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Thermodynamic Properties of Synthetic Acmite ($NaFe^{3+}Si_2O_6$)

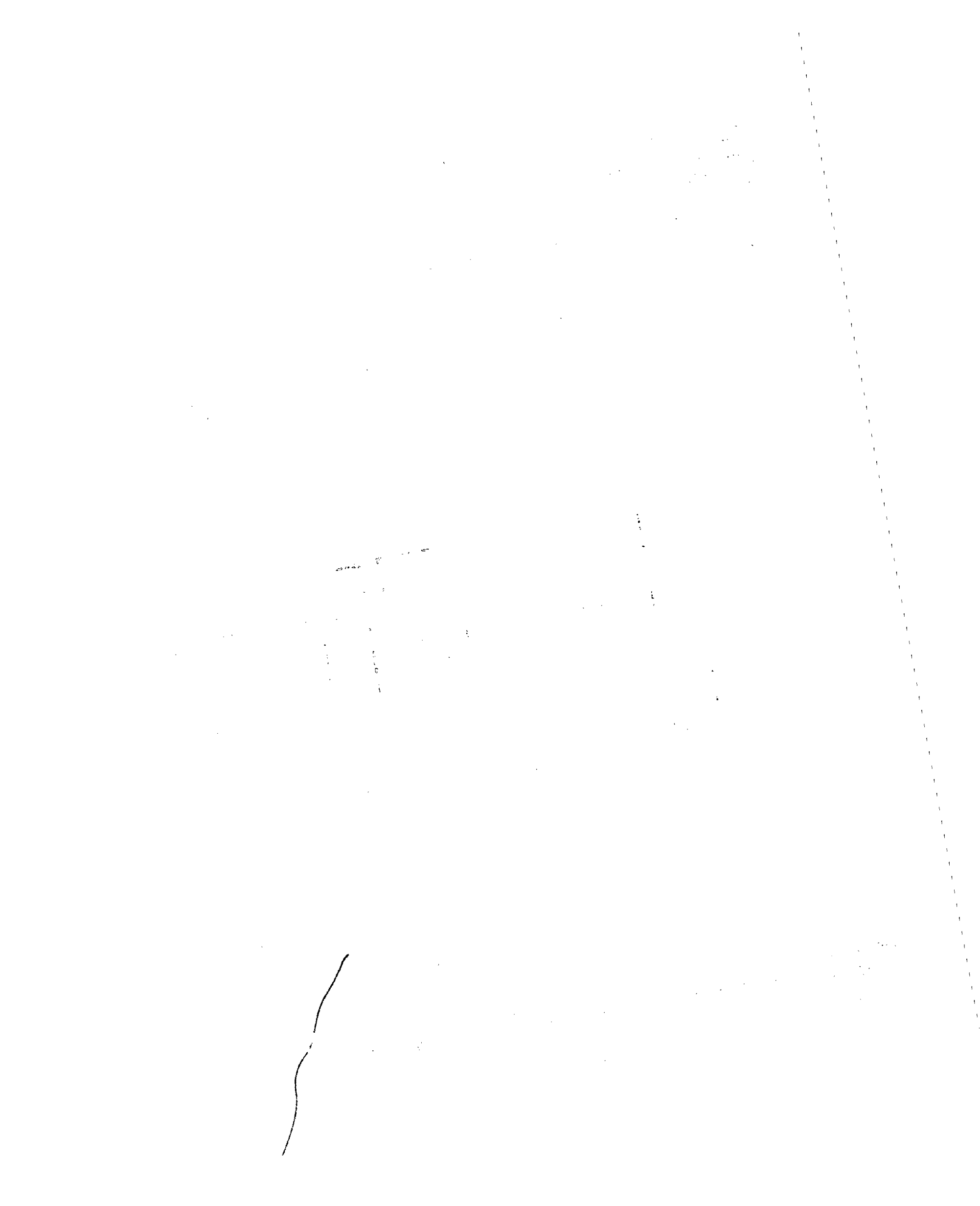By K. O. Bennington and R. R. Brown

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNITED STATES DEPARTMENT OF THE INTERIOR
James G. Watt, Secretary

