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LOW-TEMPERATURE HEAT CAPACITIES AND THERMODYNAMIC PROPERTIES OF 2,2-DIMETHYL-1,3-PROPANEDIOL

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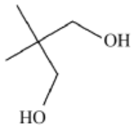
The molar heat capacities $C_{p,m}$ of 2,2-dimethyl-1,3-propanediol were measured in the temperature range from 78 to 410 K by means of a small sample automated adiabatic calorimeter. A solid–solid and a solid–liquid phase transitions were found at T=314.304 and 402.402 K, respectively, from the experimental C_p–T curve. The molar enthalpies and entropies of these transitions were determined to be 14.78 kJ mol^{-1}, 47.01 J K^{-1} mol^{-1} for the solid-solid transition and 7.518 kJ mol^{-1}, 18.68 J K^{-1} mol^{-1} for the solid–liquid transition, respectively. The dependence of heat capacity on the temperature was fitted to the following polynomial equations with least square method. In the temperature range of 80 to 310 K, $C_{p,m}$/(J K^{-1} mol^{-1})=117.72+58.8022x+3.0964x^2 +6.87363x^3–13.922x^4+9.8889x^5+16.195x^6; x=[(T/K)–195]/115. In the temperature range of 325 to 395 K, $C_{p,m}$/(J K^{-1} mol^{-1})= 290.74+22.767x–0.6247x^2–0.8716x^3–4.0159x^4–0.2878x^5+1.7244x^6; x=[(T/K)–360]/35. The thermodynamic functions H_T–$H_{298.15}$ and S_T–$S_{298.15}$, were derived from the heat capacity data in the temperature range of 80 to 410 K with an interval of 5 K. The thermostablility of the compound was further tested by DSC and TG measurements. The results were in agreement with those obtained by adiabatic calorimetry.

Keywords: *adiabatic calorimetry, 2,2-dimethyl-1,3-propanediol, DSC, heat capacity, phase transition, TG, thermodynamic properties*

Introduction

2,2-Dimethyl-1,3-propanediol [$(CH_3)_2C(CH_2OH)_2$, CAS No. 126-30-7] is an important polyhydric alcohol because of its special solid–solid phase change characterization. Its molecular formula is $C_5H_{12}O_2$ with molar mass of 104.15 g mol^{-1} and structural formula as follows:



As a solid–solid phase change material, 2,2-dimethyl-1,3-propanediol offers small volumetric change during the phase change process, lower undercooling, no leakage, smaller erosion to the device, longer lifespan, and does not have segregation or phase separation problems. It is even more important that it has higher enthalpies and lower temperature during the phase transition. 2,2-dimethyl-1,3-propanediol is receiving more and more attention due to its diverse advantages [1–4]. Moreover, it is also a raw material to prepare binary solid-solid phase change material. It is heterogeneous at low temperature, but it becomes homogeneous face-centered cubic crystal that has high symmetry and absorbs a great deal of hydrogen bond energy when the temperature rises to its solid-solid phase change temperature. Experiments show that it experiences a first-order phase transition during which the change in their Gibbs energy is zero [5].

The thermodynamic data of 2,2-dimethyl-1,3-propanediol obtained from adiabatic calorimetric method were reported in 1988 [6] and 2001 [7]. Because it is very useful in thermal energy storage, in the present study, the heat capacity and phase transition were investigated in detail with precision adiabatic calorimetric and thermal analytic technique in a wide temperature range from 78 to 410 K.

Experimental

Sample

The 2,2-dimethyl-1,3-propanediol was purchased from Tian Jin Guang Fu Fine Chemical Engineering Institute with labeled purity >99.0% mass fraction. The sample was re-crystallized and then purified by sublimation.

Adiabatic calorimetry

Heat capacity measurements were carried out in a high-precision automated adiabatic calorimeter described in detail in [8, 9]. The calorimeter was established by Thermochemistry Laboratory of Dalian Institute of Chemical Physics, Chinese Academy of Sciences in PR

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China. It mainly consisted of a sample cell, a miniature platinum resistance thermometer, an electric heater, an inner and outer adiabatic shield, two sets of chromel-copper thermocouples and a high vacuum system. Its working temperature is from 80 to 580 K [10] and the cooling medium is liquid nitrogen.

