Summary

1. Silicon tetramethyl with 0.1 mole per cent. impurity has been prepared.

2. The normal boiling point of silicon tetramethyl is 299.80±0.05°K. (26.64°C.). The vapor pressures of the liquid have been measured from 208 to 293°K. and can be represented by the equation: $\log P_{\text{mm.}} = -2346.9849/T - 12.239609 \log T + 0.00662430T + 39.038565$.

3. There are two crystalline forms of silicon tetramethyl. The stable variety (β-form) melts at 174.12±0.05°K. (−99.04°C.). The (α-form), unstable with respect to the β-form at all temperatures below the melting point of the β-form, has a melting point of 171.04±0.05°K. (−102.12° C.) and cannot be preserved more than 8° below its melting point. The equilibrium for the transition between the two forms is above the melting point of either. By thermodynamic calculation from the thermal data this temperature has been found to be 199.2±1.0°K. (−74.0°C.).

4. Silicon tetramethyl forms a minimum boiling mixture with methyl iodide boiling at 26.1±0.1°C. (1 atm.) and containing 20.1 mole per cent. of methyl iodide.

5. The eutectic (quadruple) point for the system silicon tetramethyl–methyl iodide is at 171.78±0.05°K. (−101.38°C.) and presumably involves the β-form of the former.

6. The heat capacities of both forms of the solid and of the liquid silicon tetramethyl have been determined over the range 11.5 to 295.7°K.

7. The heat of fusion of the unstable α-form of silicon tetramethyl is 1426.8±0.7 cal./mole while that of the stable β-form is 1648.0±3.5 cal./mole.

8. The heat of vaporization of liquid silicon tetramethyl at the normal boiling point has been measured calorimetrically and found to be $\Delta H_{299.8} = 5785 \pm 16.0$ cal./mole.

9. The second virial coefficient for silicon tetramethyl is − 1.208 ± 0.01 liters per mole at 296.9°K. as found from a direct determination of the density.

10. The molal entropy of the ideal gas calculated from the experimental data at the normal boiling point and 1 atmosphere is 86.04 ± 0.15 cal./deg. mole. At 227°K. and 1 atm. it is 77.78 ± 0.10 cal./deg. mole.

11. To bring the values of the entropy calculated from molecular data into agreement with the values from the calorimetric data requires the assumption of three equal potential energy maxima of 1300 ± 200 cal. hindering internal rotation of the methyl groups. These are shown probably to be due to repulsive forces.

12. The entropies of the ideal gas and the liquid at 298.16°K. are 85.79 ± 0.15 and 66.27 ± 0.15 cal./deg. mole, respectively.

STATE COLLEGE, PENNA. RECEIVED MAY 19, 1941

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Thermodynamic Properties of the Crystalline Forms of Silica

BY MAX A. MOSESMAN AND KENNETH S. PITZER

Although a rather extensive array of thermodynamic data on silica has existed for some time, a complete analysis of the relative stability of quartz, tridymite, and cristobalite has never been made. Indeed it was not possible, because the heat capacity of tridymite above 300°K. has not been determined previously. Since tridymite is the stable form in the intermediate temperature range (1140 to 1743°K.), data on this substance are very important. By combining our measurements with those of others, the heat content, $H_T - H_0$, was obtained throughout the temperature range 0 to 2000°K. The integral of this function divided by T^2 gives the free energy, $(H_0 - F_T)/T$, throughout the same range. Differences in the H_0 values for the various forms are determined from the temperatures at which two modifications are in equilibrium. Thus a rather complete analysis has been made which allows, among other things, the calculation of the trend of transition temperatures with pressure.

Each of the three principal modifications of crystalline silica shows one or more reversible transitions. These are associated with only slight changes of the structure, as compared to the relatively complete rearrangement necessary to go from one principal form to another. Our results in Fig. 1 show clearly the existence of one secondary or "high-low" transition in cristobalite at about 500–540°K. and two in tridymite near 390 and 436°K. A third transition was observed in tridymite at 498°K., which has not been previously reported. Although it may have arisen from impurities, we have been unable to explain it definitely on that basis.

Because of the very small differences in thermal properties between the different principal modifications of silica, it was essential that the measurements on each form be under exactly similar conditions. Even then the probable error for some interesting quantities equals the values themselves. Thus some of the results are only qualitative in nature; nevertheless, they would seem to be of considerable value. The possibilities of this type of analysis, when more exact data become available are also indicated.