BUREAU OF MINES
Robert C. Horton, Director

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THERMODYNAMIC PROPERTIES OF SYNTHETIC ACMITE ($NaFe^{3+}Si_2O_6$)

by

K. O. Bennington[1] and R. R. Brown[1]

ABSTRACT

The thermodynamic properties of synthetic acmite, $NaFe^{3+}Si_2O_6$, were determined by the Bureau of Mines. The enthalpy of formation was determined by hydrofluoric acid solution calorimetry. The values of the standard enthalpy of formation at 298.15 K, $\Delta Hf^{\circ}_{298.15}$, from the elements and from the oxides, $\Delta H^{\circ}_{298.15}$, are

$$\Delta Hf^{\circ}_{298.15} = -615.87 \; (\pm 0.71 \text{ kcal/mole},$$

$$\Delta H^{\circ}_{298.15} \text{ (from oxides)} = -32.08 \; \pm 0.53 \text{ kcal/mole}.$$

Various experimental data were combined with other data from the literature to calculate all the related thermodynamic properties in the range of 298 to 1,263 K. The standard Gibbs energy of formation is $\Delta Gf^{\circ}_{298.15} = -575.8$ kcal/mole.

INTRODUCTION

This Bureau of Mines investigation of the thermodynamic properties of synthetic acmite ($NaFe^{3+}Si_2O_6$) is one of a series on a slag-type pyroxenes, which includes the nearly identical mineral aegirine and the mineral hedenbergite ($CaFe^{2+}Si_2O_6$). A study of the acmite-aegirine pair was proposed to investigate the possible differences between the easily synthesized acmite and a natural aegirine. Aegirine, the subject of a forthcoming study, has not been obtainable in suitable purity to make the anticipated critical comparison. The low-temperature heat capacities and the high-temperature enthalpies for acmite have been reported by Ko (15).[2]

These pyroxene minerals readily assimilate manganese; consequently, this study contributes toward both the future investigation of some manganese minerals and the understanding of slag action in iron refining. This investigation is part of the Bureau of Mines research program for advancing mineral technology and simplifying the extraction and purification of metals and oxides.

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

MATERIALS

Acids

The hydrofluoric acid was a reagent-grade product (Mallinckrodt)[3] that was used without treatment except for dilution with distilled water to the proper strength.

Ferric Oxide

High-purity ferric oxide (Fe_2O_3) 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 (approximately 400 ppm) of manganese and silicon.

Silicon Dioxide

The silicon dioxide (SiO_2) used was from a single, natural, exceedingly clear and pure 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 until the solution remained clear; it was then digested with hydrogen peroxide 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 by the International Centre for Diffraction Data, Joint Committee on Powder Diffraction Standards (JCPDS) Powder Diffraction Fill (PDF) on card 5-490 for α-SiO_2 (alpha quartz).

Sodium Sulfate

Anhydrous, orthorhombic sodium sulfate (Na_2SO_4), referred to as Na_2SO_4 III, was prepared from Alfa ultrapure Na_2SO_4 by heating at approximately 460° C for 16 hours. After heating, it was cooled to room temperature and stored in a desiccator over freshly calcined CaO. On cooling, Na_2SO_4 I transforms (at 228° C) to Na_2SO_4 II, which transforms to the orthorhombic Na_2SO_4 III at 225° C (13). Confirmation of Na_2SO_4 III was obtained by comparing the X-ray diffraction pattern with that given on Powder Diffraction File (PDF) card 8-31.

ACMITE PREPARATION AND ANALYSIS

Preparation

Acmite ($NaFe^{3+}Si_2O_6$) was synthesized by reaction of a stoichiometric mixture of Na_2CO_3, Fe_2O_3, and silicic acid containing equivalent amounts of Na_2O, Fe_2O_3, and SiO_2. To optimize homogeneity of the mixture, the reactants were thoroughly blended by grinding before initial heat treatment. The mixture was heated in a platinum dish at 820° C for 30 min, which resulted in

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[3]Reference to specific brand names or manufacturers is made for identification only and does not imply endorsement by the Bureau of Mines.

considerable shrinkage and slight sintering of the reactants. This product was ground and thoroughly blended without dusting or loss of reactants, and then heated again at 820° C for 30 min, and for 24 hours. Next, it was heated at 870° C for 5 days, and at 900° C for 68 hours, with grinding and blending after each heating. The final grain size of the sample was between 100 and 150 mesh.

