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

The Heat Capacities of Quartz, Cristobalite and Tridymite at Low Temperatures[1]

BY C. TRAVIS ANDERSON[2]

The desirability of obtaining specific heat and entropy data on the three forms of silica was pointed out to this Laboratory some time ago by Dr. J. B. Austin of the Research Department of the United States Steel Corporation, who collaborated by preparing and furnishing the samples of cristobalite and tridymite.

The methods, apparatus and accuracy have been described previously.[3]

Materials

The sample of quartz was obtained from Utah, through the Bureau of Mines Intermountain Experiment Station at Salt Lake. It was crushed and screened to pass a 28-mesh and remain on a 35-mesh screen. It was washed with hydrochloric and nitric acids, with water and dried. An analysis of the quartz, by decomposition with hydrofluoric acid gave the impurities as 0.07%, indicating that the quartz had a purity of at least 99.93% SiO_2. Its density was found to be 2.6378 at 22.2°. The calorimeter was filled with 164.9 g.

The starting material for the samples of cristobalite and tridymite was a very pure sample of vein quartz from Lake Toxaway, North Carolina. The sample was ground to pass through a 60-mesh screen, repeatedly washed with hydrochloric acid and then dried. Analysis of the silica with hydrofluoric acid showed 99.99% SiO_2. The residue, when tested with sodium thiocyanate, showed a red coloration indicating the presence of iron.

According to Dr. Austin, the sample of cristobalite was prepared by placing the quartz in a platinum cone set into a magnesia block into which a Pt–Pt + Rh thermocouple had been inserted. The cone was covered with platinum foil resting on two porcelain rods. The assembly was placed inside a graphite tube, heated by an induction furnace for ninety minutes at 1600°. After cooling in the furnace it was removed. An analysis showed 99.99% SiO_2, the residue again showing iron. Petrographic examination showed complete conversion to cristobalite, there being only one or two grains of quartz discovered in several samples. It had a density of 2.3201 at 23.3°. A 98.9-g. sample was studied.

The preparation of the tridymite was more difficult as it was necessary to use a flux. The purified quartz was mixed with carefully purified sodium tungstate in the proportion of 6 SiO_2 to 1 Na_2WO_4, by weight. The mixture was ground in an agate mortar to pass a 200-mesh screen, placed in the platinum cone, described above, and heated in a high temperature furnace, provided with silicon carbide heating elements, for twenty-four hours at 1250°. On removing from the furnace it was washed with hot water, dried, ground again to pass 200-mesh, washed with boiling water, hydrochloric acid, again with boiling water to remove the hydrochloric acid, washed with ammonium hydroxide, again with boiling water and finally dried. Analysis of the sample showed 98.7% SiO_2, the remainder Na_2WO_4. Petrographic examination showed complete conversion to tridymite. Unfortunately the microscope showed that the remaining flux was carried in the center of the grains of tridymite. Accordingly the sample was reground in an agate mortar to pass through a 400-mesh screen. After screening it was ground for ten minutes longer. It was then subjected to the same series of washings as before. Analysis of this sample showed 99.46% SiO_2. 107.8 g. of this sample was used in the specific heat measurements. Its density was 2.2777 at 23.7°. The average deviation from the mean of the densities in six determinations each of all three materials was ±0.0001.

The Specific Heats

Specific heat measurements have been made on quartz up to about 90°K. by Nernst[4] and Wietzel[5] has reported measurements on quartz by Günther, and on cristobalite by Günther and Simon up to about 100°K.

No previous low temperature measurements have been made on tridymite. The results ob-

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[3] Anderson, THIS JOURNAL, **52**, 2296, 2712 (1930); **54**, 107 (1932); **55**, 3621 (1933).

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

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

tained in this Laboratory on the heat capacities of quartz, cristobalite and tridymite, expressed in gram calories (15°) per gram formula weight are shown in Fig. 1. The curve has been drawn through the data on quartz. The experimental values for the heat capacities are given in Tables I, II and III. The calculations were made on the basis of Si = 28.06 and O = 16.

