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By K. O. Bennington, R. R. Brown, and R. P. Beyer



UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	kcal/mol	kilocalorie per mol
cal	thermochemical calorie	K/min	kelvin per minute
cal/mol·K	calorie per mol per kelvin	mL	milliliter
g	gram	μm	micrometer
h	hour	pct	percent
J	joule	ppm	part per million
K	kelvin	wt pct	weight percent
kcal	kilocalorie		

THERMODYNAMIC PROPERTIES OF AEGIRINE

By K. O. Bennington,¹ R. R. Brown,¹
and R. P. Beyer²

ABSTRACT

The thermodynamic properties of aegirine, of composition $[(\text{Na}_{0.869}\text{Fe}_{0.7362}^{3+}\text{Fe}_{0.16}^{2+}\text{Mn}_{0.03}\text{Ca}_{0.1121})(\text{Al}_{0.141}\text{Si}_{1.9738})(\text{O}_6)]$, were experimentally determined at the Bureau of Mines as part of its efforts to advance minerals technology. The standard enthalpy of formation determined by hydrofluoric acid solution calorimetry is

$$\Delta H_f^\circ_{298} = -641.12 \pm 0.73 \text{ kcal/mol.}$$

The standard enthalpy of formation from the oxides is

$$\Delta H^\circ_{298} = -37.136 \pm 0.509 \text{ kcal/mol.}$$

Low-temperature heat capacities were determined by adiabatic calorimetry from 19.1 to 304.6 K. The derived standard entropy is $S^\circ_{298} = 38.03 \pm 0.14 \text{ cal/mol}\cdot\text{K}$. The heat capacity was measured over the range 348 to 1,198 K by differential scanning calorimetry.

These experimentally determined data were combined with data from the literature to calculate the Gibbs energies of formation and equilibrium constants of formation over the temperature range of the measurements. Standard enthalpies of formation are given as functions of temperature. The standard Gibbs energy of formation at 298.15 K is

$$\Delta G_f^\circ_{298} = -600.36 \text{ kcal/mol.}$$

INTRODUCTION

This Bureau of Mines investigation of the thermodynamic properties of aegirine $[(\text{Na}_{0.869}\text{Fe}_{0.7362}^{3+}\text{Fe}_{0.16}^{2+}\text{Mn}_{0.03}\text{Ca}_{0.1121})(\text{Al}_{0.141}\text{Si}_{1.9738})(\text{O}_6)]$ is one of a series on slag-type pyroxenes; the studies on synthetic acmite and hedenbergite have been published earlier (1-2).³ These pyroxene minerals readily assimilate manganese;

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²Chemical engineer.

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

consequently, this study contributes towards both the forthcoming investigations of some manganese pyroxenes and the understanding of slag-metal equilibria in iron refining.

MATERIALS

Aegirine

The aegirine $[(\text{Na}_{0.869}\text{Fe}_{0.7362}^{3+}\text{Fe}_{0.16}^{2+}\text{Mn}_{0.03}\text{Ca}_{0.1121})(\text{Al}_{0.141}\text{Si}_{1.9738})(\text{O}_6)]$ used for this study was obtained from Ward's,⁴ a commercial supplier. This material, which was collected at Mont Ste. Hilaire, Quebec, was made up of masses of dark green, bladed crystals with albite in the interstices. It was crushed, washed, screened, and separated. There was no evidence of alteration of any kind, nor was there any evidence of separate impurities. The X-ray diffraction pattern matched the pattern for aegirine given by the Powder Diffraction File (PDF) card 18-1222 (3).

Acids

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

Aluminum Sulfate Dodecahydrate

The aluminum sulfate dodecahydrate $(\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O})$ was prepared by first recrystallizing reagent-grade $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, 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 mol H₂O of hydration. Analysis by direct ignition showed 18.25 wt pct Al₂O₃, compared with the theoretical value of 18.26 wt pct. No significant impurities were detected spectrographically.

Calcium Oxide

Reagent-grade CaCO₃ of very high purity was roasted overnight at 970° C to provide the calcium oxide (CaO) for each determination.

Ferric Oxide

The ferric oxide (Fe₂O₃) was a high-purity product that was used without alteration except to dry to constant weight. Only α-Fe₂O₃ was detected by X-ray analysis, and the pattern matched that given on PDF card 13-534. No corrections were made for the spectrographically detected amounts (~400 ppm total) of Mn and Si.

Ferrous Sulfate Heptahydrate

The ferrous sulfate heptahydrate $(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})$ was a reagent-grade product. On analysis, it was found to have an Fe:SO₄:H₂O 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.

⁴Reference to specific brand names or manufacturers is made for identification only and does not imply endorsement by the Bureau of Mines.

Manganous Oxide

Reagent-grade MnO_2 was slowly heated in a stream of hydrogen until a temperature of $850^\circ C$ 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 manganous oxide (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.

Silica

The silica (SiO_2) used was from an exceedingly clear and pure 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 from 10 to 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 on the PDF card 5-490 for alpha-quartz.

Sodium Sulfate III

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 $460^\circ C$ for 16 h. 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 $228^\circ C$) to Na_2SO_4 II, which transforms to the orthorhombic Na_2SO_4 III at $225^\circ C$ (4). Confirmation of Na_2SO_4 III was obtained by comparing the X-ray diffraction pattern with that given on PDF card 8-31.

