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Heat capacity and thermodynamic properties for coesite and jadeite[1]

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Abstract

The heat capacities of synthetic coesite and jadeite have been measured between 340 and about 850 K by differential scanning calorimetry. The experimental data have been smoothed and an estimate has been made of heat capacities to 1800 K. The following equations represent our estimate of the heat capacities of coesite and jadeite between 298.15 and 1800 K:

$$C^{\circ}_{p}(\text{coesite}) = 124.53 - 0.00933T + 483479.3T^{-2} - 1422.58T^{-0.5}$$

$$C^{\circ}_{p}(\text{jadeite}) = 315.32 + 0.004107T - 2030508T^{-2} - 2319.28T^{-0.5}$$

Between 340 and 850 K, the equations fit the experimental values presented here with an average deviation of ±0.3 per cent. Tables of thermodynamic values for coesite and jadeite between 298.15 and 1800 K and based on literature values for the entropies and enthalpies of formation at 298.15 K are presented.

Introduction

Recently, questions have arisen (Kuskov et al., 1991, and earlier, Weaver et al. 1973 and 1979) regarding the quality of the coesite and jadeite samples upon which the presently accepted entropies and heat capacities are based (Kelley et al., 1953; Holm et al., 1967; Robie et al., 1978). The coesite sample was separated from Coconino sandstone taken from the crater near Winslow, Arizona. The jadeite is a natural sample from Burma. Coesite from Meteor Crater is thought to have been produced as a result of meteorite impact (Chao, 1967). The sample was largely composed of particles less than 0.5 microns. The concern with this sample arises from the fact that samples composed of very small particles may exhibit excess heat capacity, especially at low temperatures, as a consequence of high surface energy on the small grains (eg., Weaver et al., 1979, and Akaogi and Navrotsky, 1984). The jadeite sample appears to have significant substitution of impurities for both Na and Al (Kelley et al., 1953).

Recent reviews of the enthalpy of formation of coesite and jadeite have been completed. The CODATA Task Group on Geothermodynamic Data (Khodakovsky et al., 1995) has provided -907.8 ± 1.2 $\text{kJ}\cdot\text{mol}^{-1}$ as a recommended value for the enthalpy of formation of coesite at 298.15 K based on the difference in the enthalpy of solution of β-quartz and coesite in lead borate melt at about 975 K (Akaogi and Navrotsky, 1984, Zhidikova et al., 1988, and Kuskov et al., 1991). Hemingway and Haselton (1994) have evaluated the aqueous HF and molten salt calorimetric data for jadeite and recommend -3029.3 ± 3.6 $\text{kJ}\cdot\text{mol}^{-1}$ for the enthalpy of formation of jadeite at 298.15 K. These values are adopted here.

Samples

Coesite and jadeite were prepared in approximately one gram batches in a piston-cylinder apparatus using furnaces and pistons 2.54 cm in diameter. The furnace assemblies were similar to the low-temperature NaCl assemblies described by Bohlen (1984), except modifications had been made to allow for use of very large diameter capsules (0.375 inch OD). Temperature was measured using Pt_{100}-$Pt_{90}Rh_{10}$ thermocouples, and no correction was made for the effects of pressure and temperature gradients on emf.

Coesite was synthesized from water-clear natural quartz crystals from Jessieville, Arkansas, ground in alcohol to an average grain size of 20 microns. The quartz powder was loaded into a Au capsule (0.375 inches in diameter and 0.5 inches in length with a wall thickness of 0.008 inches) with approximately 1 wt% H_2O, and the capsules were sealed by arc welding. The samples were held at 32 kbar (nominal pressure) and 800°C for approximately 48 hours.

After synthesis, the samples were inspected carefully using optical and X-ray techniques. The syntheses yielded essentially 100% coesite crystals ranging in size from 30 - 150 microns with an average grain size estimated to be approximately 80 microns. Detailed optical examination indicated the presence of traces of quenched vapor (<<0.1 %). Coesite crystals synthesized in the same manner were studied using STEM techniques for a previous study (Bohlen and Boettcher, 1982). The results of this investigation revealed that the coesite was extremely well crystallized with remarkably few defects.

