

Thermodynamics of polymorphic transformations in silica. Thermal properties from 5 to 1070°K and pressure-temperature stability fields for coesite and stishovite*

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Abstract—Cryogenic heat-capacity measurements on coesite and stishovite provide thermodynamic properties from 5 to 350°K. The heat capacities (C_p), entropies (S°), and Gibbs energy functions [$-(G^\circ - H^\circ_0)/T$] are 10.85, 9.65, 4.124, and 10.27, 6.64, 2.362 at 298.15°K for coesite and stishovite, respectively, in cal/(mole °K). Enthalpies of transition for phase changes were determined by solution calorimetry in a lead-cadmium-borate solvent at 697°C. The following values (in kcal/mole) were obtained upon adjustment to 298.15°K: quartz \rightarrow coesite ($1.2_1 \pm 0.15$), quartz \rightarrow cristobalite ($0.6_4 \pm 0.15$), quartz \rightarrow silica glass ($2.1_5 \pm 0.15$), and cristobalite \rightarrow silica glass ($1.5_1 \pm 0.15$). The enthalpy of coesite to 1070°K and the enthalpy of transformation for stishovite-silica glass were provided by means of a novel technique, "transposed-temperature" drop calorimetry. These data permit the delineation of P - T field phase boundaries for the stable equilibria coesite-quartz and coesite-stishovite, as well as for the metastable quartz-stishovite boundary, which are in reasonable agreement with the results of recent equilibrium and formation studies.

INTRODUCTION

SILICA exists in several well-known crystalline modifications at ambient atmospheric pressure (cf. SOSMAN, 1965). As a consequence of silica's role as one of the principal rock-forming oxides, there has been longstanding interest in its chemical thermodynamics on the part of chemists and geologists alike. Nevertheless, in spite of a series of independent thermochemical studies carried out over a period of more than 50 years, there is as yet no general agreement about the enthalpies of transformation between the various low-pressure polymorphs of silica or even about its enthalpy of fusion.

During recent years the interest in the chemical thermodynamics of the silica system has been further aroused by the discovery of two new high-pressure polymorphs. First COES (1953) synthesized at pressures near 35 kb and at temperatures between 500 and 800°C a new phase which is about 10 per cent more dense than quartz. Later STISHOV and POPOVA (1961) discovered and described an even more dense modification which is formed at pressures of the order of 100 kb and temperatures of 1000-1600°C.

Since the first preparations of these phases in the laboratory, both have been

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discovered in nature and isolated from sandstone in Meteor Crater, Arizona. It is apparent that they have been formed under the transient high-temperature, high-pressure conditions generated upon meteoritic impact. These polymorphs have been given the mineralogical names *coesite* and *stishovite*. The crystal structure of coesite determined by ZOLTAI and BUEGER (1959) does not differ greatly from the structures of the low-pressure modifications of silica. The structure of stishovite determined by STISHOV and BELOV (1962) and independently by PREISINGER (1962) is that of rutile (TiO_2) and is unique among known silicon compounds in having sixfold coordination of silicon with respect to oxygen.

Since the first synthesis of coesite and stishovite, there has been great interest in determining their temperature-pressure stability fields. For example, once the quartz-coesite curve has been firmly established, the quartz-coesite transformation may eventually offer a convenient basis for calibration of solid high-pressure-high-temperature apparatus. The interest in stishovite, on the other hand, is in part motivated by the prediction that this mineral plays an important role in the chemistry of the mantle. Thus the large volume contraction associated with reactions such as:



provides a strong driving force at depths of the order of 400–1000 km below the surface of the earth (RINGWOOD, 1962). Consequently, a number of equilibrium investigations have been carried out, especially in the case of quartz-coesite which is readily accessible to modern high-pressure, high-temperature methods. There is, however, considerable disagreement among the various investigators, particularly between results obtained by piston-anvil and by piston-cylinder equipment. Hence an independent approach to this problem, such as is provided by calorimetry, is of major significance.

The conventional approach to the thermochemistry of silica and silicate minerals is based on the use of aqueous hydrogen fluoride solution calorimetry, which furnishes the essential values on enthalpies of transformation and of formation. Unfortunately, this method fails for coesite and stishovite due to the inertness of these materials to attack by aqueous hydrogen fluoride, even near 100°C.

In a recent communication, HOLM and KLEPPA (1966) have demonstrated that oxide melt solution calorimetry provides an attractive alternative for minerals which do not dissolve in aqueous hydrogen fluoride near room temperature. Using a lead-cadmium-borate solvent at 700°C, they were able to measure the enthalpies of solution of the three polymorphs of Al_2SiO_5 and of $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (mullite), which had all defied repeated attacks by the aqueous hydrogen fluoride method. Combination of the new enthalpy data with available information on the entropies and volumes of transformation enabled a calculation of the P - T diagram for this system valid over wide ranges of temperature and pressure.

In the present communication, we report the results of a related thermochemical study of coesite and stishovite, based on the combined use of adiabatic cryogenic calorimetry, high-temperature solution calorimetry, and drop calorimetry. Precise determination of the heat capacity at low temperatures permitted the evaluation of the thermal properties of these substances to about 350°K. The mineral coesite,

while thermodynamically unstable, can be maintained indefinitely at 700°C under atmospheric pressure. Its enthalpy of solution was measured at this temperature in a lead-cadmium-borate melt and compared with that obtained for pure, crystalline quartz.

The mineral stishovite will, according to SKINNER and FAHEY (1963), transform spontaneously to a glass ("stishovite glass") at elevated temperatures and atmospheric pressure. The rate of transformation depends very strongly on temperature; at 800°C the reaction is complete in 15–20 min, while at 100°C the reaction proceeds extremely slowly. The glass formed after 15–20 min at 800°C has an index of refraction of 1.461 which is very close to that of pure silica glass, 1.459.

The behavior of stishovite at elevated temperatures prevents us from studying this mineral by the oxide melt solution method. Instead we have determined the enthalpy of transformation of this mineral to stishovite glass by means of "transposed-temperature" drop calorimetry. In this approach a small sample of stishovite is first dropped from room temperature into the calorimeter at 800°C and the total enthalpy increment determined. In a second experiment the enthalpy of the transformed glass at the same temperature is measured. From the difference between these two calorimetric results we obtain the enthalpy of transformation of stishovite to glass at room temperature.