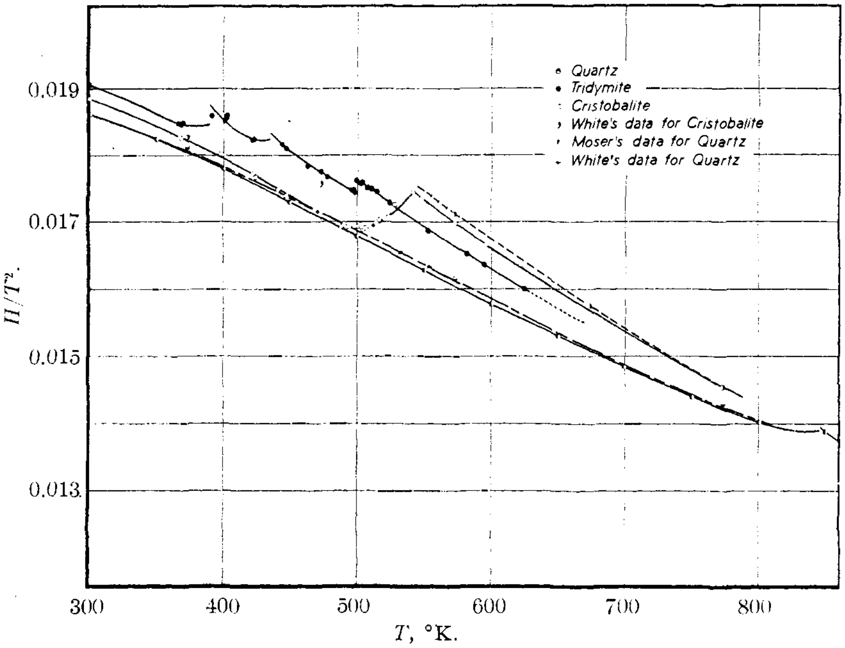

Fig. 1.—The heat content of various forms of silica.

Experimental Measurements

The heat content above that at 298°K. was determined for each modification over the range 370 to 625°K. The "method of mixtures" or transfer method was employed. This temperature range includes the various "high-low" inversions of cristobalite and tridymite whose thermal characteristics have been previously determined only approximately. Only a few measurements were made on quartz since it shows no irregularities in this range. Furthermore, Moser[1] has made heat capacity measurements throughout this range which are in reasonably good agreement with our results.

Samples.—The samples of quartz, cristobalite, and tridymite were from the same materials upon which Anderson[2] ran low temperature heat capacities. The purities of these samples, as reported by him, were 99.93, 99.99 and 99.46% for quartz, cristobalite, and tridymite, respectively. We wish to express our thanks to Dr. J. B. Austin of the Research Laboratory of the United States Steel Corporation for making available to us the same samples that he lent Dr. Anderson. We also wish to thank Dr. K. K. Kelley of the U. S. Bureau of Mines for the loan of the quartz sample.

Apparatus.—The general calorimetric set-up has been described previously.[3] Certain modifications were necessary. The calorimeter for this work consisted of a standard, narrow-necked one-pint Dewar flask, containing an electrical heater and resistance thermometer similar to that described previously. In this case these units were wound on a copper tube, bakelite varnished, and then waxed. The Dewar flask was placed within a brass can sealed water tight with adhesive tape and completely submerged in the thermostat. The lead wires and stirring shaft enter through small tubes, while a larger tube is provided for the sample. A monel screen protects the bottom of the Dewar flask from the impact of the falling sample. The amount of water in the flask was accurately reproduced for each measurement. The heat capacity of the calorimeter was determined by electrical heating as described previously.

The sample tubes contained approximately one-tenth of a mole. For temperatures up to about 285°C. the tubes were of Pyrex glass about 14 mm. in diameter and 7.5 cm. in length. For temperatures above 285°C. transparent silica tubing of similar dimensions was used. In both instances a sufficient length of tubing was taken to allow the preparation of a "blank" sample from the same piece of tubing used for the silica samples. This blank was prepared by filling the tubing with small pieces of the same tubing. Determinations on the blank were made at the same temperatures as those upon the silica samples.

The sample tubes were heated to the desired temperature by means of an electrically heated furnace mounted on the side of the water thermostat. The mounting was such that the furnace could be rotated into the proper position above the calorimeter shortly before the drop was made. The furnace consisted of a massive block of copper (9 cm. diam. by 30 cm. high), electrically heated and suitably insulated with asbestos and aluminum foil. A long hole for the sample entered from the bottom. A glass rod in a small cross hole served to support the sample tube. A calibrated copper–constantan thermocouple served as a thermometer, with one junction in a narrow, deep hole adja-

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(1) Moser, *Physik. Z.*, **37**, 737 (1936).

(2) Anderson, THIS JOURNAL, **58**, 568 (1936).

(3) Pitzer, *ibid.*, **59**, 2365 (1937).

cent to the sample. Samples were heated several hours, usually overnight, and the temperature was observed closely in the hour preceding measurement.

Special precautions were taken to limit the magnitude of errors resulting from the following sources: (1) the exact determination of the sample temperature in the furnace; (2) the loss of heat during the drop; (3) the exposure of the calorimeter to the furnace; and (4) the attainment of equilibrium within the calorimeter after the drop. On the basis of these precautions, it is estimated that the values of the heat contents obtained are accurate to 0.2%.

