prepared from the hydrate by pulverizing and heating. The salt mixtures were made up by weight and the nickel content of several melts was checked by the dimethylglyoxime method. Decomposition to water insoluble compounds was always less than 1%.

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Low Temperature Heat Capacities and Entropies at 298.15°K. of Some Crystalline Silicates Containing Calcium

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Heat capacity measurements from 51 to 298°K. were conducted for γ-calcium orthosilicate, tricalcium disilicate, diopside (calcium–magnesium metasilicate) and anorthite (calcium–aluminum silicate). The entropies at 298.15°K. are, respectively, 28.8 ± 0.2, 50.4 ± 0.3, 34.2 ± 0.2, and 48.4 ± 0.4 cal./deg. mole. Entropies of formation of the silicates from their constituent oxides are derived.

Low temperature heat capacity and entropy data are available for two varieties of calcium metasilicate[1–4] ($CaSiO_3$, wollastonite and pseudowollastonite), one variety of calcium orthosilicate[5] ($Ca_2SiO_4(\beta)$, thermodynamically unstable form), and tricalcium silicate[5] (Ca_3SiO_5). This paper reports low temperature heat capacity data and entropy evaluations at 298.15°K. for four additional crystalline silicates containing calcium, (1) the room temperature stable form of calcium orthosilicate ($Ca_2SiO_4(\gamma)$), (2) tricalcium disilicate ($Ca_3Si_2O_7$), (3) diopside ($CaMgSi_2O_6$), and (4) anorthite ($CaAl_2Si_2O_8$). No previous similar data exist for these substances, except some heat capacity values for diopside between 20 and 40°K. (reported by Wagner[2]) which are insufficient for evaluation of the entropy at 298.15°K.

Materials.—The γ-calcium orthosilicate was part of the sample described by Coughlin and O'Brien.[6] It contained 34.88% silica (theory, 34.89%) and gave an X-ray diffraction pattern that agreed with the ASTM catalog.

Tricalcium disilicate was made by heating a stoichiometric mixture of reagent-grade calcium carbonate and pure silica for a total of 80 hours at 1100–1200° and 12 hours at 1200°, with intervening grindings, mixings, analyses and adjustments of composition.[7] The final product contained 58.37% lime and 41.62% silica, as compared with the theoretical 58.33 and 41.67%. The X-ray diffraction pattern checked the ASTM catalog.

The diopside was natural mineral from Juva, Finland. It was supplied by Prof. Th. G. Sahama of the University of Helsinki, who also furnished the chemical analysis. As received, it contained 0.22% water which was removed by heating to 700° before use. It contained (on a dry basis) 25.91% lime, 18.82% magnesia, 54.78% silica, 0.68% ferric oxide, 0.07% ferrous oxide, 0.07% alumina, 0.02% manganous oxide and no titania. (The theoretical analysis for pure diopside is 25.89% lime, 18.62% magnesia and 55.49% silica.) The optical properties and density checked closely the accepted values for diopside. Further details regarding this sample are given by Juurinen and Hytonen.[8]

Anorthite was prepared by repeated sintering of a stoichiometric mixture of reagent-grade calcium carbonate, pure hydrated alumina and pure silica, with the usual intervening grinding, mixing, analysis and adjustment of composition.[9] Nine heats were made, totaling 58 hours at 1100°, 53 hours at 1200°, 6 hours at 1300°, and 10 hours at 1500°. A platinum container was used for the 1500° heats and Alundum for the others. The product analyzed 20.10% lime, 36.64% alumina, 43.02% silica and 0.20% ferric oxide. (The theoretical analysis is 20.16% lime, 36.65% alumina and 43.20% silica.) The X-ray diffraction pattern checked that given in the ASTM catalog for synthetic anorthite.

Heat-Capacity Measurements and Results.—The measurements were conducted in previously described apparatus.[10] The sample masses were as follows: γ-calcium orthosilicate, 116.94 g.; tricalcium disilicate, 114.75 g.; diopside, 209.83 g.; and anorthite, 184.02 g. All weighings were corrected to vacuum and all molecular weights conform with the 1954–55 Report on Atomic Weights.[11] The definition 0°C. = 273.15°K. was employed. The precision uncertainty in the heat capacity measurements is less than 0.1% and the absolute error is considered to be 0.3%.

The heat capacity results, expressed in defined calories (1 cal. = 4.1840 abs. joules) per deg. mole, are listed in Table I. The four substances exhibit normal heat capacity curves over the entire temperature range investigated.