MINERAL ANALYSIS AND FORMULA

Analysis

The chemical and optical analyses presented in tables 1 and 2, respectively, were made by the branch of Analytical Laboratories, U.S. Geological Survey, Menlo Park, CA. The X-ray analysis showed a barely detectable trace of an impurity, possibly $FeSiO_3$.

Formula

The formula for aegirine and the formula weight were calculated from the chemical analysis 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 (5). This procedure was described earlier by Miser (6) and Stevens (7-8) and more recently by Goff (9).

TABLE 1. - Analysis of aegirine¹

Oxide	wt pct	Extended formula ²		Charge ³	Substitution site	Adjusted formula ⁴	
		Ions	Weight, g			Ions	Weight, g
SiO ₂	51.10	1.9738	55.435	7.8951		1.9738	55.435
Al ₂ O ₃ ...	3.07	.1398	3.772	.4194		.141	3.804
P ₂ O ₅03	.0010	.031	.0049	Al ₂ O ₃		
TiO ₂84	.0244	1.168	.0975	Fe ₂ O ₃		
Fe ₂ O ₃ ...	24.21	.7037	39.300	2.1110		.7362	41.115
FeO.....	4.94	.1596	8.913	.3191		.160	8.935
MgO.....	.30						
MnO.....	.92	.0300	1.648	.0601		.030	1.648
CaO.....	2.71	.1121	4.493	.2242		.1121	4.493
Na ₂ O....	11.59	.8680	19.955	.8680		.869	19.978
K ₂ O.....	.02	.0009	.035	.0009	Na ₂ O		
CO ₂32						
H ₂ O ⁺14						
H ₂ O ⁻02						
O.....		6.000	95.996			6.000	95.996
Total ..	NAp	NAp	230.746	NAp	NAp	NAp	231.404

NAp Not applicable.

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

²Extended formula--(Na_{0.868}Fe³⁺_{0.7037}Fe²⁺_{0.1596}Mn_{0.03}Ti_{0.0244}Ca_{0.1121}K_{0.0009})(Al_{0.1398}P_{0.0010}Si_{1.9738})(O₆).

³Equivalent per formula.

⁴Adjusted formula--(Na_{0.869}Fe³⁺_{0.7362}Fe²⁺_{0.16}Mn_{0.03}Ca_{0.1121})(Al_{0.141}Si_{1.9738})(O₆).

NOTE.--Bound water, H₂O⁺, hygroscopic water, H₂O⁻, and MgCO₃ are calculated out as discrete separate impurities.

It is necessary to make several assumptions in the construction of this formula. Following Jackson (5) and Sommerfeld (10), 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 errors, and further, that if the type formula for the mineral is correctly chosen, any calculated excess of cations may be due to only analytical error. For the purposes of this study of the thermodynamic properties, the chemical analysis is considered to be absolutely accurate; consequently, information on the construction of the adjusted formula is shown in the necessary

TABLE 2. - Optical data¹ for aegirine (Mont Ste. Hilaire, Quebec)

δ.....	1.806 (3).
β.....	1.793 (2).
α.....	1.760 (2).
2V _α	62.5 (1) ^o measured, 63 ^o 14' calculated.
$\frac{r}{x} = \frac{v}{\Lambda} \frac{c}{-1.5^{\circ}}$	Strong, inclined.
y = $\frac{b}{b}$	
X.....	Olive green.
Y.....	Yellowish green.
Z.....	Yellowish brown.
X > Y > Z	

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

detail and completeness for recalculation to a different final formula.

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 (table 1). The grouping of ions into particular positions follows the example of Deer (11), who also quotes the optical data that indicate this mineral has an intermediate composition between aegirine and aegirine-augite (table 2). 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 minor impurity elements into the most likely sites. The deviations in each structural position represent the difference between the ideal stoichiometry and the sum of ions substituted per structural site. The positions, as shown in the column headed "Charge" in table 1, are shown to be almost exactly balanced.

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 impurity elements as substituted into the most likely major element sites. The difference in energy is calculated between the heats of solution, determined under similar conditions, of equal quantities of the major element that is deficient and the proxying element displacing it. The quantities of the elements and their respective heats of solution are both calculated in terms of equivalents; consequently, the corrections applied are the net energy differences for a specific number of equivalents in a particular structure position.

Phosphorus was substituted into the aluminum position by adding the equivalents per formula for phosphorus to that for aluminum, shown in the column labeled "Charge," then dividing the total by 3, the valence of aluminum, to provide the number of ions in the aluminum position in the adjusted formula. There is no convincing evidence for either placing phosphorus in the composition or omitting it as a discrete separate impurity; neither are there suitable thermodynamic data for making corrections, whether phosphorus is treated as bonded into the structure or excluded as an impurity. The error involved would be the difference between the heats of solution of equivalent amounts of the oxides of phosphorus and aluminum. The difference in atomic weight between aluminum and phosphorus results in a mineral formula weight decrease of 0.004 g, which will cause a corresponding change of ~0.002 kcal.

