

The term $(\text{OI}^-)^2/(\text{OH}^-)$, suggested by Skrabal, is shown to be negligible as compared with these two terms.

3. The heat of activation is computed from

the kinetic data at 25 and 2° to be 12,400 which is good agreement with the value obtained by Forster and Skrabal.

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[CONTRIBUTION FROM THE WESTERN REGION BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Specific Heats at Low Temperatures of Magnesium Orthosilicate and Magnesium Metasilicate¹

BY K. K. KELLEY²

Investigation of low-temperature specific heats of metallurgically important substances has been one of the programs of study of the Pacific Experiment Station of the Bureau of Mines for several years. About three years ago, the paucity of low-temperature specific-heat and entropy data for silicates led to a modest undertaking in this field, and eleven of the simpler silicates were studied. Results for three sodium silicates,³ for beryllium orthosilicate,⁴ and for iron, manganese and zirconium silicates⁵ already have been presented. The present paper reports specific-heat data in the temperature range 51° to 298°K. and the entropies of magnesium orthosilicate and magnesium metasilicate.

Materials⁶

Procedures for the preparation of these silicates are based upon the research of Jander and Wuhrer.⁷ The initial materials were (1) a good grade of finely powdered silica, which was digested overnight with 6 *N* hydrochloric acid, washed free of chlorides, dried, and heated to 800° and (2) c. p. magnesium oxide having no appreciable impurities other than water.

In the preparation of magnesium orthosilicate, a mixture of oxides containing an 0.82% excess of magnesium oxide over the theoretical 2:1 molal ratio was rotated in the chamber of a porcelain ball mill for nine hours to assure intimate mixing. (The excess magnesium oxide may have been unnecessary, but it was added to inhibit formation of magnesium metasilicate, which was present in small amounts in the best products reported by Jander and Wuhrer.) The mixture was moistened, tamped into a nickel cartridge, dried at 100°, and finally heated in a tube

furnace at 1150 ± 20° for four days under a vacuum of 10⁻⁴ mm. After this treatment the product contained 3.6% uncombined magnesium oxide. It was reground and similarly heated for five additional days at 1180 ± 10°. Analysis now gave 98.6% magnesium orthosilicate, 0.8% uncombined magnesium oxide, no free silica, and no magnesium metasilicate. A 140.83-g. sample of this product was used in the measurements.

The preparation of magnesium metasilicate was much more difficult and time-consuming. A 1:1 mixture of the oxides was made up as before in the chamber of a porcelain ball mill, tamped into a nickel cartridge, and heated in a tube furnace at 1300 ± 20° for thirteen and one-half days. At this stage no uncombined magnesium oxide remained, but 27.1% magnesium orthosilicate was present. The product was reground, reheated (this time in an Arsem furnace) for forty-five hours at 1300°, and reanalyzed. This latter procedure was repeated several times, until a virtually constant analysis was obtained. The final product analyzed 92.0% magnesium metasilicate, 5.6% magnesium orthosilicate, and 2.4% uncombined silica. Although it would have been possible, in a much longer time, to obtain a better product, the operation was so time-consuming, and so little improvement was noted in the last three stages of the regrinding-reheating process, that it appeared inadvisable to continue. It is believed that adequate results were obtained with this material, as correction was made for the uncombined silica and for magnesium orthosilicate. A 97.04-g. sample was employed in the measurements. The difficulty encountered in this preparation bears out the observations of Jander and Wuhrer, who report the persistence of magnesium orthosilicate after ten days of heating at 1170°.

Throughout the present work the analytical methods of Jander and Wuhrer were followed in minute detail. Their description is so adequate that repetition is unnecessary. The methods are not highly accurate but are good enough for most purposes. It may be of interest to record the range of variation in the above-reported analyses. In the case of the magnesium orthosilicate sample, four analyses for uncombined magnesium oxide varied from 0.75 to 0.86%, and three analyses for magnesium orthosilicate varied from 98.4 to 98.7%. For the magnesium metasilicate sample, three analyses for magnesium orthosilicate varied from 5.48 to 5.83%, three for uncombined silica varied from 2.34 to 2.49%, and three for magnesium metasilicate varied from 91.7 to 92.2%.

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(3) Kelley, *THIS JOURNAL*, **61**, 471 (1939).

(4) Kelley, *ibid.*, **61**, 1217 (1939).

(5) Kelley, *ibid.*, **63**, 2750 (1941).

(6) These materials were prepared and analyzed by Dr. G. W. Marks, Western Region, Bureau of Mines. The author gratefully acknowledges this assistance.