Heat Content Measurements.—The experimentally determined molal heat content, measured above 25°C., for cristobalite and tridymite is shown in Table I and Table II, respectively. Since quartz has been investigated rather extensively between 370 and 625°K., only two determinations on this form were made. These gave the following results: at 259.5°C., H = 3037 cal./mole; at 280.8°C., H = 3351 cal./mole.

TABLE I

THE MOLAL HEAT CONTENT ABOVE 25°C. OF CRISTOBALITE

t, °C.	H, cal./mole	t, °C.	H, cal./mole
94.0	792	230.5	2619
95.0	804	231.5	2627
124.6	1178	233.8	2673
126.0	1198	233.9	2674
148.7	1484	236.5	2725
150.5	1500	241.2	2821
167.8	1729	243.0	2865
173.6	1800	247.2	2942
195.7	2106	250.7	3013
200.5	2172	255.1	3148
217.2	2411	268.5	3449
218.9	2424	275.4	3550
221.1	2464	278.7	3581
225.2	2531	300.0	3905
228.2	2585	323.7	4261
229.1	2603	349.2	4663

TABLE II

THE MOLAL HEAT CONTENT ABOVE 25°C. OF TRIDYMITE

t, °C.	H, cal./mole	t, °C.	H, cal./mole
93.4	790	224.9	2632
95.4	815	229.0	2738
96.6	835	229.6	2751
118.1	1153	230.6	2770
128.3	1291	234.1	2812
129.1	1310	237.5	2865
129.5	1323	241.4	2926
148.2	1545	251.8	3070
149.5	1566	263.1	3184
171.0	1889	280.2	3472
173.3	1917	308.7	3900
189.5	2125	321.9	4099
199.5	2274	351.5	4550
204.4	2337		
222.6	2600		
224.6	2635		

The high temperature forms of cristobalite and tridymite are extremely similar. They may be said to differ only in the exact positions of atoms more than five times removed from one another. Hence it was not surprising to find that within our accuracy of measurement, the heat capacity of these two forms is the same. This is shown in Table III, where the values below 350°C. have been taken from a smooth curve through the experimental points. The remaining data consist of a pair of determinations at each of the temperatures. The Chromel-Alumel thermocouple used in this latter work was not precisely calibrated, but was satisfactory for determining that the tridymite and cristobalite samples were dropped from the same temperature. Our apparatus was not as well adapted to these higher temperatures, hence somewhat larger uncertainties are assigned.

TABLE III

THE DIFFERENCE IN HEAT CONTENT BETWEEN CRISTOBALITE AND TRIDYMITE ABOVE 275°C.

t, °C.	T, °K.	$(H_T - H_{298})$, cal./mole Crist.	Tridy.	$\Delta(H_T - H_{298})$, cal./mole
275	548	3539	3396	143 ± 10
300	573	3910	3761	149 ± 11
325	598	4283	4143	140 ± 12
350	623	4680	4530	150 ± 13
418	691	5710	5580	130 ± 25
484	757	6760	6610	150 ± 40
545	818	7750	7650	100 ± 50
			Weighted average	145

It was apparent from Table III that $\Delta(H_T - H_{298})$ was constant within the experimental error above 275°C., and therefore that the heat capacities of cristobalite and tridymite were equal. Furthermore, it did not seem likely that higher temperature measurements would show any observable difference. Since the heat content of cristobalite has been measured accurately by White[4] and Wietzel[5] in the very high temperature range, there seemed little purpose in extending our measurements further.

Calculations

In this section a number of thermodynamic calculations are presented.

Heat Content.—For various calculations the quantity $(H_T - H_0^0)$ is needed. This was obtained by adding to the experimental heat contents above 298°K. the value of $(H_{298}^0 - H_0^0)$.

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(4) White, *Am. J. Sci.*, [4] **47**, 44 (1919).

(5) Wietzel, *Z. anorg. Chem.*, **116**, 71 (1921).

The heat capacity data of Anderson[2] cover the range 50 to 298°K. for all three modifications. Measurements of Nernst[6] and of Gunther and Simon[7] were considered below 50°K. The region below 50°K. is quite unimportant for the heat content function, in contrast to the entropy to be mentioned below.

Graphical integration of a plot of C_p *vs.* T gave $(H^0_{298} - H^0_0)$ as 1657, 1693, and 1671 cal./mole for quartz, tridymite and cristobalite, respectively.

Free Energy and Entropy.—The equation for calculating the free energy function may be written in the forms

$$\frac{(H^0_0 - F^0_{T_1})}{T_1} = S^0_{T_1} - \frac{(H^0_{T_1} - H^0_0)}{T_1} = \int_0^{T_1} \frac{(H^0_T - H^0_0)}{T^2}\,dT \qquad (1)$$

$$S^0_{T_1} = \int_0^{T_1} C_p\,d\ln T \qquad (2)$$

It is convenient to consider the entropy at 298°K. using the low temperature heat capacities; and then to use the heat content integral above 298°K., thus

$$\frac{(H^0_0 - F^0_{T_1})}{T_1} = S^0_{298} - \frac{(H^0_{298} - H^0_0)}{298} + \int_{298}^{T_1} \frac{(H^0_T - H^0_0)}{T^2}\,dT \qquad (3)$$

Figure 1 shows the graph used for evaluating the integral in equation (3). The data of other experimenters are also shown. For quartz the results of this research lie between the values of White[4] and those obtained by integrating the data of Moser.[1] All are in reasonably good agreement. For cristobalite our values approach White's closely at the higher temperatures but disagree near the "high-low" transition. This is not a serious discrepancy, since different samples of cristobalite seldom agree exactly in this region.

