High-temperature heat capacities of corundum, periclase, anorthite, $CaAl_2Si_2O_8$ glass, muscovite, pyrophyllite, $KAlSi_3O_8$ glass, grossular, and $NaAlSi_3O_8$ glass

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Abstract

The heat capacities (C_P^0) of corundum, periclase, anorthite, $CaAl_2Si_2O_8$ glass, muscovite, pyrophyllite, $KAlSi_3O_8$ glass, and $NaAlSi_3O_8$ glass have been determined to an accuracy of ± 1.0 percent by differential scanning calorimetry between 350 and 1000 K. Our results have been combined smoothly with existing low-temperature heat capacity and entropy data, and fitted by least squares to the following equations (T in Kelvin and C_P^0 in $J/mol \cdot K$):

$$C_P^0 \text{(anorthite)} = 516.8 - 0.09249T - 1.408 \times 10^6 T^{-2} - 4588T^{-1/2} + 4.188 \times 10^{-5} T^2$$
$$(298-1800 \text{ K})$$

$$C_P^0 \text{(CaAl}_2\text{Si}_2\text{O}_8 \text{ glass)} = 375.2 + 0.03197T - 2.815 \times 10^6 T^{-2} - 2459T^{-1/2}$$
$$(298-1500 \text{ K})$$

$$C_P^0 \text{(muscovite)} = 917.7 - 0.08111T + 2.834 \times 10^6 T^{-2} - 10348T^{-1/2}$$
$$(298-1000 \text{ K})$$

$$C_P^0 \text{(pyrophyllite)} = 679.7 - 0.06412T - 6902T^{-1/2} - 5.997 \times 10^5 T^2$$
$$(298-800 \text{ K})$$

$$C_P^0 \text{(KAlSi}_3\text{O}_8 \text{ glass)} = 629.5 - 0.1084T + 2.496 \times 10^6 T^{-2} - 7210T^{-1/2} + 1.928 \times 10^{-5} T^2$$
$$(298-1300 \text{ K})$$

$$C_P^0 \text{(grossular)} = 1633.3 - 0.7599T + 9.113 \times 10^6 T^{-2} - 20783T^{-1/2} + 2.669 \times 10^{-4} T^2$$
$$(298-1200 \text{ K})$$

$$C_P^0 \text{(NaAlSi}_3\text{O}_8 \text{ glass)} = 934.4 - 0.3891T + 5.594 \times 10^6 T^{-2} - 11820T^{-1/2} + 1.476 \times 10^{-4} T^2$$
$$(298-1200 \text{ K})$$

The accuracy of the differential scanning calorimeter was checked by measuring the heat capacities of corundum and periclase and comparing these results with those published by the U. S. National Bureau of Standards. We have combined our calorimetric data for muscovite, pyrophyllite, and grossular with data from recent equilibrium studies to derive improved values for $\Delta H_{f,298}^0$ and $\Delta G_{f,298}^0$ for muscovite, pyrophyllite, and grossular. Our values for $\Delta H_{f,298}^0$ and $\Delta G_{f,298}^0$ are -5971600 ± 5180 J/mol and -5595500 ± 5190 J/mol respectively for disordered $2M_1$ muscovite, -5639800 ± 3950 J/mol and -5265900 ± 3960 J/mol respectively for pyrophyllite, and -6657100 ± 4720 J/mol and -6295300 ± 4730 J/mol respectively for grossular.

Introduction

Heat capacity values above 300 K are of fundamental importance for thermodynamic calculations of mineral equilibrium at high temperatures. Until recently the principal method of determining these data has been drop calorimetry. In this method, the sample is held at a constant (elevated) temperature, T, within a furnace and is then dropped into a receiver (calorimeter) maintained at some reference temperature, T_0, commonly 298 K. The quantity actually measured is

$$H_T^0 - H_{T_0}^0 = \int_{T_0}^{T} C_P^0 \, dT$$

The true differential heat capacity, C_P^0, is derived from these *heat content* measurements by graphical differentiation of the experimental $H_T^0 - H_{T_0}^0$ values, or by fitting the heat content data to an equation and then differentiating the equation. In either case, differentiation of the experimental $H_T^0 - H_{298}^0$ data introduces uncertainty in the derived value of C_P^0 which is approximately an order of magnitude larger than the uncertainty of the measurements. Thus, although $H_T^0 - H_{298}^0$ can with care be measured to ± 0.1 percent, the C_P^0 values derived from them have an uncertainty of the order of ± 1.0 percent. The accuracy of the derived C_P^0 values depends both upon the accuracy of the heat content measurements and upon the temperature spacing of the measurements which control the accuracy of the smoothing function. Except for the highly accurate and closely spaced measurements of Ditmars and Douglas (1971) on α-Al_2O_3 (corundum), there are probably no heat capacity values, derived from $H_T^0 - H_{298}^0$ studies, that have an uncertainty of less than 1.0 percent. See for example, Figure 7 of Ditmars and Douglas for an overall picture of the state of $H_T^0 - H_{298}^0$ calorimetric measurements.

Heat capacities can be directly measured by adiabatic calorimetry, but are not routinely determined by this method above 400 K because of greatly increased experimental difficulties. At the present time, only the adiabatic calorimeters described by Gronvold (1967) (with an upper limit of 1050 K), and by Trowbridge and Westrum (1963) (with an upper limit of 800 K) are operational. West and Westrum (1968) have discussed the problems of instrumentation connected with the construction and operation of adiabatic heat capacity calorimeters for temperatures as high as 1000 K.

Watson *et al.* (1964) introduced a new method of thermal analysis which they called differential scanning calorimetry, and O'Neill and Fyans (1971) described a much improved version of the differential scanning calorimeter (DSC). In contrast to the drop method, the differential scanning calorimeter measures C_P^0 directly and has an accuracy comparable with that obtained in all but a very few investigations where a drop calorimeter is used.

Using this method, we have determined the high-temperature heat capacities between 350 and 1000 K for corundum, periclase, anorthite, $CaAl_2Si_2O_8$ glass, muscovite, pyrophyllite, $KAlSi_3O_8$ glass, grossular, and $NaAlSi_3O_8$ glass. Using these new values with ancillary thermodynamic data from Robie *et al.* (1978a), we have derived improved values of $\Delta H_{f,298}^0$ and $\Delta G_{f,298}^0$ for $2M_1$ disordered muscovite, pyrophyllite, and grossular.

Apparatus

The calorimeter was a Perkin-Elmer Model DSC-2 differential scanning calorimeter similar to that described by O'Neill and Fyans (1971). Our heat capacity measurements were made at a heating rate of 10 K/min with a range setting of 1.25 J/min (5 mcal/sec). All samples were encapsulated in gold pans and weighed by means of either a Mettler M-5A microbalance or a Cahn Model 4100 electrobalance. Temperature calibration of the calorimeter was checked by measuring the transition temperature (extrapolated onset temperature) of the inorganic compounds supplied in the thermal standard sets, NBS-ICTA Standard Reference Materials 758 and 759 (McAdie *et al.*, 1972).

In order to check the accuracy of the differential scanning calorimeter, we have measured the heat capacities of α-Al_2O_3 (corundum) both in the form of single-crystal discs and in powder form, and compared our results with the values reported by Ditmars and Douglas (1971). We have also made a less extensive series of measurements on MgO (periclase) for comparison with the data of Victor and Douglas (1963).

Materials

Corundum (α-Al_2O_3)

The sample of single-crystal corundum was a disc of Linde synthetic sapphire 6.3 mm in diameter by 0.25 mm thick and weighed 30.20 mg. The chemical analyses given by Ditmars and Douglas (1971) indicate that the purity of Linde synthetic sapphire is 99.98 percent. Unit-cell dimensions were measured by means of an X-ray diffractometer at 296 ± 1 K using $CuK\alpha_1$ radiation and a scanning rate of $1°/$min. The cell constants were $a = 0.4760 \pm 0.0003$ and $c = 1.2993 \pm 0.0019$ nm (1 nm = 10Å). The powdered corundum was Fisher Scientific Co. reagent No. 591 (anhydrous aluminum oxide), and it weighed 28.59 mg. Chemical analyses by Fisher Scientific Co. indicate that its purity is 99.4 percent or better. Unit-cell dimensions were measured under the same conditions as those of the Linde sapphire, and they were $a = 0.4758 \pm 0.0006$ and $c = 1.2992 \pm 0.0023$ nm.

Periclase (MgO)

The single-crystal periclase sample was furnished by G. Weber (Pennsylvania State University) from material produced by an arc growth process. Its purity was comparable with commercially available high-purity MgO (Weber, 1975). The single-crystal sample was square in cross section (4.4 mm) by 0.36 mm thick and weighed 26.92 mg. The unit-cell dimension was $a = 0.4212 \pm 0.0002$ nm.

NaAlSi₃O₈ glass, KAlSi₃O₈ glass, CaAl₂Si₂O₈ glass, and anorthite

The materials used were portions of the samples used by Robie et al. (1978b) for low-temperature heat capacity studies. The $NaAlSi_3O_8$ glass and $KAlSi_3O_8$ glass were discs 6.3 mm in diameter by 0.81 mm thick and weighed 62.38 and 57.60 mg respectively. The $CaAl_2Si_2O_8$ glass and anorthite samples were -100 mesh powders, which weighed 30.37 and 29.81 mg respectively.

