

Heat capacities and entropies of phlogopite ($\text{KMg}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$) and paragonite ($\text{NaAl}_2[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$) between 5 and 900 K and estimates of the enthalpies and Gibbs free energies of formation

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Abstract

The heat capacities of phlogopite and paragonite have been measured from 5 to 1000 and 800 K, respectively, by combined cryogenic-adiabatic and differential scanning calorimetry. At 298.15 K (25°C) the molar heat capacity, C_p° , and the entropy change, $S_{298}^\circ - S_0$, are 355.1 ± 1.1 and 315.9 ± 1.0 J/(mol · K) for phlogopite and 321.5 ± 1.0 and 277.1 ± 0.9 J/(mol · K) for paragonite.

For the temperature range 298.15 to 1000 K, the molar heat capacity of phlogopite in J/(mol · K) is represented by

$$C_p^\circ = 872.13 - 0.07725T + 3.575 \times 10^{-5}T^{-2} - 8600.6T^{-0.5} (\pm 0.7 \text{ percent}).$$

For the temperature range 298 to 800 K, the molar heat capacity of paragonite is represented by

$$C_p^\circ = 688.44 + 0.03627T - 1.8604 \times 10^{-6}T^{-2} - 5816.1T^{-0.5} (\pm 0.5 \text{ percent}).$$

We have combined our calorimetric results with data from the P - T equilibrium studies of Chatterjee (1972) for the reaction



and with those of Holland (1979) for the reaction



to derive improved values for the enthalpy and Gibbs free energies of formation of paragonite. On the assumption that the paragonite formed in the equilibrium studies is disordered, in accord with crystal structure studies, our values are -5933.07 ± 4.70 and -5557.88 ± 4.70 kJ/mol for $\Delta H_{f,298}^\circ$ and $\Delta G_{f,298}^\circ$, respectively. If, however, paragonite is ordered, the correct values are -5949.33 ± 4.60 and -5568.46 ± 4.60 kJ/mol.

Introduction

As part of an ongoing study of the thermodynamic properties of the sheet-structure silicates (see Robie and Stout, 1963; Robie et al., 1976; Krupka et al., 1979) we have measured the heat capacities of phlogopite ($\text{KMg}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$) and paragonite ($\text{NaAl}_2[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$) from approximately 5 to 800 K by combined cryogenic-adiabatic and differential scanning calorimetry in order to evaluate their third-law entropies. We have combined our calorimetric results with data from experimental P_{H_2O} - T investigations using the third-law method (Robie, 1965; Krupka et al., 1979) in order to obtain values for the Gibbs free energy of formation, ΔG_f° , for phlogopite and paragonite between 298.15 and 800 K.

Paragonite is the sodium analog of muscovite and has a similar paragenesis. Although a number of equilibrium studies of the stability of paragonite at elevated temperatures exist, calorimetric data on this phase are limited to the C_p° equation of Holland (1979). The presently available thermodynamic data for paragonite are based on the

phase equilibrium studies of Chatterjee (1970, 1972) and Holland (1979) for a restricted temperature interval and are of somewhat questionable value without additional or supporting data.

Phlogopite is one of the most important of the rock-forming trioctahedral micas. It is widespread and is an important constituent in such diverse rock types as regionally metamorphosed magnesian limestones and kimberlites, where it may constitute as much as 30 volume percent of the rock (glimmerites). It is also of major commercial importance as an electrical insulator.

The only thermodynamic data available for phlogopite are estimates based on the slope of equilibrium P - T curves and a value for $\Delta G_{f,298}^\circ$ calculated by Bird and Anderson (1973) from data for the reaction 3 clinocllore + 5 muscovite = 5 phlogopite + 8 kyanite + quartz + 12 H_2O . Bird and Anderson (1973) used the equilibrium data of Bird and Fawcett (1973) for this reaction to calculate a value for ΔG_f° of phlogopite. In their calculations they used $\Delta G_{f,298}^\circ$ for clinocllore calculated by Zen (1972).

Table 1. Chemical analyses of phlogopite from Burgess, Ontario, and paragonite from Ilas de Margarita, Venezuela

	1	2	3	4	5	6	7	8	9
SiO ₂	43.20	40.3	41.18	39.66	47.16	46.7	48.02	46.36	46.90
Al ₂ O ₃	12.22	14.3	12.52	17.00	40.02	40.5	40.13	38.71	38.37
Fe ₂ O ₃		.63	.00	.27					
FeO		1.11	.30	.20		} .32	} .80	} .77	} .83
TiO ₂		1.32	.39	.56		.46		.05	.04
MnO		.03	.04						
MgO	28.98	26.4	27.32	26.49			.18	.10	.19
CaO		<.07	.00	none		.40		.22	.27
BaO		.16		.62					
Na ₂ O		.43	.88	.60	8.11	6.9	6.96	7.79	7.34
K ₂ O	11.29	10.1	11.93	9.97		.73	.64	.54	.51
H ₂ O ⁺	4.31	2.63	1.06	2.99	4.71		(3.27)*	(5.51)*	(5.60)*
H ₂ O ⁻		.91	.00			} 5.2			
F		3.2	6.74	2.24					
O=F	100.00	101.59	102.90	100.60	100.00	101.21		100.05	100.05
		1.34	2.84	.94					
		100.25	100.06	99.66					

1. KMg₃[AlSi₃O₁₀](OH)₂

2. Phlogopite, Burgess, Ontario, USNM 124158. Rapid-rock analysis, J. Marinenko, U.S. Geological Survey no. W-197309

3. " " " Jakob and Parga-Pondal (1932). Sample contains 0.54 Ti₂O₃.

4. " " " Clarke and Schneider (1890).

5. NaAl₂[AlSi₃O₁₀](OH)₂

6. Paragonite, Ilas de Margarita, Venezuela. Rapid-rock analysis, J. Marinenko, U.S. Geological Survey no. W-197310

7. " " " Microprobe analysis by L.B. Wiggins, U.S. Geological Survey.

8,9. " " " Microprobe analysis by W.V. Maresch (1972, W176-1 and W176-2).

*H₂O by difference.

Zen's value for $\Delta G_{f,298}^{\circ}$ of clinocllore differs by more than 106 kJ from the more recent values given by HENDERSON et al. (1983) which were obtained from more extensive equilibrium data and which had available measured values for the entropy and high-temperature heat capacity of clinocllore. However, for fluorphlogopite, KMg₃[Al-Si₃O₁₀]F₂, fairly extensive thermodynamic data exist (Kelley et al. (1959), with significant corrections by Robie et al. (1979).

In order to improve this situation, we have measured the heat capacities of paragonite and phlogopite over a wide temperature range to provide accurate entropies for both phases, and we have combined our C_p° and entropy data with data from earlier equilibrium studies to obtain more accurate values for the enthalpy and Gibbs free energy of formation as a function of temperature.

