{(sol,73.7^\circ)}$	-475.630	.880

$$\Delta H_{34} = \Delta H_{24} + \Delta H_{25} + \Delta H_{26} + \Delta H_{27} + \Delta H_{28} + \Delta H_{29} + \Delta H_{30} + \Delta H_{31} - \Delta H_{32} - \Delta H_{33}$$

(34) $7.971SiO_{2(c,25^\circ)} + 0.0145Al_2(SO_4)_3 12H_2O_{(c,25^\circ)} + 1.012Fe_2O_{3(c,25^\circ)}$

$+ 2.501FeSO_4 \cdot 7H_2O_{(c,25^\circ)} + 0.475Mg(OH)_{2(c,25^\circ)} + 0.1CaO_{(c,25^\circ)} + 0.95Na_2SO_{4(c,25^\circ)}$

$+ 10.7525H_2O_{(l,25^\circ)} = [(Na_{1.9}Ca_{0.1})$

$(Fe^{+3}_{2.024}Fe^{+2}_{2.501}Mg_{0.475})(Si_{7.971}Al_{0.029}O_{22.095})(OH)_{1.905}]_{(c,25^\circ)}$

$+ 3.4945H_2SO_4 7H_2O_{(l,25^\circ)}$

$\Delta H_{34} = +93.994 \pm 0.906$ kcal

The final solution after conducting reactions 24 through 31 is identical with the solution obtained after conducting reactions 32 and 33, consecutively. Therefore, the sum of the heats of reactions 32 and 33 may be subtracted from the sum of the heats of reactions 24 through 31 to obtain the heat of the overall calorimetric reaction 34. The heat is determined to be 93.994 ±0.906 kcal.

To derive the enthalpy of formation of crocidolite from the constituent elements and oxides, the enthalpy of formation of calcium oxide, sodium sulfate, and sodium oxide are required in addition to the data already presented. Table 6 lists these reactions, their enthalpy of formation values and uncertainties, and the reference to their source. The value for reaction 35 is from Parker (26), the value for reaction 36 is taken from Stull, and the value for reaction 37 was from O'Hare (24).

The combination of these and previously presented reactions and enthalpy changes in accordance with the following procedure yields $\Delta Hf^{\circ}_{298.15}$ for reaction 38, $\Delta H_{38} = \Delta H_{34} + 7.971\Delta H_{11} + 2.501\Delta H_{12} + 0.475\Delta H_{13} + 10.7525\Delta H_{14} + 1.012\Delta H_{18} + 0.95\Delta H_{38} + 0.0145\Delta H_{20} - 3.4945\Delta H_{15} + 0.1\Delta H_{35}$; the standard enthalpy of formation is $\Delta Hf^{\circ}_{298.15} = -2433.562 \pm 2.987$ kcal/mole.

The enthalpy of formation of crocidolite from the constituent oxides may be derived by the combination of reactions and enthalpy changes according to the following scheme:

$$\begin{aligned} \Delta H_{39} = {} & \Delta H_{34} + 2.501\Delta H_{12} + 0.475\Delta H_{13} + 9.8\Delta H_{14} - 3.4945\Delta H_{15} \\ & - 2.501\Delta H_{16} - 0.475\Delta H_{17} + 0.95\Delta H_{36} - 0.95\Delta H_{37} + 0.0145\Delta H_{20} \\ & - 0.0145\Delta H_{21}, \end{aligned}$$

which provides

$$\Delta Hf^{\circ}_{298.15} \text{ (oxides)} = -87.687 \pm 1.698 \text{ kcal/mole.}$$

TABLE 6. - Enthalpy of formation of crocidolite

Reaction	$\Delta H_{298.15}$, kcal/mole	Reference
(35) $Ca(c) + 1/2\ O_2(g) = CaO(c)$	-151.79 ±0.3	26
(36) $2Na(c) + S(rh) + 2\ O_2(g) = Na_2SO_4III(c)$	-331.005± .3	30
(37) $2Na(c) + 1/2\ O_2(g) = Na_2O(c)$	-99.14 ±1.0	24
$\Delta H_{38} = \Delta H_{34} + 0.1\Delta H_{35} + 0.95\Delta H_{36} + 7.971\Delta H_{11} + 2.501\Delta H_{12} + 0.475\Delta H_{13}$ $+ 10.7525\Delta H_{14} - 3.4945\Delta H_{15} + 1.012\Delta H_{18} + 0.0145\Delta H_{20}$		
(38) $7.971Si + 0.029Al + 2.024Fe + 2.501Fe + 0.475Mg + 0.1Ca + 1.9Na$ $+ 12\ O_2 + 0.9525H_2 = [(Na_{1.9}Ca_{0.1})(Fe^{+3}_{2.024}Fe^{+2}_{2.501}Mg_{0.475})$ $(Si_{7.971}Al_{0.029}O_{22.095})(OH)_{1.905}]$ $\Delta H_{38} = -2433.562 \pm 2.987$ kcal/mole		
$\Delta H_{39} = \Delta H_{34} + 2.501\Delta H_{12} + 0.475\Delta H_{13} + 9.8\Delta H_{14} - 3.4945\Delta H_{15} - 2.501\Delta H_{16}$ $- 0.475H_{17} + 0.0145\Delta H_{20} - 0.0145\Delta H_{21} + 0.95\Delta H_{36} - 0.95\Delta H_{37}$		
(39) $1.012Fe_2O_3 + 2.501FeO + 0.0145Al_2O_3 + 0.475MgO + 0.1CaO + 0.95Na_2O$ $+ 7.971SiO_2 + 0.9525H_2O = [(Na_{1.9}Ca_{0.1})(Fe^{+3}_{2.024}Fe^{+2}_{2.501}Mg_{0.475})$ $(Si_{7.971}Al_{0.029}O_{22.095})(OH)_{1.905}]$ $\Delta H_{39} = -87.687 \pm 1.687$ kcal/mole		