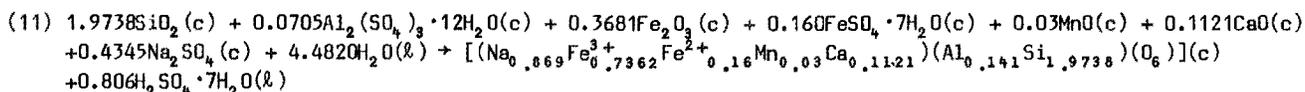
The thermal correction required by the change in gram formula weight was applied by scaling the heat of solution value for the natural mineral to the adjusted gram formula weight. This was done assuming that any vacancy sites were uniformly distributed, that the added ions are completely bonded in the 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 reaction description for the mineral, reaction 10, in the aegirine reaction scheme in table 3. The heat of solution values were determined and calculated for the formula weight of the natural mineral, and the corrections were then applied.

TABLE 3. - Reaction scheme for aegirine¹

Reaction	ΔH , kcal	Uncer- tainty (\pm), kcal
(1) $1.9738\text{SiO}_2(\text{c}) + 11.8428\text{HF}(\text{sol}) \rightarrow 1.9738\text{H}_2\text{SiF}_6(\text{sol}) + 3.9476\text{H}_2\text{O}(\text{sol})$	-64.940	0.045
(2) $0.0705\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}(\text{c}) \rightarrow 0.141\text{Al}^{3+}(\text{sol}) + 0.2115\text{SO}_4^{2-}(\text{sol}) + 0.846\text{H}_2\text{O}(\text{sol})$...	-1.220	.004
(3) $0.3681\text{Fe}_2\text{O}_3(\text{c}) + 2.2086\text{H}^+(\text{sol}) \rightarrow 0.7362\text{Fe}^{3+}(\text{sol}) + 1.1043\text{H}_2\text{O}(\text{sol})$	-15.464	.013
² (4) $0.160\text{FeSO}_4 \cdot 7\text{H}_2\text{O}(\text{c}) \rightarrow 0.160\text{Fe}^{3+}(\text{sol}) + 0.160\text{SO}_4^{2-}(\text{sol}) + 1.12\text{H}_2\text{O}(\text{sol})$	-3.219	.004
(5) $0.030\text{MnO}(\text{c}) + 0.06\text{H}^+(\text{sol}) \rightarrow 0.03\text{Mn}^{2+}(\text{sol}) + 0.03\text{H}_2\text{O}(\text{sol})$	-1.430	.008
(6) $0.1121\text{CaO}(\text{c}) + 0.2242\text{HF}(\text{sol}) \rightarrow 0.1121\text{CaF}_2(\text{p}) + 0.1121\text{H}_2\text{O}(\text{sol})$	-6.221	.007
(7) $4.482\text{H}_2\text{O}(\ell) \rightarrow 4.482\text{H}_2\text{O}(\text{sol})$	+3.693	.004
(8) $0.4345\text{Na}_2\text{SO}_4(\text{c}) \rightarrow 0.869\text{Na}^+(\text{sol}) + 0.4345\text{SO}_4^{2-}(\text{sol})$	+4.462	.007
(9) $0.806\text{H}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}(\ell) \rightarrow 1.612\text{H}^+(\text{sol}) + 0.806\text{SO}_4^{2-}(\text{sol}) + 5.642\text{H}_2\text{O}(\text{sol})$	+5.037	.016
² (10) $[(\text{Na}_{0.869}\text{Fe}^{3+}\text{Fe}^{2+}\text{Mn}_{0.03}\text{Ca}_{0.1121})(\text{Al}_{0.141}\text{Si}_{1.9738})(\text{O}_6)](\text{c})$ $+12.067\text{HF}(\text{sol}) + 3.8806\text{H}^+(\text{sol}) \rightarrow 1.9738\text{H}_2\text{SiF}_6(\text{sol}) + 0.141\text{Al}^{3+}(\text{sol}) + 0.869\text{Na}^+(\text{sol})$ $+0.8962\text{Fe}^{3+}(\text{sol}) + 0.03\text{Mn}^{2+}(\text{sol}) + 0.1121\text{CaF}_2(\text{p}) + 6\text{H}_2\text{O}(\text{sol})$	³ -105.263	.200

$$\Delta H_{11} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7 + \Delta H_8 - \Delta H_9 - \Delta H_{10}$$



$$\Delta H_{11} = +11.890 \pm 0.209 \text{ kcal.}$$

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

²Ferrous iron is oxidized in solution to ferric, which is exactly balanced and canceled in reaction 10.

³Corrected value.

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

EXPERIMENTAL DETERMINATIONS

Heats of Solution at 298.15 K

The heat of solution of aegirine was determined by hydrofluoric acid solution calorimetry. The apparatus used has been described in earlier publications (12-14). The solvent used was 948.7 g of 20.1 wt pct hydrofluoric acid to which approximately 0.60 g $\text{K}_2\text{Cr}_2\text{O}_7$ was added. The quantities of all reaction substances were stoichiometric with 0.601 g of alpha-quartz, which, when substituted into reaction 1, table 3, provides the stoichiometric molar proportions of all succeeding reactions.

Weighed amounts of solid or liquid substances to be dissolved 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 heat values as follows: (1) When several individual heat values were measured for a reaction, the precision uncertainty was taken as $2\sqrt{\sum d_i^2}/n(n-1)$, where $\sum d_i^2$ 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 and Deming (15).