In the course of the present investigation we have also determined the enthalpies of solution of quartz, cristobalite, silica glass, and stishovite glass in our oxide melt at 700°C. This permits us to compare some of our new results with data obtained by earlier workers who used the aqueous hydrogen fluoride method. Such a combined approach allows an evaluation of the chemical thermodynamics of the coesite and stishovite phases as well as the delineation of the P - T stability fields.

EXPERIMENTAL DETAILS AND RESULTS OF CRYOGENIC THERMAL MEASUREMENTS

These measurements were made at the University of Michigan.

1. *Materials*

(a) *Natural coesite*. A 100.131 g (*in vacuo*) calorimetric sample of coesite was kindly loaned by Dr. Werner Stöber and Professor Dr. Karl Thomas for these measurements. This mineral had been isolated from Coconino sandstone taken from the crater near Winslow, Arizona, where coesite was produced as a result of impact metamorphism (CHAO, 1967), i.e. by meteorite-cratering impact with the earth. The sandstone had been ground in a rubber-clad ball mill, treated with hydrochloric acid, and (since the coesite occurred as crystallites less than 1 μ in dia.) enriched by a sedimentation process. This intermediate product was subsequently treated with aqueous hydrofluoric acid to selectively remove quartz and amorphous silica (BOHN and STÖBER, 1963, 1966). X-ray diffraction indicated the absence of quartz (sensitivity limit, 0.5%). Less than 1% stishovite and less than 0.2% rutile were detected in the calorimetric sample. Electron-microscopic study of the particle size distribution by STÖBER (1965) indicated that only 4.5 per cent of the particles were larger than 0.5 μ and that the specific surface was 1.37 m²/g from a statistical survey and 7.8 m²/g on the basis of physical adsorption (BET adsorption of argon at 70°K). This represents material of smaller particle size than desirable for a thermodynamic standard state and is of particular concern because of the possible adsorption of water and/or hydroxyl (i.e. silanol) groups. The sample was held for 14 hr at 200°C in high vacuum to minimize the amount of adsorbed water.

(b) *Natural stishovite*. The calorimetric sample, 27.923 g (*in vacuo*), was isolated and loaned

to us by Stöber and Thomas. This material had also been isolated from the meteoritic impacted Coconino sandstone by further treatment of the coesite fraction (BOHN and STÖBER, 1963). It contained no quartz or coesite but traces (0.001 to 0.1%) of Al, Fe, and alkaline earth metals and a residue of 0.6% TiO₂ (rutile). Electron micrographs of the sample show the majority of the particles to be micro-crystallites of prismatic shape, with occasional extended acicular shapes. The mean geometric dia. is 0.074 μ ; the logarithmic standard deviation is 0.281. Hence the particle size distribution indicates only 0.1% greater than 0.5 μ and statistical and physical adsorption shows specific surfaces of 6.7 and 21 m²/g, respectively. The packing density was 1.6 g/ml. As in the case of coesite, this represents material of smaller particle size than desirable for a thermodynamic sample. Adsorbed water is an even more serious concern because of the large surface development of the crystallites and the not unreasonable requirement that the sample should not be heated beyond 100°C to avoid incipient decomposition at the surface of the sample. The sample was held at 100°C under high vacuum for 18 hr to minimize the adsorbed water content. From experiments reported in later sections of this paper, we estimate that the H₂O content may still approach 2 per cent.

2. Cryogenic technique

Measurements were made in the Mark II adiabatic calorimetric cryostat previously described (WESTRUM, 1962), provided with an electronic adiabatic shield control

Table 1. Heat capacities of coesite and stishovite*

<i>T</i>	<i>C_p</i>	<i>T</i>	<i>C_p</i>	<i>T</i>	<i>C_p</i>
Coesite					
Series I		11.05	0.0168	94.49	3.323
		12.18	0.0218	103.14	3.737
182.47	7.20	12.23	0.0218	111.71	4.147
191.38	7.54	13.47	0.0308	120.37	4.557
200.15	7.86	14.85	0.0438	129.05	4.963
208.83	8.17	16.38	0.0620	137.78	5.358
217.74	8.48	18.05	0.0859	146.82	5.755
226.67	8.78	19.87	0.1156	155.91	6.141
235.53	9.07	20.53	0.1271		
244.49	9.35	22.50	0.1662	Series VI	
253.60	9.63	24.74	0.2184		
262.76	9.89	27.21	0.2850	159.62	6.293
272.24	10.17	29.96	0.3701	168.74	6.665
282.07	10.43	33.06	0.4788	177.80	7.02
291.90	10.69	36.01	0.5903	187.08	7.38
301.54	10.94	39.11	0.714	196.40	7.72
311.00	11.17	43.16	0.884	205.75	8.05
320.29	11.40	47.95	1.093	214.84	8.31
329.42	11.61	53.23	1.329	223.32	8.73
		59.26	1.613	297.18	10.83
Series II		66.15	1.939	306.85	11.07
		73.33	2.280	316.69	11.32
91.08	3.163	80.74	2.648	326.50	11.54
98.69	3.525	88.77	3.051	336.94	11.77
				346.12	11.99
Series III		Series IV		Series VII	
5.83	0.0019	94.66	3.332		
6.60	0.0031	102.65	3.712		
7.35	0.0050			339.03	11.82
8.09	0.0071	Series V		346.16	12.00
8.98	0.0092				
9.97	0.0128	86.06	2.918		

Table 1 (continued)

Series I		Stishovite Series III		Series IV	
91.01	1.383	10.91	0.0159	99.94	1.708
96.15	1.566	12.29	0.0221	ΔH Run A †	
104.21	1.874	14.03	0.0306	206.78	6.657
112.61	2.221	16.02	0.0407	215.24	7.038
120.96	2.584	18.20	0.0525	223.70	7.41
129.79	2.987	20.58	0.0674	232.11	7.77
139.43	3.443	23.13	0.0827	240.71	8.13
149.31	3.917	25.89	0.1000	249.71	8.50
158.98	4.386	29.04	0.1222	259.12	8.87
168.21	4.836	32.61	0.1499	268.79	9.24
177.58	5.287	36.29	0.1845	278.54	9.59
187.10	5.741	40.17	0.2235	288.26	9.93
196.72	6.192	44.02	0.2677	298.04	10.27
206.45	6.642	48.02	0.3209		
216.28	7.071	53.11	0.3975		
		58.87	0.4965	Series V	
		65.08	0.6289	297.56	10.25
		72.51	0.803	307.34	10.57
		79.14	0.990	316.82	10.88
5.50	0.0016	86.04	1.219	325.54	11.15
7.74	0.0054	93.22	1.464	333.43	11.40
8.84	0.0079	100.64	1.738	340.70	11.62
9.30	0.0088			347.32	11.83

* Units: cal, °K, mole.