Analysis

The acmite used in this investigation was also used for the low-temperature heat-capacity measurements and the high-temperature enthalpy measurements ($\underline{15}$). Chemical analysis of the final sample showed 13.32 pct Na_2O, 34.64 pct Fe_2O_3, and 51.99 pct SiO_2, compared with theoretical values of 13.41, 34.57, and 52.02 pct, respectively. X-ray diffraction showed only acmite to be present with possibly a trace of hematite (Fe_2O_3). The line intensities and spacings observed for this material matched the pattern listed for synthetic acmite on PDF card 15-787. Spectrographic analysis showed trace impurities of Cr, Mn, and Ni estimated at 600, 200, and 200 ppm, respectively. No corrections were made for impurities or the very slight composition deviation from the theoretical values.

EXPERIMENTAL DETERMINATIONS

Heats of Formation at 298.15 K

The heat of formation of acmite was determined by hydrofluoric acid solution calorimetry. The apparatus used has been described in earlier publications ($\underline{2}$, $\underline{14}$, $\underline{19}$). The solvent used was 950 g of 20.1 wt-pct hydrofluoric acid, which contained the same amount (approximately 0.60 g) of potassium dichromate ($K_2Cr_2O_7$) used in related studies ($\underline{3}$). The quantities of all reacting substances were stoichiometric with 0.742 g of α-SiO_2, which (when substituted into reaction 1 of the Reaction Scheme table 1) provides the stoichiometric proportions for all subsequent reactions.

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 a 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. Electrical calibrations of the calorimeter were made over the temperature range of measurement.

The precision uncertainty assigned to solution heat values is twice the standard deviation. 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 thermochemical calorie (1 cal = 4.1840 j). All weighings were corrected to vacuum and molecular weights in accordance with the 1977 table of atomic weights ($\underline{12}$). Final

4

values are rounded to 10 cal. All calibrations are traceable to the National Bureau of Standards (NBS), and sample temperatures are based on the International Practical Temperature Scale of 1968 (5).

The reaction scheme for the solution calorimetric investigation is given in table 1. The symbols c, 1, and sol are used to denote substances that are crystalline, liquid, or in solution, respectively. 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 mean measured heat values and their precision uncertainties.

TABLE 1. - Reaction scheme for acmite

Reaction[1]	ΔH, kcal	Uncertainty, kcal
(1) $2SiO_2(c) + 12HF(sol) = 2H_2SiF_6(sol) + 4H_2O(sol)$......	-65.808	±0.032
(2) $1/2Fe_2O_3(c) + 3H^+(sol) = Fe^{3+}(sol) + 3/2H_2O(sol)$.....	-21.013	± .023
(3) $1/2Na_2SO_4III(c) = Na^+(sol) + 1/2SO_4^=(sol)$............	+.528	± .003
(4) $4H_2O(1) = 4H_2O(sol)$..................................	+3.280	± .004
(5) $1/2H_2SO_4 \cdot 7H_2O(1) = H^+(sol) + 1/2SO_4^=(sol)$ $+ 7/2H_2O(sol)$......................................	+3.119	± .004
(6) $NaFe^{3+}Si_2O_6(c) + 12HF(sol) + 4H^+(sol)$ $= Na+(sol)+ Fe^{3+}(sol) + 2H_2SiF_6(sol) + 6H_2O(sol)$....	-99.137	± .019

$$\Delta H_7 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_5 - \Delta H_6$$

(7) $2SiO_2(c) + 1/2Fe_2O_3(c) + 1/2Na_2SO_4(c) + 4H_2O(1)$

$= NaFe^{3+}Si_2O_6(c) + 1/2H_2SO_4 \cdot 7H_2O(1)$

$$\Delta H_7 = 13.005 \pm 0.044 \text{ kcal}$$

[1]For reactions 1 through 6, reactants are at 25° C, and reaction products at 73.7° C.