Calorimetric apparatus

Measurements of the heat capacities in the temperature range 5 to 380 K were made with the calorimeter described by Robie and Hemingway (1972) modified as discussed by Robie et al. (1976). Between 350 and 1000 K, heat capacities were determined by using a commercial differential scanning calorimeter, Perkin-Elmer DSC-2.¹ We have modified the scanning calorimeter by the addition of a digital voltmeter (Hewlett-Packard 3490A) and a desk computer (H.P. 9825T) so that all temperature and differential power data are now recorded automatically and all data reduction is done using the computer and programs written in this laboratory. The replacement of the standard chart recorder by the digital voltmeter provides a

¹ The use of trade names is for descriptive purposes only and does not imply endorsement by the U. S. Geological Survey.

significant improvement in the precision with which heat capacities may be measured, (from ± 0.9 to ± 0.4 percent).

Materials

Phlogopite

Our calorimetric sample of phlogopite was separated from a large "book" of amber-colored crystals from Burgess, Ontario, that was obtained from the U. S. National Museum (USNM 124158) through the courtesy of J. S. White, Jr. Material from this same locality has been used previously by Yoder and Eugster (1954) in studies of the stability and synthesis of phlogopite and by Hendricks and Jefferson (1939) in their classic study of the polymorphism of the micas. A chemical analysis of our sample by the method of Shapiro (1975) is given in Table 1, column 2, together with two earlier analyses of the Burgess Ontario, phlogopite, columns 3 and 4.

The sample mass, corrected for buoyancy, used for our heat capacity measurements was 33.066 g. The unit cell parameters are: $a = 0.531 \pm 0.002$ nm, $b = 0.922 \pm 0.003$ nm, $c = 1.022 \pm 0.003$ nm, and $\beta = 100.00 \pm 0.03^\circ$, and the structure type is 1M (M. R. Ross, U. S. Geol. Survey, personal communication, 1982) determined by single crystal methods.

Paragonite

The sample of paragonite used for our heat capacity measurements was separated from a schist collected by Dr. Walter Maresch (Bochum University) from the Ilas de Margarita, Venezuela. The geology and petrology of the locality have been described by Maresch (1972). Approximately 100 kg of rock was crushed in a jaw mill, and the paragonite was separated by successive passes over an asymmetric vibrating table (Faul and Davis, 1959), followed by heavy-liquid (tetrabromethane) separation, and, finally, handpicking under a binocular microscope. Analytical data for our calorimetric sample are given in Table 1, columns 6-9. Unit cell parameters are $a = 0.5130 \pm 0.0010$ nm, $b = 0.8905 \pm 0.0017$ nm, $c = 1.9342 \pm 0.0039$ nm, and $\beta = 94.5 \pm 0.2^\circ$, and the structure type is $2M_1$ (M. R. Ross, written communication, August 1982). These parameters are in good agreement with those reported by Chatterjee (1974) and Holland (1979) for synthetic $2M_1$ paragonite. The sample mass, corrected for buoyancy, used for our measurements was 27.393 g.

Experimental results 5 to 380 K and impurity corrections

The samples were heated at 120°C for 2 hours prior to loading in the low-temperature calorimeter and were sealed under approximately 25 mm pressure (3.3 kPa) of purified helium gas to promote rapid thermal equilibration. Our experimental results for the specific heat of the Burgess, Ontario, phlogopite and the Ilas de Margarita, Venezuela, paragonite, between 5 and 383 K are listed in their chronological order of measurement in Tables 2 and 3, and are shown graphically as molar heat capacities, after correction for impurities, in Figure 1. The specific heat of synthetic 1M fluorophlogopite, Kelley and others (1959) is systematically less than that of hydroxyphlogopite by 0.1 to 4.5 percent between 52 and 296 K.

In order to obtain the thermodynamic properties of

Table 2. Experimental specific heats of phlogopite from Burgess, Ontario (USNM 124158), measured by adiabatic calorimetry. The data are uncorrected for deviation from the composition $\text{KMg}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$.

T	Specific heat	T	Specific heat
K	J/(g \cdot K)	K	J/(g \cdot K)
Series 1			
50.75	0.0886	330.12	0.8820
55.04	0.1031	337.54	0.8927
59.45	0.1185	345.00	0.9029
64.41	0.1359	352.50	0.9133
69.74	0.1556	360.06	0.9231
75.01	0.1758	367.65	0.9332
80.28	0.1963	375.18	0.9424
85.58	0.2180	382.67	0.9508
90.95	0.2391		
96.41	0.2608		
101.76	0.2819		
Series 2			
94.13	0.2516	6.23	0.00092
99.92	0.2746	6.73	0.00108
105.50	0.2966	7.23	0.00117
110.80	0.3174	7.77	0.00125
116.04	0.3381	8.37	0.00139
121.28	0.3581	9.08	0.00156
126.50	0.3780	10.05	0.00185
131.74	0.3975	11.26	0.00227
136.98	0.4168	12.78	0.00298
		14.37	0.00400
		15.82	0.00515
		17.48	0.00682
		19.36	0.00925
		21.32	0.01226
		23.45	0.01585
		25.91	0.02058
		28.69	0.02654
		31.84	0.03399
		35.56	0.04538
		39.72	0.05499
		44.13	0.06774
		48.73	0.08178
Series 3			
127.00	0.3799		
132.69	0.4010		
138.10	0.4206		
143.34	0.4394		
148.62	0.4579		
153.94	0.4760		
159.32	0.4939		
164.74	0.5116		
170.20	0.5290		
175.74	0.5465		
181.17	0.5628		
187.03	0.5802		
193.88	0.5999		
		189.86	0.5884
		197.23	0.6091
		204.55	0.6290
		212.01	0.6485
		219.52	0.6676
		227.09	0.6862
		234.72	0.7042
		242.22	0.7213
		249.70	0.7378
		257.26	0.7538
		264.90	0.7694
		272.64	0.7846
		280.39	0.7993
		288.91	0.8157
		296.30	0.8287
Series 4			
302.72	0.8389		
309.76	0.8503		
316.84	0.8618		
324.05	0.8730		
331.39	0.8841		
338.77	0.8941		
		296.30	0.8287

$\text{KMg}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$ from our measured specific heats on the mineral sample having the composition of column 2, Table 1, we first normalized the heat capacity to that mass of sample which contains exactly one mole, (418.815 g) of $\text{KMg}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_{1.22}\text{F}_{.78}$ plus the associated impurities. The impurity atoms were then combined into various (fictive) oxide and silicate phases for which the heat capacity at low temperature was available; and from the heat capacity of 462.960 g of sample, we subtracted the heat capacities of the fictive impurity phases to obtain the molar heat capacity of $\text{KMg}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_{1.22}\text{F}_{.78}$. We then used the C_p° data of Kelley and others (1959) for synthetic $\text{KMg}_3[\text{AlSi}_3\text{O}_{10}]\text{F}_2$ to make the corrections for the fluorine replacement of the hydroxyl and obtain the thermodynamic properties of ideal $\text{KMg}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$.