2M₁ muscovite [KAl₂(AlSi₃O₁₀)(OH)₂] and pyrophyllite [Al₂Si₄O₁₀(OH)₂]

The materials were portions of the samples used by Robie et al. (1976) for low-temperature heat capacity measurements. The $2M_1$ muscovite was a single-crystal disc, 6.3 mm in diameter by 0.35 mm thick, and weighed 31.20 mg. The pyrophyllite was -100 mesh powder. Two samples of the pyrophyllite powder were used, and they weighed 20.80 and 24.80 mg.

Grossular (Ca₃Al₂Si₃O₁₂)

Heat capacity measurements were made on both natural and synthetic grossular. Two samples of grossular from the Jeffrey Mine, Asbestos, Quebec (NMNH 123106) were used, weighing 24.11 and 16.95 mg. The unit-cell dimension of this grossular is $a = 1.1850 \pm 0.0002$ nm. The synthetic grossular was prepared by J. J. Hemley of the U.S. Geological Survey from a gel at 923 K and 517 bars (1 bar = 10^5 pascals). Two samples weighing 17.12 and 19.88 mg were used. The unit-cell dimension of the synthetic grossular is $a = 1.1853 \pm 0.0002$ nm.

Experimental results

Our measured values of the molar heat capacities of corundum, periclase, anorthite, $CaAl_2Si_2O_8$ glass, muscovite, pyrophyllite, $KAlSi_3O_8$ glass, grossular, and $NaAlSi_3O_8$ glass are listed in Tables 1 through 9 respectively and shown graphically in Figures 1 through 3. For the sake of clarity, some of the experi-

mental C_p^0 values in Tables 1 through 9 have been omitted from Figures 1 through 3. Our measured heat capacities of anorthite, $CaAl_2Si_2O_8$ glass, and synthetic grossular were not included, because of the similarities between these data and those in Figures 2 and 3. The gram-formula weights were calculated using the 1973 atomic weights (Commission on Atomic Weights, 1974). Calorimetric unit conversion was made using 1 cal = 4.184 J. The experimental data for muscovite, pyrophyllite, $KAlSi_3O_8$ glass, and $NaAlSi_3O_8$ glass have been corrected for deviations of the samples from their ideal chemical formulae using the same approximations used by Robie et al. (1976, 1978b).

Our experimental C_p^0 values are believed to be accurate to ± 1.0 percent, based upon: (1) a comparison of our heat capacity measurements on corundum and periclase by differential scanning calorimetry with the

Table 1. Experimental heat capacities for corundum, α-Al₂O₃

Temp.	Heat capacity	Temp.	Heat capacity	Temp.	Heat capacity
K	J/(mol.K)	K	J/(mol.K)	K	J/(mol.K)
350.2	89.3	349.1	88.6	399.5	96.0
370.1	91.8	359.1	90.1	409.5	97.5
390.0	94.4	369.1	91.6	419.5	98.8
410.0	97.1	379.1	93.0	439.5	101.3
419.9	98.3	389.1	94.6	459.5	102.9
429.9	99.7	399.1	96.0	479.5	105.2
419.9	98.3	409.1	96.8	484.5	105.3
439.9	100.1	419.1	98.5	474.5	103.6
459.8	102.6	429.1	99.5	484.5	104.1
479.7	104.3	419.2	98.2	499.5	105.6
489.7	105.4	429.2	98.8	519.5	106.6
499.7	106.2	439.2	100.0	539.5	108.4
509.6	107.5	449.2	101.5	549.5	109.0
504.7	107.4	459.2	102.2	559.5	110.0
509.7	108.0	469.2	103.6	549.5	109.1
519.7	108.4	479.2	104.4	559.5	109.5
539.7	110.1	489.2	105.2	579.5	111.1
559.6	111.1	499.2	106.3	599.5	111.8
579.6	111.6	509.2	107.4	614.5	112.9
589.6	112.1	504.2	106.2	624.5	113.4
599.6	112.6	509.2	106.4	634.5	114.1
594.7	112.3	519.2	107.3	624.5	113.0
599.7	112.5	529.2	108.2	634.5	113.6
609.7	113.2	539.2	109.0	649.5	114.5
629.7	112.9	549.2	109.8	669.5	115.3
649.6	114.1	559.2	110.3	689.4	116.3
659.6	114.5	569.2	111.1	699.4	116.6
669.6	115.2	579.2	111.2	709.4	116.9
679.6	116.4	589.2	112.1	699.2	117.2
849.5	121.2	599.2	113.0	709.2	116.9
859.3	121.2	674.0	116.1	729.2	117.6
874.0	121.5	679.0	116.4	749.2	118.3
898.5	122.0	689.0	116.4	769.2	119.3
908.3	122.7	699.0	117.1	774.2	119.7
918.1	122.8	709.0	117.0	354.8	90.0
923.0	123.3	719.0	117.6	374.7	92.5
959.6	123.5	729.0	117.9	394.7	95.8
969.6	124.0	739.0	118.5	409.6	97.8
979.6	124.2	749.0	118.3	927.9	123.7
989.6	124.3	759.0	118.9	937.7	123.4
999.5	125.0	764.0	119.5	947.5	124.0
903.4	122.2	349.8	89.3	957.3	124.5
918.1	123.4				

Table 2. Experimental heat capacities for periclase, MgO

Temp.	Heat capacity	Temp.	Heat capacity
K	J/(mol.K)	K	J/(mol.K)
350.1	40.4	499.8	45.7
370.0	41.3	509.7	46.1
390.0	42.1	594.8	47.5
409.9	42.8	599.8	47.7
419.9	43.3	609.7	47.6
429.9	43.6	629.7	48.0
419.9	43.6	649.7	48.3
439.9	43.9	659.6	48.4
459.8	44.5	669.6	48.5
479.8	45.2	679.6	48.7
489.8	45.4		

values of C_P^0 calculated from the heat content data of Ditmars and Douglas (1971) for corundum, and of Victor and Douglas (1963) for periclase; and (2) a comparison of our measurements in the temperature range 350–380 K for muscovite, pyrophyllite, the three feldspar glasses, and anorthite with the values of C_P^0 determined by Robie *et al.* (1976, 1978b) by low-temperature adiabatic calorimetry (accuracy ±0.1 percent) on the same materials. Our heat capac-

Table 3. Experimental heat capacities for anorthite, CaAl₂Si₂O₈

Temp.	Heat capacity	Temp.	Heat capacity	Temp.	Heat capacity
K	J/(mol.K)	K	J/(mol.K)	K	J/(mol.K)
349.0	231.9	679.1	295.2	669.5	292.9
359.0	234.5	689.1	295.7	689.4	295.6
369.0	237.9	699.1	295.7	699.4	296.7
379.0	241.2	709.1	296.8	709.4	298.2
389.0	243.7	719.1	297.3	699.5	298.3
399.0	246.4	729.1	298.2	709.5	299.7
409.0	249.0	739.1	299.2	729.5	301.4
419.1	253.3	749.1	300.7	749.5	302.1
429.1	255.5	759.1	302.7	769.5	304.2
414.0	252.4	764.1	304.3	774.5	305.0
419.1	252.4	349.5	233.3	764.5	304.4
429.1	255.6	354.5	234.0	744.5	304.7
439.1	258.2	374.5	241.2	789.5	305.9
449.1	259.8	394.5	248.4	809.5	307.2
459.1	261.7	409.5	252.8	829.5	308.6
469.1	263.5	399.5	247.7	839.5	309.6
479.1	266.0	409.5	250.6	844.8	307.5
489.1	267.2	419.5	252.7	859.5	308.1
499.1	269.1	439.5	258.0	879.1	308.3
509.1	270.5	459.5	262.7	898.7	309.4
504.2	271.2	479.5	265.6	908.5	310.2
509.2	272.4	484.5	266.9	918.3	313.8
519.2	274.7	474.5	265.2	923.2	316.4
529.2	276.0	484.5	267.3	913.4	311.0
539.2	277.5	499.5	270.1	923.2	311.2
549.2	279.5	519.5	275.1	937.9	312.4
559.2	279.6	539.5	278.2	957.4	316.4
569.2	282.0	549.5	279.7	967.2	316.3
579.2	281.8	559.5	281.5	977.0	316.8
589.2	283.1	624.5	289.0	986.8	320.4
599.2	284.3	634.5	290.3	966.5	319.7
674.1	294.4	649.5	291.1		