Jadeite was synthesized from natural quartz from Jessieville, Arkansas, and Fisher reagent grade Al_2O_3 and $Na_2SiO_3 \cdot 5H_2O$ ground together in alcohol in stoichiometric proportions appropriate for jadeite for about 15 minutes and then dried at 100°C. The starting materials were loaded into capsules identical to those used in the synthesis of coesite, and the capsules were sealed by arc welding. No H_2O was added, and no precautions were taken to keep the starting materials especially dry. The samples were held at 22 kbar (nominal pressure) and 700°C for approximately 72 hours.

As with coesite, after synthesis the samples were inspected carefully using optical and X-ray techniques. The syntheses yielded essentially 100% jadeite crystals that were surprisingly large, ranging in size from 25 - 60 microns in the small dimension to 50 - 250 microns in the large dimension. Traces (<<0.1%) of vapor quench were also observed in the optical mounts. Electron microprobe analyses of the crystals indicated that they were stoichiometric jadeite.

A single portion of each synthesized mineral was used for the dsc heat-capacity measurements. The coesite and jadeite samples were 34.432 and 37.744 mg, respectively.

Experimental results

The differential scanning calorimeter and the procedures for measuring heat capacity have been discussed elsewhere (Hemingway et al., 1984, Krupka et al., 1979). Differences between the thermal resistance of the standard corundum sample and the jadeite sample made measurements of the jadeite heat capacity difficult.

The experimental heat capacities for coesite and jadeite are listed in Tables 1 and 2, respectively, and are presented graphically in Figures 1 and 2, also respectively. The measurements were terminated at about 850 K because there was not a significant deviation of the new experimental results from those values given in Robie et al. (1978), see Figures 2 and 3. Values of the heat capacity of coesite between 1000 and 1800 K were estimated from the heat capacities of cristobalite and silica glass, see Figure 3. For jadeite, heat capacities were estimated to 1800 K from the heat-content data provided by Kelley et al. (1953). The sets of experimental and estimated heat capacities were fit to an equation of the form suggested by Haas and Fisher (1976). The equations are:

$$C^{\circ}_{p}(\text{coesite}) = 124.53 - 0.00933T + 483479.3T^{-2} - 1422.58T^{-0.5}$$

$$C^{\circ}_{p}(\text{jadeite}) = 315.32 + 0.004107T - 2030508T^{-2} - 2319.28T^{-0.5}$$

The equations fit the experimental values to ±0.3 percent.

Smoothed values of the thermodynamic properties of coesite and jadeite estimated to 1800 K are given in Tables 3 and 4, respectively. The smoothed heat capacities are also presented graphically in Figures 1 and 2.

Discussion

Hemingway (Robie et al., 1978) estimated the heat capacity of coesite as a function of temperature between 298.15 and 1800 K based on the heat-content measurements of Holm et al. (1967) (molten-salt drop calorimetry) and smoothed heat capacity data for silica glass (Robie et al., 1978). Hemingway's estimated values (open triangles) and the values for silica glass (filled diamonds) are compared to the smoothed values given in Table 3 in Figure 3. These values are all in good agreement.

Watanabe (1982) measured the heat capacity of coesite from about 350 to 660 K, but provided only an equation representing that experimental data. Akaogi and Navrotsky (1984) used Watanabe's (1982) equation in their analysis of the quartz-coesite-stishovite transformations. A comparison of values calculated from the Watanabe (1982) equation and the smoothed data given in Table 3 is presented in Figure 3. One can easily see the rapid divergence of these values from the values selected here and from values given by Richet et al. (1982) for silica glass and cristobalite. This is not surprising as Watanabe (1982) provided data for the temperature interval of 300 to 700 K. Extrapolation of his equation to 1500 K as was done by Akaogi and Navrotsky (1984) was not a valid application of the equation.

Kuskov et al. (1991) used the equation provided by Watanabe (1982) and the heat capacity and heat-content values of Holm et al. (1967) to help derive an equation for the heat capacity of coesite that they used to 1100 K. Values calculated from this equation are compared to the smoothed values given in Table 3 in Figure 4. Although the values are higher at all temperatures, the divergence at 1100 K is not as great as is the case for the equation of Watanabe (1982) extrapolated to this temperature.