Table 3. Experimental specific heats of paragonite from Ilas de Margarita, Venezuela, measured by adiabatic calorimetry. The data are uncorrected for deviations from the composition $\text{NaAl}_2[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$.

T	Specific heat	T	Specific heat
K	J/(g·K)	K	J/(g·K)
Series I			
5.54	0.00025	135.04	0.3970
6.25	0.00036	140.71	0.4171
6.94	0.00048	146.39	0.4370
7.79	0.00058	152.01	0.4568
8.75	0.00080	157.58	0.4752
9.74	0.00108	163.12	0.4933
10.78	0.00140	168.62	0.5113
11.94	0.00168	174.19	0.5290
13.14	0.00206		
14.40	0.00262		
15.93	0.00334		
17.80	0.00457	171.75	0.5226
19.92	0.00655	177.44	0.5406
22.06	0.00897	183.12	0.5583
24.22	0.01195	188.87	0.5759
26.45	0.01555	194.52	0.5926
28.87	0.02004	200.26	0.6093
31.69	0.02610	206.46	0.6268
35.05	0.03428	212.95	0.6446
39.06	0.04498	219.33	0.6618
43.68	0.05840	225.61	0.6787
48.84	0.07444	231.80	0.6946
Series II			
306.37	0.8587	238.06	0.7107
313.46	0.8720	244.15	0.7259
321.10	0.8858	250.10	0.7403
328.78	0.8990	255.99	0.7537
336.40	0.9120	262.11	0.7678
		268.47	0.7815
Series III			
343.97	0.9241	274.76	0.7920
351.45	0.9359	280.99	0.8089
358.88	0.9482	287.28	0.8221
366.25	0.9594	293.56	0.8315
373.56	0.9699	300.22	0.8475
380.83	0.9802	306.81	0.8600
Series IV			
52.07	0.0857		
57.24	0.1036		
62.70	0.1228		
68.15	0.1427		
Series V			
Series VI			
Series VII			
Series VIII			

In order to obtain the heat capacity of $\text{KMg}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$ from our corrected results for the solid solution $\text{KMg}_3[\text{AlSi}_3\text{O}_{10}](\text{OH}_{1.22}\text{F}_{0.78})$, we have utilized the C_p° data for $\text{KMg}_3[\text{AlSi}_3\text{O}_{10}]\text{F}_2$ and assumed that these two phases obey the law of corresponding states (see Guggenheim, 1950, p. 138–144; Stout and Catalano, 1955). This assumption should be reasonably accurate inasmuch as the difference in formula weights is less than 1.0 percent, the two micas are isostructural, their molar volumes differ by only 2.4 percent, and their molar heat capacities differ by 4.5 percent or less between 50 and 300 K. The law of corresponding states asserts that for structurally similar phases, certain thermophysical properties such as the heat capacity have the same value at the same (corresponding) value of T/θ where θ is the characteristic temperature of the phase calculated from the Debye model.

In Figure 2 we show schematically the manner by which we have corrected our experimental data on the

solid solution $\text{KMg}_3[\text{AlSi}_3\text{O}_{10}](\text{OH}_{1.22}\text{F}_{0.78})$ to values for pure hydroxyphlogopite (P). From our measured values of C_p° of the solid solution and those of fluorphlogopite, we obtained the corresponding temperatures T_F and T_X at which the heat capacity of fluorphlogopite (F) and that of the solid solution (X) have the same value. We then assumed the relation $(T_X - T_F)/(T_P - T_F) = 1.22/2.00$ where the right hand side of the equation corresponds to the mole fraction of hydroxyphlogopite in our specimen and where T_P is the corresponding temperature for $\text{KMg}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$, and calculated values of T_P , obtaining the dashed curve in Figure 2. The correction was done graphically at 20-K intervals in T_F as for example as shown by T_F , T_X , and T_P . If the corresponding states model were exact, the ratio T_F/T_X would be a constant independent of temperature. In reality T_F/T_X varies by about 3 percent between 50 and 250 K.

Although our final results for C_p° of hydroxyphlogopite differ but slightly from what one would have obtained from the simpler assumption of additivity of the constituent oxide heat capacities, they do have a somewhat firmer physical justification. We also point out that, had we not made any correction for impurities, the resultant value for S_{298}° would have differed from our corrected value by only -1.3 percent.

The difference between the specific heats corrected for impurities as indicated above and the measured values was 2.4 percent at 50 K, 1 percent at 100 K, and less than 0.6 percent above 145 K. The corrected C_p° of phlogopite

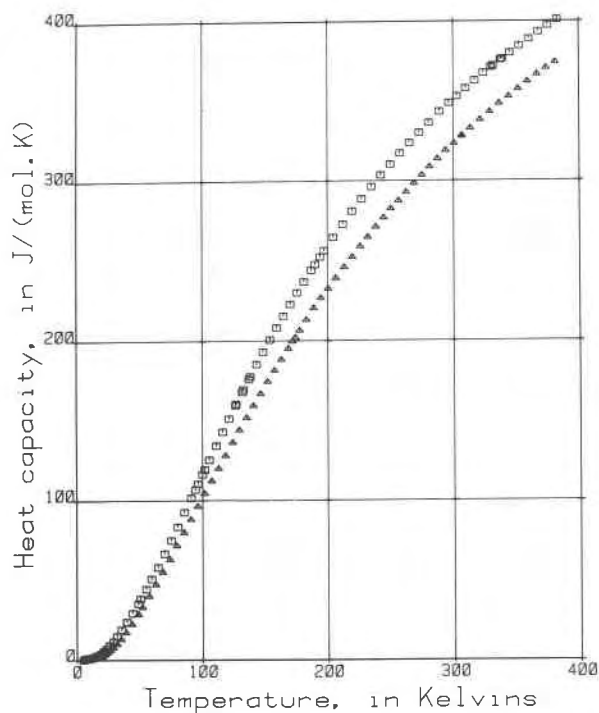


Fig. 1. Experimental molar heat capacities of phlogopite (squares) and paragonite (triangles) between 5 and 380 K.

at 298.15 K is 355.1 ± 1.1 J/(mol · K), and the corrected entropy change $S_{298}^{\circ} - S_0^{\circ}$, is 315.9 ± 1.0 J/(mol · K).

For paragonite, our experimental specific heats were corrected for deviation of the sample from the exact composition $\text{NaAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ as follows: 454.54 g of sample having the composition of column 6, Table 1, was assumed to consist of 1 mole (382.202 g) of $\text{NaAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$, 27.88 g of $\text{KAl}_2[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$, 29.17 g of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, 7.51 g of $\text{CaAl}_2\text{Si}_2\text{O}_8$, 2.08 g of TiO_2 , 1.44 g of Fe_2O_3 , 3.98 g of Al_2O_3 , and 0.28 g of CaO . The heat capacities of these fictive impurity phases were subtracted from the measured heat capacity of 454.54 g of material. The difference between the corrected and uncorrected heat capacities is 0.4 percent or less for temperatures above 52 K. At 298.15 K, the corrected C_p° for paragonite is 321.5 ± 1.0 J/(mol · K).