The measurements were conducted by means of the standard method of intermittently heating the sample and alternately measuring the temperature. The temperature difference between the sample and adiabatic shield was automatically kept to be about 10^{-3} K during the whole experiment. The temperature increment for a heating period was 2–4 K, and temperature drift was maintained about 10^{-4} K $\min^{-1}$ during each equilibrium period. The data were automatically collected through a Data Acquisition/Switch Unit (Model: 34420, Agilent USA) and processed on line by a personal computer according to the program developed in our thermochemistry laboratory [11].

The sample amount used for the heat capacity measurement is 4.07048 g, which is equivalent to 39.084 mmol based on its molar mass of 104.15 g mol^{-1}.

Thermal analysis

A differential scanning calorimeter (Model: DSC141, Setaram, France) was used to perform the thermal analysis of 2,2-dimethyl-1,3-propanediol under high purity nitrogen (99.999%) with a flow rate of 40 mL $\min^{-1}$ and heating and cooling rate of 10 K $\min^{-1}$. The mass of the sample used in the experiment was 3.08 mg.

The TG measurements of the sample were carried out by a thermogravimetric analyzer (Model: DT-20B, Shimadzu, Japan) under N_2 with a flow rate of 40 mL $\min^{-1}$ and heating rate of 10 K $\min^{-1}$. The mass of the sample used in the experiment was 11.22 mg.

Results and discussion

Heat capacity and thermodynamic functions

Experimental molar heat capacities of 2,2-dimethyl-1,3-propanediol measured by the adiabatic calorimeter over the temperature range from 78 to 410 K are listed in Table 1 and plotted in Fig. 1. From the Fig. 1, two phase transitions were observed at the temperature of 314.3 and 402.4 K, respectively. Since the melting point reported in [12] was 400.5 K, the first transition corresponds to a solid–solid phase change and the second one to a solid–liquid phase change.

The values of experimental heat capacities were fitted to the following polynomial equations with least square method.

For the solid phase over the temperature range of 80 to 310 K:

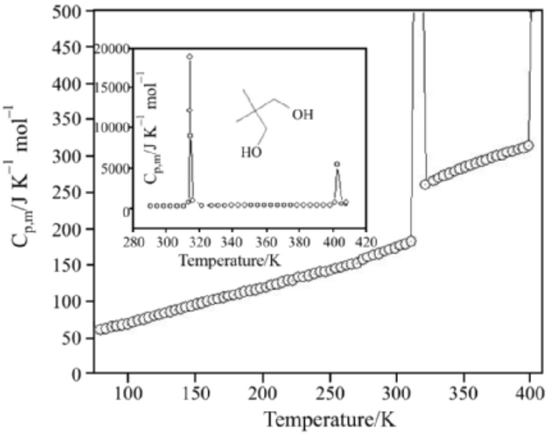

Fig. 1 Experimental molar heat capacities ($C_{p,m}$) of 2,2-dimethyl-1,3-propanediol plotted *vs*. temperature

$$C_{p,m}/(\mathrm{J\ K^{-1}\ mol^{-1}})=117.72+58.8022x+ \\ +3.0964x^2-6.87363x^3- \\ -13.922x^4+9.8889x^5+16.195x^6 \quad (1)$$

where x is the reduced temperature $x=[T-(T_{\max}+T_{\min})/2]/[(T_{\max}-T_{\min})/2]$, T is the experimental temperature, thus, in the solid-state (80 to 310 K), $x=[(T/\mathrm{K})-195]/115$, where $T_{\max}$ is the upper limit (310 K) and $T_{\min}$ is the lower limit (80 K) of the above temperature region. The correlation coefficient of the fitting $R^2=0.9937$.

For the solid phase over the temperature range of 325 to 395 K:

$$C_{p,m}/(\mathrm{J\ K^{-1}\ mol^{-1}})=290.74+22.767x-0.6247x^2- \\ -0.8716x^3-4.0159x^4-0.2878x^5+1.7244x^6 \quad (2)$$

where x is the reduced temperature, $x=[(T/\mathrm{K})-360]/35$, T is the experimental temperature, 360 is obtained from polynomial $(T_{\max}+T_{\min})/2$, 35 is obtained from polynomial $(T_{\max}-T_{\min})/2$. $T_{\max}$ and $T_{\min}$ are the upper (395 K) and lower (325 K) limit temperature respectively. The correlation coefficient of the fitting $R^2=0.9999$.

The published papers in [13–16] have used the same method to treat the $C_{p,m}$ data around the phase change temperature.

