American Mineralogist, Volume 68, pages 541–553, 1983

Heat capacity, relative enthalpy, and calorimetric entropy[1] of silicate minerals: an empirical method of prediction

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Abstract

A procedure to estimate the standard molar heat capacity, relative enthalpy, and calorimetric entropy of silicate minerals has been devised and evaluated. These are estimated by summing, in appropriate proportions, fictive molar isobaric heat capacities, relative enthalpies, and entropies evaluated for structural components of the mineral phases such as MgO-4, MgO-6, or MgO-8 where the Mg is in 4-, 6-, or 8-fold coordination, respectively. The fictive molar heat capacities and entropies were obtained from a large body of experimental calorimetric data on heat capacity, entropy, and relative enthalpy for minerals. The summation technique has a precision better than 2% for heat capacity and relative enthalpy, and 5% for entropy, relative to the data base, between 298 and 1500 K. The accuracy of prediction of molar heat capacity and relative enthalpy for mineral phases and specific heat for rocks is expected to be within 3% using this technique. The accuracy of prediction of molar calorimetric entropy is expected to be within 5% using this technique.

Tables of evaluated coefficients for the structural components of mineral phases are given. Three examples of calculations are given. (1) The estimated heat capacity of an illite is calculated and compared with experimental data which was not used in the evaluation. (2) The estimated relative enthalpy of acmite is calculated and compared with experimental data also not used in the evaluation. (3) The estimated calorimetric molar entropy of an illite is calculated and compared with data not used in the evaluation. In each of these cases, the estimated values deviate less than 2.5% from the observed values.

Introduction

The heat capacity of rocks and minerals must be known to evaluate data on both thermochemical and thermophysical properties. The heat capacity of minerals is needed to describe their entropy, enthalpy, and Gibbs energy properties as a function of temperature, to evaluate data on thermal diffusivity, and to calculate thermal diffusivity as a function of temperature.

In cases where experimental heat capacity measurements are lacking, inadequate, or unreliable, accurate estimates of these properties are needed. The estimation technique described below has an estimated accuracy better than 3 and 5%, respectively, for heat capacity and calorimetric entropy.

[1] The term "calorimetric entropy" is used as defined by Denbigh (1971, p. 419) and Ulbrich and Waldbaum (1976). Calorimetric entropy represents all contributions to entropy derived from the heat capacity integral from zero Kelvin, and includes lattice, electronic, and non-quenchable magnetic contributions to entropy.

Definitions and notation

Heat capacity is defined as the quantity of heat required to raise the temperature of a unit quantity of a substance one degree kelvin at constant pressure.

Relative enthalpy is defined as the quantity of heat required to change the temperature of a unit quantity of substance from a reference temperature (T_r) to a measurement temperature (T). Relative enthalpy is related to heat capacity by the following thermodynamic identity.

$$H_T - H_{T_r} = \int_{T_r}^{T} C_p \, dT \tag{1}$$

Calorimetric entropy is defined as

$$S_T - S_0 = \int_0^T \frac{C_p}{T} \, dT \tag{2}$$

and is determined from experimental low-temperature heat-capacity data.

0003–004X/83/0506–0541$02.00

Table 1. Experimental (and evaluated) data used to develop the functions for the fictive components

Phase	Property	No. of observations	Temperature range (K)	Reference
Akermanite	relative enthalpy	27	357-1605	Pankratz and Kelley (1964a)
	entropy	1	298	Robie et al. (1979)
Albite	apparent specific heats	14	373-1373	White (1919)
	relative enthalpy	5	472-1270	Kelley et. al. (1953)
	entropy	1	298	Robie et al. (1979)
Analbite	apparent specific heats	14	373-1373	White (1919)
	relative enthalpy	5	472-1270	Kelley et al. (1953)
	heat capacity	75	339-997	Hemingway et al. (1981)
	heat capacity	20	200-370	Openshaw et al. (1976)
Analcite	heat capacity	11	206-298	King (1955)
	entropy	1	298	Robie et al. (1979)
Andalusite	heat capacity	10	206-296	Todd (1950)
	relative enthalpy	13	397-1601	Pankratz and Kelley (1964b)
	entropy	1	298	Robie et al. (1979)
Anorthite	heat capacity	95	349-986	Krupka et al. (1979)
	heat capacity	49	202-381	Robie et al. (1978)
	apparent specific heats	17	373-1673	White (1919)
	relative enthalpy	15	400-1800	Ferrier (1969)
	entropy	1	298	Robie et al. (1979)
Anthopyllite	heat capacity	36	200-700	Krupka (1982)
	entropy	1	298	Krupka (1982)
Antigorite	heat capacity	10	206-296	King et al. (1967)
	relative enthalpy	11	405-847	King et al. (1967)
Bredigite	relative enthalpy	12	974-1690	Coughlin and O'Brien (1957)
Brucite	heat capacity	21	216-320	Giauque and Archibald (1937)
	entropy	1	298	Robie et al. (1979)
	relative enthalpy	12	350-699	King et al. (1975)
Ca-Olivine	heat capacity	10	206-296	King (1957)
	relative enthalpy	18	405-1112	Coughlin and O'Brien (1957)
	entropy	1	298	Robie et al. (1979)
Ca-Al Clinopyroxene	heat capacity	16	298-1000	Thompson et al. (1978)
	heat capacity	50	199-379	H.T. Haselton, unpublished data
	entropy	1	298	Robie et al. (1979)
Ca_2SiO_4, alpha	relative enthalpy	5	1714-1816	Coughlin and O'Brien (1957)
Ca_3SiO_5	heat capacity	9	206-296	Todd (1951)
	relative enthalpy	7	573-1773	Gronow and Schweite (1933)
Chrysotile	heat capacity	10	206-296	King et al. (1967)
Clinoenstatite	heat capacity	14	298-1600	Robie et al. (1979)
	heat capacity	9	215-295	Kelley (1943)
	relative enthalpy	13	580-1570	Wagner (1932)
	entropy	1	298	Robie et al. (1979)
Cristobalite, alpha	heat capacity	6	200-700	Robie et al. (1979)
	entropy	1	298	Robie et al. (1979)
Cristobalite, beta	heat capacity	17	400-2000	Robie et al. (1979)
Cyclowollastonite	heat capacity	7	201-295	Wagner (1932)
	relative enthalpy	12	576-1558	Wagner (1932)
	apparent specific heats	28	373-1673	White (1919)
	specific heat	6	194-298	Parks and Kelley (1926)