All energy units are expressed in terms of the defined calorie (1 cal = 4.1840 J). Weights were corrected to vacuum, and molecular weights are in accordance with the 1981 table of atomic weights (16). Final values are rounded to 0.01 kcal. 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) (17).

The reaction scheme for the solution calorimetric investigation is given in table 3. The symbols c, l, g, sol, and p in parentheses are used to denote substances that are crystalline, liquid, gas, in solution, or crystalline precipitate, respectively. The reactions are written in an abbreviated form sufficient to show that stoichiometry was maintained to permit cancellation of the reaction products. The table also contains the mean measured heat values and their precision uncertainties. Reactions 1 through 9 listed in table 3 were determined previously in this laboratory; the results have been published (18) and are adopted directly.

The heat of solution for the mineral aegirine, reaction 10, was measured in the solution after determining reaction 9. Six heat of solution measurements provided -104.269, -104.232, -104.217, -103.989, -104.035, and -104.110 kcal/mol. The mean value and precision uncertainty is -104.142 ± 0.081 kcal/mol. This heat of solution value was determined for the formula weight (230.746 g) and composition of the original mineral as represented by the extended formula in table 1. Correction of this value for 0.16 pct total water content gives 0.051 kcal for 0.369 g H₂O considered thermally equivalent to ice. The carbonate was calculated with the magnesium content to provide a 0.069-kcal correction for 1.431 g total MgCO₃, the heat of solution for MgCO₃ having been estimated as -4.05 kcal/mol. This correction procedure provided a final heat of solution value of -104.977 kcal for this mineral with the extended formula composition shown in table 1 and the corresponding formula weight of 230.746 g. This value was then adjusted for the impurity substitution (-0.013 kcal) shown in table 1, then calculated to the adjusted formula weight (231.404 g) shown in column 6. This final heat of solution value was found to be -105.263 ± 0.200 kcal. The uncertainty was increased to compensate for potential errors in the correction procedure.

The final solution after conducting reactions 1 through 8 sequentially in the original charge of acid was identical to the solution obtained after conducting reactions 9 and 10 sequentially in another charge of acid containing an equal amount of K₂Cr₂O₇. The heat of solution values were substituted into the reaction scheme and combined according to

$$\begin{aligned} \Delta H_{11} &= \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7 + \Delta H_8 - \Delta H_9 - \Delta H_{10} \\ &= +11.890 \pm 0.209 \text{ kcal,} \end{aligned}$$

to obtain the enthalpy change for reaction 11, the overall calorimetric reaction.

Standard Enthalpy of Formation

The calculation of the standard enthalpy of formation for aegirine requires additional data from the literature. All of the necessary data for the elements and oxides are taken from Pankratz (19), the data for $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and for $\text{H}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ are from Wagman (20-21), and the data for $\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ are from Ko (22). These values, with their precision uncertainties, are listed in reactions 12 through 23, table 4. The standard enthalpy of formation for aegirine was derived from a selection of these reactions and heats according to the scheme

$$\Delta H_{24} = \Delta H_{11} + 1.9738\Delta H_{12} + 0.0705\Delta H_{13} + 0.3681\Delta H_{15} + 0.16\Delta H_{16} + 0.03\Delta H_{18} \\ + 0.1121\Delta H_{19} + 0.4345\Delta H_{21} + 4.4820\Delta H_{20} - 0.806\Delta H_{23},$$

from which it follows that

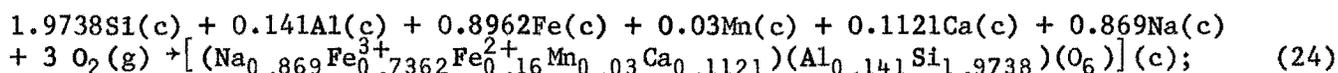
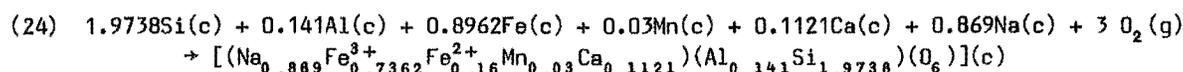