A graph similar to Fig. 1, but based completely on the data of White and Wietzel, was used for higher temperatures. As stated above, tridymite was assumed to have the same heat capacity as cristobalite in this region.

The values of the entropy at 298°K. were also needed. These were based principally on the data of Anderson.[2] That author, however, chose to neglect the available experimental data below 50.1°K. in his entropy calculations. Although they are not very precise, these older measurements of Nernst[6] and Gunther and Simon[7] appear to be reasonably consistent with Anderson's value above 50°K. Hence we believe they should be used. The revised entropy values and the manner in which they were obtained for quartz and cristobalite are shown in Table IV. The graphical integrations from 50.1 to 298.1°K. were rechecked. Our values for quartz and tridymite are identical with Anderson's; for cristobalite ours is very slightly higher. The entropy of cristobalite is very appreciably changed by this recalculation. The values of $(F^0_{298.1} - H^0_0)$ for quartz and cristobalite were then calculated to −1324 and −1367 cal./mole, respectively.

TABLE IV

ENTROPY DATA

	Quartz, cal./deg.	Cristobalite, cal./deg.
Extrap. (0–28.2°K.)	0.19	0.22
Graph. (28.2–50.1°K.)	0.51	0.59
Graph. (50.1–298.1°K.)	9.30	9.38
$S^0_{298.1}$	10.00 ± 0.1	10.19 ± 0.1
Anderson[2] $S^0_{298.1}$	10.06 ± 0.1	10.34 ± 0.1

No heat capacity data are available for tridymite below 50°K. Nevertheless, the entropy at that temperature can be fixed between certain limits. First, a plot of the fractional difference between the heat capacity of cristobalite and tridymite, from Anderson's data, shows the latter to be uniformly higher. This difference shows no tendency to change sign near or below 50°K. Nor would any sudden change be expected when comparing two very similar substances. Hence we conclude that the entropy of tridymite at 50.1°K. must be at least as great as that of cristobalite, 0.81 cal. per degree. This final conclusion would not be vitiated even if the heat capacity of tridymite should drop below that of cristobalite at very low temperatures, because the principal contribution to the entropy will come from the region just below 50°K.

The second limit is obtained by comparing the entropies of tridymite and cristobalite at 1743°K., where the two forms are in equilibrium with each other. Since cristobalite is stable above 1743°K., it must have the larger entropy at this temperature. Therefore the entropy of tridymite must be less than 37.58 cal. per degree (the value for cristobalite at 1743°K.—see equation 4). This limit reduces to 0.86 cal. per degree at 50.1°K. Thus a range of only 0.05 cal. per degree is allowed. This range is small enough to be quite satisfactory, because the experimental error is

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(6) Nernst, *Ann. Physik*, [4] **36**, 395 (1911).

(7) Simon, *ibid.*, **68**, 241 (1921).

TABLE V

THERMODYNAMIC FUNCTIONS FOR QUARTZ, TRIDYMITE AND CRISTOBALITE

Units: $(H_0^0 - F_T^0)/T$ in cal./deg. mole; $H_T^0 - H_0^0$ in kcal./mole.

	Quartz		Tridymite		Cristobalite	
T, °K.	$(H_0^0 - F_T^0)/T$	$H_T^0 - H_0^0$	$(H_0^0 - F_T^0)/T$	$H_T^0 - H_0^0$	$(H_0^0 - F_T^0)/T$	$H_T^0 - H_0^0$
298.1	4.44	1.657	4.68	1.693	4.58	1.671
300	4.48	1.676	4.72	1.713	4.62	1.691
350	5.40	2.238	5.66	2.277	5.55	2.255
400	6.30	2.851	6.59	2.961	6.46	2.879
450	7.19	3.515	7.50	3.657	7.35	3.516
500	8.04	4.218	8.39	4.404	8.21	4.231
550	8.87	4.946	9.26	5.115	9.06	5.238
600	9.68	5.695	10.09	5.864	9.91	5.982
650	10.46	6.48	10.89	6.62	10.73	6.74
700	11.21	7.29	11.66	7.40	11.51	7.52
750	11.95	8.12	12.40	8.20	12.26	8.32
800	12.66	8.98	13.11	9.01	12.99	9.13
850	13.36	10.15	13.81	9.82	13.69	9.94
900	14.05	10.96	14.47	10.64	14.37	10.76
950	14.70	11.77	15.12	11.46	15.02	11.58
1000	15.35	12.58	15.74	12.28	15.65	12.40
1100	16.57	14.23	16.93	13.94	16.85	14.06
1140	17.03	14.90	17.39	14.61	17.31	14.73
1200	17.71	15.91	18.05	15.63	17.98	15.75
1300	18.78	17.60	19.11	17.34	19.04	17.46
1400	19.79	19.30	20.11	19.06	20.05	19.18
1500	20.75	21.01	21.06	20.78	21.00	20.90
1600	21.67	22.76	21.96	22.54	21.91	22.66
1700	22.53	24.52	22.82	24.30	22.77	24.42
1743	22.89	25.28	23.17	25.07	23.13	25.19
1800	23.36	26.29	23.64	26.08	23.60	26.20
1900	24.16	28.08	24.43	27.87	24.39	27.99
2000	24.93	29.88	25.19	29.67	25.15	29.79