Low-Temperature Thermal Properties

Heat capacity measurements were made with a precision adiabatic calorimeter in the nominal temperature range 5 to 315 K. A detailed description of the apparatus is given elsewhere (31). The volume of the calorimeter sample container used was 90 ml. Heat capacity of the empty calorimeter-thermometer-heater assembly varied from 0.01 cal/K at 6 K to 9 cal/K at 300 K. A National Bureau of Standards (NBS) calibrated platinum resistance thermometer was used to determine sample temperatures according to IPTS-68 over the range 15 to 315 K. Temperatures below 15 K were measured with an NBS calibrated germanium thermometer. All auxiliary measurements related to mass, time, and electric potential are traceable to NBS calibrations.

Selected fibrous bundles of the amosite and crocidolite minerals were separately ground in a small hammermill providing a fluffy, low bulk density material of less than 0.2 mm fiber length. The pulverized minerals were compacted with a hydraulic press to form cylindrical pellets about 2.0 cm wide and 0.5 cm high. These compacts were crushed and screened to uniform-size pieces (about 0.3 cm wide) that would fit through the neck of the low-temperature calorimeter sample container. Prior to loading the processed amosite and crocidolite, granules were oven-dried in air at 110° C for 48 hours.

The sample masses of amosite and crocidolite were 29.283 and 37.137 g, respectively. About 10^{-5} g mole of helium gas was sealed with each sample after evacuating air from the sample container to facilitate thermal response during low-temperature measurements.

The results of the heat capacity measurements are tabulated in tables 7-8 for amosite and crocidolite. These experimental data are also presented in figures 1-2. The tabulated experimental data have been corrected for curvature and impurities to the adjusted formula. A slight bump was noted at about 35 K in the amosite Cp curve. In the crocidolite curve there is a definite anomaly centered at 31.3 K.

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

T, K	C_p°, cal/deg mole	T, K	C_p°, cal/deg mole	T, K	C_p°, cal/deg mole
7.76.....	2.47	40.33....	20.19	137.94....	86.91
9.28.....	3.02	44.01....	22.11	148.34....	93.74
11.02.....	3.76	47.83....	23.99	160.58....	101.40
12.80.....	4.40	52.56....	26.45	172.98....	108.80
14.59.....	5.23	58.01....	29.62	186.53....	116.50
16.26.....	6.10	63.53....	33.04	200.41....	123.90
18.24.....	7.24	69.01....	36.60	214.69....	131.30
19.91.....	8.25	77.79....	43.05	229.06....	137.90
21.89.....	9.71	85.02....	48.31	243.18....	144.30
24.15.....	11.60	91.04....	52.84	257.03....	149.70
26.83.....	12.61	97.85....	57.98	270.64....	154.80
30.05.....	14.47	106.46....	64.53	282.87....	158.90
33.34.....	16.29	116.75....	72.05	296.18....	162.80
36.74.....	18.25	127.48....	79.78	309.33....	166.40

TABLE 8. - Experimental low-temperature heat capacities of crocidolite

T, K	C_p°, cal/deg mole	T, K	C_p°, cal/deg mole	T, K	C_p°, cal/deg mole
11.77.....	2.65	33.66....	16.01	142.19....	88.62
12.81.....	3.75	35.93....	15.00	148.82....	93.28
14.06.....	4.12	40.23....	15.49	158.25....	99.11
15.38.....	4.72	45.17....	17.93	168.21....	104.80
16.75.....	5.46	50.33....	20.18	179.09....	110.90
18.04.....	6.11	55.59....	23.56	190.65....	117.20
19.46.....	6.81	61.22....	27.57	202.38....	123.20
21.12.....	7.96	66.75....	31.77	213.83....	130.10
22.91.....	9.26	72.81....	36.30	225.04....	134.20
24.57.....	10.62	79.90....	42.11	236.31....	138.80
26.97.....	12.54	85.31....	46.64	247.70....	143.40
28.35.....	14.91	94.18....	53.56	258.91....	147.80
29.48.....	16.55	103.40....	60.37	270.09....	151.90
30.67.....	18.16	112.68....	67.49	280.85....	155.90
31.64.....	18.31	122.09....	74.52	292.04....	160.20
32.36.....	17.40	131.91....	81.58	303.13....	163.20