Our smoothed value for the heat capacity of coesite at 298.15 K is lower than the measured value reported by Holm et al. (1967) by 1.3 percent, but is generally consistent with values for the other silica polymorphs. Coesite is denser than quartz, tridymite, and cristobalite, but has a higher heat capacity at 298.15 K. This is not consistent with the heat-capacity data for stishovite (Robie et al., 1978) which is also denser than coesite. Therefore, a new set of heat-capacity measurements for coesite at low temperature is needed to resolve this apparent discrepancy.

Heat capacities measured and reported here for jadeite are in good agreement with values calculated from the heat-content data reported by Kelley et al. (1953), see Robie et al. (1978). These values are compared in Figure 2.

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Table 1. Experimental heat capacities of synthetic coesite corrected for curvature. Values are listed for a sample mass of 60.084 g.

Temp.	Heat capacity	Temp.	Heat capacity	Temp.	Heat capacity
K	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	K	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	K	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
Series 1		Series 4		Series 7	
338.3	48.26	599.3	62.17	428.7	54.26
348.3	49.12	609.3	62.50	438.7	54.92
358.4	49.95	619.4	62.72	448.7	55.55
368.4	50.71	629.4	63.14	458.8	55.95
378.5	51.49	639.5	63.21	468.8	56.65
388.5	52.20	649.5	63.65	478.8	57.06
398.5	52.88	659.5	64.16	488.9	57.62
408.6	53.66	669.6	64.66	498.9	58.14
		678.6	65.24	508.0	58.77
Series 2					
		Series 5		Series 8	
488.9	57.88				
498.9	58.22	338.3	47.70	749.9	66.20
509.0	58.67	348.3	48.56	759.9	66.55
519.0	59.07	358.4	49.51	770.0	66.77
529.0	59.40	368.4	50.31	780.0	66.87
539.1	59.90	378.5	51.15	790.0	66.94
549.1	60.29	388.5	51.85	799.1	67.04
559.2	60.89	398.5	52.55		
569.2	60.96	408.6	53.24	Series 9	
579.2	61.19	418.6	53.92		
589.3	61.79	427.7	54.34	749.9	66.46
599.3	62.22			759.9	66.52
609.3	62.56	Series 6		770.0	66.67
619.4	62.83			780.0	66.77
629.4	63.36	669.6	64.68	790.0	66.86
639.5	63.81	679.6	64.78	799.1	67.09
649.5	64.29	689.7	64.94		
		699.7	65.23	Series 10	
Series 3		709.7	65.31		
		719.8	66.07	810.1	67.47
820.2	68.02	729.8	65.69	819.2	68.08
830.2	68.71	739.8	66.63		
840.2	68.90	748.9	66.67		

Table 2. Experimental heat capacities of synthetic jadeite corrected for curvature. Values are listed for a sample mass of 202.139 g.

Temp.	Heat capacity	Temp.	Heat capacity	Temp.	Heat capacity
K	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	K	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	K	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
Series 1		Series 3		Series 5	
338.3	172.43	599.3	217.09	669.6	224.35
348.3	175.28	609.3	218.21	679.6	224.74
358.4	177.91	619.4	219.35	689.7	225.66
368.4	180.73	629.4	220.21	699.7	226.62
378.5	183.07	639.5	221.58	709.7	227.24
388.5	185.66	649.5	222.22	719.8	228.03
398.5	187.98	659.5	223.67	729.8	228.30
408.6	190.45	669.6	223.42	739.8	228.94
418.6	192.99	678.6	224.36	748.9	230.03
428.7	195.39				
		Series 4		Series 6	
Series 2					
		519.0	207.88	770.0	231.49
428.7	194.07	529.0	208.59	779.0	232.49
438.7	195.59	539.1	209.84		
448.7	197.51	549.1	211.30	Series 7	
458.8	199.79	559.2	212.23		
468.8	200.91	569.2	213.15	790.0	233.82
478.8	202.39	579.2	214.79	799.1	233.77
488.9	204.63	589.3	216.66		
498.9	206.01	598.3	218.26	Series 8	
508.0	207.22				
				829.2	234.49

Table 3. Smoothed values of the thermodynamic properties for coesite. Molar mass is 60.084 g.