TABLE I

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF QUARTZ

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
53.4	1.549	98.9	3.680	197.7	7.755
56.4	1.684	107.9	4.026	216.1	8.358
60.3	1.854	122.1	4.762	234.7	8.974
65.4	2.106	134.1	5.321	252.1	9.498
72.8	2.502	143.8	5.740	272.0	10.18
80.0	2.861	156.2	6.231	285.0	10.31
87.5	3.168	169.1	6.736	296.1	10.58
		184.8	7.330		

TABLE II

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF CRISTOBALITE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
54.8	1.739	99.8	3.796	193.7	7.623
57.8	1.862	112.0	4.353	210.9	8.221
61.3	1.999	120.4	4.076	229.5	8.850
69.9	2.424	136.8	5.448	241.4	9.181
73.7	2.623	150.7	6.054	257.1	9.596
77.7	2.832	164.0	6.552	272.2	9.971
83.9	3.074	178.2	7.098	297.2	10.54
88.0	3.229			297.3	10.62

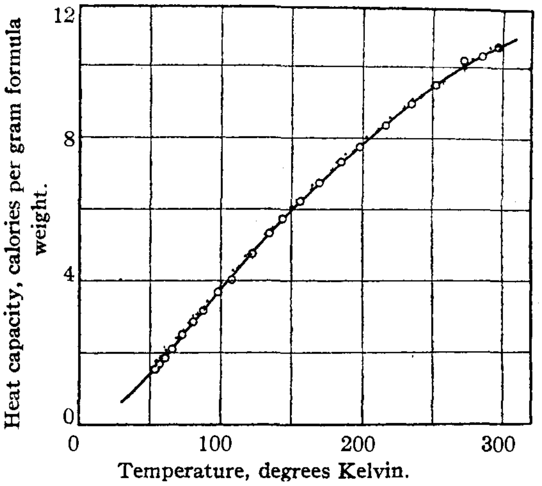
TABLE III

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF TRIDYMITE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
54.2	1.760	108.8	4.291	219.5	8.581
57.6	1.903	117.7	4.680	235.4	9.094
61.5	2.051	131.4	5.304	249.1	9.478
68.6	2.403	149.3	6.065	271.8	10.08
80.5	3.017	164.3	6.679	278.1	10.23
90.8	3.428	181.6	7.322	290.8	10.55
100.4	3.940	187.9	7.553	294.9	10.62
		202.6	8.038		

Calculation of Entropies

If an attempt is made to fit the results of these three forms of silica in the usual manner, by plotting the heat capacity against log T, a very poor fit is obtained with the Debye curve. The Debye curve will coincide with the experimental points on quartz from about 60 to 90°K. with the lower experimental points rising above the curve. If, however, three times the specific heat is plotted against the logarithm of the temperature and the experimental curve extended, excellent fits may be made on all three of these forms of SiO_2 with combinations of Debye and Einstein functions. These extended curves coincided with Debye functions having the following parameters (Θ): quartz, 166; cristobalite, 142; and tridymite, 141.



○, quartz; +, cristobalite; ●, tridymite.

Fig. 1.—The heat capacities of quartz, cristobalite and tridymite in calories per gram formula weight.

The following combinations of Debye and Einstein functions were found to fit the specific heat curves per formula weight of these forms of SiO_2.

$$C_{\text{quartz}} = \frac{1}{3} D\left(\frac{166}{T}\right) + \frac{2}{3} E\left(\frac{337}{T}\right) + E\left(\frac{658}{T}\right) + E\left(\frac{1518}{T}\right)$$

$$C_{\text{cristobalite}} = \frac{1}{3} D\left(\frac{142}{T}\right) + \frac{2}{3} E\left(\frac{339}{T}\right) + E\left(\frac{652}{T}\right) + E\left(\frac{1623}{T}\right)$$

$$C_{\text{tridymite}} = \frac{1}{3} D\left(\frac{141}{T}\right) + \frac{2}{3} E\left(\frac{331}{T}\right) + E\left(\frac{643}{T}\right) + E\left(\frac{1554}{T}\right)$$

The results of the entropy calculations, from the experimental heat capacity data, and the function sums are given in Table IV.

TABLE IV

ENTROPY DATA

	Quartz	Cristobalite	Tridymite
Extrap. (0–50.1)°K.	0.76	0.99	0.97
Graph. (50.1–298.1)	9.30	9.35	9.53
$S^\circ_{298.1}$ graphical	10.06 ± 0.1	10.34 ± 0.1	10.50 ± 0.2
$S^\circ_{298.1}$ calcd. from functions	10.06	10.32	10.52

Related Thermal Data

The heat of formation of SiO_2(cryst.) has been measured by Roth and Müller[6] who gave −204,000 cal ±2100 cal. as $\Delta H_{298.1}$ for the reaction Si(cryst.) + $O_2 \longrightarrow SiO_2$(cryst.). Using their value, the entropy of Si obtained from measurements from this Laboratory,[7] the entropy of oxygen from spectrographic data,[8] and the entropy of quartz, the free energy of formation is calculated to be −192,000 cal.