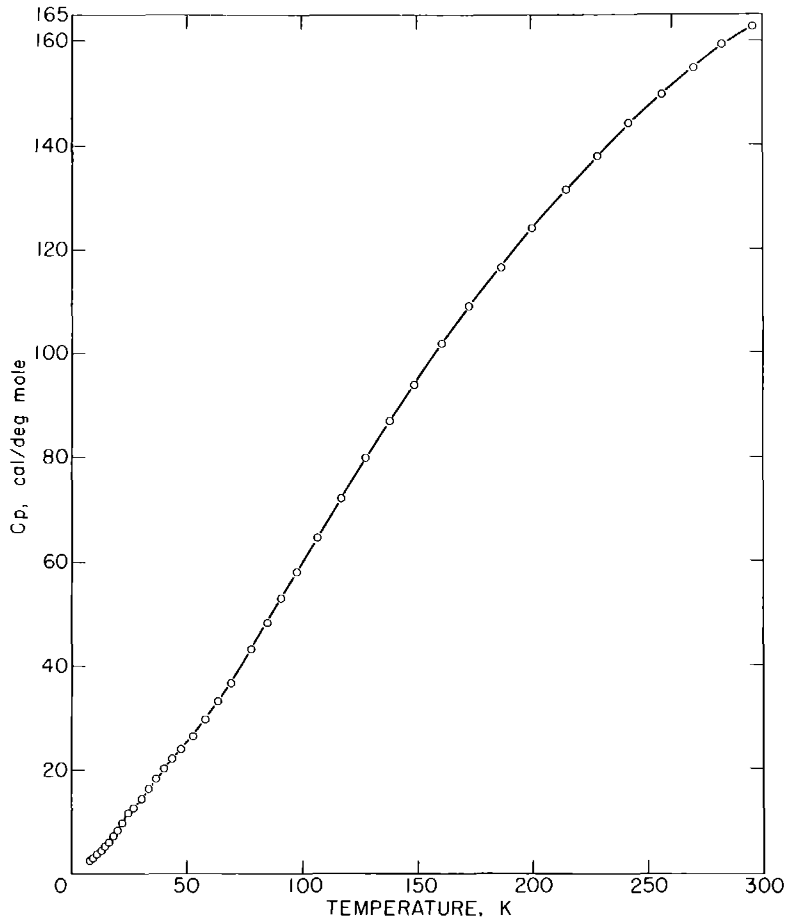

FIGURE 1. - Low-temperature heat capacity of amosite.

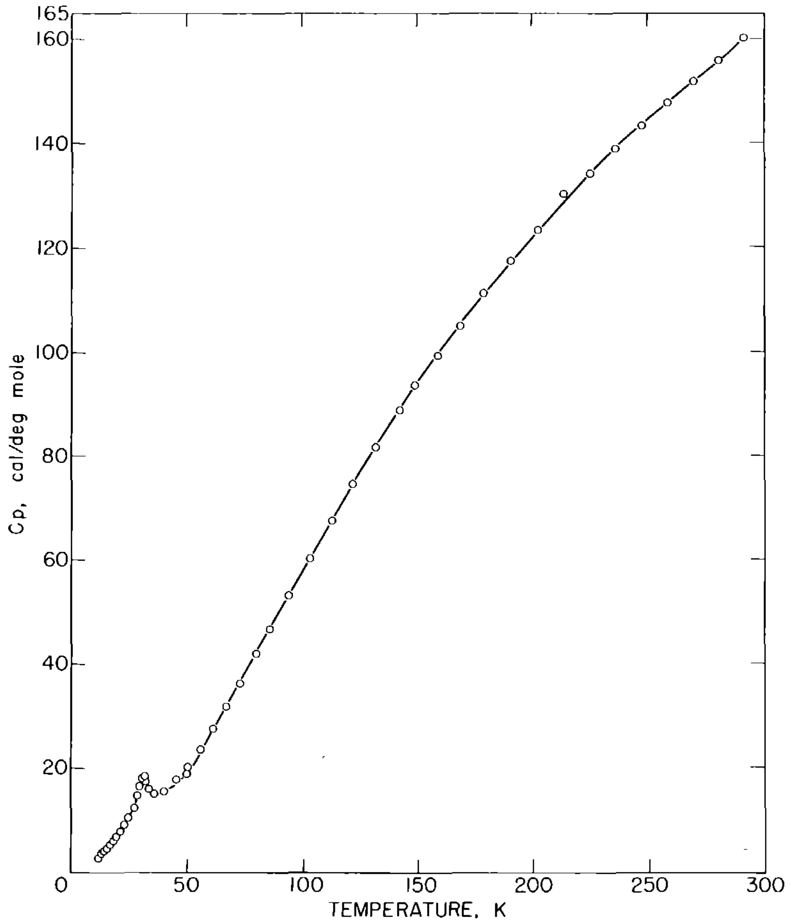

FIGURE 2. - Low-temperature heat capacity of crocidolite.

The experimental data were transformed by computer fitting to representative polynomials, which in turn were used to calculate Cp at even temperatures. These data are tabulated in tables 9-10. The entropies and related functions are also listed. Heat capacities below the temperature range of experimental values were estimated by extrapolation of Cp/T as a function of T^3.