Although no theoretical justification exists for the assumption of additivity of the heat capacities of component oxides, experiments show that this assumption is usually good to the order of 5–10 percent for temperatures above 100 K (Fig. 3).

At 100 K, the entropy of paragonite, S_{100}° , is less than 20 percent of S_{298}° , and from Figure 4, it seems reasonable to assume that the approximation of the additivity of oxide heat capacities is good to the order of 10 percent for temperatures above 100 K. Inasmuch as the total impurity correction never exceeds 2.5 percent, the corresponding uncertainty in the *corrections* should not contribute

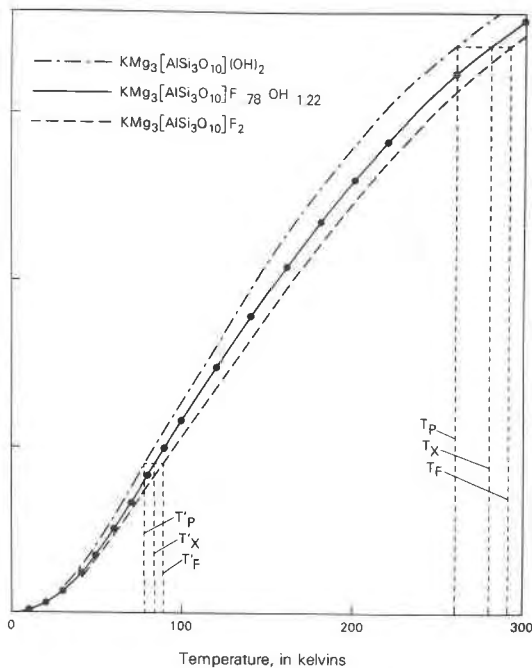


Fig. 2. Schematic of corresponding states correction for fluorphlogopite component of $\text{KMg}_3[\text{AlSi}_3\text{O}_{10}](\text{OH}_{1.22}\text{F}_{.78})$ solid solution. A description of the symbols and the procedure is given in the text.

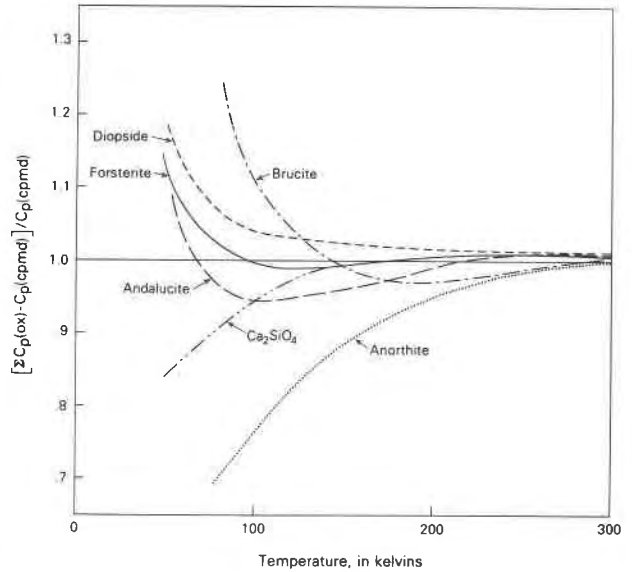


Fig. 3. Comparison of the sum of the heat capacities of oxides $\Sigma C_p(\text{ox})$ with the heat capacities of various silicates $C_p(\text{cpmd})$ as a function of temperature.

more than 0.2 percent to the final corrected values of C_p° and should not contribute more than 0.05 percent to S_{298}° . The corrected entropy change, $S_{298}^{\circ} - S_0^{\circ}$ for paragonite is 277.1 ± 0.9 J/(mol · K).

We have extrapolated our measurements to 0 kelvin using a plot of C_p°/T versus T^2 as indicated in Figure 4. For

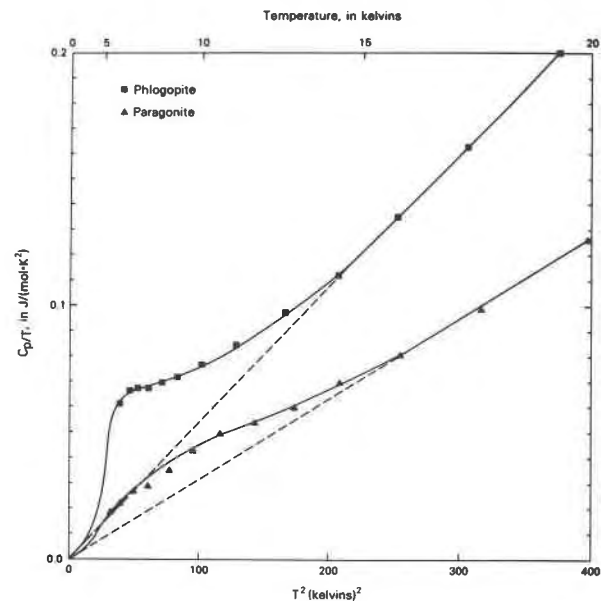


Fig. 4. C_p°/T versus T^2 extrapolation of experimental C_p° measurements to 0 kelvin for natural phlogopite and paragonite. Dashed lines represent extrapolation used to calculate entropy of the iron free phases. For phlogopite the dashed line corresponds to $\theta_D = 431$ K and for paragonite $\theta_D = 506$ K.

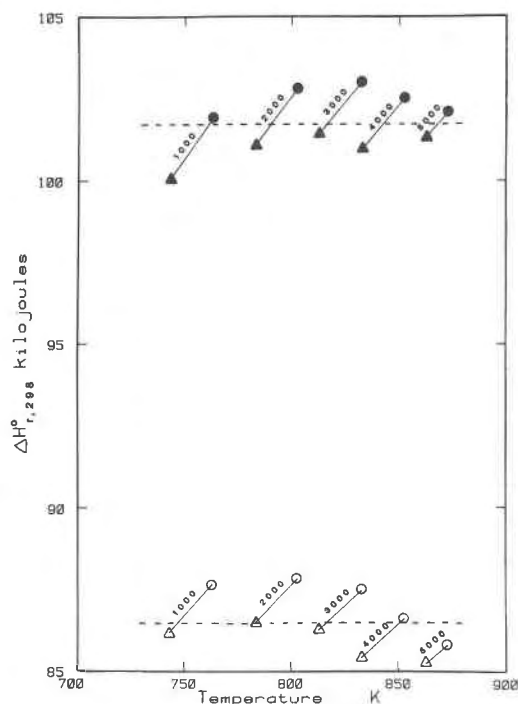


Fig. 5. Value of $\Delta H_{r,298}^\circ$ for reaction (5a) calculated from a third-law treatment of the data of Chatterjee (1972). Triangles indicate the lower temperature and circles the upper temperature for the reaction equilibrium brackets. The open symbols were calculated assuming paragonite is disordered and the solid symbols assuming paragonite is ordered. The dashed line is the average value calculated from the equilibrium data. The H_2O pressure in bars is indicated for each bracket.

a diamagnetic solid at very low temperatures, $C_p^\circ \approx aT^3$ and a plot of C_p°/T vs. T^2 should yield a straight line passing through the origin. Our data for both phlogopite and paragonite show significant deviations from this expected behavior below 15 K. We attribute these abnormalities in the C_p°/T vs. T^2 curves to the presence of the small amount of iron in solid solution in these samples leading to a Schottky-type contribution to the heat capacity at very low temperatures (see for example, Gopal, 1966, p. 102–105).