Temp.	Heat capacity	Entropy	Enthalpy function	Gibbs energy function	Formation from elements Enthalpy	Formation from elements Gibbs energy
T	C_p°	S_T°	$(H_T^\circ-H_{298}^\circ)/T$	$-(G_T^\circ-H_{298}^\circ)/T$		
K	$J \bullet K^{-1} \bullet mol^{-1}$				$kJ \bullet mol^{-1}$	
298.15	44.80	38.50	0.00	38.50	-907.8	-852.5
	±0.14	±0.62			±1.2	±1.2
300	44.97	38.78	0.28	38.50	-907.8	-852.2
400	52.69	52.84	12.47	40.37	-908.0	-833.6
500	58.18	65.22	21.09	44.12	-907.8	-815.0
600	62.20	76.20	27.63	48.57	-907.3	-796.5
700	65.22	86.02	32.79	53.23	-906.6	-778.1
800	67.53	94.89	36.99	57.89	-905.8	-759.7
900	69.31	102.95	40.49	62.46	-904.9	-741.5
1000	70.70	110.33	43.44	66.88	-904.0	-723.4
1100	71.77	117.12	45.97	71.15	-903.0	-705.4
1200	72.60	123.40	48.16	75.24	-902.1	-687.5
1300	73.23	129.24	50.07	79.17	-901.1	-669.7
1400	73.69	134.68	51.74	82.95	-900.1	-651.9
1500	74.02	139.78	53.21	86.57	-899.2	-634.2
1600	74.23	144.56	54.52	90.04	-898.4	-616.6
1700	74.33	149.07	55.68	93.38	-947.7	-598.5
1800	74.35	153.32	56.72	96.60	-946.7	-578.0
	±0.84	±1.50			±2.0	±2.0

Table 4. Smoothed values of the thermodynamic properties for jadeite. Molar mass is 202.139 g.

Temp.	Heat capacity	Entropy	Enthalpy function	Gibbs energy function	Formation from elements	
					Enthalpy	Gibbs energy
T	C_P^o	S_T^o	$(H_T^o-H_{298}^o)/T$	$-(G_T^o-H_{298}^o)/T$		
K	J•K^{-1}•mol^{-1}				kJ•mol^{-1}	
298.15	159.38	133.50	0.00	133.50	-3029.3	-2850.6
	±0.33	±0.50			±3.6	±4.0
300	160.09	134.49	0.99	133.50	-3029.3	-2849.5
400	188.31	184.80	44.63	140.17	-3033.0	-2789.1
500	205.53	228.80	75.20	153.60	-3032.7	-2728.2
600	217.46	267.38	97.97	169.41	-3031.6	-2667.4
700	226.39	301.61	115.71	185.90	-3029.8	-2606.8
800	233.43	332.31	130.00	202.31	-3027.7	-2546.5
900	239.20	360.15	141.82	218.33	-3025.5	-2486.5
1000	244.05	385.61	151.81	233.80	-3033.7	-2426.0
1100	248.23	409.07	160.39	248.68	-3031.0	-2365.3
1200	251.89	430.83	167.86	262.97	-3124.9	-2302.5
1300	255.13	451.12	174.45	276.67	-3121.0	-2234.1
1400	258.05	470.14	180.32	289.82	-3117.1	-2166.1
1500	260.69	488.03	185.59	302.44	-3113.0	-2098.2
1600	263.12	504.94	190.37	314.57	-3108.8	-2030.7
1700	265.35	520.96	194.71	326.25	-3204.9	-1962.5
1800	267.42	536.18	198.69	337.49	-3200.1	-1889.6
	±1.10	±1.60			±4.0	±4.5