TABLE 9. - Low-temperature thermodynamic properties of amosite

T, K	Cal/deg mole			Cal/mole,
	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$
10	3.27	2.84	1.31	15.33
15	5.44	4.56	2.10	36.90
20	8.34	6.49	2.95	70.86
30	14.35	11.15	4.89	187.75
35	17.23	13.58	5.96	266.77
40	19.95	16.06	7.07	359.78
45	22.58	18.57	8.21	466.13
50	25.20	21.08	9.37	585.6
60	30.85	26.16	11.74	865.2
70	37.45	31.40	14.17	1,205.9
80	44.63	36.87	16.67	1,615.9
90	52.14	42.56	19.23	2,099.6
100	59.80	48.44	21.85	2,659.2
110	67.42	54.50	24.54	3,295.4
120	74.87	60.69	27.30	4,007.0
130	82.06	66.97	30.11	4,791.9
140	88.93	73.30	32.96	5,647
150	95.49	79.66	35.87	6,569
160	101.73	86.03	38.81	7,556
170	107.68	92.37	41.76	8,603
180	113.37	98.69	44.76	9,708
190	118.82	104.97	47.76	10,870
200	124.06	111.20	50.78	12,084
210	129.09	117.37	53.80	13,350
220	133.90	123.49	56.83	14,665
230	138.47	129.54	59.86	16,027
240	142.80	135.53	62.89	17,434
250	146.87	141.44	65.91	18,882
260	150.66	147.28	68.93	20,370
270	154.19	153.03	71.94	21,895
273.15	155.25	154.82	72.83	22,382
280	157.46	158.70	74.94	23,453
290	160.49	164.28	77.92	25,043
298.15	162.78	168.76	80.34	26,361
300	163.27	169.76	80.89	26,662

TABLE 10. - Low-temperature thermodynamic properties of crocidolite

T, K	Cal/deg mole			Cal/mole,
	C_p°	S°	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$
10	2.45	1.65	0.682	9.68
15	4.59	3.04	1.23	27.16
20	7.19	4.69	1.88	56.20
25	10.82	6.69	2.64	101.24
26	11.21	7.12	2.80	112.29
36	15.08	12.23	4.72	270.30
40	16.19	13.87	5.55	332.71
45	18.03	15.88	6.59	418.03
50	20.37	17.90	7.62	513.8
60	26.40	22.12	9.68	746.3
70	33.76	26.73	11.78	1,046.3
80	41.84	31.76	13.96	1,423.9
90	50.10	37.16	16.23	1,883.7
100	58.21	42.87	18.62	2,425.5
110	65.96	48.78	21.08	3,046.6
120	73.30	54.84	23.65	3,743.2
130	80.28	60.98	26.28	4,511.4
140	86.96	67.18	28.98	5,348
150	93.41	73.40	31.73	6,250
160	99.66	79.63	34.54	7,215
170	105.70	85.85	37.37	8,242
180	111.60	92.06	40.23	9,329
190	117.20	98.24	43.12	10,473
200	122.40	104.40	46.05	11,671
210	127.30	110.50	48.98	12,920
220	131.90	116.50	51.88	14,216
230	136.20	122.50	54.86	15,557
240	140.30	128.40	57.82	16,939
250	144.30	134.20	60.75	18,362
260	148.20	139.90	63.65	19,825
270	152.00	145.60	66.61	21,326
273.15	153.20	147.30	67.42	21,806
280	155.80	151.20	69.54	22,864
290	159.20	156.70	72.43	24,439
298.15	161.70	161.10	74.74	25,747
300	162.30	162.10	75.28	26,046

The relative error of Cp measurements was estimated as 0.1 pct in the temperature range from 50 to 320 K; below 25 K, the error increases gradually to about 5 pct below 10 K. Because of the small fraction of a mole used for measurements and the relatively large molar corrections, the entropies and uncertainties assigned to amosite and crocidolite are 168.8 ±5 cal/deg-mole, and 161.1 ±4 cal/deg-mole, respectively, at 298.15 K.

High-Temperature Enthalpy Determinations

High-temperature enthalpies above 298.15 K were determined with the copper-block drop calorimeter described by Douglas and King (9). This apparatus has been modified to incorporate a more sensitive potentiometer system.

The sample containers were composed of a platinum-10-pct rhodium alloy. Enthalpies of empty containers were determined in separate experiments. The low density of the asbestos compounds of this study required determinations to be made with hammer-milled samples that were compacted and transferred directly into the sample container. They were then dried to constant weight by heating at 500 K in air for amosite and at 700 K in nitrogen for crocidolite. For either mineral, the X-ray diffraction patterns of the original and dried samples were identical. Sample masses were 13.6802 g of amosite and 12.6865 g of crocidolite.