Data used in study

Data from three general categories of experimental techniques have been used in the evaluation of the heat capacity, relative enthalpy, and entropy estimation procedure. Data from *low-temperature calorimetry* were used in the evaluation to supply accurate values of heat capacity, at temperatures generally 200–300 K, and calorimetric entropy at 298 K. Data from *differential scanning calorimetry* were used to supply values of heat capacity at temperatures of 300–800 K. Data from *drop calorimetry* were used to evaluate mineral heat capacities and relative enthalpies at temperatures generally 300–1800 K.

The data used in this study came from the sources listed on Table 1. The coordination numbers for the cations in the major mineral groups are given on Table 2.

Table 1. (continued)

Phase	Property	No. of observations	Temperature range (K)	Reference
Analcite (dehydrated)	heat capacity	10	206-296	King and Weller (1961b)
	relative enthalpy	9	407-997	Pankratz (1968)
	entropy	1	298	Robie et al. (1979)
Diaspore	heat capacity	19	340-509	Krupka (1982)
	heat capacity	10	206-295	King and Weller (1961a)
	heat capacity	215	203-345	Perkins et al. (1979)
	heat capacity	15	312-585	Mukaibo et al. (1969)
	entropy	1	298	Robie et al. (1979)
Dickite	heat capacity	10	206-296	King and Weller (1961a)
Diopside	heat capacity	14	298-1600	Robie et al. (1979)
	heat capacity	29	298-1000	Krupka et al. (1980)
	relative enthalpy	15	599-1576	Wagner (1932)
	entropy	1	29	Robie et al. (1979)
Epidote	relative enthalpy	10	335-1100	Kiseleva et al. (1974)
Fayalite	heat capacity	31	208-381	Robie and Hemingway, in review
	relative enthalpy	13	395-1370	Orr (1953)
	entropy	1	298	Robie et al. (1979)
Fluorphlogopite	heat capacity	10	206-296	Kelley et al. (1959)
	relative enthalpy	12	400-1499	Kelley et al. (1959)
	entropy	1	298	Robie et al. (1979)
Forsterite	heat capacity	9	206-295	Kelley (1943)
	relative enthalpy	16	398-1807	Orr (1953)
	entropy	1	298	Robie et al. (1979)
Gehlenite	heat capacity	10	206-296	Weller and Kelley (1963)
	relative enthalpy	15	402-1801	Pankratz and Kelley (1964a)
	entropy	1	298	Robie et al. (1979)
Gibbsite	heat capacity	23	200-479	Hemingway et al. (1977)
	heat capacity	10	205-296	Shomate and Cook (1946)
	relative enthalpy	5	322-423	Shomate and Cook (1946)
Grossular	heat capacity	1	298	Haselton and Westrum (1979)
	heat capacity	50	350-978	Krupka et al. (1979)
	heat capacity	57	200-596	Westrum et al. (1979)
	entropy	1	298	Haselton and Westrum (1979)
Halloysite	heat capacity	10	206-296	King and Weller (1961a)
High Sanidine	apparent specific heats	14	373-1373	White (1919)
	heat capacity	69	339-997	Hemingway et al. (1981)
	heat capacity	20	200-370	Openshaw et al. (1976)
Jadeite	heat capacity	10	206-296	Kelley et al. (1953)
	heat capacity	11	298-1300	Robie et al. (1979)
	entropy	1	298	Robie et al. (1979)
Kaliophilite	heat capacity	10	206-296	Kelley et al. (1953)
	relative enthalpy	23	409-1799	Pankratz (1968)
Kaolinite	heat capacity	27	340-800	Hemingway et al. (1978)
	heat capacity	10	206-296	King and Weller (1961a)
	entropy	1	298	Robie et al. (1979)
Kyanite	heat capacity	10	206-296	Todd (1950)
	relative enthalpy	12	390-1503	Pankratz and Kelley (1964b)
	entropy	1	298	Robie et al. (1979)

Evaluation of fictive molar properties

Introduction

The standard molar heat capacity and calorimetric entropy of minerals at temperatures greater than 298 K have often been approximated by summing, in appropriate proportions, the standard molar heat capacity and calorimetric entropy of their constituent oxide formula groups. The realization that the heat capacity of most substances is approximately equal to the sum of the heat capacities of its constituent oxides or elements is quite old and can be traced back to a relationship proposed by Kopp (1864). More accurate estimates often can be obtained by a mineral summation technique, in which the standard molar heat capacity or entropy of reaction among oxides and silicates of similar structural class is assumed to be zero or a function of atomic mass, ionic size and charge, and/or molar volume (Lattimer, 1952; Nriagu, 1975; Saxena, 1976; Cantor, 1973, 1977; Helgeson *et al.*, 1978).