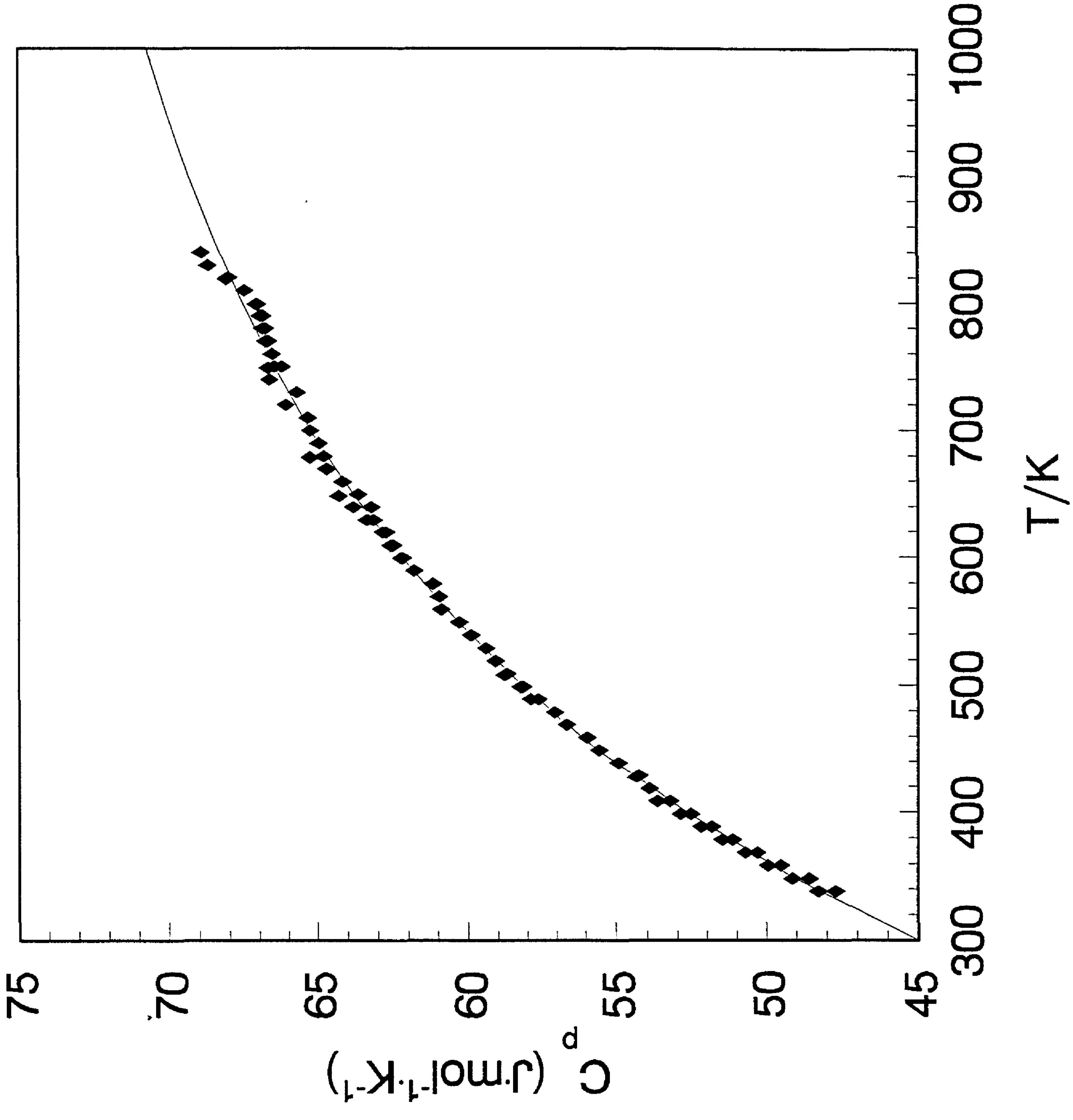

Figure 1. Heat capacities for coesite. The curve represents the smoothed values given in Table 3 for coesite and the filled diamonds represent the experimental data listed in Table 1.