(7) Jander and Wuhrer, *Z. anorg. allgem. Chem.*, **226**, 225 (1936).

Specific Heats

The previously described⁸ methods and apparatus again were employed. The specific heat results, expressed in defined calories (1 calorie = 4.1833 int. joules), are given in Table I and

TABLE I
SPECIFIC HEAT OF Mg_2SiO_4 (140.70 g.)

T , °K.	C_p , cal./deg. mole	T , °K.	C_p , cal./deg. mole	T , °K.	C_p , cal./deg. mole
53.2	1.817	114.4	9.818	216.2	22.14
57.3	2.172	124.8	11.35	226.0	23.03
61.4	2.597	134.7	12.76	236.0	23.85
65.6	3.070	145.3	14.18	246.3	24.74
70.0	3.607	155.8	15.55	256.1	25.47
75.0	4.224	165.6	16.79	266.4	26.20
80.6	4.964	175.9	17.97	276.3	27.02
85.5	5.636	185.7	19.07	286.0	27.60
94.7	6.949	196.3	20.22	295.0	28.05
104.3	8.343	206.0	21.17		

SPECIFIC HEAT OF $MgSiO_3$ (100.38 g.)

T , °K.	C_p , cal./deg. mole	T , °K.	C_p , cal./deg. mole	T , °K.	C_p , cal./deg. mole
52.7	1.508	114.9	7.171	215.9	15.29
56.5	1.757	124.5	8.090	226.2	15.95
61.1	2.108	135.3	9.109	236.3	16.51
65.7	2.493	145.2	9.982	246.1	17.10
70.6	2.921	155.4	10.86	256.4	17.62
75.5	3.366	165.5	11.71	266.3	18.10
80.6	3.842	176.7	12.56	276.3	18.71
85.4	4.294	185.8	13.23	285.9	19.08
95.1	5.242	195.9	13.99	295.3	19.45
104.7	6.163	206.2	14.67		

shown graphically in Fig. 1. The formula mass values used are 140.70 g. for magnesium orthosilicate and 100.38 g. for magnesium metasilicate

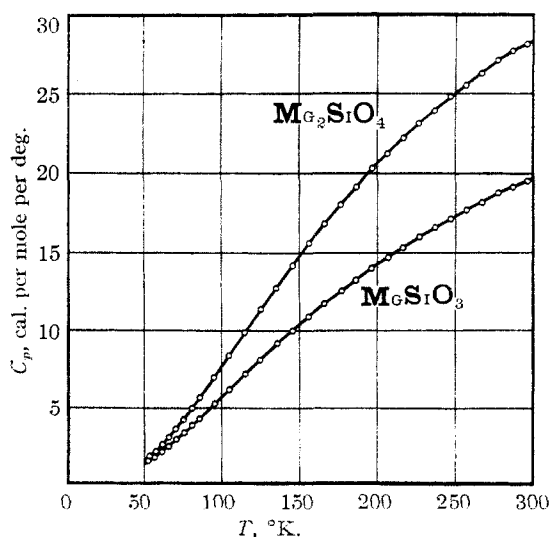


Fig. 1.—Specific heats of Mg_2SiO_4 and $MgSiO_3$.

in accordance with 1941 International Atomic Weights.

The results for magnesium orthosilicate were corrected for the previously mentioned 0.8% uncombined magnesium oxide. This correction varied from 0.10% to 0.31%, depending on the temperature. Likewise, the results for magnesium metasilicate were corrected for 5.6% magnesium orthosilicate and 2.4% uncombined silica. The combined correction varied from 1.26 to 0.05%, depending on the temperature.

Both substances exhibit normal behavior throughout the temperature range studied, and discussion of the course of their specific heat curves appears to be unnecessary.

No previous measurements have been reported for magnesium orthosilicate. A few data for magnesium metasilicate in the temperature range 21 to 36°K. were published by Wagner.⁹ His results are considerably too high in comparison with present measurements. This is not attributable to uncertainty of extrapolation as the temperature gap between the two sets of data is only 17°. Part of the discrepancy may be due to difference in physical form, but it is doubtful that this explanation alone will suffice. While one naturally would be reluctant to question the identity of Wagner's sample, it is nevertheless true that he mentions no difficulty in obtaining virtually complete reaction of the mixed oxides to form magnesium metasilicate, whereas both in the present work and in that of Jander and Wuhler the difficulties were very marked. The direction and in large part the magnitude of the discrepancy would be reconcilable with the assumption of incomplete reaction of Wagner's mixed oxides. It should be mentioned that the present data may be extrapolated nicely into the high-temperature heat content data of White,¹⁰ whose lowest measurement is at 373.16°K.