Table 1. (continued)

Phase	Property	No. of observations	Temperature range (K)	Reference
Larnite	heat capacity	10	206-296	Todd (1951)
	relative enthalpy	10	406-964	Coughlin and O'Brien (1957)
	entropy	1	298	Robie et al. (1979)
Lawsonite	heat capacity	16	206-296	King and Weller (1961b)
	heat capacity	8	298-600	Perkins et al. (1980)
	entropy	1	298	Robie et al. (1979)
Leonhardite	heat capacity	10	206-296	King and Weller (1961b)
	entropy	1	298	Robie et al. (1979)
Leucite	heat capacity	10	206-296	Kelley et al. (1953)
	relative enthalpy	21	409-1798	Pankratz (1968)
	entropy	1	298	Kelley et al. (1953)
Low Albite	heat capacity	75	339-997	Hemingway et al. (1981)
	heat capacity	20	200-370	Openshaw et al. (1976)
	entropy	1	298	Robie et al. (1979)
Margarite	heat capacity	24	200-1000	Perkins et al. (1980)
	entropy	1	298	Haas et al. (1980)
Merwinite	relative enthalpy	17	397-1601	Pankratz and Kelley (1964a)
	entropy	1	298	Robie et al. (1979)
Microcline	heat capacity	69	339-997	Hemingway et al. (1981)
	heat capacity	20	200-370	Openshaw et al. (1976)
	apparent specific heats	14	373-1373	White (1919)
	entropy	1	298	Robie et al. (1979)
Muscovite	heat capacity	62	332-967	Krupka et al. (1979)
	heat capacity	30	202-385	Robie et al. (1976)
	relative enthalpy	13	394-903	Pankratz (1964)
	entropy	1	298	Robie et al. (1979)
$Na_2Si_2O_5$	relative enthalpy	20	367-1164	Naylor (1945)
Nepheline	heat capacity	10	206-296	Kelley et al. (1953)
	entropy	1	298	Kelley et al. (1953)
Orthoenstatite	heat capacity	151	318-999	Krupka et al. (1980)
	entropy	1	298	Krupka et al. (1980)
Paragonite	heat capacity	82	200-759	R.A. Robie and B.S. Hemingway, unpub.
	entropy	1	298	R.A. Robie and B.S. Hemingway, unpub.
Phlogopite	entropy	1	298	Robie et al. (1979)
Prehnite	heat capacity	8	200-298	Perkins et al. (1980)
	heat capacity	12	298-800	Perkins et al. (1980)
	entropy	1	298	Haas et al. (1980)
Pyrope	heat capacity	9	264-345	Haselton and Westrum (1980)
	heat capacity	8	298-1000	Robie et al. (1979)
	entropy	1	298	Haselton and Westrum (1980)
Pyrophyllite	heat capacity	20	200-370	Robie et al. (1976)
	heat capacity	48	335-679	Krupka et al. (1979)
	entropy	1	298	Robie et al. (1979)
Quartz, alpha	heat capacity	5	200-600	Robie et al. (1979)
	entropy	1	298	Robie et al. (1979)

The general validity of any of these approaches is rooted in the fact that lattice vibrational modes are the dominant contribution to heat capacity and calorimetric entropy. To the degree that silicate mineral structures can be approximated as oxygen frameworks with vibrating interstitial cations, the overall lattice modes will be largely a function of the modes of the individual cation–oxygen polyhedra. It is this feature which allows the spectroscopist to identify both the coordination and composition of components in mineral phases from their spectral characteristics. This relationship also implies that the standard molar heat capacity and calorimetric entropy of minerals can be estimated by summing, in appropriate proportions, fictive molar heat capacities and calorimetric entropies for the constituent structural groups in minerals. The fictive molar heat capacities and fictive molar entropies are the average molar heat capacities and molar entropies of a component in a given coordination within the oxygen framework of the phase. Under this definition, Mg in 4-fold, 6-fold, and 8-fold coordination are listed as MgO-4, MgO-6, and MgO-8, respectively. The heat capacity and calorimetric entropy contribution of each component were found by least-squares evaluation as will be described below.

Table 1. (continued)

Phase	Property	No. of observations	Temperature range (K)	Reference
Quartz, beta	heat capacity	4	900-1200	Robie et al. (1979)
Rankinite	heat capacity	10	206-296	King (1957)
Sillimanite	heat capacity	10	206-296	Todd (1950)
	relative enthalpy	13	401-1496	Pankratz and Kelley (1964b)
	entropy	1	298	Robie et al. (1979)
Talc	heat capacity	13	200-300	Robie and Stout (1963)
	heat capacity	6	298-800	Robie et al. (1979)
	heat capacity	26	298-650	Krupka et al. (1977)
	entropy	1	298	Robie et al. (1979)
Tremolite	heat capacity	9	298-1100	Robie et al. (1979)
	heat capacity	21	298-800	Krupka et al. (1977)
	entropy	1	298	Robie et al. (1979)
Wollastonite	heat capacity	2	200-210	Cristescu and Simon (1934)
	heat capacity	7	199-303	Cristescu (1931)
	heat capacity	137	205-999	Krupka et al. (1980)
	relative enthalpy	5	573-1373	Gronow and Schweite (1933)
	relative enthalpy	13	484-1294	Southard (1941)
	relative enthalpy	7	323-1157	Roth and Bertram (1929)
	apparent specific heat	18	373-1573	White (1919)
	relative enthalpy	11	566-1383	Wagner (1932)
	entropy	1	298	Robie et al. (1979)
Zoisite	heat capacity	8	200-300	Perkins et al. (1980)
	heat capacity	11	298-730	Perkins et al. (1980)
	entropy	1	298	Haas et al. (1980)

However, the reader should be cautioned against drawing conclusions regarding possible fictive spectra for any of the fictive components presented here. While measured spectra can be integrated to supply reasonable estimates of heat capacity and entropy (Kieffer, 1979a, 1979b, 1979c, 1980), the nature of the inverse relationship indicates that heat capacity alone supplies, at best, only poor constraints on the possible vibrational modes.

This approach offers several advantages over other estimation techniques. The following problems with the other estimation techniques are eliminated:

1. The mineral summation techniques are path dependent. Results differ depending upon the specific minerals in structural classes which are used to derive estimates.

2. The mineral summation technique can produce discontinuities in the estimated heat capacity if phases in the summation have a lambda transition or phase inversion in the temperature interval of interest and no compensating corrections are applied.