† Enthalpy increment Run A: $T_1 = 104.32^\circ\text{K}$, $T_2 = 202.61^\circ\text{K}$, $H_{T_2} - H_{T_1} = 406.67$ cal/mole.

consisting of three separate channels of recording circuitry with proportional, rate, and reset actions which maintained a temperature difference of less than a millidegree and thereby reduced heat loss to the surroundings to an amount negligible in comparison with other sources of error. A special, gold-plated, copper calorimeter (laboratory designation W-35, mass 60.0 g, and a volume of 102 ml) was constructed from OFHC copper rod for measurements on coesite. A similar but smaller one was constructed to optimize results on the stishovite. It was designated W-39, had a mass of 13.1 g and a volume of 22.7 ml. Both have gold-gasketed, screw-type vacuum closures for the sample space and axial thermometer-heater wells. Temperatures determined with a capsule-type, platinum-resistance thermometer (laboratory designation A-5) are considered to be in accord with the thermodynamic temperature scale within 0.03°K from 10 to 90°K and within 0.04°K from 90 to 350°K . The heat capacity of the empty calorimeter was determined separately with appropriate small corrections for the slight differences in the amounts of helium gas (*ca.* 10 cm pressure to enhance thermal contact between calorimeter and sample) and Apiezon-T grease on the loaded and on the empty calorimeter. The heat capacity of the coesite sample is about 54% of the total at 15°K and gradually increases to about 75% above 200°K ; corresponding figures for the stishovite are 40 and 60%. Buoyancy corrections were made on the basis of densities of 2.91 and 4.28 g/ml for coesite and stishovite, respectively. All determinations of mass, voltage, current, time, and temperatures

were referred to calibrations or standardizations performed by the National Bureau of Standards.

3. Results of cryogenic calorimetry

The experimental heat-capacity values for coesite and stishovite are presented in chronological sequence at the mean temperatures of determinations in Table 1. Temperature increments employed in the measurements may usually be inferred from the differences in the adjacent mean temperatures. These data have been

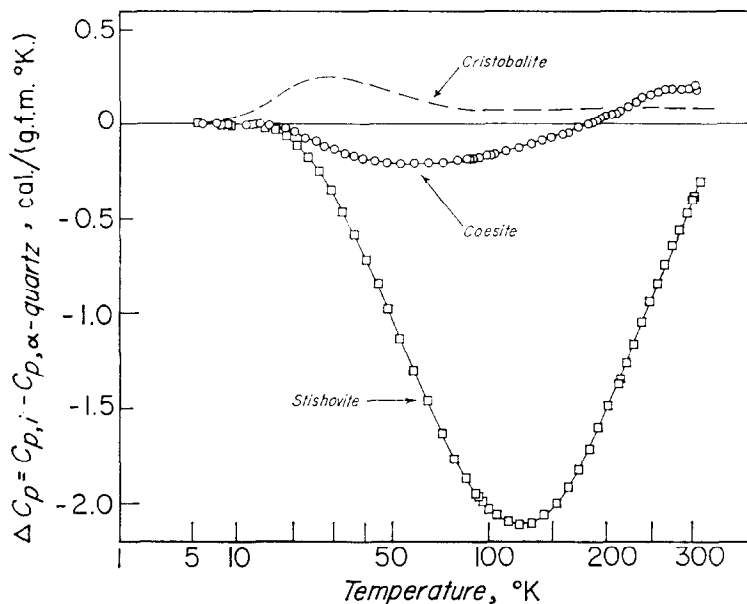


Fig. 1. Deviation of experimental heat capacities of coesite and stishovite from those of quartz(I).

adjusted for "curvature" occasioned by the finite temperature increments employed in the measurements and are considered to have a probable error decreasing from about 5% at 5°K to 1.0% at 10°K and to less than 0.2% above 20°K. They are based upon a defined thermochemical calorie equal to 4.1840 *j*, an ice point of 273.15°K, and gram formula mass (gfm) of 60.085 for SiO₂. These heat-capacity data are presented in Fig. 1 in the form of deviation curves from recent precise data for Brazilian quartz (I) (WESTRUM, 1956) and will be seen to deviate significantly over the entire temperature range. The heat-capacity values at selected temperatures in Table 2 were taken from a smooth curve obtained by a least-squares, computer-fitted polynomial function through the experimental points. The thermodynamic functions, also given at selected temperatures in this table, were obtained by integrating these data with a high-speed digital computer. The thermodynamic functions are considered to have a precision corresponding to a probable error of less than 0.1% above 100°K. However, an additional digit beyond those significant is given in Table 2 for internal consistency and to permit interpolation and differentiation. The entropies and Gibbs energies have not been adjusted for nuclear spin

and isotopic mixing contributions and are hence practical values for use in chemical thermodynamic calculations.

The presence of quartz and stishovite as impurities in the coesite sample and of rutile and water in the stishovite sample limits the accuracy which can be ascribed to these values, and uncertainties as to the exact amounts of impurities preclude adequate adjustment. We consider that these impurities will probably affect the heat capacities significantly only below 15°K and that the thermodynamic functions above 100°K are probably reliable to about $\pm 0.3\%$. However, the surface contribution to the heat capacity of the micron-sized crystallites (cf. JURA and GARLAND (1952) and BARRON *et al.* (1959) for the MgO situation) may also contribute several tenths cal/(mole °K) to the entropy. The present values may, therefore, be higher by these amounts than would be expected for ideal macroscopic crystals, the usual thermodynamic reference state.

EXPERIMENTAL DETAILS AND RESULTS OF HIGHER TEMPERATURE THERMAL MEASUREMENTS

This portion of the work was performed at the University of Chicago.