Experimental enthalpies were corrected for impurities according to the adjusted formula. The resulting standard-state enthalpy values are listed in table 11 and plotted in figures 3-4 as the function $(H_T - H_{298.15})/(T - 298.15\ K)$. These figures show no irregularities in the thermal behavior of either compound. The standard error of measurement is 0.1 pct for amosite and 0.2 pct for crocidolite. The absolute uncertainty in each case is estimated to be ±0.4 pct. Determinations for amosite were limited to 852 K, because the platinum container ruptured during heating to 903 K. Vermaas (33) determined, by differential thermal analysis (DTA), that amosite decomposes and evolves water in the temperature range of 923 to 1,008 K. The rupture of the capsule was most likely caused by this decomposition. Enthalpy experiments with crocidolite were discontinued during heating to 1,001 K, when a leak developed in the platinum capsule. The container had not swelled to the usual rupture limit, indicating that the leak probably occurred at a thin spot in the container wall. Enthalpy experiments for crocidolite were terminated well below the 1,163 to 1,234 K range where water is expelled. This temperature range, however, represents the peaks of the differential thermal analysis curves determined by Vermaas, whereas the slope began to change between 925 to 1,100 K.

TABLE 11. - Experimental enthalpies above 298.15 K

T, K	$H^\circ - H^\circ_{298}$, cal/mole	T, K	$H^\circ - H^\circ_{298}$, cal/mole
AMOSITE		CROCIDOLITE	
402.9	18,530	402.6	18,270
451.1	27,960	450.6	27,480
503.0	38,640	502.8	37,880
555.5	49,910	601.5	58,680
601.7	60,100	702.2	80,890
652.6	71,640	802.1	104,100
702.9	83,230	901.7	127,000
753.4	95,180		
802.9	107,000		
851.7	118,900		

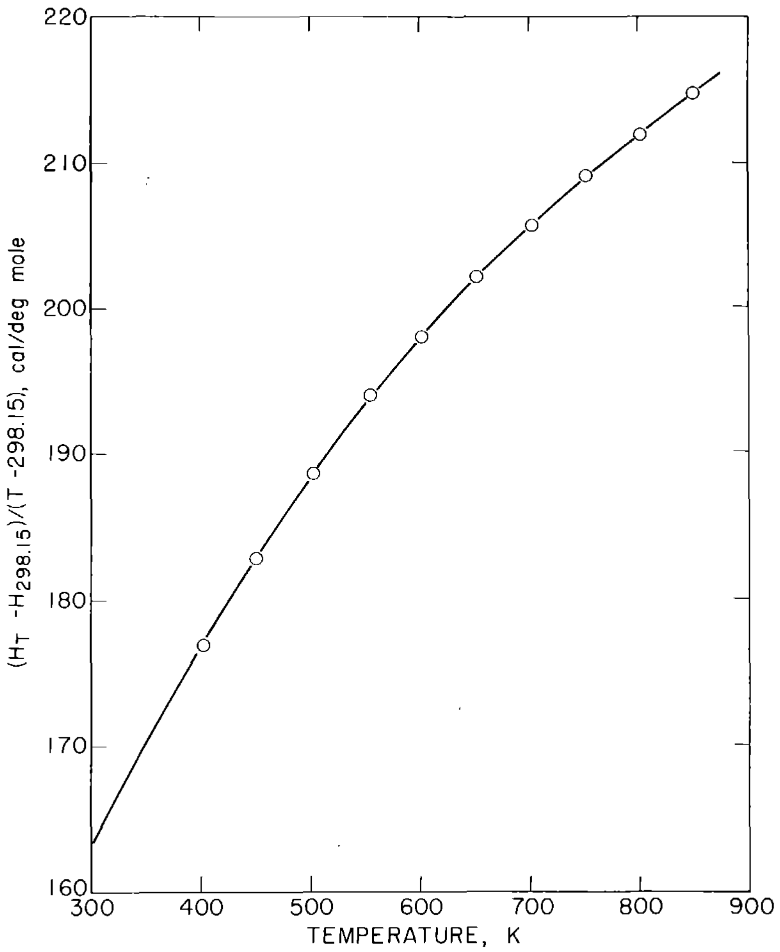

FIGURE 3. - High-temperature enthalpy function of amosite.