The following improvements are offered:

1. The summation technique provides improved accuracy relative to oxide-summation or mineral-summation techniques because the coordination of the cation is accounted for.

2. It is possible to estimate heat capacity and calorimetric entropy even though data on representative minerals in similar structural classes are not available.

3. Anomalies in the properties of reference phases or in the oxides have been removed through averaging over a large body of data.

Fitting procedure

The heat capacity and entropy properties of the fictive structural components of mineral phases have been evaluated by means of weighted, simultaneous, multiple, least-squares regression using the procedure described by Haas and Fisher (1976) and Haas *et al.* (1981). The approach and procedure given there have been followed closely and will not be described here.

The mathematical model used in the evaluation of fictive component properties is based on Equation 3 for the heat capacity of mineral phases at constant pressure:

$$C_{p(\text{phase a})} = \sum_i N_i C'_{p,i} \tag{3}$$

where: N_i represents the stoichiometric coefficient of the ith fictive structural component in mineral phase a; and $C'_{p,i}$ represents the heat capacity function for the ith fictive structural component (the superscript (′) is used here to denote properties of the fictive components);

$$C'_{p,i} = a_i + 2b_iT + c_i/T^2 + f_iT^2 + g_i/T^{1/2} \tag{4}$$

where: a_i, b_i, c_i, f_i, and g_i are coefficients fitted to each structural component and T is temperature in kelvins.

Equation 4 is a restatement of Equation 6 of Haas and Fisher (1976). The mathematical model used in regression to fit relative enthalpy is based on the thermodynamic identity

Table 2. Structural factors for common silicate minerals

Mineral group/components	Coordination number
1. Olivine group - A_2SiO_4	
A site - Mg^{2+}, Fe^{2+}, Ni^{2+}, Ca^{2+}, Mn^{2+}	6
SiO_2 site	4
2. Garnet group - $A_3B_2Si_3O_{12}$	
A site - Ca^{2+}, Fe^{2+}, Mg^{2+}, Mn^{2+}	8
B site - Al^{2+}, Fe^{3+}, Mn^{3+}	6
SiO_2 site	4
3. Mica group - $W_{0-1}Y_{2-3}(Z_4O_{10})(OH)_2$	
W site - K^{1+}, Na^{1+}, Ca^{2+}, H_3O^{2+}	8-12*
Y site - Al^{3+}, Fe^{2+}, Mg^{2+}, Fe^{3+}	6
Z site - Si^{4+}, Al^{3+}	4
OH site - hydroxyl	-
4. Silica polymorphs - SiO_2, quartz, tridymite, cristobalite	
SiO_2	4
5. Feldspar group - XZ_4O_8	
X site - K^{1+}, Na^{1+}, Ca^{2+}	6-9**
Z site - Si^{4+}, Al^{3+}	4
6. Pyroxenoid group - $A_2Z_2O_6$	
A site - Ca^{2+}, Fe^{2+}, Mg^{2+}	6
Z site - Si^{4+}	4
7. Pyroxene group - ABZ_2O_6 (C2/C symmetry)	
A site - Ca^{2+}, Na^{1+}	8
A site - Mg^{2+}, Fe^{2+}	6
B site - Mg^{2+}, Fe^{2+}, Al^{3+}	6
Z site - Si^{4+}, Al^{3+}	4
8. Kaolinite group - $M_{2-3}Z_2O_5(OH)_4$	
M site - Al^{3+}, Mg^{2+}, Fe^{2+}, Fe^{3+}	6
Z site - Si^{4+}, Al^{3+}	4
OH site - hydroxyl	-
9. Aluminosilicate minerals - $ABSi_2O_5$ (andalusite, kyanite, sillimanite)	
A site - Al^{3+}	4, 5, 6***
B site - Al^{3+}	6
SiO_2 site	4

*Coordination number of 8 used for Na and Ca, 8 used for K in muscovite, and 6 used for K in phlogopite in evaluation of component properties.
**7 used.
***Coordination numbers of 4, 5, and 6 used for sillimanite, andalusite, and kaynite, respectively.

$$H_{T(\text{phase b})} - H_{T_r(\text{phase a})} = \int_0^T C_{p(\text{phase b})}\,dT - \int_0^{T_r} C_{p(\text{phase a})}\,dT$$

In the case where phases a and b are identical, the mathematical model used to fit relative enthalpy is

$$(H_T - H_{T_r})_{(\text{phase a})} = \sum_i N_i\,(H'_{i,T} - H'_{i,T_r}) \qquad (5)$$

where: N_i represents the stoichiometric coefficient of the ith structural component in mineral phase a, and $(H'_{i,T} - H'_{i,T_r})$ represents the relative enthalpy contribution of the ith fictive structural component:

$$(H'_{i,T} - H'_{i,T_r}) = a_i(T - T_r) + b_i(T^2 - T_r^2) - c_i\left(\frac{1}{T} - \frac{1}{T_r}\right) + \frac{1}{3}f_i(T^3 - T_r^3) + 2\,g_i(T^{1/2} - T_r^{1/2}) \qquad (6)$$

where: T_r represents the reference temperature of the relative enthalpy measurement.

In the case where phases a and b are not identical (a phase inversion occurs during the measurement process), the mathematical model used to fit relative enthalpy is

$$(H_{T(\text{phase a})} - H_{T_r(\text{phase b})}) = \Delta H_r + \sum_i N_i\,(H'_{i,T} - H'_{i,T_r}) \qquad (7)$$

where: ΔH_r is the enthalpy of reaction of phase b to phase a, and the other terms are the same as in Equations 5 and 6. Equation 7 is valid because phase inversions that are rapid enough to occur during a drop calorimetry measurement for all phases studied to date do not involve a change in structural components.