TABLE 4. - Enthalpy of formation of aegirine

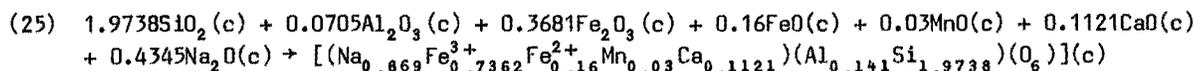
Reaction	ΔH_{298}° , kcal/mol	Uncertainty (\pm), kcal	Refer- ence
(12) $\text{Si}(c) + \text{O}_2(g) \rightarrow \text{SiO}_2(c)$	-217.720	0.34	19
(13) $2\text{Al}(c) + 3\text{S}(rh) + 12 \text{O}_2(g) + 24\text{H}_2(g) \rightarrow \text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}(c)$	-1701.51	.126	21
(14) $2\text{Al}(c) + 1.5 \text{O}_2(g) \rightarrow \text{Al}_2\text{O}_3(c)$	-400.5	.3	19
(15) $2\text{Fe}(c) + 1.5 \text{O}_2(g) \rightarrow \text{Fe}_2\text{O}_3(c)$	-197.0	.3	19
(16) $\text{Fe}(c) + \text{S}(rh) + 5.5 \text{O}_2(g) + 7\text{H}_2(g) \rightarrow \text{FeSO}_4 \cdot 7\text{H}_2\text{O}(c)$	-720.5	.14	20
(17) $\text{Fe}(c) + 0.5 \text{O}_2(g) \rightarrow \text{FeO}(c)$	-65.0	.30	19
(18) $\text{Mn}(c) + 0.5 \text{O}_2(g) \rightarrow \text{MnO}(c)$	-92.07	.30	19
(19) $\text{Ca}(c) + 0.5 \text{O}_2(g) \rightarrow \text{CaO}(c)$	-151.79	.30	19
(20) $0.5 \text{O}_2(g) + \text{H}_2(g) \rightarrow \text{H}_2\text{O}(l)$	-68.315	.01	19
(21) $2\text{Na}(c) + \text{S}(rh) + 2 \text{O}_2(g) \rightarrow \text{Na}_2\text{SO}_4 \text{ III}(c)$	-330.988	.15	19
(22) $2\text{Na}(c) + 0.5 \text{O}_2(g) \rightarrow \text{Na}_2\text{O}(c)$	-99.7	1.0	19
(23) $\text{S}(rh) + 5.5 \text{O}_2(g) + 8\text{H}_2(g) \rightarrow \text{H}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}(l)$	-687.663	.17	22

$$\Delta H_{24} = \Delta H_{11} + 1.9738\Delta H_{12} + 0.0705\Delta H_{13} + 0.3681\Delta H_{15} + 0.16\Delta H_{16} + 0.03\Delta H_{18} + 0.1121\Delta H_{19} \\ + 0.4345\Delta H_{21} + 4.4820\Delta H_{20} - 0.806\Delta H_{23}$$



$$\Delta H_{24} = -641.120 \pm 0.729 \text{ kcal/mol}$$

$$\Delta H_{25} = \Delta H_{11} + 0.0705\Delta H_{13} - 0.0705\Delta H_{14} + 0.16\Delta H_{16} - 0.16\Delta H_{17} + 0.4345\Delta H_{21} - 0.4345\Delta H_{22} \\ - 0.806\Delta H_{23} + 4.482\Delta H_{20}$$



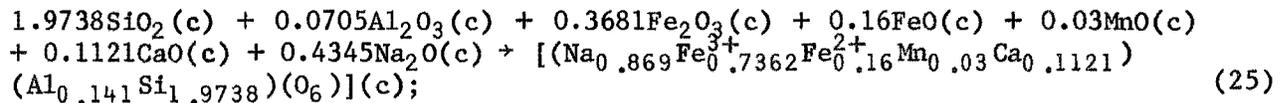
$$\Delta H_{25} = -37.136 \pm 0.509 \text{ kcal/mol}$$

for which

$$\Delta H_{f298}^{\circ} = -641.120 \pm 0.729 \text{ kcal/mol.}$$

The enthalpy of formation for aegirine, from the constituent oxides, may be derived by a combination of selected reaction and enthalpy changes according to the scheme

$$\Delta H_{25} = \Delta H_{11} + 0.0705\Delta H_{13} - 0.0705\Delta H_{14} + 0.16\Delta H_{16} - 0.16\Delta H_{17} + 4.482\Delta H_{20} \\ + 0.4345\Delta H_{21} - 0.4345\Delta H_{22} - 0.806\Delta H_{23};$$



$$\Delta H_{298}^{\circ} (\text{from oxides}) = -37.136 \pm 0.509 \text{ kcal/mol.}$$

Low-Temperature Thermal Properties

The heat capacity of aegirine was measured by adiabatic calorimetry over the range 19.1 K to 304.6 K. Design and operational details of this calorimeter have been described previously (23).

The aegirine sample for the low-temperature measurements was dried at 383 K overnight before loading into a 90-mL copper calorimeter vessel. Prior to sealing, the loaded calorimeter was evacuated and backfilled with 1.3×10^{-4} mol He to enhance the heat transfer. An aegirine sample of 144.8180 g was used. The experimental heat capacities are listed chronologically in table 5.

TABLE 5. - Experimental low-temperature heat capacities of aegirine

T, K	Cp°, cal/mol·K	T, K	Cp°, cal/mol·K	T, K	Cp°, cal/mol·K
SERIES I		SERIES II		SERIES II--Con.	
19.10	0.989	48.84	3.902	188.00	28.961
20.80	.993	51.55	4.434	196.01	29.993
22.39	1.014	55.93	5.174	203.81	30.970
24.20	1.071	60.54	6.205	211.42	31.896
26.28	1.169	65.54	7.095	218.87	32.745
28.43	1.308	71.07	8.234	226.17	33.565
30.75	1.497	77.08	9.444	233.35	34.317
33.23	1.745	83.63	10.801	240.40	35.115
37.75	2.304	90.81	12.324	247.34	35.816
39.89	2.536	98.68	13.965	254.17	36.627
43.23	3.013	107.18	15.622	260.10	37.078
46.72	3.636	116.01	17.345	265.96	37.625
50.59	4.381	124.92	19.015	272.56	38.227
54.83	5.022	133.92	20.652	279.09	38.793
59.39	5.853	143.43	22.282	285.56	39.331
		153.14	23.844	291.97	40.048
		162.50	24.485	298.31	40.580
		171.26	26.806	304.60	41.187
		179.76	27.848		

Heat capacity measurements were discontinued below 19 K, owing to poor thermal equilibrium. The heat capacity below 19 K was determined by graphical extrapolation using a C_p°/T -versus- T^2 plot.