1. Materials

(a) *Quartz*. Two different samples of quartz were employed:

(1) Natural quartz(I). A sample provided by Dr. D. R. Waldbaum was powdered crystalline (-200 +325 mesh) Brazilian quartz of the type used in the oscillator plate industry. It contained less than 0.003% B and less than 0.001% of all other detected impurities (Al, Ca, Ba, Cu) according to a semiquantitative spectrographic analysis furnished by Dr. Waldbaum.

(2) Synthetic quartz(II). This material was furnished by Dr. R. C. Newton. It was a very fine crystalline powder prepared by heating silicic acid (Mallinckrodt AR) for 2.5 hr at 700°C and 15 kb.

(b) *Cristobalite*. The cristobalite was prepared from quartz(I) by heating the sample for 24 hr at 1470 \pm 20°C.

(c) *Coesite*. We had available small amounts of three different samples of this substance:

(1) Natural coesite. This had been isolated from the sandstone of Meteor Crater, Arizona, and was a gift from Dr. W. Stöber. The natural coesite is a powder of very fine particle size, which was unsuitable for precise solution calorimetry. On the other hand, our measurements of the high-temperature heat content of coesite were based on this material.

(2) Synthetic coesite(I). This material was a gift from Dr. F. R. Boyd of the Geophysical Laboratory, Washington, D. C. It had been prepared at 1300–1400°C and 40 kb from purified crystalline quartz powder.

(3) Synthetic coesite(II). This material was a gift from Dr. R. C. Newton. It was prepared by heating silicic acid (Mallinckrodt AR) for 2 hr at 700°C and 40 kb. As received, this substance contained small amounts of graphite introduced through the preparation. The graphite was removed completely upon heating the sample in air at 700°C for some hours.

(d) *Stishovite*. A small sample of this mineral isolated from the sandstone of Meteor Crater was furnished by Dr. W. Stöber.

All crystalline samples were identified by X-ray powder diffraction and showed no lines other than those of the crystal in question.

(e) *Stishovite glass*. This glass was obtained by heating the stishovite powder in the calorimeter for 1 hr at 800°C. It was expected that this material might have properties slightly different from those of the usual silica glass.

(f) *Silica glass*. This material was prepared by pulverizing clean, thin-walled fused silica tubing from the Lamp Glass Division of the General Electric Company in an agate mortar.

Table 2. Molal thermodynamic functions for coesite and stishovite*

T	C_p	S	$H^\circ - H_0^\circ$	$-(G^\circ - H_0^\circ)/T$
		Coesite		
(5)	0.0017	0.0005	0.002	0.0001
10	0.0116	0.0039	0.029	0.0010
15	0.0456	0.0140	0.158	0.0034
20	0.1162	0.0358	0.546	0.0085
25	0.2265	0.0729	1.387	0.0174
30	0.3735	0.1266	2.873	0.0309
35	0.5504	0.1971	5.171	0.0494
40	0.749	0.2834	8.413	0.0731
45	0.963	0.3839	12.69	0.1019
50	1.185	0.4968	18.06	0.1357
60	1.644	0.7532	32.19	0.2167
70	2.118	1.0419	50.98	0.3136
80	2.612	1.3568	74.62	0.4241
90	3.110	1.693	103.2	0.5462
100	3.588	2.046	136.7	0.6785
110	4.065	2.410	175.0	0.8192
120	4.538	2.784	218.0	0.9673
130	5.004	3.166	265.7	1.122
140	5.456	3.553	318.0	1.282
150	5.892	3.945	374.8	1.446
160	6.311	4.338	435.8	1.614
170	6.716	4.733	501.0	1.786
180	7.11	5.128	570.1	1.961
190	7.49	5.523	643.1	2.138
200	7.85	5.916	719.8	2.317
210	8.21	6.308	800.1	2.498
220	8.56	6.698	883.9	2.680
230	8.89	7.085	971.2	2.863
240	9.21	7.471	1062	3.047
250	9.52	7.853	1155	3.232
260	9.82	8.232	1252	3.417
270	10.10	8.608	1352	3.602
280	10.38	8.981	1454	3.787
290	10.64	9.349	1559	3.973
300	10.90	9.714	1667	4.158
273.15	10.19	8.73	1384	3.660
298.15	10.85	9.65	1647	4.124
350	12.09	11.485	2242	5.080

Table 2 (continued)

Stishovite				
(5)	0-0015	0-0005	0-002	0-0001
10	0-0122	0-0039	0-029	0-0009
15	0-0353	0-0129	0-144	0-0033
20	0-0635	0-0268	0-390	0-0073
25	0-0944	0-0443	0-784	0-0129
30	0-1295	0-0645	1-341	0-0198
35	0-1713	0-0875	2-090	0-0278
40	0-2216	0-1136	3-069	0-0369
45	0-2809	0-1430	4-321	0-0470
50	0-3497	0-1761	5-893	0-0582
60	0-5191	0-2541	10-20	0-0841
70	0-740	0-3500	16-45	0-1150
80	1-018	0-4663	25-19	0-1514
90	1-346	0-6047	36-97	0-1939
100	1-712	0-7652	52-24	0-2428
110	2-111	0-9468	71-32	0-2984
120	2-541	1-1487	94-55	0-3607
130	2-998	1-3699	122-2	0-4297
140	3-470	1-609	154-6	0-5053
150	3-951	1-865	191-7	0-5874
160	4-436	2-136	233-6	0-6756
170	4-920	2-419	280-4	0-7698
180	5-402	2-714	332-0	0-8695
190	5-878	3-019	388-4	0-9746
200	6-346	3-332	449-5	1-085
210	6-804	3-653	515-3	1-199
220	7-25	3-980	585-6	1-318
230	7-69	4-312	660-2	1-441
240	8-11	4-648	739-2	1-568
250	8-51	4-987	822-3	1-698
260	8-90	5-328	909-4	1-831
270	9-28	5-672	1000	1-967
280	9-64	6-016	1095	2-105
290	9-99	6-360	1193	2-246
300	10-33	6-705	1295	2-389
273-15	9-40	5-78	1030	2-010
298-15	10-27	6-64	1276	2-362
350	11-91	8-42	1851	3-128

* Units: cal, °K, mole.