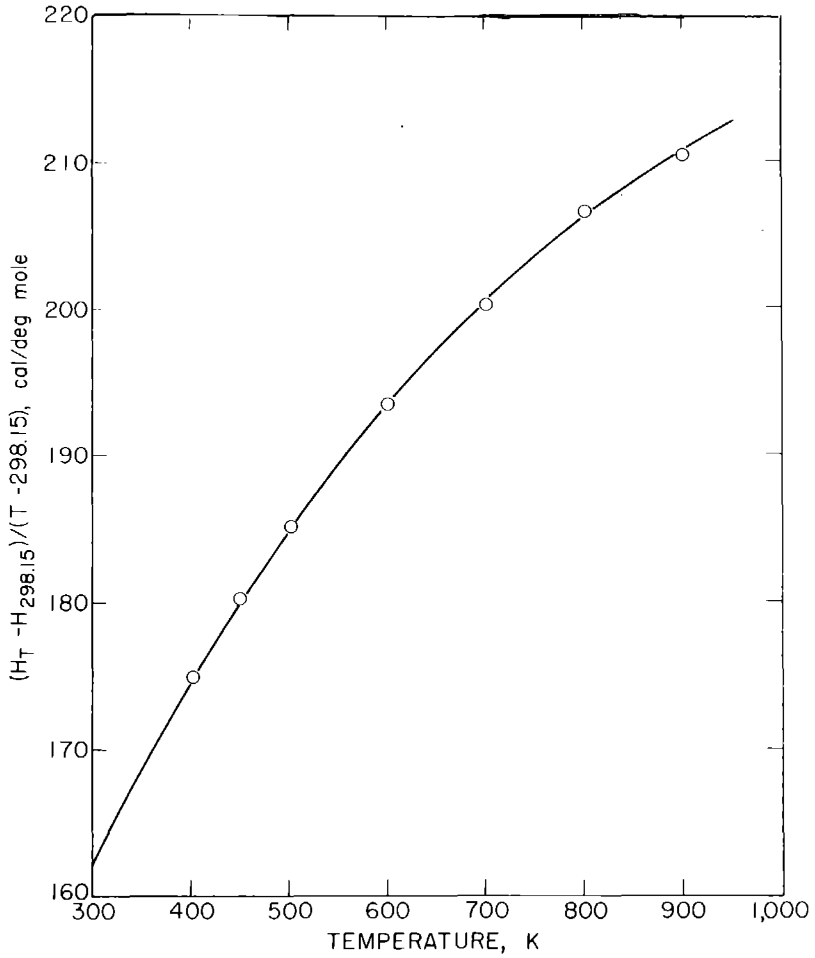

FIGURE 4. - High-temperature enthalpy function of crocidolite.

Polynomial functions (16) were fitted to the experimental enthalpy values with the aid of a computer. These functions were used to calculate smooth enthalpy increments above 298.15 K at selected temperatures, and to derive related thermodynamic properties which appear in tables 12-13 for amosite and crocidolite.

The standard form equations derived by Kelley's method (17) to represent the smooth enthalpy increments follow. Both the percent average deviation of the equation from the experimental enthalpy data and the temperature range of validity are given in parentheses.

Amosite: $H_T^\circ - H_{298.15}^\circ = 180.763T + 42.492 \times 10^{-3}T^2 + 38.491 \times 10^5 T^{-1} - 70{,}582$ cal/mole (0.4 pct, 298 - 1,000 K)

Crocidolite: $H_T^\circ - H_{298.15}^\circ = 191.906T + 27.490 \times 10^{-3}T^2 + 41.423 \times 10^5 T^{-1} - 73{,}554$ cal/mole (0.6 pct, 298 - 1,100 K).

TABLE 12. - Enthalpies and Gibbs energies for the formation of amosite from the elements $5.3966Fe(c) + 1.5209Mg(c) + 0.0825Mn(c) + 7.9163Si(c) + 0.0837Al(c) + 12O_2(g) + 0.98185H_2(g) = [(Fe^{+2}_{5.2766}Mg_{1.5209}Fe^{+3}_{0.12}Mn_{0.0825})(Si_{7.9163}Al_{0.0837}O_{22.0363})(OH)_{1.9637}](c)$

T, K	Cal/deg mole			Kcal/mole			Log Kf
	C_p°	S°	$-(G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔHf°	ΔGf°	
298.15....	162.8	168.8	168.8	0	-2,419.2	-2,260.1	1,656.70
300.......	163.3	169.8	168.8	.30	-2,419.3	-2,259.1	1,645.75
400.......	189.8	220.5	175.5	18.00	-2,419.2	-2,205.7	1,205.14
500.......	209.6	265.1	189.1	38.02	-2,417.7	-2,152.5	940.86
600.......	223.5	304.6	205.1	59.71	-2,415.4	-2,099.6	764.78
700.......	233.4	339.9	221.9	82.58	-2,412.7	-2,047.2	639.16
800.......	241.1	371.6	238.7	106.30	-2,409.9	-1,995.2	545.06
900.......	247.3	400.3	255.0	130.80	-2,407.3	-1,943.4	471.92
[1] 922.......	248.2	406.3	258.5	136.25	-2,406.8	-1,932.1	457.98
922.......	248.2	406.3	258.5	136.25	-2,410.0	-1,932.1	457.98
[2] 933.52....	248.7	409.4	260.4	139.11	-2,409.8	-1,926.1	450.93
933.52....	248.7	409.4	260.4	139.11	-2,410.0	-1,926.1	450.93
[3] 980.......	250.7	421.5	267.7	150.68	-2,409.2	-1,902.1	424.19
980.......	250.7	421.5	267.7	150.68	-2,409.2	-1,902.1	424.19
1,000......	251.6	426.6	270.9	155.70	-2,408.9	-1,891.7	413.43

[1] Melting point of Mg.
[2] Melting point of Al.
[3] Transition point of Mn.