Table 4. Experimental heat capacities for CaAl₂Si₂O₈ glass

Temp.	Heat capacity	Temp.	Heat capacity	Temp.	Heat capacity
K	J/(mol.K)	K	J/(mol.K)	K	J/(mol.K)
349.1	230.9	699.1	298.3	624.5	290.3
359.1	233.6	709.1	299.6	634.5	292.2
369.1	238.0	719.1	299.8	649.5	292.8
379.1	241.2	729.1	301.4	669.5	294.4
389.1	243.7	739.1	302.0	689.4	298.4
399.1	246.5	749.1	302.7	699.4	299.1
409.1	250.1	759.1	304.4	709.4	300.3
419.1	252.5	764.1	306.4	699.5	298.9
429.1	254.7	349.5	232.8	709.5	301.3
414.1	251.7	354.5	234.5	729.5	303.3
419.1	252.4	374.5	240.0	749.5	305.2
429.1	255.5	394.5	246.5	769.5	307.1
439.1	258.5	409.5	251.1	774.5	307.6
449.1	260.0	399.5	246.2	764.5	307.6
459.1	261.8	409.5	249.0	774.5	306.9
469.1	264.0	419.5	251.5	789.5	308.0
479.1	266.0	439.5	257.0	809.5	312.1
489.1	267.9	459.5	262.5	829.5	313.1
499.1	270.3	479.5	266.2	839.5	314.2
509.1	272.0	484.5	267.5	844.8	311.2
504.2	270.7	474.5	263.5	859.5	312.8
509.2	272.0	484.5	265.8	898.7	315.0
519.2	273.8	499.5	268.0	908.5	316.7
529.2	276.4	519.5	272.9	918.3	318.5
539.2	277.4	539.5	276.8	923.2	317.6
549.2	280.8	549.5	278.5	913.4	315.7
559.2	281.8	559.5	279.6	923.2	317.2
569.2	283.1	549.6	278.6	937.9	319.0
579.2	283.9	559.6	280.0	996.6	322.4
589.2	286.0	579.6	283.7	957.4	319.9
599.2	286.7	599.6	287.6	967.2	318.8
674.1	295.2	614.5	289.4	977.0	321.9
679.1	295.3	624.5	290.6	986.8	325.6
689.1	296.5	634.5	292.1	996.5	323.8

ity measurements on corundum agree with the values reported by Ditmars and Douglas (1971) for the certification of Standard Reference Material 720 with an average deviation of 0.3 percent.

Previous studies

Pankratz (1964) measured the relative enthalpy $H_T^0 - H_{298}^0$ of a muscovite sample at approximately 100 K intervals between 400 and 903 K. Heat capacities calculated from his derived C_P^0 equation are smaller than those obtained directly in this investigation by 1.2 percent at 500 K and 1.8 percent at 900 K. Although his muscovite sample was less pure than the muscovite sample we used, his data were not corrected for the deviation of the sample from the exact stoichiometric formula KAl₂(AlSi₃O₁₀)(OH)₂ as were our data.

White (1919) measured $H_T^0 - H_{273}^0$ of anorthite, NaAlSi₃O₈ glass, CaAl₂Si₂O₈ glass, and KAlSi₃O₈ glass at 200 K intervals to 1673 K, 1173 K, 973 K, and 1373 K respectively. From these data Kelley (1960) derived approximate heat capacity equations for each compound which give values agreeing with

Table 5. Experimental heat capacities for muscovite, $KAl_2(AlSi_3O_{10})(OH)_2$

Temp.	Heat capacity	Temp.	Heat capacity
K	J/(mol.K)	K	J/(mol.K)
332.5	349.5	639.6	464.7
342.5	354.5	659.6	471.1
362.6	364.3	679.7	471.8
382.6	371.9	674.7	469.4
392.6	379.9	679.7	469.3
397.6	383.1	699.7	475.1
374.6	370.0	719.7	479.1
384.6	376.7	739.7	483.0
394.6	382.4	759.7	486.3
409.6	390.4	779.7	489.7
429.6	400.1	689.7	475.3
449.6	409.1	699.7	475.3
469.6	417.2	719.7	478.7
439.6	404.2	739.7	483.7
449.6	407.1	759.7	486.6
459.6	411.6	769.6	489.0
474.7	418.7	779.6	493.8
489.7	423.0	759.6	482.3
509.7	428.8	769.6	482.3
529.7	433.4	789.6	483.3
524.7	435.0	819.6	490.8
529.7	437.1	829.6	494.9
539.7	439.0	869.3	499.5
559.7	443.0	879.2	495.6
579.8	449.2	899.0	499.5
599.8	453.3	908.9	506.6
619.8	459.7	923.3	507.6
584.6	461.6	933.1	500.2
594.6	454.7	942.8	504.0
599.6	453.8	957.6	513.5
619.6	459.6	967.4	520.6

our measurements to within ±2.5 percent up to 1000 K. Ferrier (1969) measured $H_T^0 - H_{298}^0$ of synthetic anorthite to 1850 K and $CaAl_2Si_2O_8$ glass to 1500 K with a precision of approximately 2.0 percent. Ferrier, unfortunately, presented his data only in the form of graphs and equations.

Westrum et al. (1978) have measured the heat capacity of grossular from Asbestos, Quebec between 5 and 600 K by precise adiabatic calorimetry. Their results were corrected for deviation of the sample from the exact formula $Ca_3Al_2Si_3O_{12}$. Our measured heat capacities on synthetic grossular are in agreement with these smoothed, composition-corrected values to within an average deviation of 1.0 percent between 350 and 600 K.

Kushov (1973) determined the specific heat of natural pyrophyllite over the range of 298–773 K by thermal analysis. Kushov's heat capacity values were not used in this study, because his pyrophyllite sample deviates significantly with respect to silicon and aluminum from the ideal composition of py-

rophyllite, and his heat capacity values show a large scatter.

Thermodynamic functions

Our results for anorthite, $CaAl_2Si_2O_8$ glass, muscovite, $KAlSi_3O_8$ glass, grossular, and $NaAlSi_3O_8$ glass between 350 and 1000 K, and for pyrophyllite between 350 and 650 K were combined with the low-temperature heat capacity values of Robie et al. (1976, 1978b) and Westrum et al. (1978), and were fit by least squares to the equation

$$C_P^0 = A + BT + CT^{-2} + DT^{-1/2} + ET^2$$

suggested by Haas and Fisher (1976). Only four terms were used if a fifth term made no significant contribution to the statistical fit, i.e., no significant decrease in the root mean square percent deviation. The curve fitting was accomplished by means of the computer program HINC written by D. W. Osborne of Argonne National Laboratory and modified by B. S. Hemingway. The equations were constrained to join smoothly with the C_P^0 values between 300 and

Table 6. Experimental heat capacities for pyrophyllite, $Al_2Si_4O_{10}(OH)_2$

Temp.	Heat capacity	Temp.	Heat capacity
K	J/(mol.K)	K	J/(mol.K)
335.9	320.5	382.6	341.0
355.8	329.6	392.6	345.8
375.7	339.7	374.5	338.9
395.6	347.6	384.6	344.0
415.6	354.3	394.6	348.4
435.5	362.3	409.6	354.9
455.4	370.2	429.6	363.4
475.3	374.3	449.6	371.9
495.2	384.8	469.6	381.4
515.1	393.3	439.6	364.9
335.9	317.1	449.6	371.6
355.8	328.6	459.6	376.8
375.7	337.6	474.6	382.6
395.6	347.4	489.7	386.6
415.6	356.7	509.7	388.8
434.4	365.1	529.7	392.4
455.4	371.9	524.7	395.6
475.3	380.4	529.7	397.2
495.2	386.6	539.7	399.2
515.1	391.9	559.8	404.0
332.5	314.4	579.8	409.2
342.5	321.4	599.8	415.4
362.6	331.5	619.8	420.8
		659.6	429.1
		679.6	429.7

370 K obtained by accurate low-temperature adiabatic calorimetry.

For anorthite, $CaAl_2Si_2O_8$ glass, $KAlSi_3O_8$ glass, and $NaAlSi_3O_8$ glass, the curve-fitting processes were extended to 1800 K, 1500 K, 1300 K, and 1200 K respectively, using the heat content data of White (1919) and Ferrier (1969). White's $H_T^0 - H_{273}^0$ data were corrected to the 1973 values of the atomic weights, recalculated to $H_T^0 - H_{298}^0$ values, and fitted by least squares to the equation

$$H_T^0 - H_{298}^0 = G + AT + \frac{B}{2} T^2$$
$$- CT^{-1} + 2DT^{1/2} + \frac{E}{3} T^3$$

with the constraints that $H_T^0 - H_{298}^0 = 0$ at 298.15 K and that C_P^0 at 298.15 K is equal to the value given by Robie et al. (1978b). Heat capacity values derived from this equation were added to the heat capacities obtained by differential scanning calorimetry.