The excess heat capacity (and entropy) arising from these Schottky contributions is in addition to the excess lattice heat capacity caused by the replacement of magnesium by iron (in phlogopite) and must also be corrected for in order to obtain C_p° and the entropy for pure $KMg_3[AlSi_3O_{10}](OH)_2$ and $NaAl_2[AlSi_3O_{10}](OH)_2$. This correction was made by extrapolating smoothly the C_p°/T versus T^2 curve from temperatures above the anomalous region to $C_p^\circ/T = 0$ at zero kelvin as indicated by the dashed lines in Figure 4. The dashed lines correspond to θ_D values of 431 and 506 K for hydroxyphlogopite and paragonite respectively.

For phlogopite, the difference in the entropy at 15 K calculated for the solid (experimental) and dashed (ex-

cluding the Schottky anomaly) curve corresponds to ≈ 0.2 J/(mol · K) and is in reasonable agreement with that calculated for the replacement of 0.015 moles of Mg^{2+} by Fe^{2+} (i.e., $0.015 R \ln 5 = 0.2$ J/(mol · K)) and is, we believe, justification of our use of the extrapolation represented by the dashed curves in Figure 5. For paragonite, the difference in the entropy at 15 K calculated from the dashed and solid curves is 0.13 J/(mol · K).

Experimental results 350 to 1000 K

Above 350 kelvin we also measured the heat capacities of phlogopite and paragonite using a differential scanning calorimeter. The samples were enclosed in gold pans and were studied at a heating rate of 10 K/min and a sensitivity of 1.25 J/min. The sample of phlogopite weighed 22.14 mg and that of paragonite 22.50 mg. Our experimental results for phlogopite and paragonite, uncorrected for deviation from the ideal formulas, are listed in Tables 4 and 5, respectively. Our results were fit by least squares to the equation

$$C_p^\circ = a + bT + c/T^2 + dT^{-0.5} \quad (1)$$

which was constrained to join smoothly with the values obtained from our more accurate low-temperature adia-

Table 4. Experimental specific heats of phlogopite from Burgess, Ontario, measured by differential scanning calorimetry. Data are uncorrected for deviation from the formula $KMg_3[AlSi_3O_{10}](OH)_2$.

Temp Kelvins	C_p° J/(g·K)	Temp Kelvins	C_p° J/(g·K)
349.7	0.9228	649.7	1.127
359.7	0.9396	659.7	1.132
369.7	0.9551	669.7	1.132
379.7	0.9364	679.7	1.138
389.7	0.9785	689.7	1.145
399.7	0.9873	699.7	1.150
409.7	0.9942	709.7	1.154
419.7	1.002	719.7	1.160
429.7	1.009	729.7	1.165
439.7	1.017	739.7	1.168
449.7	1.020	749.7	1.173
459.7	1.034	759.7	1.167
469.7	1.039	769.7	1.173
479.7	1.053	779.7	1.180
489.7	1.054	789.7	1.179
499.7	1.061	799.7	1.177
469.9	1.039	869.6	1.187
479.8	1.047	879.4	1.195
489.8	1.054	889.3	1.200
499.8	1.060	899.2	1.205
509.8	1.064	909.1	1.215
519.8	1.070	918.9	1.219
529.8	1.077	928.8	1.228
539.8	1.082	938.7	1.231
549.8	1.088	948.6	1.227
559.8	1.092	958.4	1.232
569.8	1.099	968.3	1.227
579.8	1.103	978.2	1.232
589.7	1.106	988.1	1.236
599.7	1.110	997.8	1.237
609.7	1.118	898.9	1.210
619.7	1.122	889.0	1.196
629.7	1.127	879.1	1.187
639.7	1.134	859.3	1.187
649.7	1.140	849.4	1.182
619.8	1.119	839.5	1.178
629.8	1.123	809.5	1.174

batic calorimetry between 300 and 370 K. Between 298 and 1000 K the molar heat capacity of ideal hydroxyphlogopite may be represented by the equation

$$C_p^\circ = 872.13 - 0.07725T + 3.575 \times 10^{-5}T^{-2} - 8600.6T^{-0.5} \quad (2)$$

with an average deviation ± 0.7 percent, and that for ideal paragonite between 298 and 800 K by the equation

$$C_p^\circ = 688.44 + 0.03627T - 1.8604 \times 10^6T^{-2} - 5816.1T^{-0.5} \quad (3)$$

with an average deviation of ± 0.5 percent.

Our high-temperature heat capacities for paragonite differ from those calculated from the equation given by Holland (1979) for a synthetic paragonite by -1.3 percent at 400 K, -1.4 percent at 600 K, and $+0.8$ percent at 800 K. At 800 K, our value for $S_{800}^\circ - S_{298}^\circ$ is 1 percent (i.e., 4.5 J/(mol · K)) less than that obtained from Holland's equation.

Thermodynamic properties of KMg₃[AlSi₃O₁₀](OH)₂ (phlogopite) and NaAl₂[AlSi₃O₁₀](OH)₂ (paragonite)

Our experimental data for phlogopite and paragonite, corrected for curvature and impurities and extrapolated to 0 kelvin, were smoothed graphically (using a mechanical spline) below 30 K and by orthogonal polynomial

Table 5. Experimental specific heats of paragonite from Ilas de Margarita, Venezuela, measured by differential scanning calorimetry. Data are uncorrected for deviation from the formula NaAl₂[AlSi₃O₁₀](OH)₂

Temp Kelvins	C _p ^o J/(g·K)	Temp Kelvins	C _p ^o J/(g·K)
339.7	0.9228	569.8	1.145
349.7	0.9338	579.8	1.151
359.7	0.9416	589.7	1.158
369.7	0.9268	599.7	1.164
379.7	0.9702	609.7	1.170
389.7	0.9861	619.7	1.180
399.7	0.9982	629.7	1.192
409.7	1.012	639.7	1.201
419.7	1.021	649.7	1.210
429.7	1.027	619.8	1.194
439.7	1.036	629.8	1.202
449.7	1.040	639.7	1.208
459.7	1.064	649.7	1.214
469.7	1.064	659.7	1.217
479.7	1.079	669.7	1.222
489.7	1.089	679.7	1.228
499.7	1.103	689.7	1.228
469.9	1.072	699.7	1.230
479.8	1.081	709.7	1.235
489.8	1.090	719.7	1.238
499.8	1.097	729.7	1.244
509.8	1.101	739.7	1.246
519.8	1.108	749.7	1.250
529.8	1.115	759.7	1.251
539.8	1.121	769.7	1.260
549.8	1.127	779.7	1.271
559.8	1.135		

curve fitting (Justice, 1969) between 30 and 380 K and were used to generate the thermodynamic functions at integral temperatures listed in Tables 6 and 7. In both tables, the function $S_T^\circ - S_0^\circ$ is tabulated and not the absolute entropy.