The values for the heat capacity and related functions were obtained by smoothing the data using a computer program by Justice (24). The results are listed in table 6. All of the experimental heat capacity values are shown in figure 1. The overall uncertainties from the low-temperature adiabatic calorimeter are ± 1 pct from 19 to 50 K, ± 0.2 pct from 50 to 200 K, and ± 0.1 pct from 200 to 300 K.

High-Temperature Thermal Determination

The heat capacity was also measured with a differential scanning calorimeter (DSC) over the range 323 to 1,223 K. The DSC, a model TA2000C manufactured by the Mettler Corp., has a nominal operating range of 298 to 1,473 K.

A 0.11867-g sample of aegirine was used in a platinum capsule. Both the full and empty capsule, along with a reference sample of Al_2O_3 , were measured. The DSC was operated with argon at a scan rate of 10 K/min in 50-K steps from 323 to 1,223 K. The data were analyzed according to the "enthalpy method," as described by Mraw and Naas (25). The accuracy of the heat capacity values was determined by measuring the properties of MgO and comparing the measured values with accepted values from Pankratz (19). The uncertainties of the heat capacity values are ± 3 pct from 323 to 700 K and ± 1 pct from 700 to 1,223 K. The experimental heat capacity values are listed in table 7 and plotted in figure 1. The values in table 7 are reported to five significant figures only for internal consistency of the table and should not be construed as being more accurate than the quoted uncertainty. Smooth values are shown in table 6.

Enthalpies and Gibbs Energies of Formation and Reaction

The experimentally determined thermal data for aegirine--the enthalpy of formation, the low-temperature heat capacity, 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, Gibbs energies of formation, and other relevant properties as a function of temperature. The thermodynamic properties for the formation of aegirine from the elements and oxides are presented in tables 8 and 9, respectively. Aegirine is shown to be stable throughout the range of the measurements.

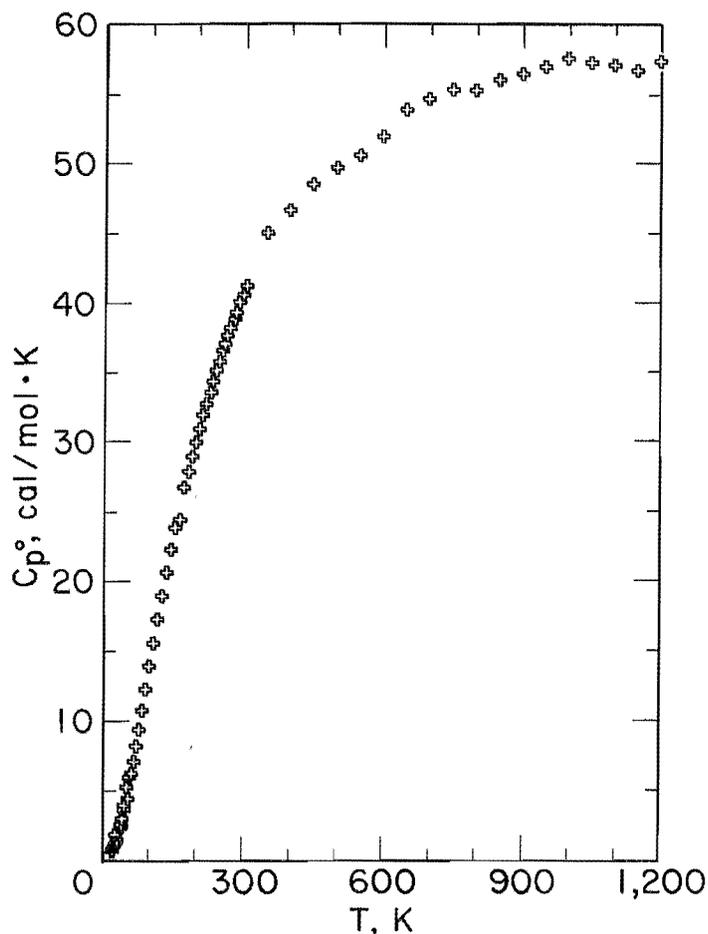


FIGURE 1. - Experimental heat capacity values.