Ferrier (1969) only gave four-term polynomial equations for $H_T^0 - H_{298}^0$ values of anorthite and

Table 7. Experimental heat capacities for $KAlSi_3O_8$ glass

Temp.	Heat capacity	Temp.	Heat capacity
K	J/(mol.K)	K	J/(mol.K)
350.2	228.6	669.7	296.2
370.1	236.2	689.7	298.4
390.0	243.1	699.7	297.7
410.0	248.7	709.7	298.5
419.9	251.0	689.8	295.8
429.9	253.4	699.8	296.6
419.9	249.6	719.9	297.4
439.9	254.8	739.9	299.4
459.8	259.3	759.9	302.3
479.8	264.1	770.0	304.4
489.8	264.8	780.0	305.3
499.8	267.4	759.9	301.7
509.7	269.4	770.0	302.9
504.7	267.2	790.0	304.3
509.7	267.7	810.0	305.7
519.7	269.0	820.0	306.1
539.7	272.8	830.1	306.1
559.6	275.0	864.7	306.7
579.6	277.6	874.6	307.9
589.6	278.0	888.0	310.3
599.6	282.5	908.9	309.6
594.8	283.7	918.7	308.6
599.7	284.0	899.1	307.9
609.7	285.0	908.9	307.6
629.7	286.8	928.6	309.4
649.7	288.1	938.4	310.8
659.6	289.0	948.2	312.4
674.6	291.2	923.7	313.5
679.6	291.5	933.5	313.6
619.7	286.8	948.2	313.5
629.7	290.0	958.0	314.0
649.7	293.8	967.9	314.5

Table 8a. Experimental heat capacities for synthetic grossular, $Ca_3Al_2Si_3O_{12}$

Temp.	Heat capacity	Temp.	Heat capacity
K	J/(mol.K)	K	J/(mol.K)
350.2	371.1	669.6	464.0
370.1	379.9	679.6	467.9
390.0	392.6	619.8	453.6
410.0	401.0	629.8	454.5
419.9	403.8	649.7	458.3
429.9	408.7	669.7	460.4
419.9	401.8	689.7	462.3
439.9	410.0	699.7	462.8
459.8	419.6	709.7	465.4
479.7	424.9	759.7	468.0
489.7	424.4	769.7	463.4
499.7	429.7	789.6	465.7
509.6	430.8	819.6	472.9
504.7	434.4	829.6	477.6
509.7	438.8	869.3	494.8
519.7	440.5	879.2	491.4
539.7	446.9	899.0	495.7
559.6	450.7	908.9	497.2
579.6	452.7	918.8	492.1
589.6	452.9	903.7	480.1
599.6	451.6	918.4	480.5
594.7	456.7	938.0	481.2
599.7	458.5	947.8	485.4
609.7	457.9	952.7	482.2
629.7	459.9	962.5	481.8
649.6	462.4	977.2	489.7
659.6	462.1	987.1	485.6

$CaAl_2Si_2O_8$ glass which reportedly fit his data to ± 2 percent. Values calculated from his equations were included with the data sets from our measurements and those of White for the final curve fitting.

Our results for synthetic grossular and natural grossular from Asbestos, Quebec, were separately combined with low-temperature heat capacity values of Westrum et al. (1978) and fitted by least squares to the general C_P^0 equation. Because of the greater accuracy of the data by Westrum et al. (1978), their C_P^0 values were weighted by a factor of three in the curve-fitting process. The equation for the natural grossular was not used for the derivation of the thermodynamic functions because the sample lacked chemical characterization.

The final C_P^0 equations for anorthite, $CaAl_2Si_2O_8$ glass, muscovite, pyrophyllite, $KAlSi_3O_8$ glass, grossular, and $NaAlSi_3O_8$ glass are listed in Table 10. The errors in the derived thermodynamic functions are estimated to be ± 0.7 percent in C_P^0 and $(H_T^0 - H_{298}^0)/T$, and ± 0.3 percent in S_T^0 and $(G_T^0 - H_{298}^0)/T$ between 300 and 1000 K. Tabulated values of the thermodynamic functions C_P^0, $(H_T^0 - H_{298}^0)/T$, S_T^0,

Table 8b. Experimental heat capacities for grossular from Jeffrey mine, Asbestos, Quebec

Temp.	Heat capacity	Temp.	Heat capacity
K	J/(mol.K)	K	J/(mol.K)
349.1	354.9	484.5	415.1
359.1	361.1	499.5	418.4
369.1	365.1	519.5	422.7
379.1	369.2	539.5	429.9
389.1	375.7	549.5	432.9
399.1	378.7	559.5	435.7
409.1	384.0	549.5	430.9
419.1	388.5	559.5	433.0
429.1	391.8	579.5	437.0
504.2	421.9	599.5	441.3
509.2	422.2	614.5	444.6
519.2	422.4	624.5	445.8
529.2	426.7	634.5	448.3
539.2	429.3	624.5	443.2
549.2	432.4	634.5	445.4
559.2	434.6	649.5	448.7
569.2	436.2	669.5	451.6
579.2	437.6	689.4	456.0
589.2	440.9	699.4	457.7
599.2	444.1	709.4	459.5
594.0	442.2	699.2	457.7
599.0	444.7	709.2	461.5
609.0	448.2	729.2	460.7
619.0	450.7	749.2	464.1
629.0	453.0	769.2	467.8
639.0	454.9	774.2	470.6
649.0	456.0	763.6	467.5
659.0	456.8	774.6	468.3
669.0	458.5	789.6	469.7
679.0	457.9	809.6	473.7
349.8	358.5	829.7	476.1
354.7	361.0	839.7	476.3
374.7	371.4	959.6	493.3
394.7	383.1	969.6	495.0
409.6	387.3	979.6	489.5
399.5	384.1	989.6	495.5
409.5	388.6	999.5	498.0
419.5	393.5	903.4	488.7
439.5	402.2	918.1	497.3
459.5	408.0	927.9	492.3
479.5	414.3	937.7	493.7
484.5	416.4	947.5	495.8
474.5	412.4	957.3	494.9

and $(G_T^0 - H_{298}^0)/T$ derived from the C_P^0 equations in Table 10 are given in Robie *et al.* (1978a).

Third-law derivation of $\Delta H_{f,298}^0$ and $\Delta G_{f,298}^0$ for muscovite, pyrophyllite, and grossular

It has been shown (for example, Darken and Gurry, 1953; Lewis and Randall, 1961, p. 177; Robie, 1965; Stull and Prophet, 1971, p. 5) that the so-called third-law method provides a rigorous means of extracting values of the enthalpy of reaction at 298.15 K, $\Delta H_{r,298}^0$, from equilibrium measurements. It also simultaneously furnishes a critical test of the accuracy of the equilibrium data. This approach is based

on a knowledge of the entropies and heat capacities (as a function of temperature) for all the phases involved in the equilibrium. For a reaction like the dehydration of muscovite or pyrophyllite, in which none of the phases is a solid solution, a value of the enthalpy of reaction at 298.15 K, $\Delta H_{r,298}^0$, can be calculated from *each* equilibrium bracket using the relation

$$-\Delta H_{r,298}^0 = T\Delta \ [(G_T^0 - H_{298}^0)/T] + \int_1^P \Delta V_T^0 dP$$
$$+ RT \ln f(T, H_2O) \qquad (1)$$

where ΔV_T^0 is the difference in the molar volumes of the solid phases in the reaction. For the pressure range over which equilibrium measurements exist for the dehydration of muscovite and pyrophyllite, the approximation can be made that

$$\int_1^P \Delta V_T^0 dP \approx (P - 1) \ \Delta V_{298}^0$$

Table 9. Experimental heat capacities for NaAlSi$_3$O$_8$ glass

Temp.	Heat capacity	Temp.	Heat capacity
K	J/(mol.K)	K	J/(mol.K)
350.2	228.3	759.6	305.3
370.1	236.1	764.6	305.3
390.0	243.3	619.7	289.8
410.0	249.0	629.7	291.1
419.9	251.4	649.7	294.3
429.9	253.9	669.7	296.6
419.9	249.0	689.7	298.2
439.9	254.1	699.7	299.9
459.8	258.5	709.7	301.9
479.8	263.3	689.8	297.6
489.8	264.0	699.8	298.9
499.8	266.6	719.9	298.8
509.7	268.5	739.9	300.5
504.7	267.1	760.0	304.3
509.7	267.6	770.0	306.9
519.7	268.8	780.0	307.1
539.7	272.5	760.0	303.5
559.6	274.5	770.0	304.2
579.6	276.9	810.0	309.2
589.6	279.3	820.1	310.2
599.6	281.7	830.1	310.9
594.8	282.9	864.7	312.8
599.8	283.3	874.6	313.1
609.7	284.2	889.3	314.9
629.7	286.1	908.9	316.2
649.7	286.6	918.8	317.4
659.6	289.3	899.0	314.7
674.6	290.5	908.9	317.3
679.6	290.9	928.6	319.5
674.6	286.1	938.9	318.2
679.6	294.3	948.2	318.6
689.6	297.4	923.7	317.1
709.6	299.3	933.5	318.6
729.6	302.9	948.2	320.1
749.6	305.9	958.0	320.7
		967.9	321.4

The value of $\Delta H^0_{r,298}$ calculated by this method is independent of the enthalpies of formation and their associated errors for the reacting phases. The third-law method uses the difference of Gibbs free-energy functions, $\Delta[(G^0_T - H^0_{298})/T]$, which is derived solely from heat capacity data, usually the most accurate of the data used in a thermodynamic calculation. The difference of Gibbs free-energy functions, which are given in most tabulations of thermodynamic properties, is a continuous, monotonically changing function of temperature and varies nearly linearly at high temperatures. Figure 4 shows the variation of the differences of the Gibbs free-energy functions with respect to temperature for two mineral reactions discussed later. Values of the Gibbs free-energy function can be easily interpolated, which results in an accurate integration of the entropy contribution of a reaction.