At room temperature the heat capacities of these silicates do not differ greatly from the sums for their constituent oxides. The difference is smallest for anorthite (0.2%) and greatest for γ-calcium orthosilicate (2.5%). It is of interest to note that the heat capacity of the γ-variety of calcium orthosilicate is lower than that of the β-variety[5] by amounts ranging from 1.4% at 298°K. to 12.4% at 50°K.; this is to be expected as the β-variety is thermodynamically unstable. Diopside may be considered as composed of one mole each of calcium metasilicate and magnesium metasilicate. In comparison with wollastonite and clinoenstatite[4] its heat capacity is lower by 0.5% at 298°K. and 23.8% at 50°K. Anorthite may be compared with its so-

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TABLE I

HEAT CAPACITIES (CAL./DEG. MOLE)

T. °K.	C_p	T. °K.	C_p	T. °K.	C_p
$Ca_2SiO_4(\gamma)$ (mol. wt. 172.25)					
54.15	3.837	114.77	13.73	216.34	24.97
58.76	4.565	124.82	15.18	226.17	25.76
63.28	5.306	135.85	16.66	236.41	26.49
67.99	6.104	145.64	17.94	245.95	27.13
72.82	6.927	155.82	19.17	256.38	27.83
77.28	7.680	165.95	20.29	266.21	28.47
82.42	8.549	175.76	21.32	276.10	29.05
86.78	9.278	185.92	22.32	286.70	29.66
94.74	10.60	196.02	23.21	296.22	30.26
104.93	12.24	206.24	24.12	298.15	(30.31)
$Ca_3Si_2O_7$ (mol. wt. 288.42)					
53.45	7.075	114.56	24.02	216.22	42.54
57.86	8.269	124.51	26.42	226.31	43.78
62.42	9.594	136.28	29.01	236.14	44.97
67.14	10.99	145.77	31.06	245.95	46.03
71.75	12.36	155.90	33.05	256.41	47.27
76.28	13.66	165.77	34.83	266.23	48.24
80.68	14.95	175.89	36.53	276.18	49.25
85.24	16.24	185.89	38.15	286.69	50.23
95.04	18.97	195.82	39.63	296.15	51.19
105.04	21.72	206.31	41.12	298.15	(51.24)
$CaMgSi_2O_6$ (mol. wt. 216.58)					
53.83	3.618	114.71	15.42	216.42	31.58
58.40	4.378	124.66	17.37	226.05	32.73
63.33	5.232	135.80	19.46	235.88	33.82
68.23	6.140	145.58	21.25	245.64	34.83
72.87	7.022	155.87	22.99	256.29	35.95
77.47	7.918	165.78	24.59	266.14	36.91
82.52	8.921	175.86	26.11	276.08	37.85
87.18	9.855	186.01	27.60	286.63	38.77
94.82	11.41	195.86	28.96	295.98	39.66
105.11	13.51	206.24	30.34	298.15	(39.80)
$CaAl_2Si_2O_8$ (mol. wt. 278.22)					
53.43	7.263	114.84	21.79	215.93	40.05
57.84	8.340	124.75	23.93	226.04	41.55
62.14	9.392	136.11	26.28	235.89	42.87
66.41	10.45	145.47	28.18	245.73	44.11
70.92	11.53	155.60	30.10	256.12	45.43
75.70	12.73	165.80	31.96	266.09	46.72
81.13	14.04	175.97	33.70	276.13	47.99
85.78	15.22	185.90	35.38	286.47	49.14
94.74	17.30	195.83	36.97	295.93	50.23
105.23	19.70	206.17	38.60	298.15	(50.46)

dium-analog, albite ($NaAlSi_3O_8$).[12] The latter has the lower heat capacity down to about 175°K.; at lower temperatures the order is reversed.

Entropies at 298.15°K.—The entropy increments for the measured range, 51–298.15°K., were obtained by Simpson-rule integrations of plots of C_p against log T. Values for the range 0–51°K. were extrapolated. For use in extrapolation, the following empirical Debye and Einstein function sums were found to fit the measured data for the two calcium silicates and diopside to within the limits indicated in parentheses

$Ca_2SiO_4(\gamma)$: $D(231/T) + 3E(358/T) + 3E(896/T)$, (1.2%)

$Ca_3Si_2O_7$: $D(176/T) + 4E(283/T) + 4E(586/T) + 2E(950/T)$, (0.8%)

$CaMgSi_2O_6$($^1/_2$ mole): $D(312/T) + 2E(480/T) + E(871/T) + E(1290/T)$, (0.7%)

In the case of anorthite, the extrapolation of entropy was made by the comparison method of Kelley, Parks and Huffman,[13] as described by Kelley and co-workers[12] for alkali aluminum silicates. The entropy calculations are summarized in Table II.

TABLE II

ENTROPIES AT 298.15°K. (CAL./DEG. MOLE)

Substance	0–51°K. (extrap.)	51–298.15°K. (meas.)	$S^0_{298.15}$
$Ca_2SiO_4(\gamma)$	1.32	27.53	28.8 ± 0.2
$Ca_3Si_2O_7$	2.64	47.71	50.4 ± .3
$CaMgSi_2O_6$	1.22	32.94	34.2 ± .2
$CaAl_2Si_2O_8$	3.70	44.75	48.4 ± .4

Employing entropy data given by Kelley[4] (except for aluminum oxide for which the value of Kerr, Johnston and Hallett[14] is adopted), the following entropies of formation from the constituent oxides at 298.15°K. are obtained (cal./deg. mole): -0.2 for γ-calcium orthosilicate, 1.9 for tricalcium disilicate, 1.9 for diopside, and 6.7 for anorthite. The entropy of formation of diopside from wollastonite and clinoenstatite at 298.15°K. is -1.6 cal./deg. mole. The conversion of γ- to β-calcium orthosilicate involves an entropy change of 1.7 cal./deg. mole at 298.15°K. Also at this temperature, anorthite has an entropy 1.8 cal./deg. mole lower than that of its sodium analog (albite).

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