approximately this large for any of the principal calculations of interest. We somewhat arbitrarily selected 0.83 cal. per degree for this entropy of tridymite at 50.1°K., and verified that this value was consistent with a reasonable extrapolation of the heat capacity data from higher temperatures. Using the value 9.53 cal. per degree for the graphical integration from 50.1 to 298.1°K., $S_{298.1}^0$ for tridymite is 10.36 ± 0.15 cal. per degree. Anderson's previous value was 10.50 ± 0.2 e. u.

For convenience in thermodynamic calculations at various temperatures from 298.1 to 2000°K., the functions $(H_0^0 - F_T^0)/T$ and $(H_T^0 - H_0^0)$ are presented in Table V. The data are given to the second or third decimal place because of their relative accuracy for certain calculations. Their absolute accuracy is nearer ±0.1 cal./degree. The entropy at any temperature may be obtained readily from the functions tabulated.

$$S_T^0 = (H_0^0 - F_T^0)/T + (H_T^0 - H_0^0)/T \qquad (4)$$

Energy Differences between the Modifications.—We are now in a position to compute the differences in heat content between the three crystalline modifications of silica at the absolute zero. This is done by noting that at the transition temperature the free energy change between the two forms in equilibrium is zero.

The temperature of equilibrium between quartz and tridymite was recently determined to be 867 ± 3° by Kracek[8] in excellent agreement with Fenner's[9] older value of 870 ± 10°. For the tridymite-cristobalite point, Fenner[9] gives 1470 ± 10°.

These calculations are shown in Table VI. Also included there are values for the standard heat and free energy differences at 298.1°K. These were also obtained by use of the functions in Table V. The uncertainties shown in Table VI are estimated probable errors. It is impossible to give useful upper limits of error.

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[8] Kracek, THIS JOURNAL, **61**, 2863 (1939).

[9] Fenner, *Am. J. Sci.*, **36**, 331 (1913).

TABLE VI

SOME THERMODYNAMIC CONSTANTS FOR THE CRYSTALLINE FORMS OF SILICA. UNITS: CAL. PER MOLE

Reaction	ΔH_0^0	ΔH_{298}^0	ΔF_{298}^0
Quartz = Tridymite	410 ± 50	446	338
Tridymite = Cristobalite	-70 ± 50	-92	-40
Quartz = Cristobalite	340 ± 50	354	298

The Heat of Fusion of Silica.—A great many discordant values can be quoted for the heat of fusion of silica. By use of the data in Table VI all values are reduced to heats of fusion of cristobalite and are listed in Table VII. This is of course the only form which reaches true equilibrium with the liquid. The melting point is given as 1713 ± 5° by Greig,[10] in good agreement with the value of Ferguson and Merwin,[11] 1710 ± 10°

TABLE VII

THE HEAT OF FUSION OF CRISTOBALITE. UNITS: CAL. PER MOLE

Method	Observer	ΔH_{1983}
Heats of solution in HF aq.		
Vitreous–Cristobalite	Wietzel[5]	1,000
	Troitzsch[12]	1,700
Vitreous–Tridymite	Troitzsch[12]	3,900
Vitreous–Quartz	Wietzel[5]	2,300
	Mulert[13]	2,200
	Ray[14]	5,700
	Troitzsch[12]	3,000
Heats of solution in Na_2CO_3		
Vitreous–Quartz	Chernobaev[15]	900
Freezing Point Lowering		
Alkali oxides	Kracek[16]	1,835

The results listed in Table VII were obtained by two general methods. The first involves the heats of solution in HF or Na_2CO_3 of both crystalline form and vitreous silica, together with the relative heat capacities up to the melting point. In all cases Wietzel's[5] values are used for the heat capacities. It is seen easily that the various values by this method are quite discordant, even when the work of a given observer is considered by itself. This was not so apparent previously, because only in this research have relatively reliable energy differences between the crystalline forms become available. Whether the difficulties arose through different impurities in the various samples, or from other sources, it is not possible to say definitely.