TABLE 6. - Thermodynamic functions of aegirine

T, K	Cp°, cal/mol·K	S°(T)-S°(0), cal/mol·K	-[G°(T)-H°(0)]/T, cal/mol·K	H°(T)-H°(0), kcal/mol
20	0.959	0.885	0.379	0.010
25	1.139	1.116	.503	.015
30	1.449	1.349	.625	.022
35	1.922	1.606	.746	.030
40	2.553	1.902	.872	.041
45	3.315	2.245	1.005	.056
50	4.170	2.638	1.148	.075
60	5.976	3.560	1.471	.125
70	8.082	4.637	1.844	.196
80	10.185	5.853	2.268	.287
90	12.241	7.172	2.739	.399
100	14.243	8.566	3.251	.532
110	16.187	10.015	3.800	.684
120	18.067	11.505	4.380	.855
130	19.880	13.023	4.986	1.045
140	21.623	14.560	5.615	1.252
150	23.293	16.110	6.263	1.477
160	24.890	17.664	6.927	1.718
170	26.413	19.219	7.604	1.975
180	27.861	20.771	8.293	2.246
190	29.236	22.314	8.990	2.532
200	30.541	23.847	9.695	2.831
210	31.777	25.367	10.405	3.142
220	32.947	26.873	11.119	3.466
230	34.057	28.362	11.837	3.801
240	35.112	29.834	12.556	4.147
250	36.117	31.288	13.276	4.503
260	37.079	32.723	13.997	4.869
270	38.006	34.140	14.717	5.245
273.15	38.292	34.583	14.943	5.364
280	38.905	35.539	15.435	5.629
290	39.787	36.919	16.152	6.022
298.15	40.499	38.032	16.735	6.350
300	40.661	38.283	16.867	6.425
325	42.540	41.614	18.644	7.465
350	44.149	44.827	20.400	8.549
375	45.527	47.921	22.132	9.671
400	46.713	50.898	23.837	10.824
425	47.737	53.761	25.514	12.005
450	48.630	56.516	27.160	13.210
475	49.414	59.166	28.776	14.436
500	50.111	61.719	30.359	15.680
550	51.315	66.554	33.433	18.217
600	52.348	71.064	36.383	20.809
650	53.278	75.291	39.215	23.450
700	54.136	79.271	41.935	26.135
750	54.930	83.034	44.551	28.862
800	55.647	86.602	47.068	31.627
850	56.264	89.995	49.495	34.425
900	56.754	93.225	51.835	37.251
950	57.092	96.304	54.095	40.098
1,000	57.268	99.237	56.279	42.958
1,100	57.179	104.695	60.437	48.684
1,200	56.895	109.657	64.335	54.386

TABLE 7. - Experimental high-temperature heat capacities of aegirine

T, K	Cp°, cal/mol·K	T, K	Cp°, cal/mol·K	T, K	Cp°, cal/mol·K
348	45.053	648	53.907	948	56.993
398	46.675	698	54.690	998	57.541
448	48.589	748	55.332	1,048	57.269
498	49.689	798	55.284	1,098	57.083
548	50.567	848	56.037	1,148	56.694
598	51.911	898	56.448	1,198	57.389

TABLE 8. - Standard formation data for aegirine, reaction
 $[1.9738\text{Si}(c,l) + 0.141\text{Al}(c,l) + 0.8962\text{Fe}(c,l) + 0.03\text{Mn}(c,l) + 0.1121\text{Ca}(c,l,g) + 0.869\text{Na}(c,l,g) + 3\text{O}_2(g) \rightarrow (\text{Na}_{0.869}\text{Fe}_{0.7362}^{3+}\text{Fe}_{0.16}^{2+}\text{Mn}_{0.03}\text{Ca}_{0.1121})(\text{Al}_{0.141}\text{Si}_{1.9738})(\text{O}_6)(c)]$

T, K	cal/mol·K			kcal/mol			Log Kf
	Cp°	S°	-(G° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔHf°	ΔGf°	
298.15	40.499	38.032	38.032	0.000	-641.120	-600.365	440.073
300.00	40.661	38.283	38.033	.075	-641.125	-600.111	437.175
¹ 371.00	44.958	47.448	38.972	3.145	-641.215	-590.395	347.787
371.00	44.958	47.448	38.972	3.145	-641.756	-590.395	347.787
400.00	46.713	50.898	39.713	4.474	-641.759	-586.380	320.379
500.00	50.111	61.719	43.059	9.330	-641.610	-572.544	250.256
600.00	52.348	71.064	46.966	14.459	-641.352	-558.756	203.524
700.00	54.136	79.271	51.007	19.785	-641.055	-545.015	170.159
² 720.00	54.438	80.800	51.813	20.871	-640.993	-542.272	164.600
720.00	54.438	80.800	51.813	20.871	-641.018	-542.272	164.600
800.00	55.647	86.602	55.006	25.277	-640.764	-531.313	145.146
900.00	56.754	93.225	58.891	30.901	-640.491	-517.646	125.700
³ 933.61	56.927	95.309	60.164	32.811	-640.430	-513.059	120.101
933.61	56.927	95.309	60.164	32.811	-640.794	-513.059	120.101
⁴ 980.00	57.165	98.081	61.894	35.464	-640.727	-506.700	112.998
980.00	57.165	98.081	61.894	35.464	-640.743	-506.701	112.998
1,000.00	57.268	99.237	62.629	36.608	-640.743	-503.965	110.140
⁵ 1,043.00	57.230	101.647	64.188	39.070	-640.831	-498.082	104.367
1,100.00	57.179	104.695	66.210	42.334	-640.840	-490.295	97.411
⁶ 1,112.00	57.145	105.315	66.628	43.020	-640.832	-488.654	96.038
1,112.00	57.145	105.315	66.628	43.020	-641.061	-488.653	96.037
⁷ 1,177.00	56.960	108.555	68.855	46.727	-640.969	-479.745	89.080
1,177.00	56.960	108.555	68.855	46.727	-661.204	-479.745	89.080
⁸ 1,185.00	56.938	108.941	69.125	47.182	-661.177	-478.512	88.251
1,185.00	56.938	108.941	69.125	47.182	-661.370	-478.512	88.251
1,200.00	56.895	109.657	69.627	48.036	-661.298	-476.200	86.727

¹ Melting point for Na.² α-β transition point for Ca.³ Melting point for Al.⁴ α-β transition point for Mn.⁵ Curie temperature for Fe.⁶ Melting point for Ca.⁷ Boiling point for Na.⁸ α-β transition point for Fe.