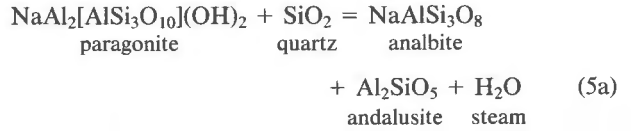
The crystal structure of 2M₁ paragonite has been refined by Burnham and Radoslovich (1964) by X-ray studies and by Sidorenko et al. (1974) by electron diffraction. Hazen and Burnham (1973) and Joswig (1972) have refined the structure of 1M phlogopite by X-rays and neutron diffraction, respectively, and McCauley et al. (1973) have refined the structure of fluorophlogopite (1M). All these investigators concur that the tetrahedral aluminum atoms are randomly distributed in both these mica

Table 6. Molar thermodynamic properties of hydroxyphlogopite KMg₃[AlSi₃O₁₀](OH)₂. Formula weight = 417.262 g mol⁻¹. Entropy and Gibbs energy function are not corrected for possible zero-point entropy.

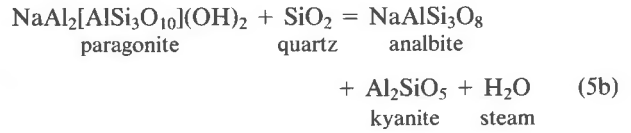
Temp. K	Heat capacity C _p ^o	Entropy (S _T ^o - S ₀ ^o) J/(mol·K)	Enthalpy function (H _T ^o - H ₀ ^o)/T	Gibbs energy function -(G _T ^o - H ₀ ^o)/T
5	0.082	0.026	0.019	0.007
10	0.620	0.208	0.155	0.053
15	2.008	0.686	0.511	0.175
20	4.497	1.571	1.167	0.404
25	8.198	2.952	2.185	0.767
30	12.83	4.842	3.561	1.282
35	18.20	7.218	5.264	1.955
40	24.04	10.03	7.241	2.784
45	30.29	13.21	9.452	3.763
50	36.93	16.75	11.86	4.882
60	51.23	24.72	17.22	7.508
70	66.63	33.77	23.16	10.60
80	82.71	43.71	29.60	14.11
90	99.13	54.40	36.41	17.99
100	115.6	65.70	43.51	22.19
110	132.0	77.49	50.81	26.68
120	148.1	89.67	58.25	31.42
130	163.8	102.1	65.77	36.38
140	179.0	114.8	73.32	41.53
150	193.7	127.7	80.85	46.84
160	208.0	140.7	88.35	52.30
170	221.9	153.7	95.80	57.88
180	235.5	166.8	103.2	63.56
190	248.4	179.8	110.5	69.34
200	260.7	192.9	117.7	75.19
210	272.3	205.9	124.8	81.11
220	283.2	218.8	131.7	87.07
230	293.6	231.6	138.6	93.08
240	303.8	244.3	145.2	99.12
250	313.7	257.0	151.8	105.2
260	323.4	269.4	158.2	111.3
270	332.5	281.8	164.5	117.3
280	341.1	294.1	170.6	123.4
290	349.0	306.2	176.7	129.5
300	356.4	318.1	182.5	135.6
310	363.4	329.9	188.2	141.7
320	370.1	341.6	193.8	147.8
330	376.6	353.1	199.3	153.8
340	382.8	364.4	204.6	159.8
350	388.8	375.6	209.7	165.8
360	394.6	386.6	214.8	171.8
370	400.4	397.5	219.7	177.8
380	404.2	408.3	224.6	183.7
273.15	335.3	285.7	166.4	119.3
298.15	355.1	315.9	181.4	134.5

Table 7. Molar thermodynamic properties of paragonite $\text{NaAl}_2[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$. Formula weight = $382.202 \text{ g mol}^{-1}$. Entropy and Gibbs energy function are not corrected for possible zero-point entropy.

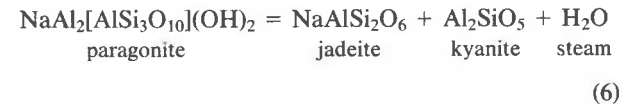
Temp.	Heat capacity	Entropy	Enthalpy function	Gibbs energy function
T	C_P°	$(S_T^\circ - S_0^\circ)$	$(H_T^\circ - H_0^\circ)/T$	$-(G_T^\circ - H_0^\circ)/T$
K		J/(mol·K)		
5	0.032	0.011	0.008	0.003
10	0.282	0.090	0.068	0.022
15	1.004	0.318	0.240	0.078
20	2.477	0.787	0.596	0.191
25	4.979	1.581	1.197	0.384
30	8.409	2.779	2.101	0.678
35	12.90	4.405	3.316	1.089
40	18.11	6.460	4.833	1.628
45	23.89	8.923	6.625	2.298
50	30.11	11.76	8.659	3.099
60	43.43	18.41	13.33	5.082
70	57.52	26.16	18.63	7.528
80	72.09	34.78	24.40	10.39
90	86.91	44.13	30.52	13.61
100	101.7	54.05	36.90	17.16
110	116.4	64.44	43.46	20.98
120	130.7	75.18	50.14	25.05
130	144.7	86.20	56.88	29.33
140	158.3	97.42	63.63	33.79
150	171.6	108.8	70.39	38.41
160	184.5	120.3	77.12	43.17
170	197.0	131.8	83.81	48.04
180	209.1	143.5	90.44	53.02
190	220.8	155.1	96.99	58.09
200	232.0	166.7	103.5	63.23
210	242.7	178.3	109.8	68.43
220	253.1	189.8	116.1	73.68
230	263.1	201.3	122.3	78.98
240	272.7	212.7	128.4	84.32
250	281.9	224.0	134.3	89.68
260	290.6	235.2	140.2	95.06
270	299.1	246.4	145.9	100.5
280	307.3	257.4	151.5	105.9
290	315.2	268.3	157.0	111.3
300	322.9	279.1	162.4	116.7
310	330.2	289.8	167.7	122.1
320	337.1	300.4	172.9	127.5
330	343.6	310.9	178.0	132.9
340	350.0	321.2	182.9	138.3
350	356.3	331.5	187.8	143.7
360	362.5	341.6	192.6	149.0
370	368.2	351.6	197.2	154.4
380	373.7	361.5	201.8	159.7
273.15	301.7	249.8	147.7	102.2
298.15	321.5	277.1	161.4	115.7



and



and



together with the requisite thermodynamic data for jadeite, quartz, corundum, and steam, tabulated by Robie et al. (1979), for analbite from Hemingway et al. (1981), and for andalusite and kyanite from Robie and Hemingway (1984) in a third-law analysis of the equilibrium data to obtain the enthalpy of formation at 298.15 K ($\Delta H_{f,298}^\circ$).