The other general method is that of the freezing point lowering with various solutes. Kracek[16] considered the solutions of the various alkali and alkaline earth oxides, and concluded that only rubidium and cesium oxides formed reasonably ideal solutions with silica. His value for the heat of fusion was obtained from these two.

Since this last value given by Kracek represents a fair mean of all the data, and because it is not contradicted by any other good freezing point data, we shall take it as the most probable value. It is shown in Table VIII along with the transition data. Some other characteristics of the fusion process are listed there also.

The Heats of Transition.—The changes in heat content, given in Table VIII, for the "high-low" transition in cristobalite and those in tridymite, were read off a plot of the heat content data of Tables I and II. Smooth curves were drawn through the points above and below each transition, and extrapolated to the transition temperature. The curves from above and below were so nearly parallel that no ambiguity arose. The uncertainties given should cover any calorimetric errors; however, no estimate can be made of the effect of impurities or methods of preparation on these quantities.

No value is given for the quartz transition because it occurs over such a wide temperature range.

The heats of the transitions between the principal forms were calculated from the data in Tables V and VI. The errors listed in Table VIII are estimated probable errors. The only maximum limits of error that can be given are that these quantities must be positive and that the sum of the quartz–tridymite and the tridymite–cristobalite transition heats must not be larger than about 500 cal. This last statement of course presumes that no gross errors exist in the higher temperature heat capacity and equilibrium data.

The entropies of transition were calculated direactly from the heats and temperatures. The volume changes are taken from the data summarized by Sosman.[17] The pressure-temperature trends of the transitions were calculated from the thermodynamic formula $dP/dT = \Delta S/\Delta V$. The significance of this calculation for a gradual transition, such as that in cristobalite, is subject to some question. For the transitions between the

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(10) Greig, *Am. J. Sci.*, **13**, 1 (1927).

(11) Ferguson and Merwin, *ibid.*, **46**, 417 (1918).

(12) Troitzsch, Dissertation, Leipzig, 1936.

(13) Mulert, *Z. anorg. allgem. Chem.*, **75**, 198 (1912).

(14) Ray, *Proc. Roy. Soc.* (London), **A101**, 509 (1922).

(15) Chernobaev, *Rev. Metall.*, **107**, 729 (1905).

(16) Kracek, THIS JOURNAL, **52**, 1436 (1930).

(17) Sosman, "The Properties of Silica," Chemical Catalog Co., New York, N. Y., 1927, p. 361.

TABLE VIII

THERMODYNAMIC CONSTANTS FOR TRANSITIONS AND MELTING; BASIS, ONE MOLE

Substances	t, °C.	T, °K.	ΔH, cal.	ΔS, cal./deg.	ΔV, cc.	dP/dT, atm./deg.	General nature
α to β cristobalite	225 to 262	498 to 535	310 ± 20	0.60	0.8	31	Gradual, rapid
α to β_1 tridymite	~117	~390	70 ± 10	.18	~.05	~150	Rapid
β_1 to β_2 tridymite	~163	~436	40 ± 10	.09	~.05	~75	Rapid
β_2 to β_3 (?) tridymite	225	498	45 ± 10	.09	?	?	Sharp, rapid
Quartz to tridymite	867	1140	120 ± 50	.11	3.75	1.2	Very slow
Tridymite to cristobalite	1470	1743	50 ± 50	.03	~−0.1	~−12	Very slow
Quartz to cristobalite (metastable below 650 atm.)	1027	1300	200 ± 50	.15	3.65	1.7	"Very slow"
Cristobalite to liquid	1713	1986	1835	.92	~0.05	~760	
Quartz to liquid (metastable below 1170 atm.)	1610	1883	2035	1.08	3.7	12.1	

principal forms, however, these data should be of some interest. On the basis of the extensive data of Bridgman[18] one may presume that these pressure–temperature lines for the transitions will run very nearly straight up to a few thousand atmospheres. On this basis Fig. 2 was constructed. The trend of the melting point with pressure is also shown on Fig. 2.

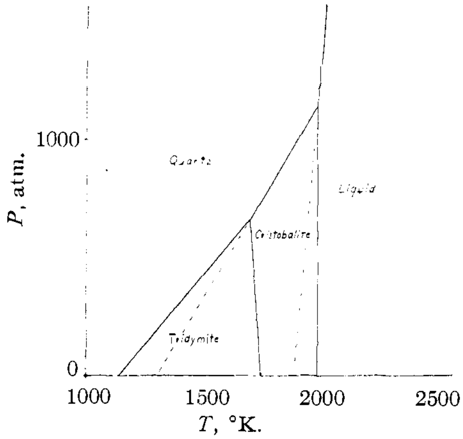

Fig. 2.—The effect of pressure on the stability of various forms of silica.

The accuracy of the lines in Fig. 2 is certainly not very great. Nevertheless, it is sufficient to show that quartz will be the stable form in equilibrium with the liquid at moderately high pressures. The triple point liquid–cristobalite–quartz is calculated to be at 1988 ± 10°K. and 1160 ± 500 atm. The triple point cristobalite–tridymite–quartz is not well defined by our results at all. The slope of the tridymite–cristobalite line may have almost any value although it appears to be definitely negative.