TABLE 13. - Enthalpies and Gibbs energies for the formation of crocidolite from the elements $4.525\mathrm{Fe(c)} + 7.971\mathrm{Si(c)} + 0.475\mathrm{Mg(c,l)} + 1.9\mathrm{Na(c,l)} + 0.1\mathrm{Ca(c)} + 0.029\mathrm{Al(c)} + 12\mathrm{O_2(g)} + 0.9525\mathrm{H_2(g)}$
$= [(\mathrm{Na_{1.9}Ca_{0.1}})(\mathrm{Fe^{+3}_{2.024}Fe^{+2}_{2.501}Mg_{0.475}})$
$(\mathrm{Si_{7.971}Al_{0.029}O_{22.095}})(\mathrm{OH})_{1.905}](\mathrm{c})$

T, K	Cal/deg mole			Kcal/mole			Log Kf
	C°_p	S°	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	ΔHf°	ΔGf°	
298.15....	161.7	161.1	161.1	0	-2,433.6	-2,269.8	1,663.81
300.......	162.3	162.1	161.1	.30	-2,433.6	-2,268.8	1,652.82
[1]371[1]......	179.1	198.5	164.9	12.48	-2,433.9	-2,229.7	1,313.48
371.......	179.1	198.5	164.9	12.48	-2,435.1	-2,229.7	1,313.48
400.......	186.0	212.2	167.8	17.77	-2,435.1	-2,213.7	1,209.51
500.......	204.0	255.7	181.1	37.31	-2,434.2	-2,158.4	943.44
600.......	217.0	294.1	196.8	58.39	-2,432.5	-2,103.4	766.16
700.......	225.9	328.3	213.2	80.56	-2,430.4	-2,048.7	639.63
[2]720.......	227.0	334.7	216.5	85.09	-2,429.9	-2,037.8	618.56
720.......	227.0	334.7	216.5	85.09	-2,430.0	-2,037.8	618.56
800.......	231.5	358.8	229.4	103.50	-2,428.2	-1,994.2	544.79
900.......	234.8	386.3	245.4	126.80	-2,426.4	-1,940.1	471.12
[3]922.......	235.2	392.0	248.9	131.97	-2,426.1	-1,928.3	457.08
922.......	235.2	392.0	248.9	131.97	-2,427.1	-1,928.3	457.08
[4]933.52....	235.4	394.9	250.6	134.68	-2,426.9	-1,922.0	449.97
933.52....	235.4	394.9	250.6	134.68	-2,427.0	-1,922.0	449.97
1,000.....	236.6	411.2	260.8	150.40	-2,426.4	-1,886.1	412.21
[5]1,043.....	237.2	421.2	267.2	160.59	-2,426.6	-1,862.8	390.33
1,100.....	237.9	433.8	275.5	174.10	-2,426.3	-1,832.1	364.00

[1] Melting point of Na.
[2] Transition point of Ca.
[3] Melting point of Mg.
[4] Melting point of Al.
[5] Curie temperature of Fe.

Enthalpies and Gibbs Energies of Formation and Reaction

The experimental data for amosite and crocidolite presented in the previous section of this report may be combined with the necessary data for the constituent elements and oxides to permit the calculation of enthalpies and free energies of formation. Table 14 gives the data sources for the reaction constituents not previously quoted. The type of transition or phase change is indicated with each element or compound. The type of data used, whether complete thermodynamic, entropy, enthalpy, or high- and low-temperature calorimetric, is listed as well as the number of the reference. Selected data were corrected according to the International Temperature Scale of 1968 (8).

TABLE 14. - Auxiliary thermodynamic data

Element or compound and transition	Function	Source	Reference No.
CaO	$\Delta H^\circ f_{298}$	Parker, Wagman, and Evans	26
Fe(α)		Hultgren, Desai, Hawkins, Gleiser, Kelley, and Wagman.	13
FeO	$Fe_{0.947}O$	Kelley and King	18
	$\Delta H^\circ f$	Wagman, Evans, Parker, Halow, Bailey, and Schumm.	36
	S_{298}	Stull and Prophet	30
Fe_2O_3(α,β)	HT	Coughlin	6
	$H^\circ f_{298}$	Wagman, Evans, Parker, Halow, Bailey, and Schumm.	36
	S_{298}	.....do	36
		Stull and Prophet	30
Fe_3O_4(α,β)	LT	Westrum and Grønvold	37
	HT	Coughlin	6
	$H^\circ F_{298}$	Coughlin, King, and Bonnickson	5
O_2		Stull and Prophet	30
H_2(g)		.....do	30
H_2O(l,g)	Liquid	Ginnings and Furukawa	10
	Gas	Stull and Prophet	30
	$\Delta H^\circ vap_{298}$	Wagman, Evans, Parker, Halow, Bailey, and Schumm.	35
	S_{298}	.....do	35
Mg(s,l)		Hultgren, Desai, Hawkins, Gleiser, Kelley, and Wagman.	13
MgO(s)	LT	Barron, Berg, and Morrison	2
	HT	Pankratz and Kelley	25
		Victor and Douglas	34
	$\Delta H^\circ f_{298}$	Stull and Prophet	30
Na(s,l)		Hultgren	12
Na_2O(α,β)	$\Delta H^\circ f$	O'Hare	24
	S°		
	H_T-H_{298}	Stull and Prophet	30
Si(s,l)	0, 100, 200 K	Hultgren, Desai, Hawkins, Gleiser, Kelley, and Wagman.	13
		Stull and Prophet	30
SiO_2(α,β)	$\Delta H^\circ f_{298}$	Wise, Feder, and Hubbard	38
		Stull and Prophet	30

Tables 12 and 15 give the enthalpy and Gibbs energy values for the formation of amosite from the constituent elements and oxides. For the formation reaction from the elements, the enthalpy changes and Gibbs energies are similar and fairly constant over the range of the measurements which indicates that amosite is stable relative to the elements. The Gibbs energy values for the formation from the oxides show that the stability of amosite relative to the oxides decreases with increasing temperature to approximately 924 K, the point where the Gibbs energy of formation is zero.