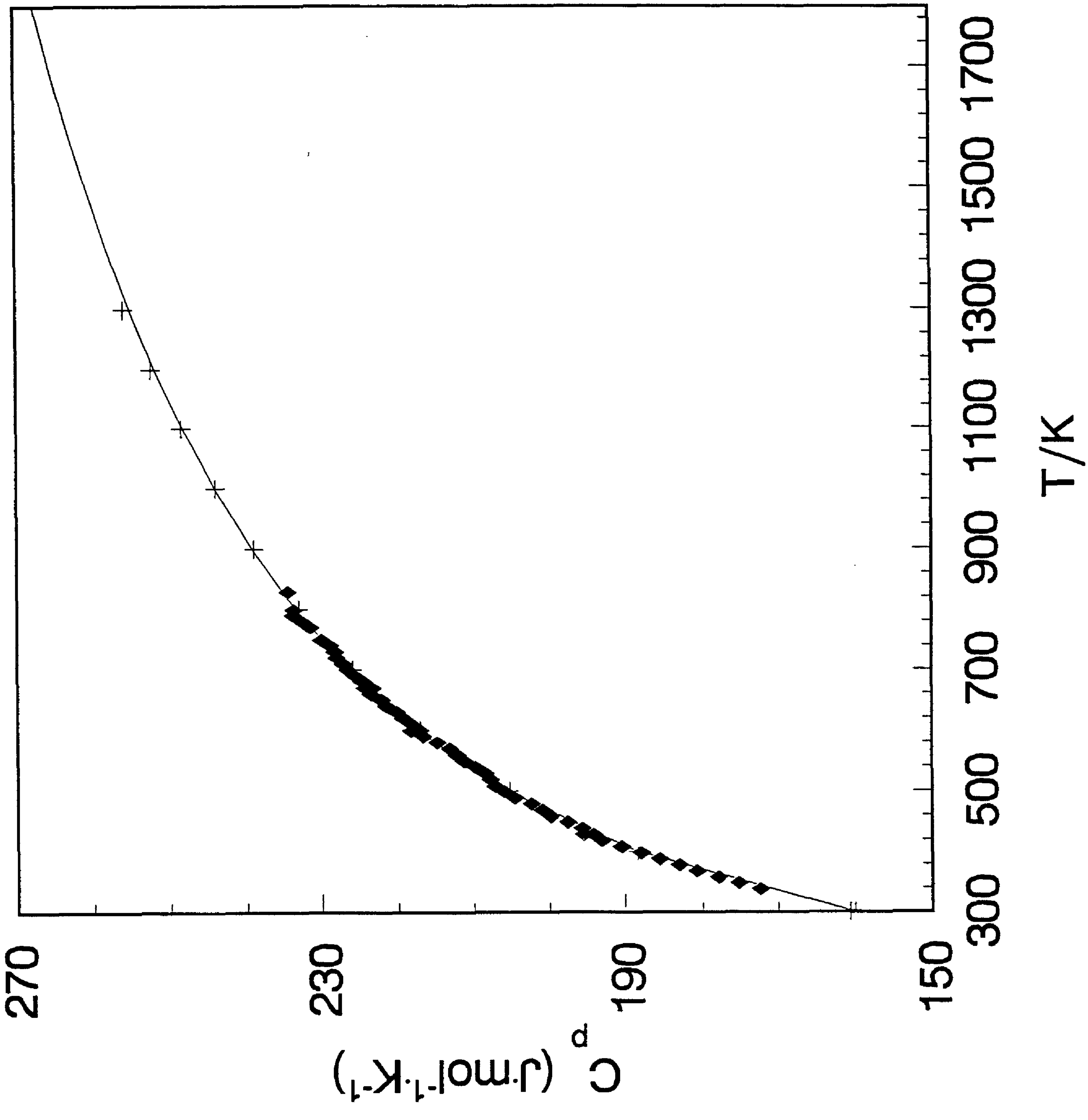

Figure 2. Heat capacities for jadeite. The curve represents the smoothed values given in Table 4 for jadeite, the plus symbol represents values given by Robie et al. (1979) and based on the data of Kelley et al. (1953), and the filled diamonds represent the data given in Table 2.