Relative Stabilities of the Various Modifications; Standard Free Energies of Formation.—Although the data in Tables V and VI provide a complete description of the relative stability of the various crystalline forms of silica, it seems desirable to show this graphically with a single function and to include the vitreous form. The vapor pressure is probably the most real measure, but it cannot be computed with any accuracy. A quantitative function which serves almost as well is the standard free energy difference between the forms. The change in free energy for the formation of each other form from cristobalite was calculated from Tables V, VI and VIII and is plotted in Fig. 3. These curves may be regarded as showing relative vapor pressures. Sharp breaks are shown at the "high-low" inversions even though these should be somewhat gradual in some cases. The transition in cristobalite at 530°K. increases the slope of the other curves, while transitions in the other substances decrease the slopes of their respective curves. Stable transitions between forms are indicated by arrows from below; metastable transitions by arrows from above.

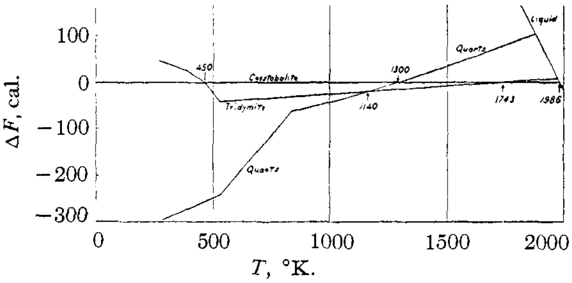

Fig. 3.—The free energy of formation of various forms of silica from cristobalite.

The cristobalite–tridymite transition at 450°K. has never been suggested before as far as we know. At this low temperature, there seems little hope of direct verification of this result.

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[18] Bridgman, "The Physics of High Pressure," The Macmillan Co., New York, N. Y., 1931, p. 232.

The curve for liquid or vitreous silica in the high temperature region is also shown in Fig. 3. The metastable melting points of quartz and tridymite are found to be 1883 and 1976°K., respectively. Ferguson and Merwin[11] reported 1943 ± 10°K. for the latter. Our value is higher than theirs by somewhat more than their indicated experimental error. It is interesting to note that, neglecting heat capacity differences, the heat of fusion of cristobalite and the heat of transition from tridymite are related to the temperature of transition and the melting points of each form by the equation

$$\Delta H_{\text{trans.}} = \Delta H_{\text{fusion}} \left(\frac{T_{\text{M. P. Cr.}} - T_{\text{M. P. Tr.}}}{T_{\text{M. P. Tr.}} - T_{\text{trans. Tr.}-\text{Cr.}}} \right) \left(\frac{T_{\text{trans. Tr.}-\text{Cr.}}}{T_{\text{M. P. Cr.}}} \right)$$

If the difference between the melting points of tridymite and cristobalite could be determined with precision, this equation would probably give the best value for the heat of this transition. The use of Ferguson and Merwin's melting points, however, leads to a heat of transition which seems much too large, and which could be true only if the heat capacities of tridymite and cristobalite differ considerably from one another in the high temperature range. Therefore we believe the values given above are the more probable ones.

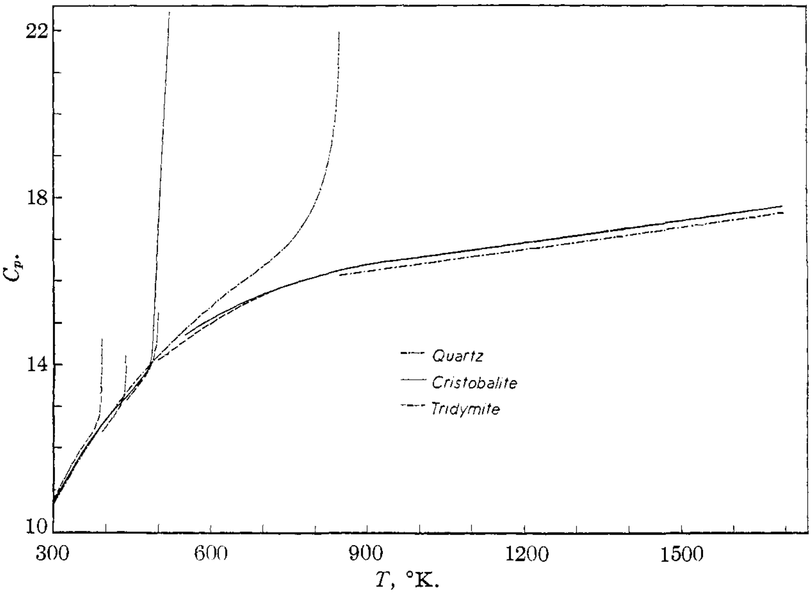

Fig. 4.—The heat capacity of crystalline silica.

The melting point of quartz has never been observed accurately because of the tendency of cristobalite to crystallize in this region.