The mathematical model used in the regression step 2a to fit calorimetric entropy (at 298.15 K) is

$$(S_T - S_0)_{(\text{phase a})} = \sum_i N_i\,S'_i \qquad (8)$$

where: N_i represents the stoichiometric coefficient of the ith fictive structural component in mineral phase a, and S_i represents the calorimetric entropy contribution of the ith fictive structural component.

$$S'_i = a_i \ln T + 2b_iT - c_i/T^2 + e_i + f_iT^2/2 - 2g_i/T^{1/2} \qquad (9)$$

Equations 4, 6 and 9 are smoothing functions and have no theoretical basis beyond the thermodynamic identities shown in Equations 1 and 2. In our work, data at temperatures below 200 K were not considered. Above 200 K, the functions readily describe most data. In order to avoid overfitting of the data, nonsignificant constants have been eliminated from the general equation wherever they were not needed to describe the properties of a phase or fictive component. This is particularly common for the f_iT^2 term in Equation 2. Removal of this term eliminated any rapid excursions of the calculated values in the temperature region around and above the highest experimental temperature. Equations 4, 7, and 9 have been fit within the temperature range represented for each fictive structural component and should not be extended indiscriminately to higher or lower temperatures.

Table 3. Component coefficients to estimate mineral heat capacity and entropy (joules/mol.-Kelvin)

Component	a	b	c	e	f	g
Al_2O_3-4*	1.56985D+02	6.34774D-03	0.00000D+00	-9.92000D+02	0.00000D+00	-1.37221D+03
Al_2O_3-5	2.05756D+02	-7.82311D-03	0.00000D+00	-1.34963D+03	0.00000D+00	-2.08406D+03
Al_2O_3-6	2.22740D+02	-8.20451D-03	0.00000D+00	-1.50724D+03	0.00000D+00	-2.46456D+03
CaO-6	7.88255D+01	-1.91875D-03	0.00000D+00	-4.80538D+02	0.00000D+00	-6.22865D+02
CaO-7	7.88255D+01	-1.91875D-03	0.00000D+00	-4.71709D+02	0.00000D+00	-6.22865D+02
CaO-8	8.36079D+01	-2.97891D-03	1.96615D+04	-5.15167D+02	0.00000D+00	-7.16401D+02
Fe_2O_3-4/6	3.18412D+02	-4.89380D-02	4.17088D+05	---------**	2.57115D-05	-3.30795D+03
FeO-6	8.11612D+01	0.00000D+00	0.00000D+00	-4.85209D+02	0.00000D+00	-6.51941D+02
fluorine	1.39627D+01	1.28265D-02	0.00000D+00	-5.22387D+01	0.00000D+00	0.00000D+00
hydrate	5.69125D+01	0.00000D+00	0.00000D+00	-3.00702D+02	0.00000D+00	-2.63847D+02
hydroxyl	1.29124D+02	-6.01221D-03	6.32070D+05	-8.86693D+02	0.00000D+00	-1.64532D+03
K_2O-8	7.71711D+00	5.27163D-02	0.00000D+00	1.08368D+02	0.00000D+00	6.56875D+02
K_2O-6	4.24609D+01	1.70942D-02	0.00000D+00	-1.25937D+02	0.00000D+00	1.71435D+02
MgO-4	4.30846D+01	7.44796D-04	0.00000D+00	-2.06902D+02	0.00000D+00	0.00000D+00
MgO-6	8.99331D+01	-3.19321D-03	0.00000D+00	-5.88796D+02	0.00000D+00	-8.72529D+02
MgO-8	4.78300D+01	0.00000D+00	-8.10599D+05	-2.45321D+02	0.00000D+00	0.00000D+00
Na_2O-6	5.80738D+01	1.24598D-02	0.00000D+00	-2.26355D+02	0.00000D+00	-4.58234D+01
Na_2O-7	5.80738D+01	1.24598D-02	0.00000D+00	-2.51172D+02	0.00000D+00	-4.58234D+01
Na_2O-8	5.80738D+01	1.24598D-02	0.00000D+00	-2.59204D+02	0.00000D+00	-4.58234D+01
SiO_2-4	1.09383D+02	-2.77591D-03	0.00000D+00	-7.04147D+02	0.00000D+00	-1.08305D+03

*The number after the "-" in each component name indicates the coordination number of the component.
**Dashes indicate coefficient value has not been determined.

Haas (1974) described the mechanics used to fit the model to discrete experimental observations in detail. Data were weighted by the reciprocal of the precision; the higher (smaller in magnitude) the precision, the higher (larger in magnitude) the weight. The use of weighting served two purposes. First, it allowed the simultaneous fitting of different properties that have large variations in magnitude. An example is the simultaneous fitting of relative enthalpy data that could exceed 7 megajoules/mol and heat capacity data that are generally less than 1 kilojoule/mol-K. Second, weighting constrained the solution towards the more precise observations. This was particularly desirable where precise data from low-temperature, adiabatic calorimetry were being matched with the less precise data from differential scanning calorimetry or from drop calorimetry.

The author's stated precision was used in the first fitting of a data set from a particular reference. In subsequent cycles this would be modified *if* logic or other data showed the author's estimate to be abnormally small or large.

Results

Table 3 gives the coefficients for the heat-capacity function, Equation 2, and for the entropy function, Equation 4. They are given for the 20 different fictive components allowed in this study. Figure 1 contrasts the standard errors of estimate for 86 data sets using the average error in the fictive molar heat-capacity summation and the average error in the oxide heat-capacity summation as coordinates. The oxide sum calculations were corrected to remove the effects of lambda transitions occurring in the temperature intervals of interest. The dashed lines represent a 2% error of estimate for the data sets. On Figure 1, only 15 sets, a little more than 17%, lie outside the 2% bracket, that is, lie outside the vertical dashed lines, for the fictive method. However, 35 sets, a little more than 41%, lie outside the 2% brackets (the horizontal dashed lines) for the oxide method. Clearly, an estimate using the summation of the fictive component heat capacities is a significant improvement over a summation using the oxide heat capacities. Because the mineral-