2. Solution calorimetry

The calorimeter used throughout the present work and the experimental procedures adopted were similar to those of YOKOKAWA and KLEPPA (1964). All experiments were performed at $697 \pm 2^\circ\text{C}$. Calibration was by the gold-drop method, based on the enthalpy equation for pure gold given by KELLEY (1960). The solvent was prepared from reagent grade lead(II) oxide, cadmium(II) oxide, and boric acid in the approximate ratio $9 \text{ PbO} : 3 \text{ CdO} : 4 \text{ B}_2\text{O}_3$. In previous work (HOLM and KLEPPA, 1966) the heat of solution of quartz in a melt of this composition was found to be -3.64 kcal/mole. This value was obtained using a melt of slightly more basic character than in the present work. At the composition used, the heat

Table 3. Enthalpy of solution data at $697 \pm 2^\circ\text{C}$ for silicon dioxide phases

Material	$\Delta H_{s_{970}}$, kcal/mole					Mean*
	Expt. No. 1	No. 2	No. 3	No. 4	No. 5	
Quartz(I)	-3.0	-3.0	-3.0	-3.2		$-3.0_5 \pm 0.1$
Quartz(II)	-2.8	-2.8	-2.8			-2.8 ± 0.1
Cristobalite(I)	-3.4	-3.5	-3.6			-3.5 ± 0.1
Coesite(I)	-3.7	-3.7	-3.8	-3.8		$-3.7_5 \pm 0.1$
Coesite(II)	-3.5	-3.5	-3.5	-3.6		$-3.5_3 \pm 0.1$
Stishovite glass	-4.3	-4.4	-4.5	-4.5	-4.5	$-4.4_5 \pm 0.1_5$
Silica glass	-4.5	-4.5	-4.5			-4.5 ± 0.1

* The uncertainties quoted in the last column are the estimated limits of error. Due to the possible presence of small systematic uncertainties resulting from the drift of the apparatus zero, the estimated errors tend to be somewhat larger than indicated by the random error.

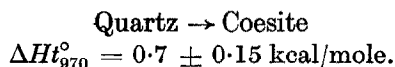
of solution of silica is quite sensitive to even small variations in the composition of the melt.

In each solution experiment a small quartz, cristobalite, coesite, or glass sample (0.7–1.0 m-mole) was dissolved in 40 g of melt (about 250 m-mole of oxides). The results obtained in the solution experiments are summarized in Table 3.

It will be seen from the data given in Table 3 that the results obtained in experiments with quartz(II) and coesite(II) are about 0.2 kcal less negative than those obtained for quartz(I) and coesite(I), respectively. Quartz(II) and coesite(II), which were prepared at 700°C , had particules ranging in size from about 1 to 10μ . On the other hand, coesite(I), which had been synthesized at much higher temperatures, consisted of a generally coarser powder. We have no definite explanation for the different values observed for the two sets of powders, although it could be due to the difference in particle size. This problem has been studied recently in the case of MgO. For this oxide NAVROTSKY and KLEPPA (1966) found a significantly more endothermic enthalpy of solution in lead-cadmium-borate for powders fired at 700°C than for those fired at high temperature (up to 1400°C). Moreover, a powder of very fine particle size has frequently been found to be disadvantageous in this calorimeter, possibly due to surface tension effects. It is also possible that the large specific surface favors chemisorption of water, even at 700°C .

It should be noted that the difference in the enthalpy of solution values for

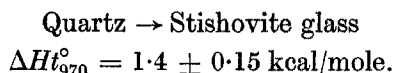
quartz(II) and coesite(II) is similar to the corresponding difference for quartz(I) — coesite(I). We accordingly adopt for the enthalpy of transformation:



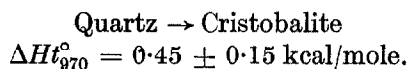
By taking into account our enthalpy data for coesite at 970°K (see below), we derive for the same process at 298°K:

$$\Delta H_{298}^{\circ} = 1.2_1 \pm 0.15 \text{ kcal/mole.}$$

The last two lines of Table 3 give data on the heat of solution of stishovite glass and of silica glass in our calorimetric solvent. It is apparent that the values do not differ significantly. This suggests that, thermodynamically, stishovite glass is virtually identical with regular silica glass. By comparison of our result for stishovite glass with that for pure crystalline quartz(I), $-3.0_5 \pm 0.1$ kcal/mole, we may write for the process



Using the enthalpies of quartz and silica glass at 970° (JANAF THERMOCHEMICAL TABLES, 1965), this enthalpy change may be referred to 298°K. For quartz \rightarrow stishovite glass, $\Delta H_{298}^{\circ} = 2.1 \pm 0.15$ kcal/mole, and for quartz \rightarrow silica glass, 2.15 ± 0.15 kcal/mole. These values are in good agreement with that of HUMMEL and SCHWIETE (1959), who report 2.27 ± 0.2 kcal/mole on the basis of aqueous hydrogen fluoride solution calorimetry and review earlier calorimetric data for this transformation. They are also in excellent agreement with that of KRACEK (1953), 2.18 kcal/mole at 74.7°C, which was not included in the review by HUMMEL and SCHWIETE.

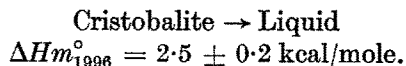


On the basis of enthalpy data given by KELLEY (1960), this is converted to:

$$\Delta H_{298}^{\circ} = 0.64 \pm 0.15 \text{ kcal/mole.}$$

The latter value is in reasonable agreement with that calculated by MOSESAN and PITZER (1941) ($\Delta H_{298}^{\circ} = 0.35$ kcal/mole) from third-law entropies and the transformation temperature and is in excellent agreement with the calorimetric value of KRACEK (1953), 0.63 kcal/mole. The calorimetric value of HUMPHREY and KING (1952) is somewhat larger ($\Delta H_{298}^{\circ} = 0.93 \pm 0.52$ kcal/mole). However, other calorimetric investigators have reported much larger enthalpies of transformation. The data are reviewed by HUMMEL and SCHWIETE (1959).