The temperature, enthalpy and entropy of solid–solid and solid–liquid phase transitions

The molar enthalpies and entropies of the solid–solid and solid–liquid phase transitions, $\Delta_{trs}H_m$, $\Delta_{trs}S_m$, $\Delta_{fus}H_m$ and $\Delta_{fus}S_m$ of the compound were derived according to the following Eqs (3)–(6):

$$\Delta_{trs}H_m = \\ =\frac{Q_1-n\int_{T_i}^{T_{trs}}C_{p,m}(s)\mathrm{d}T-n\int_{T_{trs}}^{T_j}C_{p,m}(s)\mathrm{d}T-\int_{T_i}^{T_j}C_p(1)\mathrm{d}T}{n} \quad (3)$$

Table 1 Experimental molar heat capacity of 2,2-dimethyl-1,3-propanediol (M=104.15 g mol^{-1})

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}	T/K	$C_{p,m}$/J K^{-1} mol^{-1}
79.898	61.07	167.168	103.9	254.630	145.9	331.173	269.6
83.981	62.63	171.124	105.5	258.605	147.3	335.068	273.2
87.869	64.85	175.040	107.8	262.648	149.4	339.010	276.0
91.882	66.43	178.911	109.3	266.666	151.8	343.007	279.2
95.964	68.08	182.880	111.1	270.634	153.1	346.971	282.2
99.907	69.43	186.952	113.7	274.531	157.9	350.911	284.7
103.772	71.74	190.997	115.1	278.579	161.4	354.827	287.4
107.759	74.37	194.977	116.4	282.685	164.0	358.719	289.9
111.782	75.75	198.897	118.0	286.743	166.3	362.663	292.4
115.729	78.22	202.782	119.7	290.755	169.5	366.662	294.9
119.570	80.30	206.776	123.0	294.707	171.6	370.632	297.7
123.487	82.36	210.847	124.4	298.617	173.7	374.574	300.2
127.511	84.20	214.858	126.4	302.596	177.0	378.479	302.3
131.444	86.10	218.831	129.0	306.633	179.2	382.361	305.0
135.296	88.31	222.772	129.6	310.626	183.2	386.302	306.6
139.260	90.45	226.669	133.7	313.382	666.9	390.270	309.4
143.315	92.34	230.531	133.9	314.184	12108	394.221	311.3
147.300	94.33	234.600	135.6	314.304	18801	398.157	314.5
151.225	96.47	238.792	138.9	314.461	8992	401.175	655.7
155.094	98.04	242.883	140.6	315.864	937.8	402.402	5383
159.063	100.3	246.825	140.6	321.396	261.0	405.023	505.6
163.146	102.3	250.744	143.2	327.328	266.1	407.478	502.7
						407.782	639.4

Table 2 Thermodynamic parameters of 2,2-dimethyl-1,3-propanediol gained from heat capacity measurements

Thermodynamic parameters	T_{trs}/K	T_m/K	$\Delta_{trs}H_m$/kJ mol^{-1}	$\Delta_{trs}S_m$/J K^{-1} mol^{-1}	$\Delta_{fus}H_m$/kJ mol^{-1}	$\Delta_{fus}S_m$/J K^{-1} mol^{-1}
Value	314.304	402.402	14.78	47.01	7.518	18.68

$$\Delta_{trs}S_m = \frac{\Delta_{trs}H_m}{T_{trs}} \tag{4}$$

$$\Delta_{fus}H_m = \frac{Q_2 - n\int_{T_k}^{T_m} C_{p,m}(s)\mathrm{d}T - n\int_{T_m}^{T_f} C_{p,m}(l)\mathrm{d}T - \int_{T_k}^{T_f} C_p(2)\mathrm{d}T}{n} \tag{5}$$

$$\Delta_{fus}S_m = \frac{\Delta_{fus}H_m}{T_m} \tag{6}$$

where T_i is a temperature slightly lower than the solid–solid transition temperature, T_j a temperature slightly higher than the solid–solid transition temperature, T_{trs} and T_m are solid–solid and solid–liquid transition temperature, respectively, T_k a temperature slightly lower than the solid–liquid transition temperature, T_f a temperature slightly higher than the solid–liquid transition temperature, Q_1 the total energy introduced into the sample cell from T_i to T_j, Q_2 the total energy introduced into the sample cell from T_k to T_f, $C_p(1)$ the heat capacity of the sample cell from T_i to T_j, $C_p(2)$ the heat capacity of the sample cell from T_k to T_f, $C_{p,m}(s)$ the heat capacity of the sample in solid phase from T_i to T_m, $C_{p,m}(l)$ the heat capacity of the sample in liquid phase from T_m to T_f and n is molar amount of the sample. The heat capacity polynomials mentioned above were used to calculate the smoothed heat capacities, and were numerically integrated to obtain the values of the standard thermodynamic functions above T=298.15 K. The calculated results are listed in Table 2.