Values of the enthalpy of formation, $\Delta H^0_{f,298}$, are derived for muscovite, pyrophyllite, and grossular, based on: (1) recent equilibrium studies, (2) values of the Gibbs energy function, $(G^0_T - H^0_{298})/T$, calculated

Fig. 2. Experimental molar heat capacities, C^0_P, of muscovite [$KAl_2(AlSi_3O_{10})(OH)_2$], pyrophyllite [$Al_2Si_4O_{10}(OH)_2$], and $KAlSi_3O_8$ glass from Tables 5, 6 and 7, respectively, obtained by DSC. Above 298 K, the solid curves are generated from the C^0_P equations given for muscovite, pyrophyllite, and $KAlSi_3O_8$ glass in Table 10. Below 298 K, the curves are from the data of Robie *et al.* (1976) for muscovite and pyrophyllite, and from the data of Robie *et al.* (1978b) for $KAlSi_3O_8$ glass.
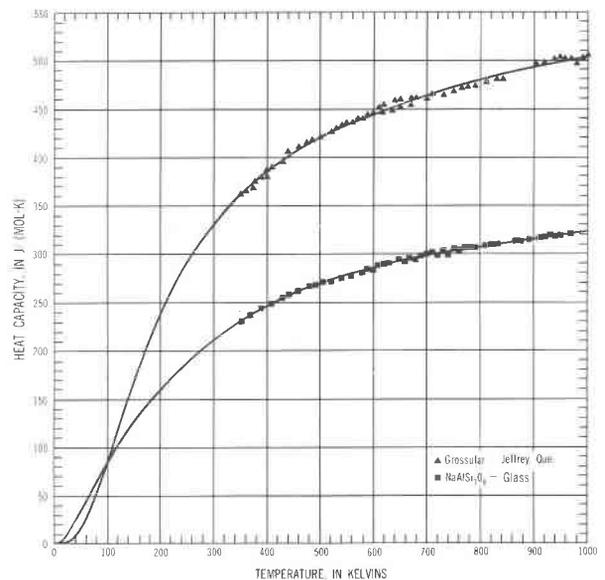
Fig. 3. Experimental molar heat capacities, C^0_P, of grossular ($Ca_3Al_2Si_3O_{12}$) from Jeffrey mine, Asbestos, Quebec, and of $NaAlSi_3O_8$ glass from Table 9 obtained by DSC. For grossular, the solid curve is the least-squares fit of the results of Westrum *et al.* (1978) and the experimental data listed in Table 8B. For $NaAlSi_3O_8$ glass, the solid curve above 298 K is generated from the C^0_P equation given for $NaAlSi_3O_8$ glass in Table 10. The solid curve below 298 K is from the data of Robie *et al.* (1978b) on the same sample of $NaAlSi_3O_8$ glass.

Fig. 1. Experimental molar heat capacities, C^0_P, of corundum (α-Al_2O_3) and periclase (MgO) obtained by differential scanning calorimetry (DSC). For corundum, the solid curve is from the values given by Ditmars and Douglas (1971). For periclase, the solid curve is from the work of Victor and Douglas (1963) above 273.15 K, and Barron *et al.* (1959) below 273.15 K.

Table 10. Molar heat capacity equations obtained by a least-squares fit to the experimental C_P^o data for anorthite, $CaAl_2Si_2O_8$ glass, muscovite, pyrophyllite, $KAlSi_3O_8$ glass, grossular, and $NaAlSi_3O_8$ glass

Compound	Temperature range of equation	Aver. % deviation between data and equation	Equations for C_P^o in J/(mol.K)
Anorthite $CaAl_2Si_2O_8$	(298 - 1800 K)	0.5	$C_P^o = 516.8 - 0.09249T - 1.408 \times 10^6 T^{-2} - 4588T^{-\frac{1}{2}} + 4.188 \times 10^{-5} T^2$
$CaAl_2Si_2O_8$ glass	(298 - 1500 K)	0.7	$C_P^o = 375.2 + 0.03197T - 2.815 \times 10^6 T^{-2} - 2459T^{-\frac{1}{2}}$
Muscovite (2M$_1$) $KAl_2(AlSi_3O_{12})(OH)_2$	(298 - 1000 K)	0.4	$C_P^o = 917.7 - 0.08111T + 2.834 \times 10^6 T^{-2} - 10348T^{-\frac{1}{2}}$
Pyrophyllite $Al_2Si_4O_{10}(OH)_2$	(298 - 800 K)	0.3	$C_P^o = 679.7 - 0.06412T - 6902T^{-\frac{1}{2}} - 5.997 \times 10^5 T^2$
$KAlSi_3O_8$ glass	(298 - 1300 K)	0.4	$C_P^o = 629.5 - 0.1084T + 2.496 \times 10^6 T^{-2} - 7210T^{-\frac{1}{2}} + 1.928 \times 10^{-5} T^2$
Grossular* $Ca_3Al_2Si_3O_{12}$	(298 - 1200 K)	1.0	$C_P^{o*} = 1633.3 - 0.7599T + 9.113 \times 10^6 T^{-2} - 20783T^{-\frac{1}{2}} + 2.669 \times 10^{-4} T^2$
Grossular** (Asbestos, Quebec)	(298 - 1000 K)	0.6	$C_P^{o**} = 630.4 + 0.1300T - 3.695 \times 10^6 T^{-2} - 4534T^{-\frac{1}{2}}$
$NaAlSi_3O_8$ glass	(298 - 1200 K)	0.3	$C_P^o = 934.4 - 0.3891T + 5.594 \times 10^6 T^{-2} - 11820T^{-\frac{1}{2}} + 1.476 \times 10^{-4} T^2$

* C_P^o equation used to derive the thermodynamic functions listed in Table 15.

** The C_P^o data for the grossular sample from Asbestos, Quebec, were not corrected for composition. The C_P^o
 equation was used only to derive the smooth curve for grossular in Figure 5.

from precise heat capacity measurements, and (3) previously-published values for the enthalpies of formation at 298.15 K of the ancillary reactants. The Gibbs energy functions of muscovite, pyrophyllite, grossular, and anorthite are derived from the C_P^o equations obtained in this study; those of corundum are from Ditmars and Douglas (1971); those of wollastonite, quartz, andalusite, and steam are tabulated in Robie et al. (1978a); and those of high sanidine are from values given by Hemingway, Krupka and Robie (unpublished data, 1976). Values for the fugacity of water, $f(T, H_2O)$, were taken from Burnham et al. (1969). The molar volumes, V_{298}^o, of the solid phases at 298.15 K and 1 bar pressure were taken from several sources. We have used 22.688±0.001 cm³, 25.575±0.007 cm³, and 51.53±0.04 cm³ as the molar volumes for low quartz, corundum, and andalusite, respectively, taken from the compilation of Robie et al. (1967). For the molar volume of 2M$_1$ muscovite, we used 140.73±0.20 cm³, which is the average of the volumes obtained from the cell parameters of Chatterjee and Johannes (1974), Robie et al. (1976), and Güven (1971). For pyrophyllite, we averaged the unit-cell volume data of Wardle and Brindley (1972)

and Taylor and Bell (1971) to obtain a molar volume of 127.82±0.29 cm³. For high sanidine, we used a molar volume of 108.91±0.04 cm³, which is an average calculated from the unit-cell volumes of Openshaw et al. (1976), Stewart and Wright (1974), and Chatterjee and Johannes (1974).

Chatterjee and Johannes (1974) investigated the reactions

muscovite $\rightleftharpoons$ high sanidine

$$+ \text{ corundum } + \text{ steam} \quad (2)$$

and

muscovite + quartz $\rightleftharpoons$ high sanidine

$$+ \text{ andalusite } + \text{ steam} \quad (3)$$
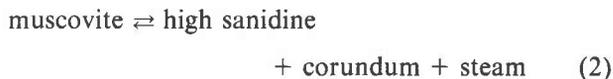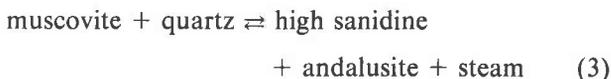
Reaction (2) was studied in the PH_2O range of 1000 to 8000 bars, at temperatures between 873 and 1073 K. They gave the uncertainties for the experimental pressures and temperatures obtained for reaction (2) as ±100 bars and ±6 K at $PH_2O < 8000$ bars, and ±100 bars and ±10 K at $PH_2O = 8000$ bars. Reaction (3) was studied in the PH_2O range of 500 to 5000 bars, at temperatures between 793 and 973 K. For
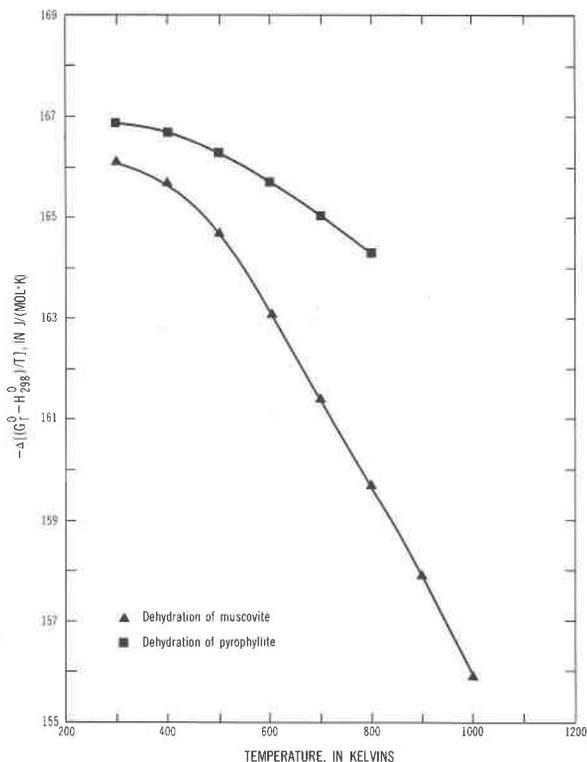
Fig. 4. Plot of the difference of the Gibbs free-energy functions, $-\Delta[(G_T^\circ - H_{298}^\circ)/T]$, with respect to temperature for two reactions studied in this paper. The triangles represent the dehydration reaction muscovite $\rightleftharpoons$ high sanidine + corundum + H_2O. The squares represent the dehydration reaction pyrophyllite $\rightleftharpoons$ andalusite + 3 quartz + H_2O.