The experimentally determined heat-of-solution data together with the precision uncertainties used for the reactions listed in table 1 are listed in table 2. Confirmatory measurements were made on reaction 1, and the results (the last three values) were averaged with previously published values, which were determined under identical conditions. The heat of solution of Fe_2O_3 (reaction 2) was determined for this study as was the heat-of-solution reaction for Na_2SO_4 III (reaction 3) and the dilution reaction for H_2O (reaction 4). The heat of mixing for $H_2SO_4 \cdot 7H_2O$ (reaction 5) was previously determined (3). The heat of solution for the synthetic acmite was made in the solution following reaction 5. These were the only determinations made in this charge of acid, the sulfuric acid mixture having been added before the measurements were made on the synthetic acmite.

TABLE 2. - Experimental heats of solution, kilocalorie per mol

SiO_2, reaction 1	Fe_2O_3, reaction 2	Na_2SO_4 III, reaction 3	H_2O reaction 4	$H_2SO_4 \cdot 7H_2O$, reaction 5	$NaFe^{3+}Si_2O_6$ reaction 6
-32.876	-42.005	+1.066	+0.822	6.230	-99.162
-32.914	-42.029	1.057	.821	6.242	-99.132
-32.901	-42.114	1.060	.821	6.239	-99.161
-32.952	-42.114	1.047	.820	6.228	-99.101
-32.889	-41.944	1.052	.819	6.243	-99.131
-32.881	-42.936	1.051	.821	6.249	-99.137
	-42.046				
-32.900	-42.027				
-32.923					
-32.904					
Mean -32.904	-42.026	+1.056	+0.820	+6.239	-99.137
±.016	±.047	±.006	±.001	±.007	±.019

The final solution from reactions 1 through 4 was identical with the solution resulting from the combination of reactions 5 and 6. These reactions and their heats were therefore combined as indicated, according to the scheme

$$\Delta H_7 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_5 - \Delta H_6,$$

to obtain the resulting reaction 7, the overall calorimetric reaction with a heat change of 13.009 ±0.044 kcal.

The Standard Enthalpy of Formation

To derive the standard enthalpy of formation for acmite, additional enthalpy-of-formation data are required from the literature. Following are the necessary data and sources that are presented in table 3: alpha quartz (α-SiO_2) from Wise (26), ferric oxide (Fe_2O_3) from Wagman (21), sodium sulfate (Na_2SO_4 III) from JANAF tables (7), water (H_2O) and sulfuric acid ($H_2SO_4 \cdot 7H_2O$) from Wagman (20), and sodium oxide (Na_2O) from O'Hare (17).

TABLE 3. - Enthalpy of formation for acmite

Reaction	$\Delta H_{298.15}$, kcal/mol	Uncertainty, kcal	Reference
(8) Si(c) + O$_2$ (g) = SiO$_2$(c).....................	-217.720	±0.34	26
(9) 2Fe(c) + 1 1/2 O$_2$(g) = Fe$_2$O$_3$(c).............	-197.0	± .30	21 .
(10) 2Na(c) + S(rh) + 2O$_2$(g) = Na$_2$SO$_4$III(c)......	-331.005	± .30	7
(11) H$_2$(g) + 1/2 O$_2$(g) = H$_2$O(l)..................	-68.315	± .01	20
(12) 8H$_2$(g) + S(rh) + 5 1/2 O$_2$(g) = H$_2$SO$_4$·7H$_2$O(l)	-687.663	± .17	20
(13) 2Na(c) + 1/2 O$_2$(g) = Na$_2$O(c)................	-99.70	±1.00	17

$$\Delta H_{14} = \Delta H_7 + 1/2\Delta H_{10} + 4\Delta H_{11} - 1/2\Delta H_{12} + 2\Delta H_8 + 1/2\ \Delta H_9$$

(14) 2Si(c) + Fe(c) + Na(c) + 3O$_2$(g) = NaFe^{3+}Si$_2$O$_6$(c)
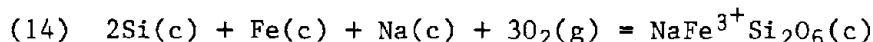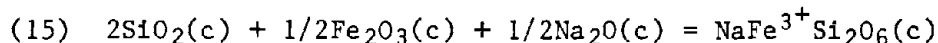
$$\Delta H_{14} = -615.866\ \pm0.719\ \text{kcal/mol} = -615.87\ \pm0.72\ \text{kcal/mol}$$

$$\Delta H_{15} = \Delta H_7 + 1/2\Delta H_{10} + 4\Delta H_{11} - 1/2\Delta H_{12} - 1/2\Delta H_{13}$$