We used the relation (Robie and Stout, 1963)

$$-\Delta H_{298}^\circ = T\Delta[(C_T^\circ - H_{298}^\circ)/T] + \int_1^P \Delta V dP + RT \ln f_{\text{H}_2\text{O}}$$

to calculate values of ΔH_{298}° for the reaction from each of the bracketing equilibrium values. Reaction (4) has been investigated by Chatterjee (1970) and by Ivanov and Gusynin (1970). Chatterjee (1972) has determined the

Table 8. Third-law calculation of $\Delta H_{f,298}^\circ$ for the reaction paragonite + quartz = analbite + andalusite (or kyanite) + H_2O from the equilibrium P - T data of Chatterjee (1972), reactions (5a) and (5b).

T	$P_{\text{H}_2\text{O}}$	$\Delta[(C_T^\circ - H_{298}^\circ)/T]$	$(P-1)\Delta\bar{V}/T$	$R \ln f_{\text{H}_2\text{O}}$	$\Delta H_{f,298}^\circ$		
K	bars	J/K	J/K	J/K	kJ		
		disordered	ordered		disordered	ordered	
Reaction (5a)							
74.3	1000	-165.30	-184.00	-0.32	49.78	86.15	100.05
76.3	1000	-165.00	-183.70	-0.32	50.58	87.63	101.90
78.3	2000	-164.67	-183.37	-0.65	55.10	86.44	101.09
80.3	2000	-164.32	-183.02	-0.66	55.79	87.80	102.82
81.3	3000	-164.12	-182.82	-0.98	59.27	86.23	101.43
83.3	3000	-163.70	-182.40	-0.99	59.93	87.43	103.01
83.3	4000	-163.70	-182.40	-1.32	62.79	85.38	100.95
85.3	4000	-163.26	-181.96	-1.33	63.33	86.57	102.52
86.3	5000	-163.03	-181.73	-1.66	66.23	85.20	101.33
87.3	5000	-162.80	-181.50	-1.66	66.47	85.76	102.08
Reaction (5b)							
84.3	5000	-154.40	-173.10	-5.48	65.73	80.22	95.99
89.8	5000	-153.10	-171.80	-5.52	67.29	82.58	99.37
87.3	6000	-153.70	-172.40	-6.60	68.97	80.56	96.89
90.3	6000	-152.97	-171.67	-6.62	69.64	81.87	98.76
89.3	7000	-153.25	-171.95	-7.71	71.79	80.45	97.15
91.3	7000	-152.70	-171.40	-7.73	72.20	81.23	98.30

structures. This disorder is frozen in at low temperatures and, accordingly, to our measured values of $S_T^\circ - S_0^\circ$, one must add a configurational term to account for this disorder (see below).

Inasmuch as the enthalpy of formation of paragonite has not yet been determined calorimetrically, we have combined our entropy and heat capacity data with equilibrium studies for the reactions



and

equilibrium curve for reaction (5a and 5b), and Holland (1979) has studied reaction (6).

For each reaction, the calculations were made by assuming (a) that paragonite is Al/Si ordered, i.e., $S_{298}^{\circ} = 277.1 \text{ J}/(\text{mol} \cdot \text{K})$, and (b) that paragonite is disordered and accordingly $S_0^{\circ} \neq 0$ but has a zero-point entropy of $18.7 \text{ J}/(\text{mol} \cdot \text{K})$ corresponding to the completely random distribution of the tetrahedral aluminum atoms and that, therefore, $S_{298}^{\circ} = 295.8 \text{ J}/(\text{mol} \cdot \text{K})$. Because the temperature ranges of the equilibrium data for reactions (4) and (5a and 5b) are essentially the same, we have assumed that the $\text{NaAlSi}_3\text{O}_8$ phase is analbite in both equilibria. The results for the calculation using Chatterjee's (1970, 1972) equilibrium data are listed in Tables 8 and 9. The data of Burnham et al. (1969) were used for the properties of H_2O and the molar volume of paragonite was taken from Chatterjee (1974).

For these calculations, the heat capacity of paragonite was extrapolated to 1000 K by assuming C_p° to vary linearly above 800 K with a slope, dC_p°/dT , evaluated from equation (3) at 775 K. The equations used to fit our high-temperature C_p° measurements are intended only for representation within the stated temperature limits and should not be used to extrapolate C_p° beyond the stated limits.

In Figure 5 we show the resultant values for $\Delta H_{f,298}^{\circ}$ for both ordered and disordered models of paragonite calcu-

lated from Chatterjee's data for reaction (5a). The mean values for the enthalpy of reaction (5a) at 298.15 K are $86.46 \pm 0.58 \text{ kJ}$ and $101.72 \pm 0.58 \text{ kJ}$, and those of reaction (5b) at 298.15 K are $81.15 \pm 0.75 \text{ kJ}$ and $97.74 \pm 1.04 \text{ kJ}$, each respectively, for disordered and ordered paragonite. Using our calculated value for $\Delta H_{f,298}^{\circ}$ for reaction (5b) based on the disordered model for paragonite together with the necessary data for kyanite and andalusite from Robie and Hemingway (1984) and for the other phases from the tables of Robie et al. (1979), we obtain $\Delta H_{f,298}^{\circ} = -5932.50 \pm 4.20 \text{ kJ/mol}$; for the ordered model, we obtain $-5949.06 \pm 4.30 \text{ kJ/mol}$. Similarly, from reaction (4), we obtain $\Delta H_{f,298}^{\circ} = -5932.87 \pm 4.00 \text{ kJ/mol}$ (disordered) and $-5949.26 \pm 4.00 \text{ kJ/mol}$ (ordered), and from reaction (5a), we obtain $-5933.71 \pm 4.20 \text{ kJ/mol}$ (disordered) and $-5948.97 \pm 4.20 \text{ kJ/mol}$ (ordered).