reaction (3), the uncertainties are given as ± 50 bars and ± 6 K at $P \leq 2000$ bars, and ± 100 bars and ± 6 K at $P > 2000$ bars. Our calculations of the enthalpies of reactions (2) and (3) at 298.15 K, based on the equilibrium results of Chatterjee and Johannes (1974), are shown in Tables 11 and 12 respectively. The uncertainties for the average values of $\Delta H_{r,298}^0$ represent two standard errors (twice the standard deviation of the mean).

The calculated values of $\Delta H_{r,298}^\circ$, especially for reaction (2), show a drift with temperature and pressure. Calculations by Zen (1977), using the same experimental data, show a similar variation in the values of $\Delta G_{f,298}^\circ$ of muscovite calculated by the method described by Fisher and Zen (1971). This suggests an error with either the model chosen for the third-law calculation and/or the experimental data. Chatterjee and Johannes (1974, p. 89) give equations for the equilibrium constants for reactions (2) and (3) obtained by a linear least-squares fit to their experimental brackets. These equations may be rewritten in

terms of $\Delta G_{r,T}^\circ$ and then differentiated with respect to temperature to obtain the entropy change for the reaction, $\Delta S_{r,T}^\circ$ using the relation

$$(\partial \Delta G_T^\circ / \partial T)_P = -\Delta S_{r,T}^\circ$$

The value calculated from Chatterjee and Johannes' equations for $\Delta S_{r,1000}^\circ$ of reaction (2) is 164.2 J/K and for $\Delta S_{r,900}^\circ$ of reaction (3) is 159.6 J/K. Values of $\Delta S_{r,T}^\circ$ can also be calculated using the value for S_{298}° of sanidine given by Chatterjee and Johannes and the auxiliary entropy data from the same source used by Chatterjee and Johannes, i.e. Robie and Waldbaum (1968). From these data, $\Delta S_{r,1000}^\circ$ of reaction (2) is 155.4 J/K and $\Delta S_{r,900}^\circ$ of reaction (3) is 155.0 J/K. However, Hemingway and Robie (1977) point out that Chatterjee and Johannes used an incorrect value for S_{298}° of sanidine. The value of $\Delta S_{r,1000}^\circ$ for reaction (2) is 137.2 J/K and $\Delta S_{r,900}^\circ$ for reaction (3) is 139.0 J/K, based on: (1) S_{298}° values for sanidine from Openshaw et al. (1976) and for muscovite from Robie et al. (1976); (2) S_T° values for sanidine from Hemingway, Krupka and Robie (unpublished data, 1976) and for muscovite from this study; and (3) S_{298}° and S_T° values for andalusite, corundum, quartz, and steam from Robie et al. (1978a). These values are very different from those calculated from the equations of the equilibrium constants.

The reason for these discrepancies is not clear. The model chosen for the third-law calculations considers

Table 11. Calculation of $\Delta H_{r,298}^\circ$ for reaction (2)*, muscovite $\rightleftharpoons$ high sanidine + corundum + H_2O

T	P	$\Delta\left[\frac{(G_T^\circ - H_{298}^\circ)}{T}\right]$	$\frac{(P-1)\Delta V_{298}^\circ}{T}$	f_{T,H_2O}	$R\ln f_{T,H_2O}$	$\Delta H_{r,298}^\circ$
K	bars	J/K	J/K	bars	J/K	J
873	1000	-158.4	-0.7336	631.0	53.61	92120
883	1000	-158.2	-0.7252	646.0	53.80	92830
913	2000	-157.6	-1.404	1171	58.75	91530
933	2000	-157.2	-1.373	1230	59.16	92750
943	3000	-157.0	-2.039	1859	62.59	90950
953	3000	-156.8	-2.017	1903	62.79	91510
963	4000	-156.6	-2.662	2736	65.80	90000
983	4000	-156.2	-2.608	2856	66.16	91070
993	5000	-156.0	-3.227	3964	68.89	89700
1003	5000	-155.8	-3.195	4040	69.04	90220
1013	6000	-155.6	-3.796	5474	71.57	88970
1023	6000	-155.4	-3.759	5576	71.72	89450
1053	8000	-154.8	-4.870	9813	76.42	87660
1073	8000	-154.4	-4.779	10096	76.66	88540

Average $\Delta H_{r,298}^\circ$ = 90520 ± 840 J

*The experimental brackets for reaction (2) are from the data of Chatterjee and Johannes (1974).

Table 12. Calculation of $\Delta H^\circ_{r,298}$ for reaction (3)*, muscovite + quartz $\rightleftarrows$ high sanidine + andalusite + H_2O

T	P	$\Delta\left[\frac{(G^\circ_T-H^\circ_{298})}{T}\right]$	$\frac{(P-1)\Delta V^\circ_{298}}{T}$	f_{T,H_2O}	$R\ln f_{T,H_2O}$	$\Delta H^\circ_{r,298}$
K	bars	J/K	J/K	bars	J/K	J
793	500	−160.2	−0.1924	340.0	48.47	88750
833	500	−159.4	−0.1831	369.0	49.15	91990
823	1000	−159.6	−0.3711	550.5	52.47	88470
843	1000	−159.2	−0.3623	585.0	52.98	89850
863	2000	−158.8	−0.7081	1015	57.56	87980
878	2000	−158.4	−0.6960	1062	57.93	88820
893	3000	−158.1	−1.027	1630	61.50	87180
912	3000	−157.7	−1.004	1724	61.96	88330
933	4000	−157.3	−1.310	2551	65.22	87130
943	4000	−157.1	−1.296	2612	65.42	87680
963	5000	−156.6	−1.587	3728	68.38	86480
978	5000	−156.3	−1.562	3849	68.64	87260

Average $\Delta H^\circ_{r,298}$ = 88330 ± 850 J

*The experimental brackets for reaction (3) are from the data of Chatterjee and Johannes (1974).

muscovite and sanidine to be completely disordered with respect to Al/Si. The crystal structure determinations for $2M_1$ muscovite by Güven (1971) using X-ray diffraction and by Rothbauer (1971) using neutron diffraction indicate complete disorder of the Al and Si atoms in the $2M_1$ muscovite structure. Because the Al/Si disorder might be an artifact of the symmetry restrictions used in the data reduction by Güven (1971), Guggenheim and Bailey (1975) re-refined the $2M_1$ muscovite structure in the subgroup symmetry Cc using Rothbauer's intensity data. Their subgroup refinement also shows an Al/Si disorder in the $2M_1$ muscovite structure. Without structural data on the muscovite produced by Chatterjee and Johannes in their run products, we had to assume that their muscovite is a $2M_1$ muscovite with complete Al/Si disorder.

Chatterjee and Johannes also report the cell dimensions and the long-range order parameter Z (Thompson, 1969; Hovis, 1974) for four sanidines produced by reaction (2). The narrow range of these values suggests the sanidines are completely disordered with respect to Al/Si over the entire range of their experiments.

The experimental run times used by Chatterjee and Johannes decrease significantly as the temperatures and pressures of their experiments increase. Experimental run times, however, can be an important factor in interpreting the final results as recently shown in a study on ferrierites by Cormier and Sand (1976). Velde (1965) has also shown that the stability of the

different muscovite polytypes is a function of temperature, pressure, and time. Chatterjee and Johannes used X-ray diffraction to identify the phases in the run products and to establish the direction of the reaction. It would be almost impossible to identify a muscovite polytype other than $2M_1$ muscovite if it comprises only 10 or 20 percent of the total amount of muscovite in an X-ray diffractogram which also contains all of the phases in reaction (2) or (3).