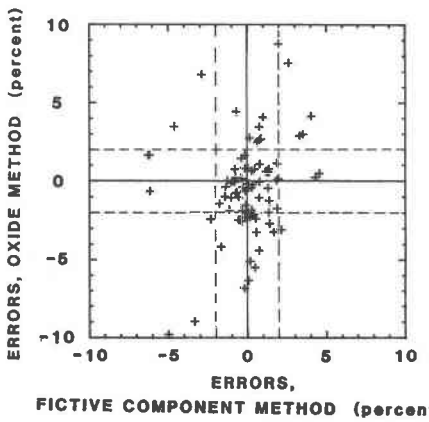

Fig. 1. Plots of the percentage errors for estimates averaged over the temperature range of the data set of the oxide-summation method against the fictive component method for 86 sets of heat-capacity data. Each (+) symbol represents the standard error of estimate, in percent, averaged over the temperature range of each set used and, therefore, represents as few as one or more than 100 observations. The vertical dashed lines emphasize 2% error for estimates using the fictive component method. The horizontal dashed lines emphasize 2% error of estimates using the oxide summation method. Less than half as many sets lie outside of the 2% envelope for the fictive component method than do for the oxide summation method.

Table 4. Part a. Conversion of the analyses to the number of moles of each oxide

Oxide	Wt %	Adjusted mols (n)
SiO_2	51.62	7.0202
TiO_2	0.92	0.0939
Fe_2O_3	1.63	0.0834
Al_2O_3	23.96	1.9203
FeO	0.29	0.0327
MgO	3.83	0.7763
CaO	0.47	0.0686
MnO	0.01	0.0008
Na_2O	0.14	0.0188
K_2O	8.12	0.7044
H_2O^+	5.00	2.2676
F	0.74	0.3187
H_2O^-	2.90	
P_2O_5	0.09	
Subtotal	99.72	
Less O	0.31	
Total	99.41	

summation technique of Helgeson *et al.* (1978) is path-dependent, a similar analysis is not available.

Figure 2 contrasts the standard errors of estimate for 45 data sets using the error in the fictive molar-entropy summation and the error in the oxide-entropy summation as coordinates. The dashed lines represent a 5% error of estimate for the data sets. Seven sets, approximately 16%, lie outside the 5% brackets for the fictive component method; whereas 20 sets, approximately 40% lie outside the 5% brackets for the oxide method.

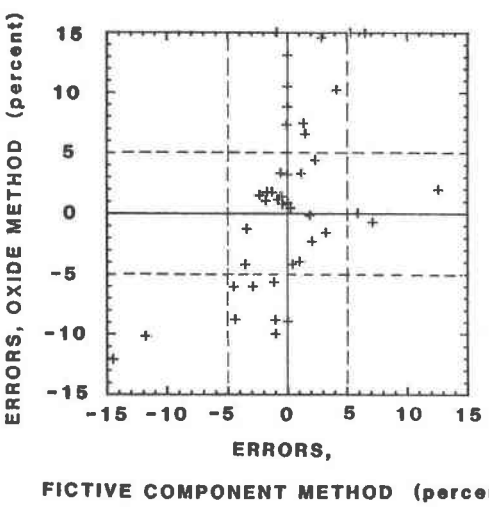

Fig. 2. Plots of the percentage errors for estimates from the oxide summation method against the percentage errors for estimates from the fictive component method for 45 sets of molar calorimetric entropy data at 298.15 K. The vertical dashed lines emphasize 5% error of estimates using the fictive component method. The horizontal dashed lines emphasize 5% error of estimates using the oxide summation method. Less than half as many sets lie outside of the 5% envelope for the fictive component method than do for the oxide summation method.

Procedures to calculate estimated molar heat capacities, relative enthalpies, and calorimetric molar entropies for minerals

Heat capacity

The molar heat capacity of silicate minerals as a function of temperature can be estimated using Equations 3 and 4. The coefficients a, b, c, e, f, and g for each structural component i can be found in Table 3. Table 2 contains a list of common silicate minerals defined in terms of their structural components. Other information regarding the structure of silicate minerals can be found in Papike and Cameron (1976) and Ulbrich and Waldbaum (1976).

As an example, the estimated heat capacity of an impure illite is calculated and compared with the measured values of Robie *et al.* (1976). The chemical analysis of the illite studied by Robie *et al.* was recast into the following generalized formula. The chemical analysis and adjusted molar formula are shown in Table 4a.

$$(K,Na,H_3O)_{x+y}[Al_{4-x}(Fe,Mg,Ca,Mn)_x][Si_{8-y-z}Ti_z(Al,Fe)_y]\,O_{20}(OH,F)_4$$

Table 4. Part b. Calculation of the constants a, b, c, f, and g for use in Equation 4 to calculate the heat capacity of illite of the composition given in part a of this table

Structural component	n'	n'·a_i	n'·b_i x10^{+3}	n'·c_i x10^{-5}	n'·f_i x10^{+5}	n'·g_i x10^{-3}
SiO_2-4	7.1141	778.16	-19.7481	0.0	0.0	-7.70493
TiO_2 included in SiO_2-4						
Fe_2O_3-4	0.0834	26.56	-4.0814	0.34785	21.4434	-0.27588
Al_2O_3-4	0.3596	56.45	2.2826	0.0	0.0	-0.49345
Al_2O_3-6	1.5607	347.63	-12.8048	0.0	0.0	-3.84644
FeO-6	0.0328	2.66	0.0	0.0	0.0	-0.02138
MgO-6	0.7763	69.82	-2.4789	0.0	0.0	-0.67734
CaO-6	0.0686	5.41	-0.1316	0.0	0.0	-0.04273
MnO included in FeO-6						
Na_2O-8	0.0188	1.09	0.2342	0.0	0.0	-0.00086
K_2O-12	0.7044	5.44	37.1334	0.0	0.0	0.46270
H_2O hydrate	0.4269	24.30	0.0	0.0	0.0	-0.11264
H_2O hydroxyl	1.8407	237.68	-11.0667	11.63451	0.0	-3.02854
F	0.3187	4.45	4.0878	0.0	0.0	0.0
H_2O^- corrected by Robie et al. (1979) to remove effect.						
P_2O_5 neglected in these calculations.						
		a	b	c	f	g
Constants for equation 2		1559.65	-6.5735 x10^{-3}	11.98236 x10^{+5}	21.4434 x10^{-5}	-15.74149 x10^{+3}