TABLE 15. - Enthalpies and Gibbs energies for the formation of amosite from the oxides $5.2766FeO(c) + 1.5209MgO(c) + 0.06Fe_2O_3(c) + 0.0825MnO(c) + 7.9163SiO_2(c) + 0.04185Al_2O_3 + 0.98185H_2O(l,g) = [(Fe^{+2}_{5.2766}Mg_{1.5209}Fe^{+3}_{0.12}Mn_{0.0825})(Si_{7.9163}Al_{0.0837}O_{22.0363})(OH)_{1.9637}](c)$

T, K	Kcal		Log K	T, K	Kcal		Log K
	ΔH°	ΔG°			ΔH°	ΔG°	
298.15	-30.9	-26.3	19.28	700	-41.6	-10.2	3.18
300	-31.0	-26.3	19.16	800	-41.6	-5.8	1.58
[1]373.15	-32.2	-25.0	14.64	[2]847	-41.8	-3.7	.95
373.15	-41.8	-25.0	14.64	847	-43.2	-3.7	.95
400	-41.9	-23.8	13.00	900	-42.5	-1.1	.27
500	-42.1	-19.2	8.39	[3]960	-41.8	1.6	-.36
600	-41.9	-14.7	5.35	1,000	-41.2	3.4	-.74

[1] Boiling point of water.

[2] Transition point of quartz.

[3] Transition point of Fe_2O_3.

The enthalpies and Gibbs energies for the reactions forming crocidolite from the constituent elements and oxides are presented in tables 13-16. Crocidolite is shown to remain stable relative to both the elements and oxides throughout the range of the data.

TABLE 16. - Enthalpies and Gibbs energies for the formation of crocidolite from the oxides $2.501FeO(c) + 1.012Fe_2O_3(c) + 0.475MgO(c) + 0.95Na_2O(c,l) + 0.1CaO(c) + 0.0145Al_2O_3(c) + 7.971SiO_2(c) + 0.9525H_2O(g) = [(Na_{1.9}Ca_{0.1}(Fe^{+3}_{2.024}Fe^{+2}_{2.501}Mg_{0.475})(Si_{7.971}Al_{0.029}O_{22.095})(OH)_{1.905}](c)$

T, K	Kcal		Log K	T, K	Kcal		Log K
	ΔH°	ΔG°			ΔH°	ΔG°	
298.15	-87.7	-84.0	61.57	[2]847	-103.0	-61.6	15.89
300	-87.7	-84.0	61.19	847	-104.3	-61.6	15.89
[1]373.15	-89.0	-82.9	48.55	900	-104.7	-59.0	14.33
373.15	-98.3	-82.9	48.55	[3]960	-105.5	-56.0	12.75
400	-98.5	-81.8	44.69	1,000	-105.6	-53.9	11.78
500	-99.2	-77.5	33.88	[4]1,023.7	-105.7	-52.7	11.25
600	-99.8	-73.1	26.63	1,023.7	-106.1	-52.7	11.25
700	-100.7	-68.7	21.45	1,100	-106.4	-48.7	9.68
800	-102.0	-63.9	17.46				

[1] Boiling point of water.

[2] Transition point of quartz.

[3] Transition point of Fe_2O_3.

[4] Transition point of Na_2O.

DISCUSSION

There are no known previously published thermodynamic data on the two amphibole asbestos minerals studied, amosite and crocidolite. The thermodynamic properties of a pure iron grunerite were calculated by Melnick (22) from equilibrium data. He reported that S°_{298} = 187.0 cal/deg mole; ΔH°_{298} = -2,294.0 cal/mole, and ΔG°_{298} = -2,141.0 cal/mole. He also reported that the mineral is stable to 923 to 943 K, where it decomposes to fayalite, quartz, and water. Vermaas indicated that grunerite, of unreported composition, has a peak temperature before decomposition of 1,103 K.

The characteristic products of the thermal decomposition of amosite are magnetite, cristobalite, and water. This mineral structure breakdown reaction did not take place because of insufficient oxygen in the sealed platinum capsule for the oxidation of iron prior to the release of water. The enthalpy and Gibbs energies of formation from this study show amosite to be stable to approximately 924 K.

The decomposition reaction for crocidolite includes acmite ($NaFeSi_2O_6$) as one of the products in addition to hematite, silica, and water. Evaluation of this reaction will be made upon completion of a study of the thermodynamic properties of acmite. Crocidolite is shown in this study to be stable throughout the temperature range of the data.

Gibbs energies of formation and decomposition involving various constituents of these strong and flexible fiber amphibole asbestos minerals are presented to provide insight into their development. These data also provide a choice of conditions and starting materials for perfecting a synthetic preparation process.

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