0.02 E. U. as compared with the previous "best" values of 12.5 E. U. selected by Kelley on the basis of the earlier work of several other investigators.

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[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heat Capacities at Low Temperatures and Entropies at 298.16°K. of Andalusite, Kyanite, and Sillimanite

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This paper presents low-temperature heat-capacity data and entropy values at 298.16°K. for three crystalline modifications of aluminum silicate (Al_2SiO_5), namely, andalusite, kyanite and sillimanite. The heat capacities of all three substances were studied previously by Simon and Zeidler,[1] and their data were used by Kelley[2,3] in evaluating the entropies at 298.16°K. These entropy values range from 20.7 to 27.0 E.U., the spread being 6.3 units. The magnitude of the variation appears unaccountably high, which was one of the factors justifying the present work.

Materials.—The materials used in this investigation were natural minerals from the following sources: andalusite, Standish, Maine; kyanite, Celo Mines, Burnsville, N. C.; and sillimanite, Benson Mines, N. Y. They were supplied to us by the Geophysical Laboratory of the Carnegie Institution of Washington, where they had been subjected to careful purification and microscopic examination. Subsequently, complete chemical analyses also were furnished.[4] These appear in Table I and may be compared with the theoretical composition, 62.93% Al_2O_3 and 37.07% SiO_2.

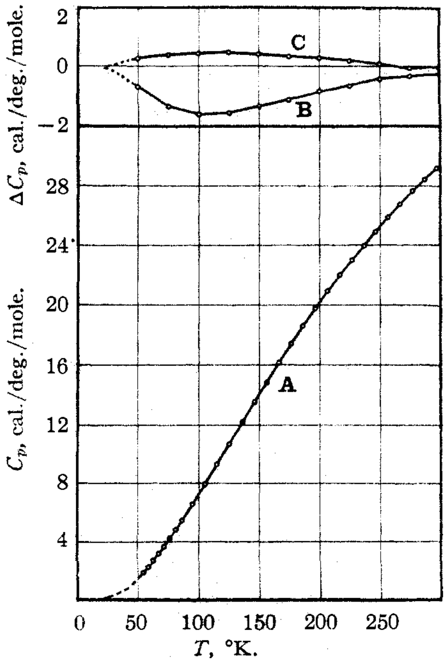

Fig. 1.—Heat capacities: curve A, C_p (andalusite); curve B, C_p (kyanite) − C_p (andalusite); curve C, C_p (sillimanite) − C_p (andalusite).

TABLE I

CHEMICAL ANALYSES (WEIGHT %, DRY BASIS)

	Andalusite	Kyanite	Sillimanite
Al_2O_3	63.15	63.20	61.80
SiO_2	36.84	36.90	36.44
TiO_2	Trace[a]	None	None
FeO	None	None	0.14
Fe_2O_3	0.11	0.10	0.98
MgO	Trace	None	0.24
CaO	0.02	0.05	0.07
MnO	Trace	None	0.04
Na_2O	None	None	Trace
K_2O	None	None	None
P_2O_5	....	....	0.28
F	....	....	0.04
Total	100.12	100.25	100.03

[a] "Trace" means < 0.01%.

According to microscopic examinations, the andalusite contained a few muscovite inclusions, the kyanite contained less than 0.2% unidentified inclusions, and the sillimanite contained less than 0.7% wagnerite inclusions. The samples were heated 4 hours at 540°, to remove moisture, before enclosing in the calorimeter.

Heat Capacities.—The heat-capacity measurements were made with previously described apparatus.[5] The results, expressed in defined calories (1 calorie = 4.1833 int. joules) per deg. per mole (162.00 g.), are listed in Table II. The masses of materials employed were 198.61 g. of andalusite, 212.19 g. of kyanite, and 207.71 g. of sillimanite. No corrections were applied for deviations of the chemical analyses from the theoretical composition. Figure 1 shows the results for andalusite plotted against temperature and also the curves for the difference in heat capacity between andalusite and kyanite and between andalusite and sillimanite. This method of plotting is more informative in this instance than a single plot of this size showing all three individual heat-capacity curves.

The heat-capacity values of Simon and Zeidler[1] deviate markedly from the present work. Thus, for andalusite their results range from 97% higher at the lower end of the common temperature range to 11% higher at the upper end of the common temperature range. Similar comparison for kyanite shows their results are from 31 to 2% higher,

(1) F. Simon and W. Zeidler, *Z. physik. Chem.*, **123**, 383 (1926).

(2) K. K. Kelley, *U. S. Bur. Mines Bull.* 350 (1932).

(3) Kelley, *ibid.*, 394 (1936); *ibid.*, 434 (1941).

(4) The author expresses his thanks to Th. G. Sahama, Professor of Geochemistry, University of Helsinki, Finland (formerly Visiting Investigator at the Geophysical Laboratory), and to L. H. Adams, Director, Geophysical Laboratory, for their kind coöperation and interest.

(5) K. K. Kelley, B. F. Naylor and C. H. Shomate, *U. S. Bureau of Mines Tech. Paper* 686 (1946).

TABLE II

MOLAL HEAT CAPACITIES (0°C. = 273.16°K.)