If one considers muscovite as an ordered phase (for example, 3T muscovite) and subtracts out the configurational-entropy contribution for the Al/Si disorder, the calculated $\Delta H^\circ_{r,298}$ values for reactions (2) and (3) show little or no variation with respect to temperature. The slopes of the calculated reaction curves are then consistent with the experimental results. However, these $\Delta H^\circ_{r,298}$ values result in two different $\Delta H^\circ_{f,298}$ values for muscovite, which are both considerably more negative than the value given by Hemingway and Robie (1977) for a $2M_1$ muscovite. Until a detailed structure analysis is made on the final synthetic muscovite produced in the equilibrium investigations, we submit that the only logical model to use in the thermodynamic calculation is that of the Al/Si-disordered $2M_1$ muscovite.

The mean value of $\Delta H^\circ_{r,298}$ for reaction (3) (Table 12), 88330±850 J, was combined with the values of $\Delta H^\circ_{f,298}$ for quartz, andalusite, and steam from Robie et al. (1978a), and for sanidine (Z = 0.12±0.02) from Hemingway and Robie (1977) to yield a value of −5966500±4040 J/mol for the $\Delta H^\circ_{f,298}$ of muscovite from the elements. Hemingway and Robie obtained a value of −5976700±3240 J/mol for the $\Delta H^\circ_{f,298}$ of muscovite, from a recalculation of the solution calorimetry of Barany (1964), based on their new measurements of the enthalpies of formation of gibbsite, and the heat of solution of quartz.

The mean of the calorimetric value of $\Delta H^\circ_{f,298}$ for muscovite (Hemingway and Robie, 1977) and the $\Delta H^\circ_{f,298}$ value calculated from reaction (3) is −5971600±5180 J/mol. We believe that this represents the best value now available for $\Delta H^\circ_{f,298}$ of disordered $2M_1$ muscovite. The equilibrium curves for reactions (2) and (3), calculated from this value of $\Delta H^\circ_{f,298}$ and the high-temperature values of the Gibbs energy functions (Figs. 5 and 6), are in rather poor agreement with the experimental data of Chatterjee and Johannes (1974) for reaction (2) and in fair agreement with their data for reaction (3). Montoya and Hemley (1975) give a temperature of 873 K at 1000 bars for the breakdown of $2M_1$ muscovite in the presence of quartz [reaction (3)]. Our calculated equi-
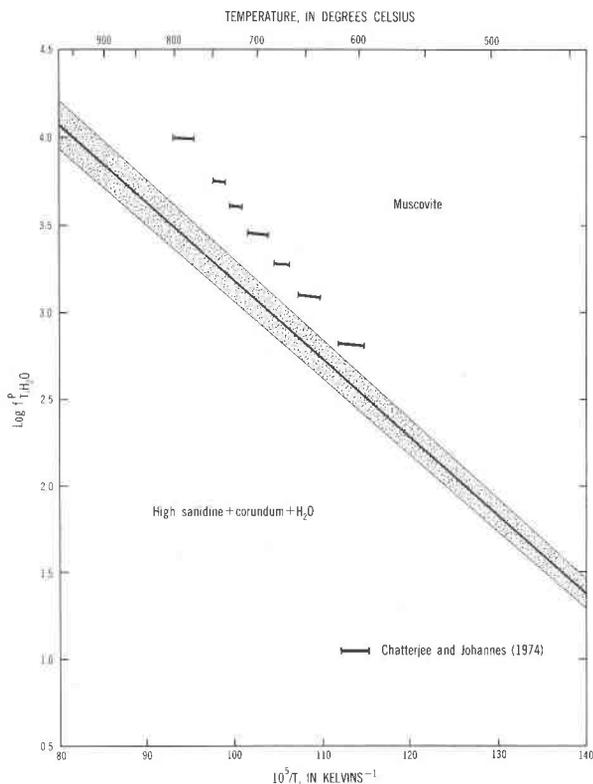
Fig. 5. Plot of log $f(T,H_2O)vs.T^{-1}$ for the reaction muscovite ⇌ high sanidine + corundum + H₂O. The equilibrium curve was calculated from the $\Delta H^\circ_{f,298}$ of muscovite as determined in this study. The stippled area represents the uncertainty contributed by the thermodynamic functions in the calculation of the curve. The experimental brackets are from the data of Chatterjee and Johannes (1974).

librium curve for reaction (3) (Fig. 6) is in agreement with this value.

The mean value of $\Delta H^\circ_{f,298}$ of muscovite was combined with the values for the entropies of muscovite (Table 12) and its constituent elements (Robie et al., 1978a) to obtain −5595500±5190 J/mol for the Gibbs free energy of formation, $\Delta G^\circ_{f,298}$, for disordered 2M₁ muscovite. The range of $\Delta G^\circ_{f,298}$ values for muscovite calculated by Zen (1977) from the experimental data of Chatterjee and Johannes agree very well with the value obtained in this study. Zen's $\Delta G^\circ_{f,298}$ values for muscovite vary between −5597500±4600 J/mol and −5600300±5900 J/mol.

Hemley (1967), Kerrick (1968), and Haas and Holdaway (1973) have studied the equilibrium

pyrophyllite ⇌ andalusite + 3 quartz + steam (4)

at temperatures between 638 and 736 K and in the PH_2O range of 1000 to 7000 bars. Values of the

Gibbs energy functions for pyrophyllite from this study and for andalusite, quartz, and steam (Robie et al., 1978a) were combined with the experimental data in a third-law calculation to obtain $\Delta H^\circ_{r,298}$ for the reaction (Table 13). Two distinct sets of $\Delta H^\circ_{r,298}$ values can be calculated from the three sets of experimental data. Neither set of $\Delta H^\circ_{r,298}$ values shows any significant variation with temperature. The average value of $\Delta H^\circ_{r,298}$ derived from the data of Hemley (1967) and Kerrick (1968) is 79670±1100 J, whereas that calculated from results of Haas and Holdaway (1973) is 77440±370 J. The set of experimental brackets from Hemley and Kerrick and the set from Haas and Holdaway are each *internally consistent*. As Kerrick and Haas and Holdaway used the same experimental technique, we have no basis for favoring either set of experimental values. Equilibrium curves for reaction (4) calculated from each average value of $\Delta H^\circ_{r,298}$ we determined are shown in Figure 7.
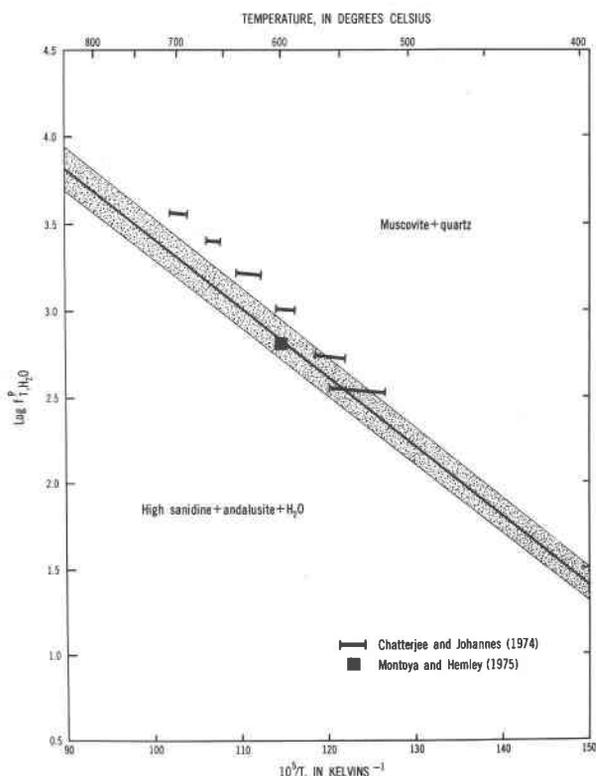
Fig. 6. Plot of log $f(T,H_2O)vs.T^{-1}$ for the reaction muscovite + quartz ⇌ high sanidine + andalusite + H₂O. The equilibrium curve was calculated from the $\Delta H^\circ_{f,298}$ of muscovite determined in this study. The stippled area represents the uncertainty contributed by the thermodynamic functions in the calculation of the curve. The experimental brackets are from the data of Chatterjee and Johannes (1974). The solid square represents the experimental point taken from Montoya and Hemley (1975).

Table 13. Calculation of $\Delta H^\circ_{r,298}$ for reaction (4), pyrophyllite $\rightleftarrows$ andalusite + 3 quartz + H_2O

T	P	$\Delta\left[\dfrac{(G^\circ_T - H^\circ_{298})}{T}\right]$	$\dfrac{(P-1)\Delta V^\circ_{298}}{T}$	f_{T,H_2O}	$R\ln f_{T,H_2O}$	$\Delta H^\circ_{r,298}$
K	bars	J/K	J/K	bars	J/K	J
638	1000*	-165.44	-1.322	199.5	44.03	78300
668	1000*	-165.23	-1.263	252.8	46.00	80490
668	1800**	-165.23	-2.274	358.0	48.90	79230
698	1800**	-165.02	-2.176	440.3	50.61	81380
688	3900**	-165.09	-4.785	919.0	56.73	77840
718	3900**	-164.88	-4.585	1098.3	58.22	79870
				Average $\Delta H^\circ_{r,298}$	= 79520 ± 1090 J	
643	2400***	-165.41	-3.150	376.5	49.31	76680
665	2400***	-165.25	-3.046	446.6	50.73	78180
668	3500***	-165.23	-4.423	694.8	54.41	76980
678	3500***	-165.16	-4.358	744.5	54.98	77660
687	4800***	-165.10	-5.898	1252	59.30	76740
697	4800***	-165.03	-5.814	1329	59.80	77400
728	7000***	-164.81	-8.118	3203	67.11	77040
736	7000***	-164.75	-8.030	3323	67.42	77540
				Average $\Delta H^\circ_{r,298}$	= 77280 ± 360	

*Experimental bracket is a revised value by Hemley (personal commun., 1976) for that given in Hemley (1967).

