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HEAT CAPACITIES AND PHASE TRANSITIONS OF 1,1,1-TRIHYDROXYMETHYLPROPANE AND PENTAERYTHRITOL OVER THE SUPERAMBIENT TEMPERATURE RANGE

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ABSTRACT

The heat capacities of 1,1,1-trihydroxymethylpropane and pentaerythritol were measured over the superambient temperature range by means of an automated adiabatic calorimeter. The 1,1,1-trihydroxymethylpropane melted at 333.40 K with an enthalpy of fusion of 21.45 kJ mol^{-1}, while the pentaerythritol showed a solid–solid transition at 461.60 K with an enthalpy of transition of 41.38 kJ mol^{-1}.

INTRODUCTION

The solid–solid transitions in the solid solutions composed of 1,1,1-trihydroxymethylpropane and pentaerythritol have been determined in the laboratory by means of an adiabatic calorimeter [1]. To understand the nature of the solid–solid transitions in the solid solutions, the thermal data of the two pure constituents should be available. However, calorimetric data for 1,1,1-trihydroxymethylpropane are not available while there are only early calorimetric data for pentaerythritol in the literature [2]. Therefore, heat capacities and phase transition parameters for the two compounds were measured by means of an automated adiabatic calorimeter.

EXPERIMENTAL

Samples for this work were prepared according to the following methods. 1,1,1-Trihydroxymethylpropane reagent (No. 1 Reagent Manufactory, Shanghai) was recrystallized from dry ether. The purity of the calorimetric sample of the compound was found to be 99.12 mol% from analysis of its equilibrium melting curve, as described later in this paper. Pentaerythritol reagent (No. 1 Reagent Manufactory, Shanghai) was sublimed and recrystal-

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TABLE 1

Experimental molar heat capacities of 1,1,1-trihydroxymethylpropane

T (K)	$C_{p,m}$ ($J\ K^{-1}\ mol^{-1}$)	T (K)	$C_{p,m}$ ($J\ K^{-1}\ mol^{-1}$)	T (K)	$C_{p,m}$ ($J\ K^{-1}\ mol^{-1}$)
270.89	187.36	317.80	243.73	332.72	15104
276.31	189.49	321.48	277.02	332.81	24185
283.49	189.56	322.89	297.24	332.87	26362
289.46	197.04	323.26	313.33	332.93	27473
295.64	200.52	326.29	560.41	334.84	517.20
301.29	213.79	327.35	775.57	339.66	363.10
306.75	231.98	331.59	2420.9	344.62	373.67
309.94	218.06	332.27	6147.8	349.46	374.79
312.56	220.62	332.56	10418	354.22	374.00
316.69	238.80				

lized twice from distilled water. The purity of the calorimetric sample of the compound was found to be 99.96% by chemical analysis [3].

The heat capacities and phase transition parameters were measured by means of an automated adiabatic calorimeter [4]. The calorimetric cell, made of silver, contained 20.4317 g (0.15227 mol) of the 1,1,1-trihydroxymethylpropane or 75.7521 g (0.55638 mol) of the pentaerythritol. The cryostat included an adiabatic shield and a guard shield, together with heaters, three unheated radiation shields and a vacuum can. Four similar adiabatic control circuits were used to control the temperatures of the guard shield and of the three parts (the top, bottom and cylindrical middle parts) of the adiabatic shield. Each control circuit consisted of a modified DWT-702 precise temperature regulator (No. 6 Automatic Meter Plant, Shanghai) and a thermocouple pile. A 25 Ω platinum resistance thermometer used in the calorimeter was calibrated on the basis of the IPTS-68 temperature scale.

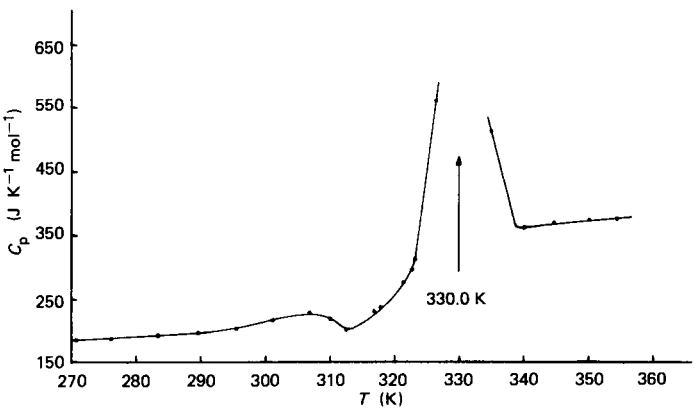

Fig. 1. Experimental molar heat capacity of 1,1,1-trihydroxymethylpropane.

TABLE 2

Experimental molar heat capacities of pentaerythritol

T (K)	$C_{p,m}$ ($J\ K^{-1}\ mol^{-1}$)	T (K)	$C_{p,m}$ ($J\ K^{-1}\ mol^{-1}$)	T (K)	$C_{p,m}$ ($J\ K^{-1}\ mol^{-1}$)
277.05	178.22	386.91	250.39	461.54	56037
287.22	183.17	392.14	257.10	461.56	58541
292.73	188.08	397.29	261.20	461.60	85494
298.98	188.40	402.91	262.55	461.63	72651
305.53	194.36	408.25	266.83	461.67	45098
309.14	196.86	413.51	271.10	461.71	33409
314.42	203.57	418.62	275.96	462.16	2403.1
319.53	204.31	425.40	280.21	462.80	1055.2
329.57	208.31	431.15	290.87	464.90	386.56
334.60	210.41	437.27	298.51	468.02	384.00
339.51	214.65	443.58	306.98	469.78	380.76
344.42	220.96	449.77	316.99	473.83	383.08
349.24	226.86	455.69	329.71	474.28	385.11
354.20	225.96	459.80	908.31	479.16	385.14
360.05	231.43	461.14	5994.0	480.18	385.70
364.68	235.70	461.34	11841	489.19	387.70
370.17	238.17	461.41	13268	494.76	390.28
375.87	241.31	461.43	21088	501.70	391.53
381.44	246.83	461.48	28185	509.99	390.91

The operation of the calorimeter was checked by means of the measurement of the heat capacities of α-Al_2O_3.