(15) 2SiO$_2$(c) + 1/2Fe$_2$O$_3$(c) + 1/2Na$_2$O(c) = NaFe^{3+}Si$_2$O$_6$(c)

$$\Delta H_{15} = -32.076\ \pm0.53\ \text{kcal/mol} = -32.08\ \pm0.53\ \text{kcal/mol}$$

The standard enthalpy of formation for acmite was derived from these reactions and heats, according to the scheme

$$\Delta H_{14} = \Delta H_7 + 2\Delta H_8 + 1/2\Delta H_9 + 1/2\Delta H_{10} + 4\Delta H_{11} - 1/2\Delta H_{12},$$

from which it follows that

$$2Si(c) + Fe(c) + Na(c) + 3O_2(g) \rightarrow NaFe^{3+}Si_2O_6(c), \tag{14}$$
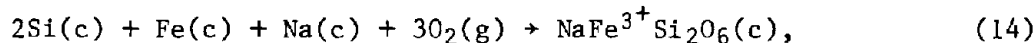
for which

$$\Delta Hf^{o}_{298.15} = -615.87\ \pm0.71\ \text{kcal/mol}.$$

The enthalpy of formation for acmite from the constituent oxides may be derived by the combination of reactions and enthalpy changes, according to the scheme

$$\Delta H_{15} = \Delta H_7 + 1/2\Delta H_{10} + 4\Delta H_{11} - 1/2\Delta H_{12} - 1/2\Delta H_{13},$$

from which it follows that

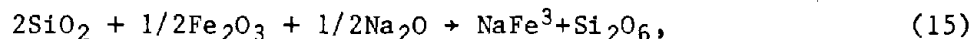$$2SiO_2 + 1/2Fe_2O_3 + 1/2Na_2O \rightarrow NaFe^{3+}Si_2O_6, \tag{15}$$

for which

$$\Delta H^0_{298} \text{ (from oxides)} = -32.08 \pm 0.53 \text{ kcal/mol.}$$

Enthalpies and Gibbs Energies of Formation and Reaction

The experimental low-temperature heat capacity, high-temperature enthalpy, and heat-of-formation data for acmite may be combined with the necessary data for the constituent elements and oxides to permit the calculation of enthalpies, Gibbs energies of formation and other relevant properties as a function of temperature. Table 4 presents the information on thermodynamic data for reaction constituents not previously quoted.

TABLE 4. – Auxiliary thermodynamic data

Element or compound	Function	Source	Reference
Fe (c,l)	All data...................	Hultgren........................	11
Fe_2O_3(c)	ΔHf^0_{298}.....................	NBS 270-4......................	21
	Low temperature Data (LT).	Westrum and Grvold.............	23
	High Temperature Data (HT)	Coughlin, King, and Bonnickson.	6
Na(c,l,g)	All data...................	JANAF NSRDS–NBS 37.............	7
Na_2O(c)	ΔHf^0_{298}.....................	O'Hare and Wagman..............	17,22
Na_2O(c)	S°.........................	Grimley and Margrave...........	10
	Cp°........................	JANAF NSRDS–NBS 37.............	7
	HT.........................	Fredrickson and Chasanov.......	9
O_2(g)	All data...................	JANAF..........................	8
Si(c,l)	All data...................	Hultgren.......................	11
	LT.........................	JANAF..........................	7
$SiO_2(\alpha,\beta)$	ΔHf^0_{298}.....................	Wise...........................	26
	S°.........................	NBS-270-3......................	20
	LT.........................	Anderson.......................	1
	HT.........................	Moser..........................	16
	HT.........................	Roth and Bertram...............	18
	HT.........................	White..........................	24
	HT.........................	Wietzel........................	25

The thermodynamic properties for the formation of acmite from the elements and oxides are presented in tables 5 and 6, respectively. The thermodynamic data from Ko (15) are repeated here in calories for convenience.