The various enthalpies of transformation referred to 298°K are summarized in Table 4 which also contains data relating to stishovite (see below). Using the available enthalpy data for cristobalite and silica glass between 970°K and the melting point of cristobalite, 1996°K, we obtain for the process:



This result may be compared with the generally accepted value for the enthalpy of melting of cristobalite, 1.84 kcal/mole, calculated by KRACEK (1930) from cryoscopic data. This value also was derived by FØRLAND (1964) on the basis of a recent re-analysis of the available cryoscopic data for silica-rich solutions. It should be noted, however, that RICHARDSON (1953) and LUMSDEN (1966) calculated the cristobalite enthalpy of melting as 3.6 kcal/mole from a different analysis of KRACEK's cryoscopic data.

Table 4. Enthalpies of reaction at 298°K for transformations involving the modifications of silica

Reaction	ΔH_{298}° , kcal/mole
Quartz \rightarrow Cristobalite	0.6 ₄ \pm 0.15
Quartz \rightarrow Coesite	1.2 ₁ \pm 0.15
Quartz \rightarrow Silica glass	2.1 ₅ \pm 0.15
Quartz \rightarrow Stishovite	11.8 \pm 0.3
Cristobalite \rightarrow Silica glass	1.5 ₁ \pm 0.15

3. Transposed-temperature drop calorimetry

The present work involves two different types of drop calorimetric experiments, both using a transposed-temperature drop method; in each case material was dropped from a known temperature near 300°K into a high-temperature calorimetric receiver. The two types of experiments were designed to determine the enthalpy of coesite at temperatures up to 800°C and the enthalpy of transformation of stishovite to glass.

(a) *Enthalpy of coesite.* About 250 mg of natural coesite was placed in a platinum capsule (5 mm dia., 25 mm length, and 0.07 mm wall thickness). After filling the capsule, the open end was squeezed completely closed with a three-jaw chuck. The filled capsule was then dried to constant weight at 700°C. In an actual drop experiment the filled capsule was dropped into the calorimeter through a fused silica tube of 8 mm i.d. The capsule was received within the entrant, silica-glass-lined well of a silver cylinder (16 mm dia. \times 100 mm length) in the calorimeter proper. Since our present concern is primarily with the difference in enthalpy between quartz and coesite, we also carried out completely analogous experiments in which the capsule was filled with about 250 mg of pure, crystalline quartz(I) powder. The results of all these experiments are recorded in Table 5. Because a small discrepancy between our data for quartz and those calculated from the values given in the JANAF TABLES obtains at the lower temperatures, our data for coesite listed in the last column of Table 5 are referred to the enthalpy of quartz given in the JANAF TABLES.

(b) *Transformation of stishovite to the glassy phase.* For each experiment about 150 mg of stishovite powder was placed in a platinum capsule of 3.5 mm dia., 25 mm length, and 0.07 mm wall thickness and sealed in the manner described for coesite. Prior to each drop experiment the capsule and contents were maintained in a vacuum at 50°C overnight and then dried for 1 hr at 105–110°C. This treatment still left some water in the sample. Attempts at drying the capsule at 150°C did not reduce the water content significantly, but resulted in some transformation of stishovite to glass. Therefore, the water-containing samples dried at 110°C were dropped into the calorimeter at 800°C, and the weight-loss due to the vaporization of water was

determined. This weight-loss represented about 2.2% of the total weight of the sample. A correction was then applied for the thermal effect associated with transforming the (assumed) liquid water in the sample at 25°C to gaseous water at 800°C. The results of these experiments are recorded in Table 6. The quantities given in this

Table 5. Enthalpy data for quartz and coesite

$T(^{\circ}\text{K})$	$H_T^{\circ} - H_{298}^{\circ}$ kcal/mole			
	Quartz		Coesite*	
	This work	JANAF	This work	This work, adjusted
298	0	0	0	0
577	3.65	3.70	3.59 ± 0.02 (3)	3.64
731	6.13	6.16	5.96 ± 0.02 (3)	5.99
968	10.39	10.40		
972		10.46	9.94 ± 0.03 (4)	9.95
1072			11.65 ± 0.02 (2)	11.65

* Quoted uncertainties are average deviations from the mean. Numbers in parentheses represent numbers of experiments performed. The adjusted values are referred to JANAF TABLES (1965) selected values for quartz.

Table 6. Results of transposed-temperature drop calorimetric experiments with stishovite, 1072°K

No.	Wt of sample (mg)	Wt loss (mg)	Dry stishovite (m/mole)	ΔH_{t_1}	ΔH_2^*	ΔH_3^{\dagger}	$\Delta H_{t_4}^{\ddagger}$	ΔH_{t_5}	ΔH_{298}° § (kcal/mole)
				(obs)	(calc)	(calc)	(obs)	(net)	
1	166.86	3.30	2.7233	22.12	13.37	3.20	31.62	-26.07	-9.57
2	153.30	2.85	2.5050	20.59	12.87	2.76	29.08	-24.12	-9.63
3	143.25	3.05	2.3343	19.64	12.44	2.96	27.10	-22.86	-9.79
4	138.01	3.27	2.2434	20.84	13.03	3.17	26.57	-21.93	-9.77
Mean									-9.69 ± 0.12

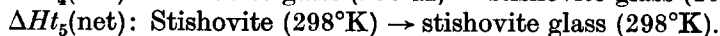
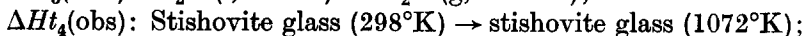
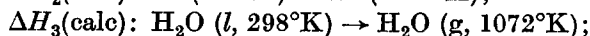
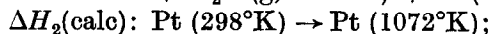
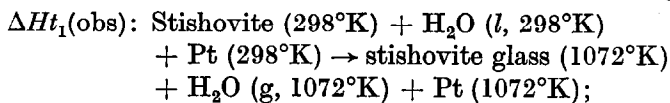
* ΔH_2 is based on KELLEY's (1960) equation for the heat content of platinum.

† ΔH_3 is based on the heat content data for H_2O given in the JANAF TABLES (1965).

‡ ΔH_{t_4} is based on the mean value of the enthalpy of stishovite glass obtained in the present work, 11.61 kcal/mole at 1072°K.