**Experimental brackets from Kerrick (1968).

***Experimental brackets from Haas and Holdaway (1973).

The mean of the two average values of $\Delta H^\circ_{r,298}$ for reaction (4) is 78400±1850 J. We believe that this represents the best value for $\Delta H^\circ_{r,298}$ for reaction (4) and is a fair representation of the state of the art of phase equilibrium measurements for pyrophyllite. Combining this value with the $\Delta H^\circ_{f,298}$ values adopted by Robie et al. (1978a) for quartz, andalusite, and steam, the enthalpy of formation of pyrophyllite from the elements is −5639800±3950 J/mol. The enthalpy of formation of pyrophyllite was combined with the entropies for pyrophyllite and its constituent elements (Robie et al., 1978a) to obtain a value of −526900±3960 J/mol for $\Delta G^\circ_{f,298}$ of pyrophyllite.

Newton (1966), Hays (1967), Boettcher (1970), and Windom and Boettcher (1976) have determined the equilibrium curve shown in Figure 8 for the reaction

grossular + quartz $\rightleftarrows$ anorthite + 2 wollastonite   (5)

at temperatures between 875 and 1575 K, and in the pressure range of 2000 to 19500 bars. Extension of the equilibrium curve to a pressure of one bar passes through 800±15 K. From this extrapolation and the relation

$$\Delta G^\circ_{r,T} = \Delta H^\circ_{r,298} + T\Delta[(G^\circ_T - H^\circ_{298})/T]$$

we calculate $\Delta H^\circ_{r,298}$ equal to 54300±1800 J/mol for the enthalpy change for reaction (5). This value, combined with the enthalpies of formation at 298.15 K for wollastonite and quartz (Robie et al., 1978a) and anorthite (Hemingway and Robie, 1977) yields −6657100±4720 J/mol for $\Delta H^\circ_{f,298}$ of grossular. From the entropies and molar volumes of the phases at 800 K (Table 14), the initial slope of the equilibrium curve (i.e., at 1 bar pressure) was calculated using the relation

$$dP/dT = \Delta S^\circ_{800}/\Delta V^\circ_{800}$$

$$= (68.5 \text{ J/mol} \cdot \text{K})/(32.1 \text{ cm}^3) = 21\pm4 \text{ bar/K}$$

This value agrees, within the combined experimental uncertainty, with the line drawn through the experimental P–T data, 26±2 bar/K. Combining this result with the entropies of the elements, wollastonite, and
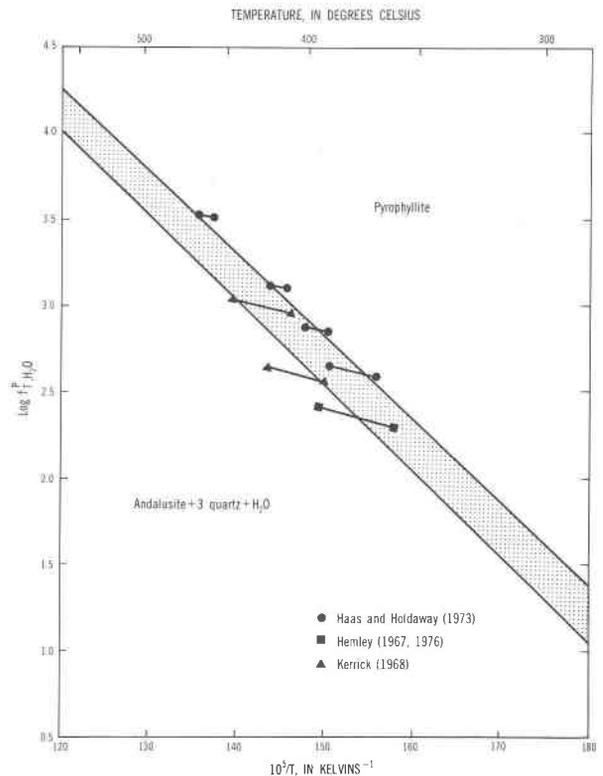
Fig. 7. Plot of log $f(T,H_2O)$ vs. T^{-1} for the reaction pyrophyllite $\rightleftarrows$ andalusite + 3 quartz + H_2O. The equilibrium curve at the lower temperatures was calculated from the average $\Delta H^\circ_{r,298}$ for the dehydration of pyrophyllite determined from the experimental data of Haas and Holdaway (1973). The other equilibrium curve was calculated from the average $\Delta H^\circ_{r,298}$ for the same reaction using the data of Hemley (1967; personal communication, 1976) and Kerrick (1968).

quartz (Robie *et al.*, 1978a) and our new entropy and enthalpy values for anorthite and grossular yields $\Delta G^\circ_{f,298}$ equal to -6295300 ± 4730 J/mol for grossular.

Summary

By combining data from recent equilibrium studies with new heat capacity values for anorthite, muscovite, pyrophyllite, and grossular, improved values of $\Delta H^\circ_{f,298}$ and $\Delta G^\circ_{f,298}$ for muscovite, pyrophyllite, and grossular were calculated by means of the third-law method. The best value for $\Delta H^\circ_{f,298}$ of disordered $2M_1$ muscovite from the elements is -5971600 ± 5180 J/mol, which is the mean of the calorimetric value of $\Delta H^\circ_{f,298}$ for muscovite given by Hemingway and Robie (1977) and the value of $\Delta H^\circ_{f,298}$ derived from reaction (3). The new value of $\Delta H^\circ_{f,298}$ of muscovite yields a value of -5595500 ± 5190 J/mol for the Gibbs free energy of formation, $\Delta G^\circ_{f,298}$, for disordered $2M_1$ muscovite. Similarly, an improved value for $\Delta H^\circ_{f,298}$ of pyrophyllite is -5639800 ± 3950 J/mol. This value and the appropriate entropy data were combined to obtain a value of -5265900 ± 3960 J/mol for $\Delta G^\circ_{f,298}$ of pyrophyllite. A new value of -6657100 ± 4720 J/mol was determined for $\Delta H^\circ_{f,298}$ of grossular. The value of $\Delta G^\circ_{f,298}$ of grossular was calculated to be -6295300 ± 4730 J/mol.

Table 14. Thermodynamic constants used in determining $\Delta H^\circ_{f,298}$ of grossular

Compound	S°_{800} J/(mol·K)	V°_{800}* cm^3	$(G^\circ_{800} - H^\circ_{298})/T$ J/(mol·K)
Anorthite $CaAl_2Si_2O_8$	460.7	101.4	−290.0
Wollastonite $CaSiO_3$	186.3	40.38	−118.4
Grossular $Ca_3Al_2Si_3O_{12}$	665.3	126.7	−397.7
α-Quartz SiO_2	99.58	23.36	−61.23

*The thermal expansion data which was used are from:

    Anorthite -- Czank and Schulz (1971)

    Wollastonite -- H. T. Evans, Jr. (unpub. data, 1977)

    Grossular -- Skinner (1956)

    α-Quartz -- Skinner (1966)

Acknowledgments

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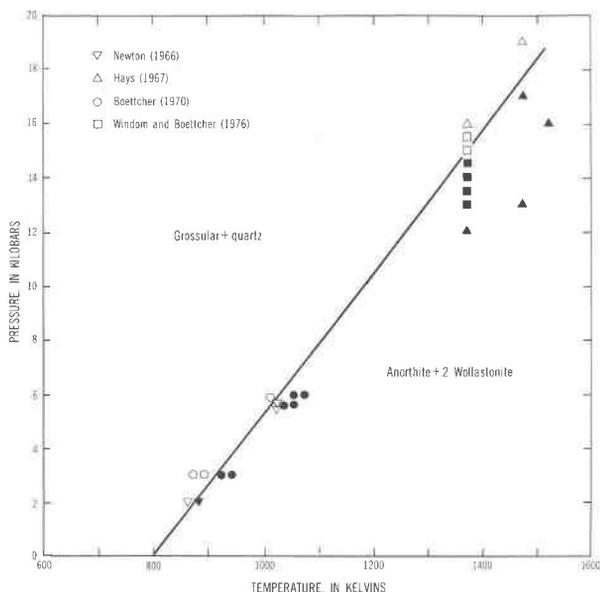
Fig. 8. Plot of the *P–T* conditions for the reaction grossular + quartz $\rightleftarrows$ anorthite + 2 wollastonite. The equilibrium curve was extrapolated to 800 ± 15 K and 1 bar using the experimental data of Newton (1966), Hays (1967), Boettcher (1970), and Windom and Boettcher (1976).

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