T, °K.	Cp, cal./deg.	T, °K.	Cp, cal./deg.	T, °K.	Cp, cal./deg.
Andalusite (Al_2SiO_5)					
54.90	1.920	114.62	9.247	216.2	22.00
58.90	2.296	124.7	10.65	226.1	22.98
62.98	2.701	135.9	12.19	236.2	23.97
67.23	3.184	145.9	13.52	245.8	24.91
71.69	3.656	155.7	14.81	256.2	25.88
76.41	4.229	165.9	16.13	266.2	26.74
81.00	4.798	176.0	17.41	276.1	27.61
86.29	5.430	185.9	18.58	286.2	28.39
94.80	6.550	195.9	19.76	296.2	29.19
104.81	7.899	206.2	20.91	(298.16)	(29.34)
Kyanite (Al_2SiO_5)					
54.76	1.089	114.62	7.650	216.1	21.26
58.83	1.355	124.87	9.103	226.0	22.37
63.05	1.670	141.9	11.58	236.0	23.42
67.56	2.044	146.7	12.24	245.6	24.41
71.97	2.447	155.9	13.54	256.0	25.50
76.26	2.874	166.4	15.01	266.0	26.42
80.72	3.345	175.9	16.32	276.1	27.27
86.06	3.936	186.0	17.58	286.3	28.13
95.04	5.022	195.8	18.84	296.3	28.95
104.61	6.274	206.2	20.10	(298.16)	(29.10)
Sillimanite					
54.40	2.179	114.82	9.750	216.2	22.22
58.48	2.583	124.7	11.10	226.6	23.25
62.53	3.008	136.0	12.65	236.3	24.14
67.00	3.506	146.3	14.01	246.2	25.06
71.52	4.037	155.8	15.24	256.2	25.98
76.00	4.589	165.9	16.53	266.1	26.83
80.86	5.183	175.9	17.76	276.2	27.63
86.07	5.850	186.4	18.96	286.3	28.39
95.40	7.084	196.1	20.05	296.5	29.19
104.80	8.373	206.6	21.23	(298.16)	(29.31)

and for sillimanite from 44 to 4% higher. Simon and Zeidler mention that the scatter in their results for andalusite and sillimanite was greater than usual because of the limited quantities of materials available for their measurements. Their values for kyanite do deviate least from the present results, but the improvement is not enough to make this a major factor. Nothing was said in their paper with regard to any examinaton for purity. However, unless their materials were grossly impure, one would not expect to account for a major portion of the deviations upon the basis of purity.

The results in the present paper have been examined critically and absolutely no grounds were found for doubting their accuracy. The precision error in the measurements is less than 0.1% and they are considered accurate in the absolute sense to within 0.3% on the average.

Entropies at 298.16°K.—The entropy increments between 51.00° and 298.16°K. were obtained by numerical integration of plots of Cp against log T, using Simpson's rule. The increments between 0° and 51.00°K. were obtained through the use of the empirical Debye and Einstein function sums listed below. These empirical function sums fit the data over the entire measured temperature range within the maximum deviation indicated in parentheses.

Andalusite: $D\left(\frac{311}{T}\right) + 3E\left(\frac{485}{T}\right) + 4E\left(\frac{1035}{T}\right)$ (2.5%)

Kyanite: $D\left(\frac{395}{T}\right) + 4E\left(\frac{569}{T}\right) + 4E\left(\frac{1271}{T}\right)$ (1.4%)

Sillimanite: $D\left(\frac{292}{T}\right) + 3E\left(\frac{468}{T}\right) + 4E\left(\frac{1048}{T}\right)$ (0.5%)

Table III contains the entropy results.

TABLE III

MOLAL ENTROPIES, CAL./DEG.

	Andalusite	Kyanite	Sillimanite
0°–51.00°K. (extrap.)	0.62	0.33	0.73
51.00°–298.16° (meas.)	21.66	19.69	22.24
$S^0_{298.16}$	22.28 ± 0.10	20.02 ± 0.08	22.97 ± 0.10

The extrapolated portions of the entropy are about 2.8, 1.6 and 3.2%, respectively, of the totals at 298.16°K. The spread in the entropies of the three substances is 2.95 units, which appears entirely reasonable in comparison with values for other compounds having two or more crystalline modifications.[6]

Related Thermal Data.—Column (2) of Table IV lists heats of formation from the elements and from the oxides (corundum and quartz), in accordance with the National Bureau of Standards Tables.[7] Entropies of formation from the elements and from the oxides are in column (3), the necessary auxiliary data being taken from Kelly's[6] compilation. Column (4) gives the derived free energies of formation from the elements and from the oxides. It is not possible to assign limits of error to the heat values, or consequently to the free-energy values. The errors probably are large enough that no significance should be attached to the indicated differences in heats or free energies of formation of the three substances.

TABLE IV

THERMAL DATA

Substance	$\Delta H^0_{298.16}$, cal./mole	$\Delta S^0_{298.16}$, cal./deg./mole	$\Delta F^0_{298.16}$, cal./mole
	From elements		
Andalusite	−642,200	−118.3	−606,900
Kyanite	−642,700	−120.5	−606,800
Sillimanite	−648,900	−117.6	−613,800
	From oxides		
Andalusite	−37,700	−0.2	−37,600
Kyanite	−38,200	−2.5	−37,500
Sillimanite	−44,400	0.5	−44,500

Summary

The heat capacities of three crystalline modifications of aluminum silicate (andalusite, kyanite and sillimanite) were measured in the temperature range 52 to 298°K.

Entropies at 298.16°K., computed from the heat-capacity data, are 22.28 ± 0.10, 20.02 ± 0.08, and 22.97 ± 0.10 E. U., for andalusite, kyanite and sillimanite, respectively.

Free energy of formation values at 298.16°K. were obtained from the entropies and literature results for the heats of formation.

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(6) The known values are included in the compilation of K. K. Kelley, *U. S. Bureau of Mines Bull.*, 477 (1950).

(7) National Bureau of Standards, "Tables of Selected Values of Chemical Thermodynamic Properties," Series I, Tables 59-2 and 59-9 (Sept. 30, 1949); Table 24-2 (Sept. 30, 1948).