§ For the reaction stishovite \rightarrow stishovite glass.

table represent the thermal effects associated with the following processes:



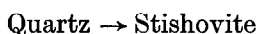
$$\Delta H_{t_1} - (\Delta H_2 + \Delta H_3 + \Delta H_{t_4}) = \Delta H_{t_5}.$$

In the last column of Table 6 the molal enthalpy increment associated with reaction 5 is given. The mean of the four separate experiments is -9.69 ± 0.12 kcal/mole.

By taking into account the enthalpy change associated with the process:



for which $\Delta H_{298}^{\circ} = 2.1$ kcal/mole, the value of ΔH_{298}° for the process



is 11.8 ± 0.3 kcal/mole.

CALCULATION OF THE PRESSURE-TEMPERATURE DIAGRAMS FOR EQUILIBRIA AMONG THE SILICA POLYMORPHS

From the low-temperature heat capacities of coesite and stishovite and the resultant third-law entropy values plus the higher-temperature enthalpies of coesite

Table 7. Enthalpies and entropies of transformation of quartz to coesite and stishovite

T (°K)	Quartz \rightarrow Coesite		Quartz \rightarrow Stishovite	
	ΔSt° * (cal/(mole °K))	ΔHt° (kcal/mole)	ΔSt° * (cal/(mole °K))	ΔHt° (kcal/mole)
0	0	1.2 ₂	0	12.1 ₇
298	-0.23	1.2 ₁	-3.24	11.7 ₉
577	-0.36	1.1 ₅	—	—
731	-0.53	1.0 ₄	—	—

* All values of ΔSt° are based on the standard entropy of quartz as obtained by WESTRUM (1967), $S_{298,15}^{\circ} = 9.88$ cal/(mole °K).

(cf. Table 4), we have calculated the entropy of this substance up to 731°K.

The presently available enthalpies and entropies of quartz to coesite and stishovite are summarized in Table 7. On the basis of these data, the Gibbs energies (ΔGt_T°) for the quartz-coesite, coesite-stishovite, and quartz-stishovite transformations may be calculated at the indicated temperatures and at 1 atm pressure:

$$\Delta Gt_T^{\circ} = \Delta Ht_T^{\circ} - T\Delta St_T^{\circ}.$$

At any other pressure the Gibbs energy may be obtained from the expression:

$$\Delta Gt_T^P = \Delta Gt_T^{\circ} + \int_{P=1}^{P=P} \Delta Vt_T dP. \quad (1)$$

For equilibrium between the two phases $\Delta Gt_T^{P_{eq}} = 0$.

In a zeroth order approximation of the equilibrium pressure we may neglect the dependence of ΔVt_T on temperature and pressure and simply set $\Delta Vt_T = \Delta Vt_{298}^{\circ}$, the volume increment at 298°K and 1 atm. Generally, since $P_{eq} \gg 1$, we have in this approximation:

$$P_{eq} = -\Delta Gt_T^{\circ} / \Delta Vt_{298}^{\circ} = -\frac{\Delta Ht_T^{\circ} - T\Delta St_T^{\circ}}{\Delta Vt_{298}^{\circ}}.$$

The values of ΔV_{298}° for the processes considered are readily calculated from the molal volumes (22.69 cm³ for quartz, 20.64 cm³ for coesite, and 14.01 cm³ for stishovite) listed by ROBIE and BETHKE (1962).

When, as in the cases under consideration, the pressures are high and the compressibility differences between the phases in equilibrium are significant, it is of importance also to take into account the dependence of $\Delta V_{T,P}$ on pressure. Among the silica polymorphs of interest, detailed compressibility information is available only for quartz, for which we may write:

$$-\frac{\Delta V}{V^{\circ}} = aP + bP^2 + cP^3. \quad (2)$$

Similar equations may be expected to apply for the other substances too. For pressures up to 100 kb the experimental values of $\Delta V/V^{\circ}$ for quartz are represented to a good approximation by the following values of the coefficients: $a = 27 \times 10^{-4}$ kb⁻¹, $b = 24 \times 10^{-6}$ kb⁻², and $c = 12 \times 10^{-8}$ kb⁻³. The values of a and b are those used by BIRCH (1966) to give an analytical expression for $\Delta V/V^{\circ}$ between 0 and 40 kb. We have also obtained the quoted value of c by considering more recent experimental results at significantly higher pressures. At 80 kb, for example, the mentioned values of a , b and c yield $\Delta V/V^{\circ} = -0.123$, in good agreement with the recent measurements of MCWHAN (1967) who found -0.125 .

Unfortunately, we do not as yet have similar detailed knowledge about the compressibility of coesite and stishovite. However, according to a very recent unpublished determination by JAMESON (1966), the value of $\Delta V/V^{\circ}$ for stishovite at 80 kb is about -0.02 , i.e. 1/6 of the value for quartz. We are not aware of any PV data for coesite. On the other hand, in view of the well-known correlation between molal volume and compressibility, we have estimated the compressibility of coesite to be about 80 per cent of that of quartz.

For convenience, if we now assume that the ratios of the coefficients b/a and c/a in equation (2) are the same for the three modifications considered, we shall be able to make a somewhat improved calculation of the equilibrium pressures for the three equilibria of interest. When improved compressibility data for coesite and stishovite become available, a more refined calculation can be carried out.

The calculated P - T diagram for coesite-quartz, covering the temperature range 0-731°K, is presented in Fig. 2. Calculations at temperatures significantly higher than these are not possible due to the α - β quartz transformation at 848°K. The lighter continuous curve in Fig. 2 represents the calculated equilibrium curve with compressibility neglected, while the bolder continuous curve includes this correction. The difference in pressure between the two curves is about 2 kb. For each of the calculated points in Fig. 2 we have indicated the magnitude of the estimated error, ± 3 kb. This is based principally on our assessment of the estimated error in the enthalpy of transformation. It does not include the small uncertainties associated with the entropy of transformation.