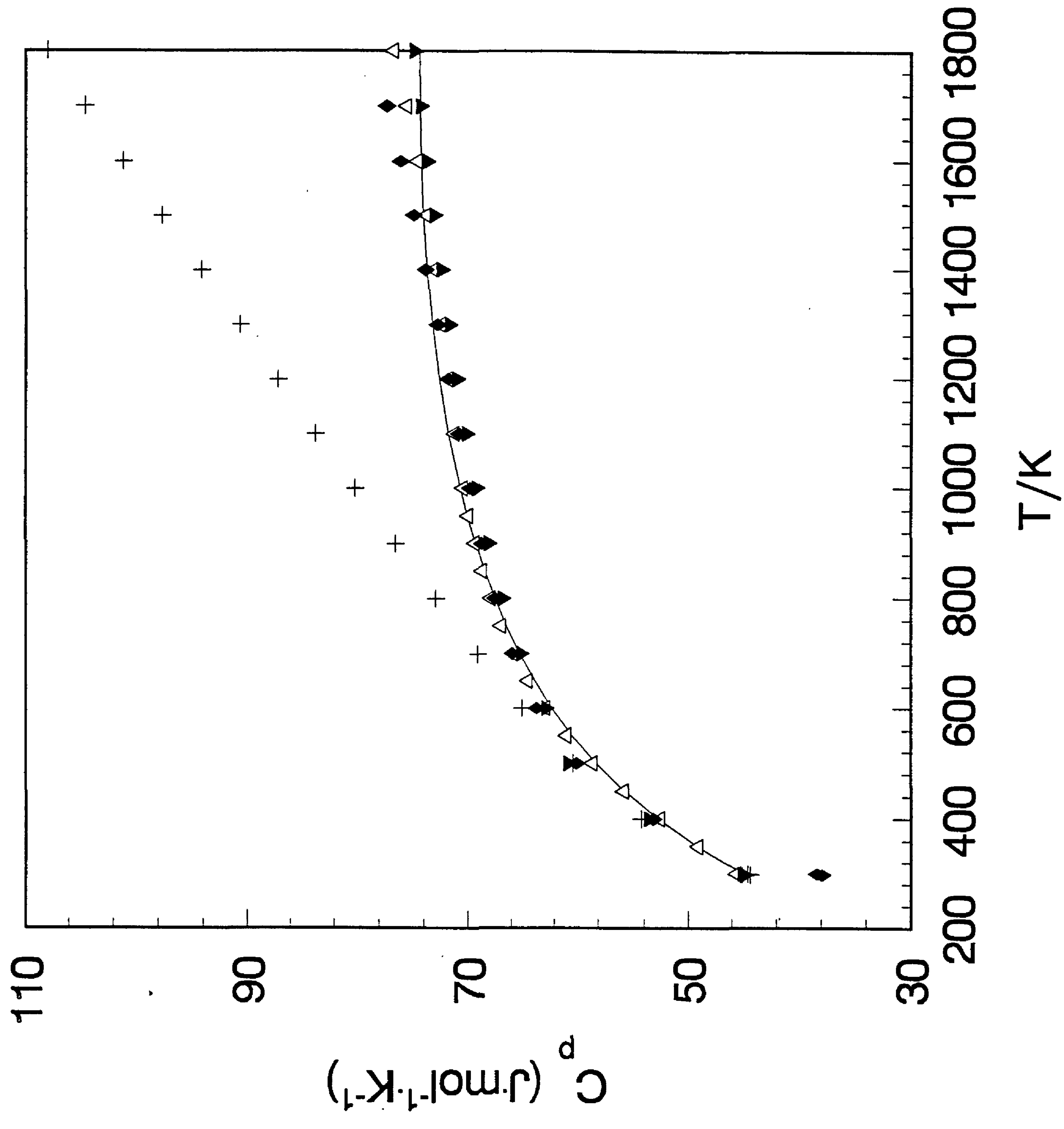

Figure 3. Heat capacities for coesite, cristobalite, and silica glass. The curve represents the smoothed values given in Table 3 for coesite, the open triangles represent the estimate given by Hemingway in Robie et al. (1979) for coesite, and the plus symbols represent values for coesite calculated from the equation used by Akaogi and Navrotsky (1984) and attributed to Watanabe (1982). The solid symbols are values given by Richet et al. (1982) for silica glass (diamond) and cristobalite (inverted triangle).