The thermodynamic functions of the 2,2-dimethyl-1,3-propanediol relative to the reference temperature 298.15 K were calculated in the temperature range of 80–410 K with an interval of 5 K, using the polynomial equation of heat capacity and thermodynamic relationships as follows.

Before solid–solid phase transition,

$$H_T - H_{298.15} = \int_{298.15}^{T} C_{p,m}(s)\mathrm{d}T \tag{7}$$

$$S_T - S_{298.15} = \int_{298.15}^{T} (C_{p,m}(s)/T)\mathrm{d}T \tag{8}$$

Table 3 Calculated thermodynamic functions of 2,2-dimethyl-1,3-propanediol

T/K	$C_{p,m}$/ J K^{-1} mol^{-1}	H_T–$H_{298.15}$/ kJ mol^{-1}	S_T–$S_{298.15}$/ J K^{-1} mol^{-1}	T/K	$C_{p,m}$/ J K^{-1} mol^{-1}	H_T–$H_{298.15}$/ kJ mol^{-1}	S_T–$S_{298.15}$/ J K^{-1} mol^{-1}
80	61.27	–25.09	–135.9	245	143.1	–8.333	–30.69
85	63.15	–24.78	–132.1	250	145.5	–7.611	–27.77
90	65.28	–24.46	–128.4	255	147.9	–6.878	–24.86
95	67.57	–24.12	–124.8	260	150.4	–6.132	–21.96
100	69.99	–23.78	–121.3	265	152.8	–5.374	–19.06
105	72.49	–23.42	–117.8	270	155.4	–4.603	–16.18
110	75.03	–23.05	–114.4	275	158.0	–3.820	–13.31
115	77.59	–22.67	–111.0	280	160.8	–3.023	–10.44
120	80.16	–22.28	–107.7	285	163.7	–2.212	–7.569
125	82.71	–21.87	–104.4	290	167.0	–1.385	–4.700
130	85.25	–21.45	–101.1	295	170.6	–0.5414	–1.822
135	87.77	–21.02	–97.80	298.15	173.2	0	0
140	90.28	–20.57	–94.56	300	174.7	0.3218	1.075
145	92.76	–20.12	–91.34	305	179.5	1.207	4.002
150	95.24	–19.65	–88.15	310	184.9	2.118	6.977
155	97.71	–19.16	–84.98	315	phase transition	–	–
160	100.2	–18.67	–81.38	320	phase transition	–	–
165	102.6	–18.16	–78.71	325	263.9	17.95	57.29
170	105.1	–17.64	–75.60	330	268.6	19.29	61.36
175	107.6	–17.11	–72.52	335	273.0	20.64	65.43
180	110.1	–16.57	–69.45	340	277.0	22.02	69.50
185	112.6	–16.01	–66.40	345	280.7	23.41	73.57
190	115.2	–15.44	–63.36	350	284.1	24.82	77.64
195	117.7	–14.86	–60.34	355	287.5	26.25	81.69
200	120.3	–14.26	–57.33	360	290.7	27.70	85.73
205	122.9	–13.66	–54.34	365	294.0	29.16	89.77
210	125.4	–13.03	–51.35	370	297.2	30.64	93.79
215	128.0	–12.40	–48.38	375	300.3	32.13	97.80
220	130.6	–11.75	–45.41	380	303.4	33.64	101.8
225	133.1	–11.10	–42.45	385	306.2	35.16	105.8
230	135.6	–10.42	–39.50	390	309.0	36.70	109.8
235	138.1	–9.739	–36.55	395	311.8	38.25	113.7
240	140.6	–9.0421	–33.62	400	phase transition	–	–
				405	phase transition	–	–