Similar calculations were also made using Holland's (1979) data for the breakdown of paragonite to jadeite and kyanite. For these calculations, we used values for the fugacity of H_2O calculated by J. L. Haas, Jr. (U. S. Geol. Survey, written communication, July 1980) using the equation of state proposed by Haar et al. (1980). The fugacities obtained from their equation of state agree with those given by Delany and Helgeson (1978) to within 0.3 percent in the range 23 to 26 kilobars and at temperatures of 800 to 1000 K. The pressure-temperature correction to the volume change for the solid phases for reaction (6) was made using the thermal expansion and compressibility data tabulated by Holland (1979).

Our third-law calculation leads to an enthalpy change for reaction (6) at 298.15 K of $65.50 \pm 1.25 \text{ kJ/mol}$ if paragonite is disordered and $82.32 \pm 0.75 \text{ kJ}$ if paragonite is ordered. These values were used to calculate $\Delta H_{f,298}^{\circ}$ of paragonite together with the necessary enthalpies of formation for kyanite from Robie and Hemingway (1984) and for steam from Robie and others (1979) and for jadeite from Hemingway et al. (1981), and lead to $\Delta H_{f,298}^{\circ}$ (disordered) = $-5933.21 \pm 4.70 \text{ kJ/mol}$ and $\Delta H_{f,298}^{\circ}$ (ordered) = $-5950.03 \pm 4.60 \text{ kJ/mol}$.

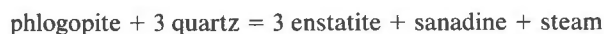
If the equilibrium brackets are correct, then the combined equilibrium and calorimetric data should provide a means of checking the state of the tetrahedral Al/Si order in paragonite (and phlogopite). The results of our calculations are somewhat ambiguous, principally because of the width of the "equilibrium" brackets. The data for reactions (4), (5a,b), and (6) are in reasonable agreement, as noted previously by Holland (1979), but do not clearly exclude either the ordered or disordered model for paragonite, i.e., both models lead to values for $\Delta H_{f,298}^{\circ}$ that vary somewhat with the equilibrium temperature. For reactions (4), (5a,b), and (6), the ordered model actually gives a slightly better fit to the equilibrium data contrary to what the crystal structure data would lead us to expect. The average values of $\Delta H_{f,298}^{\circ}$ obtained from the combined data of (4), (5a,b), and (6) are $-5933.07 \pm 4.70 \text{ kJ/mol}$ and $-5949.33 \pm 4.60 \text{ kJ/mol}$, respectively, for the disordered and ordered models. The equivalent values for

Table 9. Third-law calculation of $\Delta H_{f,298}^{\circ}$ for the reaction paragonite = analbite + corundum + steam from the experimental brackets of Chatterjee (1970), reaction (4), and for the reaction paragonite = jadeite + kyanite + steam from the experimental brackets of Holland (1979), reaction (6).

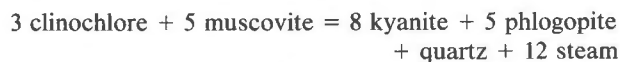
T	$P_{\text{H}_2\text{O}}$	$\Delta[(C_p^{\circ} - H_{298}^{\circ})/T]$		$(p-1)\Delta\bar{V}/T$	$R \ln f_{\text{H}_2\text{O}}$	$\Delta H_{f,298}^{\circ}$	
		J/K	J/K			J/K	kJ
K	bars	disordered	ordered			disordered	ordered
Reaction (4)							
803	1000	-166.10	-184.80	-0.65	51.91	92.36	107.36
823	1000	-165.69	-184.39	-0.65	52.47	93.83	109.22
828	2000	-165.58	-184.28	-1.30	56.59	91.54	107.02
848	2000	-165.17	-183.87	-1.30	57.16	92.90	108.75
853	3000	-165.07	-183.77	-1.96	60.48	91.18	107.13
873	3000	-164.66	-183.36	-1.97	61.00	92.47	108.79
898	5000	-164.14	-182.84	-3.30	67.07	90.47	107.26
913	5000	-163.73	-182.43	-3.30	67.40	91.25	108.32
893	6000	-164.24	-182.94	-3.96	69.43	88.62	105.32
923	6000	-163.44	-182.14	-3.97	70.05	90.17	107.43
923	7000	-163.73	-182.43	-4.64	72.38	88.96	106.22
943	7000	-162.87	-181.57	-4.65	72.74	89.65	107.28
Reaction (6)							
823	24000	-104.07	-122.77	-80.22	103.98	66.10	81.49
823	26000	-104.07	-122.77	-86.91	107.46	68.74	84.13
873	24000	-103.08	-121.78	-75.63	103.76	65.43	81.76
873	25500	-103.08	-121.78	-80.35	106.24	67.39	83.71
923	24000	-101.87	-120.57	-71.53	103.50	64.52	81.78
923	25000	-101.87	-120.57	-74.51	105.08	65.81	83.07
973	23000	-100.43	-119.13	-65.03	101.68	62.06	80.25
973	24500	-100.43	-119.13	-69.27	103.97	63.96	82.15

$\Delta G_{f,298}^{\circ}$ are -5557.88 ± 4.70 and -5568.46 ± 4.60 kJ/mol for the disordered and ordered models respectively.

Unfortunately, no direct calorimetric data exist for the enthalpy of formation for hydroxyphlogopite. To obtain $\Delta H_{f,298}^{\circ}$ of phlogopite we have combined our heat capacity and entropy data with the P - T data of Wood (1976), and of Wones and Dodge (1977) for the reaction



From Wood's equilibrium data, we obtained 130.8 and 111.3 kJ for the enthalpy change for the above reaction depending, respectively, upon whether we assume Al/Si in phlogopite is ordered or disordered. From Wones and Dodge's (1977) data we calculate 136.3 and 115.6 kJ respectively for the enthalpy of this reaction for ordered and disordered phlogopite. If we simply average the results of Wood, and of Wones and Dodge and combine them with the data tabulated in Robie et al. (1979) for quartz, clinoenstatite, sanidine, and H_2O and assuming a negligible difference for $\Delta H_{f,298}^{\circ}$ between clinoenstatite and orthoenstatite, we obtain for ordered phlogopite $S_{298}^{\circ} = 315.9 \pm 1.0$ J/(mol · K), $\Delta H_{f,298}^{\circ} = -6246.1 \pm 6.4$ kJ/mol, and $\Delta G_{f,298}^{\circ} = -5860.5 \pm 6.5$ kJ/mol, and for a completely Al/Si disordered phlogopite $S_{298}^{\circ} = 334.6 \pm 1.0$ J/(mol · K), $\Delta H_{f,298}^{\circ} = -6226.0 \pm 6.4$ kJ/mol, and $\Delta G_{f,298}^{\circ} = -5846.0 \pm 6.5$ kJ/mol. We have not used the data of Bird and Fawcett (1973) for the reaction



to calculate a value for ΔG_f° for phlogopite because the state of tetrahedral Al/Si order in clinocllore, muscovite, and phlogopite are unknown and the difference in ΔG_f° between an ordered and a fully disordered clinocllore is approximately 37 kJ/mol (Henderson et al., 1983).

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