The experimental heat capacities for 1,1,1-trihydroxymethylpropane and

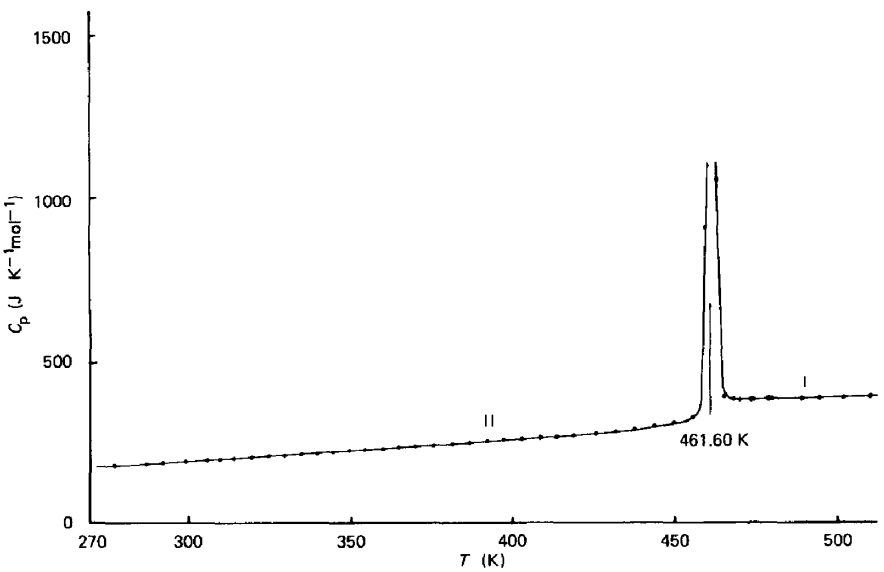

Fig. 2. Experimental molar heat capacity of pentaerythritol. I and II indicate different solids.

TABLE 3

Transition parameters of 1,1,1-trihydroxymethylpropane and pentaerythritol

T_{trs} (K)	T_1 (K)	T_2 (K)	$\Delta_{trs}H_m$ (kJ mol^{-1})	$\Delta_{trs}S_m$ (J K^{-1} mol^{-1})
1,1,1-trihydroxymethylpropane: melting transition				
333.40	325.59	337.35	21.98	
	323.12	337.39	20.82	
	318.41	334.74	21.55	
			Mean: 21.45 ± 0.42	64.3 ± 1.2
Pentaerythritol: solid–solid transition				
461.60	410.96	471.74	41.26	
	410.00	472.84	41.50	
			Mean: 41.38 ± 0.24	89.64 ± 0.52

pentaerythritol are listed in Tables 1 and 2, respectively. The deviation between the experimental points in 'non-phase-transition' regions and their smoothed values is within ±0.3%.

The experimental heat capacities for the two compounds are also shown in Figs. 1 and 2. From these figures, except for a small hump in the heat capacity curve in Fig. 1, a phase transition can be found for each compound with the temperature of the maxima occurring at 330.02 K for the 1,1,1-trihydroxymethylpropane and at 461.60 K for the pentaerythritol. From macroscopic observations, the transition is a melting transition for the former and a solid–solid transition for the latter.

Direct enthalpy measurements were made on the two compounds and the parameters of the phase transitions thus obtained are given in Table 3, in which T_1 and T_2 are the starting and finishing temperatures of the experiments, respectively, in the direct enthalpy measurements. The 'normal heat

TABLE 4

Fractional melting of 1,1,1-trihydroxymethylpropane

T (K)	F	$1/F$
330.629	0.1990	5.0250
332.077	0.2954	3.3851
332.466	0.4038	2.4763
332.683	0.5163	1.9370
332.860	0.6297	1.5881
332.920	0.8592	1.1639
332.975	0.9737	1.0270

Triple point of sample: 333.02 K
Triple point of pure compound: 333.40 K
Purity of sample: 99.12 mol%

capacities' in the transition regions were obtained by the extrapolation of the experimental heat capacities in the non-transition regions.

The purity of the calorimetric sample for 1,1,1-trihydroxymethylpropane was determined using the data listed in Table 4. The linearity of the plot of melting temperature versus reciprocal fraction melted ($1/F$) indicates 0.88 mol% impurity in this sample. Extrapolation of this plot also yields the true triple-point temperature of this sample and that of the pure substance as 333.02 and 333.40 K, respectively.

DISCUSSION

Although the two compounds under investigation are polybasic alcohols, their crystallographic natures seem to be different. Because of its low entropy of fusion (13.4 J K^{-1} mol^{-1}), the pentaerythritol crystal is considered to be a plastic crystal, while 1,1,1-trihydroxymethylpropane is a stable crystal, with a high entropy of fusion (64.34 J K^{-1} mol^{-1}) according to the result obtained in this paper. Thus, the absence of a solid–solid transition above 270 K for 1,1,1-trihydroxymethylpropane can be explained, and the small hump at 309 K in the heat capacity curve possibly derives from an impurity in the sample.

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