Figure 2 also contains the P - T curves given in six different equilibrium studies of this system carried out during the past ten years, as well as a single high-temperature, high-pressure point reported recently by BOYD *et al.* (1966). It will be seen that the results of the earlier studies generally fall into two distinct groups. The

studies by MACDONALD (1956), by GRIGGS and KENNEDY (1956), and by DACHILLE and ROY (1959), all of which were based on the piston-anvil method, give somewhat lower transformation pressures than the more recent investigations of BOYD and ENGLAND (1960), of KITAHARA and KENNEDY (1964), and of TAKAHASHI (1963), who all used the piston displacement approach. Our calculated values of the transformation pressures fall somewhat above those obtained by the other investigators. However, when the many sources of error are taken into account, we consider the agreement to be reasonably satisfactory. This is particularly true with respect to

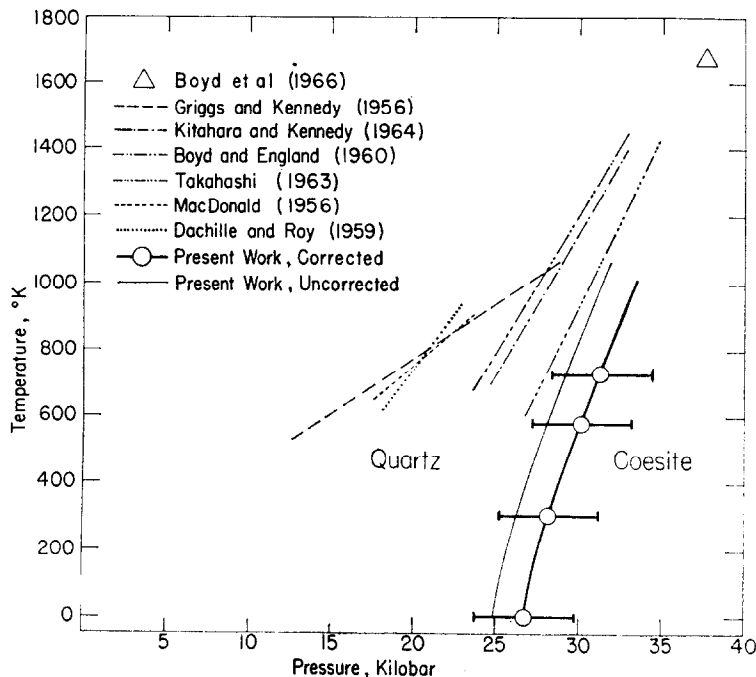


Fig. 2. P - T stability fields for the quartz-coesite equilibrium calculated from thermodynamic data reported in the present work.

the work of TAKAHASHI and the recent high-temperature, high-pressure point of BOYD *et al.* On the other hand, the discrepancy seems somewhat too large to support the use of the presently available quartz-coesite curves for P - T calibration.

Calculated P - T curves for coesite-stishovite and for the metastable equilibrium quartz-stishovite are presented in Fig. 3. The temperature range of the calculated data is restricted to 0-345°K, since we do not have enthalpies and entropies for stishovite at higher temperatures. Due to the very high pressures and the large compressibility differences, the compressibility corrections in these cases are quite large, of the order of 10 kb. We estimate that the uncertainty in the corrected values of P is of the order of ± 5 kb.

Experimental information on these transformations is both exiguous and uncertain and usually is a report only of the temperature and pressure ranges at which stishovite does or does not form. We have included in Fig. 3 the results of STISHOV and POPOVA (1961) [recalculated on the basis of the new pressure scale of KENNEDY and LAMORI

(1961)], of WENTORF (1962), and of SCLAR and co-workers (1962). The agreement between these studies and the new thermodynamic data is as good as could be expected. Figure 3 also includes an estimated equilibrium curve for coesite–stishovite, given by STISHOV (1963) on the basis of his high-temperature, high-pressure results plus an estimate of the entropy of stishovite at 298°K. His estimate

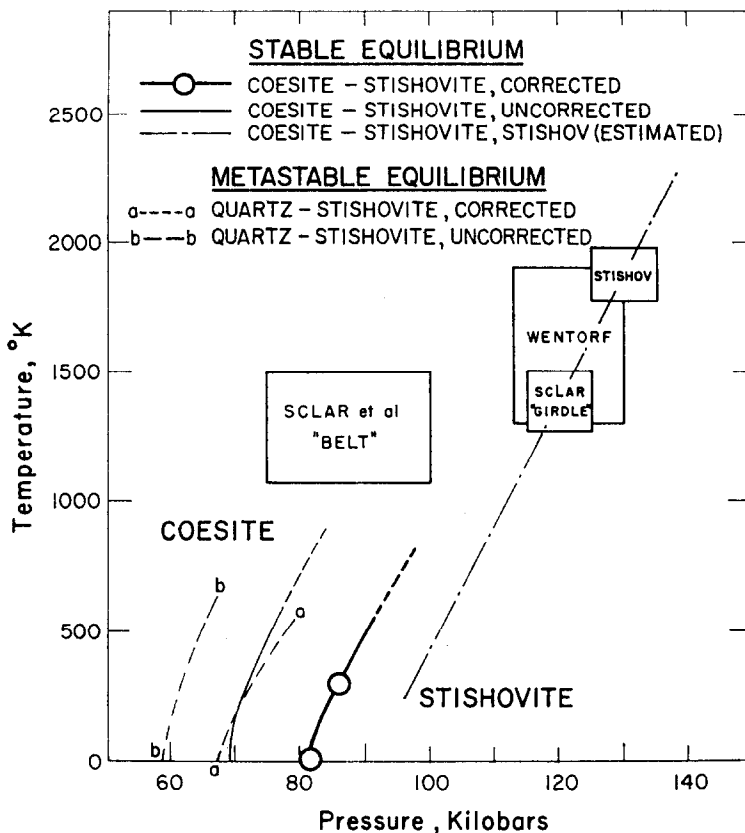


Fig. 3. P - T stability fields for the coesite–stishovite equilibrium and for the metastable equilibrium quartz–stishovite calculated from thermodynamic data reported in the present work.

of 6.28 cal/(mole °K) does not differ much from the experimental value, 6.64 cal/(mole °K). This agreement accounts for the fact that Stishov's estimated P - T curve and our own calculated curve are nearly parallel at 298°K. It should be noted, however, that our data show that at 298°K the heat capacity of stishovite is still significantly less than that of coesite [10.27 as compared to 10.85 cal/(mole °K)]. Therefore, the slope of the equilibrium curve ($dT/dP = \Delta Vt/\Delta St$) may be expected to become somewhat smaller at temperatures higher than 298°K.

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