Heat Capacity.—Although all of the essential calculations have been completed, it is of some interest to give approximate values for the differential heat capacity of the various forms above 300°K. These results are shown in Fig. 4. At the lower temperatures the data for quartz are those of Moser. Otherwise the slope of the heat content–temperature curve was taken graphically. These latter results were checked by plotting and integrating, whereupon the original heat contents were reproduced within reasonable error. Our data show definitely that the heat capacity of cristobalite rises markedly below the transition at 535°K. Figure 4 shows similar behavior for tridymite below the first and second transitions, although our data do not definitely establish this result. The third transition of tridymite appears perfectly sharp with no change in heat capacity.

Before concluding this section on thermodynamic calculations, the writers wish to mention the work of Dr. K. K. Kelley[19] in this field. Although we eventually based almost all of our calculations on original data, his summaries were a great help in the preliminary stages of the work.

Discussion

Although a number of the results obtained, particularly those of Fig. 2, should be of interest in geological phenomena, such discussions will be omitted at least from the present paper. However, a few comments on the high-low transitions will be included, particularly from the point of view of the structural changes involved. The crystal structure researches of Nieuwenkamp[20] have explained beautifully the nature of the cristobalite transition. In the high temperature form the oxygen atoms can be considered to be revolving in small circular orbits whose centers lie on the direct line between silicon atoms. The radius of these orbits is 0.4 Å. so that the Si–O–Si bond angle is about 150°. In the low temperature form this rotation has stopped and the entire structure

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[19] Kelley, Bur. of Mines, Bull. 350, 371, 383, 393 and 394 (1932–1936).

[20] Nieuwenkamp, *Z. Krist.*, **92**, 82 (1935); **96**, 454 (1937).

collapsed into a less symmetrical form, which nevertheless retains the 150° bond angle. Transitions associated with the beginning of rotation usually show the gradual character observed in cristobalite.

Because of the great similarity between the high temperature forms of tridymite and cristobalite, it may be assumed safely that the transitions are similar in nature even though no detailed crystal structure analysis is available. It is interesting to note that, while in cristobalite all oxygen atoms are identically situated, in tridymite there are two groups whose surroundings are not absolutely the same. Possibly one group of oxygen atoms starts to revolve in the small orbits at the 117° transition, and the other group begins at 163°.

Apparently, when the oxygen atoms stop revolving, tridymite is not able to collapse to as stable a structure as cristobalite. This is indicated by the fact that, while tridymite is lower in energy content in the high temperature form, cristobalite is lower in energy at low temperatures. The fact that the oxygen atoms begin to revolve at lower temperatures in tridymite than in cristobalite is also in agreement with this idea.

The general picture just outlined leaves no place for the new transition in tridymite at 225°. This would be only a minor consideration, but the fact that none of the earlier workers observed this effect casts considerable doubt on its existence as a true property of tridymite. On the other hand, our calorimetric observations show it to be a very definitely real effect in our sample. We then sought to explain this transition on the basis of probable or even relatively improbable impurities, but failed. Hence we can only suggest that this inversion may be really a property of tridymite, but that it should be verified further before being accepted definitely as such.

Finally, a few remarks concerning possible improvements in the thermal data on silica may not be amiss. The unsatisfactory state of the calorimetric data on the heat of fusion has already been mentioned; also the possible use of a precise value of the difference between the cristobalite and tridymite melting points. Other than this, little would be added to the general picture by isolated measurements. To give really precise values for many of the quantities of interest, it would be necessary to know more accurately the differences in heat capacity of the three forms over the whole temperature range. Because these differences are frequently less than one per cent., this would be a difficult problem.

Summary

An extensive analysis is given of the thermodynamic properties of the various crystalline forms of silica. The new experimental data presented are the heat content above 25° of quartz, tridymite, and cristobalite. For each of the latter modifications about thirty experimental values are given in the range 90–350°. In the range 400–550° the difference between the heat content of tridymite and cristobalite was measured.

These results were combined with data from the literature to yield values of the following quantities for quartz, tridymite, and cristobalite: the heat content function $(H^0_T - H^0_0)$, the free energy function $(H^0_0 - F^0_T)/T$, the entropy, and the heat capacity for each form over the range 298–2000°K. The heat content differences between the three forms are given for 0° and 298°K. All heat of fusion data are reduced to a comparable basis and a best value selected. The temperatures, the heat, entropy, and volume changes, and the pressure–temperature coefficients are given for the various transitions between the principal modifications, and for transitions within one principal modification. The standard free energy differences between the modifications are calculated and plotted chiefly to show the stability relationships between the various forms.

Among the results obtained are the minimum pressure under which liquid silica freezes directly to quartz and the metastable melting points of quartz and tridymite at 1 atm. pressure. It was found that cristobalite is more stable than tridymite, not only above 1743°K., but also below 450°K.

The low temperature transitions of cristobalite and tridymite are discussed in terms of the beginning of a revolution of oxygen atoms in small circular orbits.

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