The composition of the illite studied by Robie *et al.* (1976) recast into the above molar formula is

$$(K_{1.41},Na_{0.04},H_3O_{0.28})[Al_{3.12}(Fe_{0.03},Mg_{0.78},Ca_{0.07})][Si_{7.11}(Al_{0.72},Fe_{0.17})]O_{20}(OH_{3.68},F_{0.32})$$

Part b of the table shows the procedure for getting the constants for illite of the cited composition for use in Equation 4, above. The analysis was chosen because (1) Robie *et al.* (1976) used this sample to measure the heat capacity between 15 and 380 K and (2) these data were not used to evaluate the fictive component functions given in Table 3.

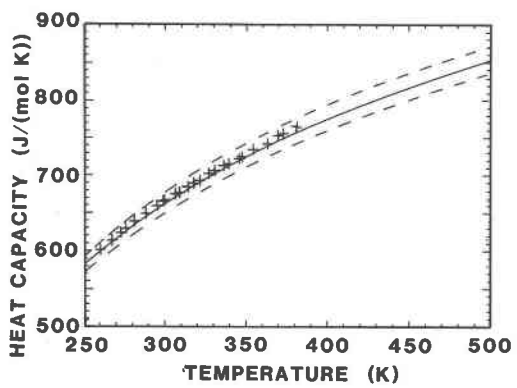

Fig. 3. Plot of the experimental and estimated heat capacities for an illite sample used by Robie *et al.* (1976). They are shown by + and a solid line, respectively. The analysis of the illite is given on Table 4a, column 2. The dashed lines represent an error of 2% about the estimated heat-capacity function. The function departs from the experimental data by about 0.9%.

Table 5. Calculation of the constants a, b, c, f, and g for use in Equations 5 and 6 to calculate the relative heat content of acmite ($NaFe^{3+}Si_2O_6$).

Structural component	Moles (n_i)	n_i·a_i x10^{-2}	n_i·b_i x10^{+3}	n_i·c_i x10^{-5}	n_i·f_i x10^{+5}	n_i·g_i x10^{-3}
Na_2O-8	0.5	0.29037	6.22990	0.0	0.0	-0.02291
Fe_2O_3-6	0.5	1.59206	2.44690	2.08544	1.28558	-1.65398
SiO_2-4	2.0	2.18766	-5.55182	0.0	0.0	-2.16610
		a	b	c	f	g
Constants for equation 5		4.07009 x10^{2}	3.12498 x10^{-3}	2.08544 x10^{+5}	1.28558 x10^{-5}	-3.84299 x10^{+3}

Part b of Table 4 shows the calculation of the coefficients a, b, c, f, and g for use in Equation 4 to calculate the heat capacity of the illite of the composition given in Table 4a. Column 2 of Table 4, part b (labeled n′) contains the moles of each structural component in this illite. Columns 3 through 7 of part b were obtained by multiplying the constants a through f of Table 3 by n′. The columns 3 through 7 were summed to get the constants for illite for use in Equation 2. The heat capacity of illite at any desired temperature was then calculated.

Figure 3 shows the experimental data of Robie *et al.* (1976) adjusted to the formula weight of 790.39 gm, the formula weight derived from this analysis. The solid line is the estimated value derived from the above constants. The dashed lines in Figure 3 represent a deviation of 2% from the calculated curve. The departure of the estimated values from the observed values is about 0.9%. This is a marked improvement over other methods where similar data for phases, especially those that have hydroxyl ions, can be estimated only poorly.

The estimation of the molar calorimetric entropy of an illite of this composition would follow the same approach and the procedure described in the entropy section.

Relative enthalpy

The molar relative enthalpy of silicate minerals can be estimated using Equations 5 and 6. The coefficients a, b, c, e, f, and g for each structural component i can be found in Table 3. Table 2 contains a list of common silicate minerals defined in terms of their structural components. Other information regarding the structure of silicate minerals can be found in Papike and Cameron (1976) and Ulbrich and Waldbaum (1976).

As an example, Table 5 shows the calculation procedure for estimating the relative enthalpy of acmite ($NaFe^{3+}Si_2O_6$). Acmite was chosen because experimental data on the relative enthalpy of acmite were not used to evaluate the estimation functions given in Table 3. As the calculation is for a stoichometric end-member phase,

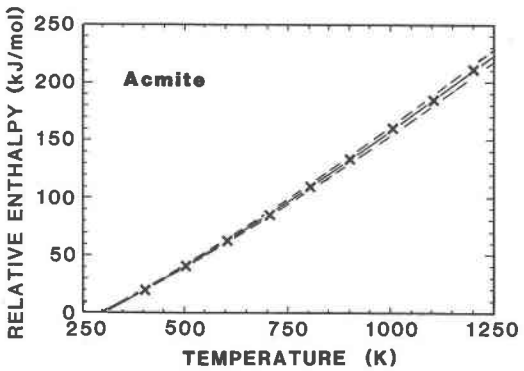

Fig. 4. Plot of experimental and estimated relative enthalpies (H_T-$H_{298.15}$) for acmite ($NaFe^{3+}Si_2O_6$). The estimated values were calculated using equations 5 and 6 and the coefficients listed in Table 5 and are shown by a solid line. The dashed lines represent an error of 2% about the estimated relative enthalpy function. The experimental measurements of Ko *et al.* (1977) on a synthetic acmite are shown by x. The function departs from the experimental data by about 0.4%.

the computational procedure is straightforward. The coefficients, a, b, c, f, and g used to describe the relative enthalpy of acmite are calculated by summing the products of the moles of each component i in one mole of acmite and the coefficients, a_i . . . g_i, for each component i. Figure 4 compares the calculated relative enthalpies with measured relative enthalpies (Ko *et al.*, 1977) for acmite. The dashed lines in Figure 4 represent a deviation of 2% from the calculated curve. Note that the measured relative enthalpy values lie well within this 2% window.