TABLE 5. – Standard formation data for acmite, reaction

$$2Si(s,l) + Fe(c,l) + Na(c,l,g) + 3O_2(g) = NaFe^{3+}Si_2O_6(c)$$

T, K	cal/mol·K			kcal/mol			Log Kf
	Cp°	S°	$-(G°-H^\circ_{298})/T$	$H°-H^\circ_{298}$	ΔHf°	ΔGf°	
298.15	40.607	40.622	40.622	0.	-615.870	-575.855	422.108
300	40.771	40.874	40.624	.075	-615.875	-575.606	419.323
[1]371	45.115	50.062	41.563	3.153	-615.956	-566.067	333.456
371	45.115	50.062	41.563	3.153	-616.578	-566.067	333.456
400	46.889	53.524	42.306	4.487	-616.577	-562.119	307.123
500	50.959	64.449	45.669	9.390	-616.382	-548.518	239.754
600	53.985	74.020	49.613	14.644	-615.995	-534.981	194.864
700	56.321	82.524	53.717	20.165	-615.491	-521.517	162.823
800	58.153	90.169	57.804	25.892	-614.928	-508.130	138.813
900	59.606	97.106	61.792	31.783	-614.371	-494.813	120.156
1,000	60.778	103.449	65.645	37.804	-613.913	-481.540	105.239
[2]1,043	61.198	106.017	67.257	40.426	-613.846	-475.850	99.708
1,100	61.754	109.289	69.351	43.932	-613.604	-468.329	93.047
[3]1,177	62.414	113.489	72.102	48.713	-613.114	-458.172	85.074
1,177	62.414	113.489	72.102	48.713	-636.399	-458.172	85.074
[2]1,185	62.482	113.912	72.382	49.213	-636.327	-456.961	84.276
1,185	62.482	113.912	72.382	49.213	-636.542	-456.960	84.276
1,200	62.611	114.699	42.907	50.151	-636.379	-454.692	82.810
1,263	63.123	117.916	75.073	54.111	-635.677	-454.170	77.031

[1]Melting point for sodium.
[2]Transition points for iron.
[3]Boiling point for sodium.

TABLE 6. - Formation data for acmite from the oxides, reaction

$$2SiO_2(c) + 0.5Fe_2O_3(c) + 0.5Na_2O(c)$$

$$= NaFe^{3+}Si_2O_6(c)$$

T, K	cal/mol·K			kcal/mol			Log Kf
	$Cp°$	$S°$	$-(G°-H_{298}°)/T$	$H°-H_{298}°$	$\Delta Hf°$	$\Delta Gf°$	
298.15	40.607	40.622	40.622	0.	-32.080	-32.432	23.773
300	40.771	40.874	40.624	.075	-32.083	-32.436	23.630
400	46.889	53.524	42.306	4.487	-32.234	-32.531	17.774
500	50.959	64.449	45.669	9.390	-32.453	-32.583	14.242
600	53.982	74.020	·49.613	14.644	-32.732	-32.582	11.868
700	56.321	82.524	53.717	20.165	-33.082	-32.530	10.156
800	58.153	90.169	57.804	25.892	-33.588	-32.417	8.856
[1]847	58.836	93.508	59.693	28.641	-34.023	-32.333	8.343
847	58.836	93.508	59.693	28.641	-34.373	-32.332	8.342
900	59.606	97.106	61.792	31.783	-34.603	-32.201	7.819
[2]960	60.309	100.977	64.121	35.382	-34.973	-32.030	7.292
960	60.309	100.977	64.121	35.382	-34.973	-32.030	7.292
1,000	60.778	103.449	65.645	37.804	-35.017	-31.017	6.973
1,100	61.754	109.289	69.351	43.932	-35.140	-31.591	6.276
1,200	62.611	114.699	72.907	50.151	-35.352	-31.259	5.693
1,263	63.123	117.916	75.073	54.111	-35.578	-31.042	5.371

[1]Transition point for SiO_2.
[2]Transition point for Fe_2O_3.

DISCUSSION

The enthalpy-of-formation data are presented in this investigation and combined with the published high- and low-temperature thermodynamic data (15) that were determined on the same sample of synthetic acmite. No similar data were found in the literature.

The experimental high-temperature enthalpy data were terminated at a temperature slightly below 1,263 K, the reported melting point of acmite (NaFe^{3+} Si$_2$O$_6$) (4). Synthetic acmite is shown to be stable throughout the range of the data.

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