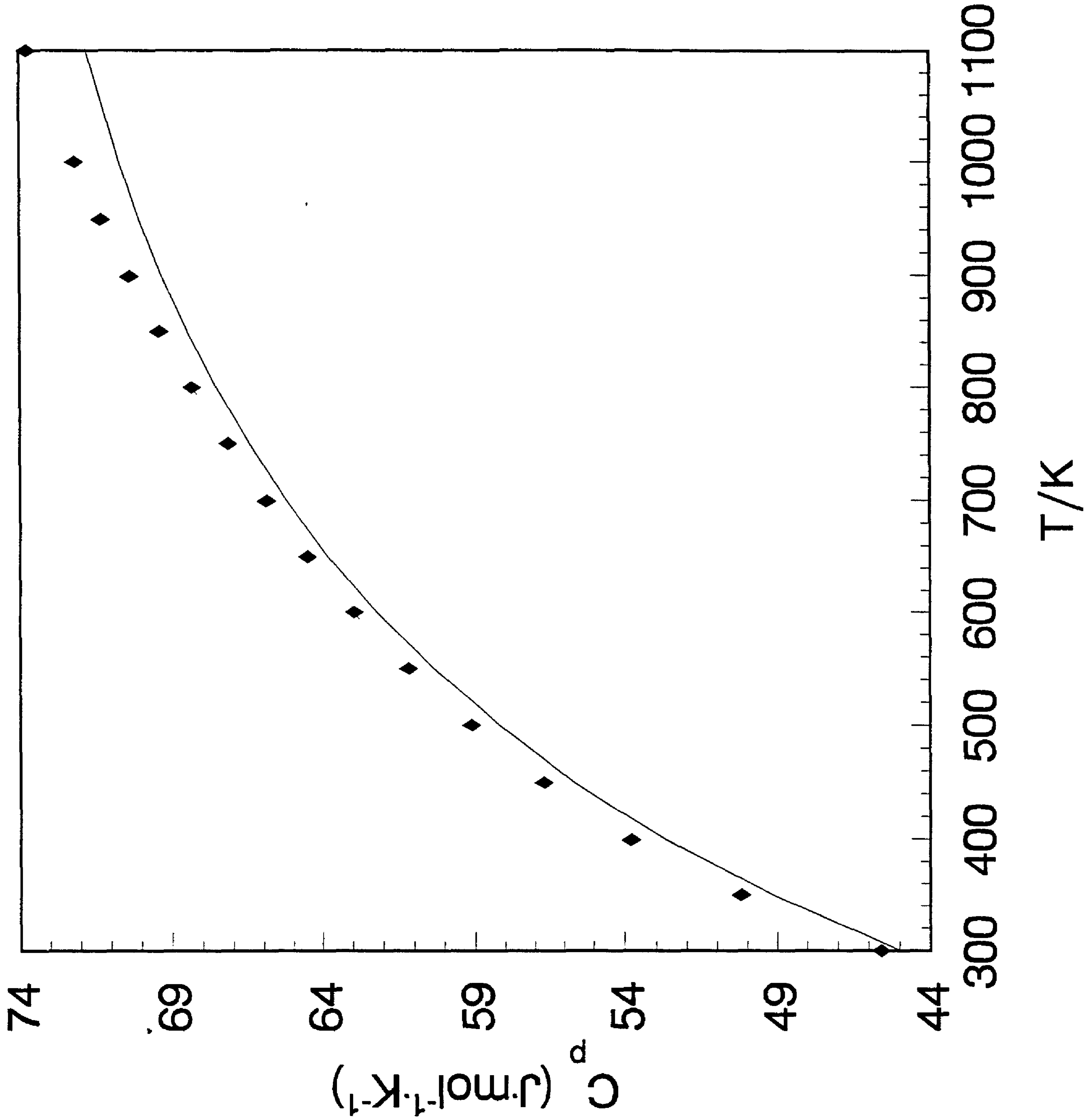

Figure 4. Heat capacities for coesite. The curve represents the smoothed values given in Table 3 for coesite. The filled diamonds represent the equation derived by Kuskov et al. (1991).