Entropies

The results of entropy calculations are given in Table II. The entropy increments between 50.12 and 298.16°K. were obtained graphically from plots of C_p against $\log T$. The extrapolated portion for magnesium orthosilicate was based on the function $\sum D(310/T) + 4E(509/T)$, which represents adequately measured specific heats up to 150°K. The extrapolation of the magnesium metasilicate results was made with the function

(9) Wagner, *Z. anorg. allgem. Chem.*, **208**, 1 (1932).

(10) White, *Am. J. Sci.*, **47**, 1 (1919).

(8) Kelley, *This Journal*, **63**, 1137 (1941).

sum $D(333/T) + 2E(494/T) + 2E(1058/T)$, which fits the data over the entire experimental range of temperature. In both instances only the Debye function is of importance in the extrapolation of entropy.

TABLE II
ENTROPIES AT 298.16°K. (CAL./DEG. MOL.)

	Mg ₂ SiO ₄	MgSiO ₃
0-50.12°K. (extrap.)	0.60	0.49
50.12-298.16°K. (graph)	22.15	15.73
$S_{298.16}$	22.7 ± 0.2	16.2 ± 0.2

Discussion

It is interesting to note that the entropy difference between these two magnesium silicates, 6.5 ± 0.4 , is virtually the same as the entropy of magnesium oxide,¹¹ 6.55 ± 0.15 . Analogous observations may be made from available data for sodium metasilicate and sodium disilicate³ and from available data for the basic carbonate and the basic sulfates of lead.¹¹ It would appear that

(11) Kelley, *Bureau of Mines Bull.*, 434, 1941, 115 pp.

if the entropy of one compound in a series of compounds formed from two oxides is known, then the others may be computed approximately merely by adding (or subtracting) the entropies of the oxides in accordance with the compositions of the compounds. This statement may be useful in estimating free energies of silicates, especially at the present time, as the available heat of formation data for silicates are generally so inaccurate that in comparison even appreciable errors in the assigned entropies cannot contribute much to the errors in free energies calculated from the relationship $\Delta F^\circ = \Delta H - T\Delta S$.

Summary

The specific heats of Mg₂SiO₄ and MgSiO₃ have been measured in the temperature range 51 to 298°K.

The corresponding entropies have been computed as $S_{298.16} = 22.7 \pm 0.2$ for Mg₂SiO₄ and $S_{298.16} = 16.2 \pm 0.2$ for MgSiO₃.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Heat Capacity and Entropy, Heats of Transition, Fusion and Vaporization and the Vapor Pressures of Cyclopentane. Evidence for a Non-planar Structure

BY J. G. ASTON, HERMAN L. FINK AND S. C. SCHUMANN

A preliminary statement has been given already of evidence¹ which indicates that the cyclopentane ring is non-planar. The evidence consisted essentially of the results of a determination of the symmetry number of cyclopentane by a comparison, at three temperatures, of its entropy, as calculated from the spectroscopic and molecular data, with that obtained using the third law of thermodynamics and thermal data down to 11.8°K. The present paper presents the data on which the comparisons were based along with calorimetric determinations of the heat of vaporization of cyclopentane at 298.16°K.

Preparation and Purification of Cyclopentane.

—A highly purified sample of cyclopentane was furnished us through the kindness of Professor M. R. Fenske of the Petroleum Refining Laboratory of this college. The cyclopentane, prepared by Mr. R. B. Richards, had been obtained by decomposition of dicyclopentadiene and subsequent

hydrogenation of the cyclopentadiene formed, followed by fractionation through an eighty-plate column. After being dried over phosphorus pentoxide and freed from the last traces of air by repeated freezings and evacuations to 10^{-6} mm. of mercury, about 43 cc. of the material was condensed in a weighed glass sample bulb and then introduced into the calorimeter in the customary manner.² The sample bulb was of the type described already.² In addition to the sealed off side-tube through which it was filled this bulb had a main tube with an inner sealed capillary, which was broken open by moving a piece of iron sealed in glass along a side arm with the aid of a solenoid after sealing to the calorimeter filling line. The pure cyclopentane was thus distilled into the calorimeter without coming into contact with anything but glass (the manometric mercury excepted).

The Heat Capacity Measurements.—The apparatus, methods, accuracy and temperature

(1) Aston, Schumann, Fink and Doty, *THIS JOURNAL*, **63**, 2029 (1941).

(2) Aston and Eidinoff, *ibid.*, **61**, 1533 (1939).