Entropy

The calorimetric molar entropy of silicate minerals can be estimated using Equations 8 and 9. The coefficients a, b, c, e, f, and g for each structural component i can be found in Table 3. Table 2 contains a list of common silicate minerals defined in terms of their structural components. Other information regarding the structure of silicate minerals can be found in Papike and Cameron (1976) and Ulbrich and Waldbaum (1976). In addition, Ulbrich and Waldbaum (1976) present structural information on silicate minerals needed to correct calorimetric entropy to third-law entropy.

The general procedure for the estimation of the molar calorimetric entropy for a phase would follow the same approach described in the calculation of estimated heat capacity of illite and relative enthalpy of acmite.

As an example, Table 6a shows the calculation procedure to estimate the calorimetric molar entropy of an ideal illite ($K_3Al_7Mg(Si_{14}Al_2)O_{40}(OH)_8$). Measured data on the calorimetric molar entropy of illite were excluded from the evaluation. Table 6b compares the observed value for the calorimetric molar entropy of illite (Robie *et al.*, 1976) with estimated values using (1) the estimation technique described here, (2) the estimation technique described by Helgeson *et al.* (1978), and (3) estimation based on sum of oxide entropies. The estimated molar entropy of illite at 298.15 K (1127.8 J/mol · K) differs by 2.1% from the measured molar entropy (1104.2±6.0 J/mol · K, Robie *et al.*, 1976).

Conclusions

A technique utilizing fictive structural components can provide accurate estimates of heat capacity and calorimetric entropy for silicate minerals. The properties of the fictive components were obtained from a multiple, least-squares regression of a large body of experimental data on silicate minerals. The uncertainty of estimate using this technique is approximately 2% for heat capacity and 5% for calorimetric entropy. The calculation procedure is easy to perform and is path independent. One restriction

Table 6. Part a. Calculation of the constants a. b, c, f, and g for use in Equation 9 to calculae the calorimetric entropy of illite ($K_3Al_7Mg(Si_{14}Al_2)O_{40}(OH)_8$) at 298.15 K.

Structural component	Moles (n_i)	$n_i \cdot a_i$ x10^{-2}	$n_i \cdot b_i$ x10^{+3}	$n_i \cdot c_i$ x10^{-6}	$n_i \cdot e_i$ x10^{-3}	$n_i \cdot f_i$	$n_i \cdot g_i$ x10^{-3}	S_{298} J/mol·K	$n_i \cdot S_{298}$ J/mol·K
K_2O-8	1.5	0.11576	79.07445	0.0	0.16255	0.0	0.98531	107.687	161.53
Al_2O_3-6	3.5	7.79590	-28.71579	0.0	-5.27534	0.0	-8.26596	42.411	148.44
MgO-6	1	0.89933	-3.13921	0.0	-0.58880	0.0	-0.87253	22.766	22.77
Al_2O_3-4	1	1.56985	6.34474	0.0	-0.99200	0.0	-1.37221	65.162	65.16
SiO_2-4	14	15.31362	-38.86274	0.0	-9.85806	0.0	-15.16270	42.865	600.11
Hydroxyl	4	5.16496	-24.04884	2.52828	-3.54677	0.0	-6.58128	32.437	129.75
		a	b	c	e	f	g		
Constants for equation 9		3.08594 x10^{+3}	-9.39839 x10^{-3}	2.52828 x10^{+6}	-2.00984 x10^{+4}	0.0	-3.16294 x10^{+4}		
Entropy at 298.15 K									1127.8

Table 6. Part b. Comparison of the observed calorimetric molar entropy of illite ($K_3Al_7Mg(Si_{14}Al_2)O_{40}(OH)_8$) with estimated values calculated from (1) the technique described here, (2) the technique described by Helgeson *et al.* (1978), and (3) the sum of oxide entropies.

	Observed*	Estimated (This paper)	Estimated** (Helgeson technique)	Estimated*** (Oxide sum)
Calorimetric entroy (at 298.15 K) J/mol·K	1104.2 ± 6.0	1127.8	1131.7	1164.1
Estimated value-observed value		23.6	27.5	59.9
Percent error		2.14	2.49	5.42

*Data from Robie et al. (1979).
**Calculated using the method of Helgeson et al. (1978), volume and entropy data from Robie et al. (1979), molar volume for illite of 558.3 ± 0.3 cm^3/mol from Guven (1972), and the reaction illite = 3 muscovite + brucite + 5 quartz.
***Oxide data, except H_2O, from Robie et al. (1979). A value of (S_{298}-S_0) for crystalline H_2O (ice) of 44.7 J/mol·K, calculated from information in Giauque and Stout (1936) was used in the calculation.

in use is that the crystal structure of the mineral phase in question must be sufficiently well known so that the appropriate coordination polyhedra (fictive components) may be defined.

Acknowledgments

We are grateful to R. A. Robie, B. S. Hemingway, and H. T. Haselton for making experimental results available prior to publication. Their kindness has provided critical information that greatly improved the results of this study. Reviews and comments by B. S. Hemingway, E. C. Robertson, S. W. Kieffer, H. C. Helgeson, B. R. Lipin, and A. Navrotsky greatly improved the manuscript. However, as always, only we, the authors, are responsible for any errors in judgment.

Financial support for this work has come in part from the National Bureau of Standards, U.S. Department of Commerce, under purchase order NB81NAGH5955 and NB82NAGK5391.

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Manuscript received, March 31, 1982;
accepted for publication, December 22, 1982.