TABLE 9. - Formation data for aegirine from the oxides
 $[1.9738\text{SiO}_2(\text{c}) + 0.0705\text{Al}_2\text{O}_3(\alpha, \beta) + 0.3681\text{Fe}_2\text{O}_3(\text{c}) + 0.16\text{FeO}(\text{c}) + 0.03\text{MnO}(\text{c}) + 0.1121\text{CaO}(\text{c})$
 $+ 0.4345\text{Na}_2\text{O}(\text{c}) + (\text{Na}_{0.669}\text{Fe}_{0.7362}^{3+}\text{Fe}_{0.16}^{2+}\text{Mn}_{0.03}\text{Ca}_{0.1121})(\text{Al}_{0.141}\text{Si}_{1.9738})(\text{O}_6)(\text{c})]$

T, K	cal/mol·K			kcal/mol			Log Kf
	Cp°	S°	-(G° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔHf°	ΔGf°	
298.15	40.499	38.032	38.032	0	-37.136	-36.587	26.818
300.00	40.661	38.283	38.033	.075	-37.140	-36.585	26.652
400.00	46.713	50.898	39.713	4.474	-37.298	-36.377	19.875
500.00	50.111	61.719	43.059	9.330	-37.547	-36.120	15.788
600.00	52.348	71.064	46.966	14.459	-37.921	-35.800	13.040
700.00	54.136	79.271	51.007	19.785	-38.424	-35.409	11.055
800.00	55.647	86.602	55.006	25.277	-39.103	-34.933	9.543
847.00	56.167	89.794	56.848	27.905	-39.618	-34.670	8.946
¹ 847.00	56.167	89.794	56.848	27.905	-39.963	-34.670	8.946
900.00	56.754	93.225	58.891	30.901	-40.288	-34.332	8.337
² 960.00	57.062	96.903	61.152	34.321	-40.744	-33.920	7.722
960.00	57.062	96.903	61.152	34.321	-40.744	-33.920	7.722
1,000.00	57.268	99.237	62.629	36.608	-40.915	-33.632	7.350
1,100.00	57.179	104.695	66.210	42.334	-41.414	-32.882	6.533
1,200.00	56.895	109.657	69.627	48.036	-42.104	-32.078	5.842

¹α-β transition point for SiO₂.

²Transition point for Fe₂O₃.

DISCUSSION

An excellent discussion of aegirine pyroxenes appears in Deer (11). The analysis (table 1) for this sample of aegirine, perhaps with slightly higher-than-average Al content, compares favorably with several of those that are presented. Although this specimen does contain significant Ca, it is high in Na and qualifies for containing a high percentage of the acmite (NaFe³⁺Si₂O₆) molecule; consequently, a comparison of some thermal properties of aegirine and synthetic acmite was made.

A study on the thermodynamic properties of synthetic acmite was completed in this laboratory and the results have been published (1). The standard enthalpy of formation was found to be

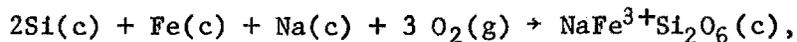
$$\Delta H_{298}^{\circ} = -615.87 \pm 0.71 \text{ kcal/mol.}$$

The analysis of the mineral aegirine used in this investigation (table 1) may be adjusted to pure acmite by substituting elements in the composition into the major sites as previously described. After making the associated thermal adjustments for these substitutions and the formula weight correction, the heat of solution value for pure aegirine was calculated to be -99.368 ± 0.200 kcal/mol. This value, substituted into reaction 10, table 3, in the reaction scheme for aegirine, along with ideal composition numbers for reactions 1, 3, and 8, provides a value of $+13.214 \pm 0.206$ kcal for the overall calorimetric reaction.

The standard enthalpy of formation of pure aegirine may be calculated according to the scheme

$$\begin{aligned}\Delta H_{298}^{\circ} \text{ (pure aegirine)} &= (+13.214 \pm 0.206) + 1/2\Delta H_{21} + 4\Delta H_{20} \\ &+ 2\Delta H_{12} + 1/2\Delta H_{15} - 1/2\Delta H_{23},\end{aligned}$$

which provides the reaction



for which

$$\Delta H_{298}^{\circ} \text{ (pure aegirine)} = -615.649 \pm 0.737 \text{ kcal/mol.}$$

This substantial agreement between the standard enthalpy of formation values for synthetic acmite and aegirine adjusted to the end member composition provides a reasonable endorsement for the synthesis and characterization procedures and for the adjustments made in the substitution and recalculation procedure.

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