Summary

The heat capacities of quartz, cristobalite and tridymite from about 50 to 300°K. have been determined and their corresponding entropies calculated as 10.06, 10.34 and 10.50, respectively.

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[6] Roth and Müller, *Z. physik. Chem.*, **A144**, 256 (1929).

[7] Anderson, THIS JOURNAL, **52**, 2301 (1930).

[8] Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

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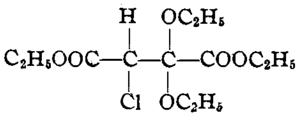
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF BRYN MAWR COLLEGE AND THE UNIVERSITY OF ILLINOIS]

Products of the Reaction of Ethyl Dichloroacetate with Alcoholic Sodium Ethoxide

BY ARTHUR C. COPE

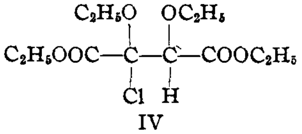
The reaction of ethyl dichloroacetate with alcoholic sodium ethoxide, which might be expected to be a practical method for the synthesis of ethyl diethoxy acetate, actually gives poor yields of the expected ester plus larger quantities of a higher boiling ester. Wohl and Lange[1] originally made this observation, and expressed the opinion that the high boiling material was formed by an acetoacetic ester condensation of the ethyl diethoxyacetate first produced, giving the keto ester $(C_2H_5O)_2CHCOC(OC_2H_5)_2COOC_2H_5$ (I). Their analysis, however, approached the formula $C_{12}H_{21}O_6Cl$, indicating that one of the ethoxyl groups was largely replaced by chlorine. Since recent work[2] has shown that monocarboxylic esters with only one alpha hydrogen atom do not undergo the acetoacetic ester condensation, structure I cannot be correct. Evidence which establishes the correct structure of the high boiling condensation product is presented in this paper.

The high boiling product decomposes slightly on distillation in vacuum. Zeisel determinations made on samples from successive distillations showed that each fractionation diminished the ethoxyl content. Material distilled rapidly at low pressures (0.1 to 2 mm.) gave analyses corresponding to the presence of four ethoxyl groups and the formula $C_{12}H_{21}O_6Cl$. The nature of the decomposition occurring during distillation was determined by heating samples at atmospheric pressure and identifying the products. The decomposition proceeded readily at 170 to 220° with the evolution of carbon monoxide, ethylene and a small amount of carbon dioxide. A low boiling distillate which was largely ethyl alcohol plus smaller quantities of ethyl formate and ethyl carbonate collected, and a high boiling liquid residue remained. Fractionation separated this residue into two portions. The lower boiling fraction was identified as ethyl chloromalonate by saponification to the acid and decarboxylation to chloroacetic acid. The higher boiling fraction was proved to be ethyl α-chloro-β-ethoxymaleate, $C_2H_5OOCCCl{=}C(OC_2H_5)COOC_2H_5$ (II), by saponification to the acid, which on heating gave α-chloro-β-ethoxymaleic anhydride. The isolation of this substituted maleic ester in 58% yield indicates the nature of the carbon chain in the original ester, which must therefore be a chlorodiethoxysuccinic ester, III or IV. Structure IV is improbable, since α-chloro ethers are usually too reactive to permit their isolation from alcoholic solution. III would be expected to lose alcohol on heating giving II; simultaneous loss of ethylene and carbon monoxide would explain the formation of the ethyl chloromalonate. Conclusive evidence that III is the correct structure for the high boiling condensation product was ob-



$$\begin{array}{ccccc} & \text{H} & & \text{OC}_2\text{H}_5 & \\ & | & & | & \\ \text{C}_2\text{H}_5\text{OOC}- & \text{C} & - & \text{C} & -\text{COOC}_2\text{H}_5 \\ & | & & | & \\ & \text{Cl} & & \text{OC}_2\text{H}_5 & \end{array}$$

III



$$\begin{array}{ccccc} & \text{C}_2\text{H}_5\text{O} & & \text{OC}_2\text{H}_5 & \\ & | & & | & \\ \text{C}_2\text{H}_5\text{OOC}- & \text{C} & - & \text{C} & -\text{COOC}_2\text{H}_5 \\ & | & & | & \\ & \text{Cl} & & \text{H} & \end{array}$$

IV

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[1] Wohl and Lange, *Ber.*, **41**, 3612 (1908).

[2] McElvain, THIS JOURNAL, **51**, 3124 (1929).