After solid–solid phase transition,

$$H_T - H_{298.15} = \\ = \int_{298.15}^{T_i} C_{p,m}(s)\mathrm{d}T + \Delta_{trs}H_m + \int_{T_j}^{T} C_{p,m}(s)\mathrm{d}T \qquad (9)$$

$$S_T - S_{298.15} = \int_{298.15}^{T_i} (C_{p,m}(s)/T)\mathrm{d}T + \\ +\Delta_{trs}H_m/T_{trs} + \int_{T_j}^{T} (C_{p,m}(s)/T)\mathrm{d}T \qquad (10)$$

where T_i is a temperature slightly lower than the solid–solid transition temperature, T_j a temperature slightly higher than the solid–solid transition temperature; $\Delta_{trs}H_m$ is the molar enthalpy of solid–solid phase transition; $\Delta_{fus}H_m$ is the molar enthalpy of fusion; T_{trs} is the temperature of solid–solid phase transition.

- The thermodynamic functions, H_T–$H_{298.15}$, S_T–$S_{298.15}$, are listed in Table 3.

In order to compare our results with literature values, the data reported by Zhang *et al.* [6], Kamae *et al.* [7] and present work are listed in Table 4. From the table, it can be seen that T_{trs}, $\Delta_{trs}H_m$, $\Delta_{trs}S_m$ of the phase transition at about 314 K are in well accordance with each other, but for the phase transition at about 403 K, T_{trs} of our work is lower slightly than that reported by

Zhang, while the $\Delta_{trs}H_m$ and $\Delta_{trs}S_m$ are slightly higher than the values reported by Zhang.

Thermal analysis

From the DSC curve in Fig. 2, two sharply endothermic peaks were observed with the peak temperature of 315.31 and 403.14 K respectively, which were consistent with the value (314.30, 402.40 K) obtained from the adiabatic calorimetric measurements. Results were listed in Table 4. The data from our present work and DSC are well consistent but slightly higher than the data in literature.

From the TG curve in Fig. 3, it can be seen that the mass loss of the sample starts at about 410 K and completely loss the mass at about 450 K.

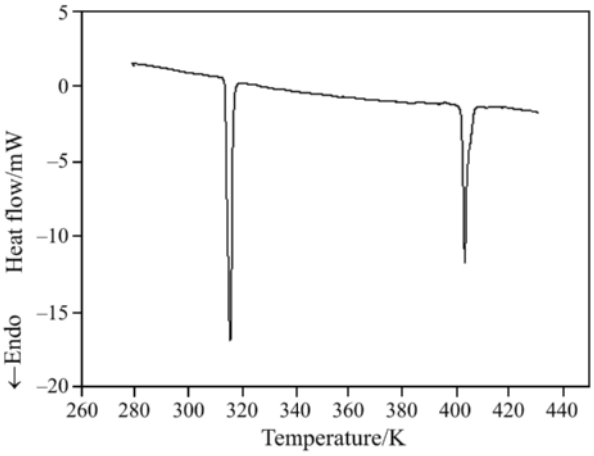

Fig. 2 DSC curves of 2,2-dimethyl-1,3-propanediol

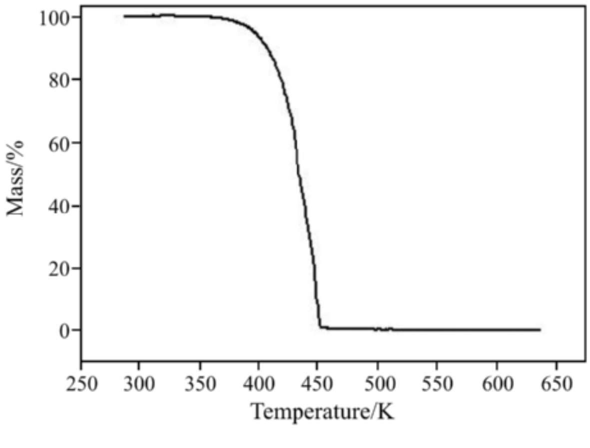

Fig. 3 TG curves of 2,2-dimethyl-1,3-propanediol

Table 4 Transition temperatures and thermochemical properties of 2,2-dimethyl-1,3-propanediol

T_{trs}/K	$\Delta_{trs}H_m$/ kJ mol^{-1}	$\Delta_{trs}S_m$/ J K^{-1} mol^{-1}	Ref./remark
60.4	0.177	2.93	Kamae *et al*. [7]
314.5	12.5	39.1	Kamae *et al*. [7]
314.8	12.41	39.4	Zhang *et al*. [6]
314.30	14.78	47.01	present work
315.31	13.54	42.94	DSC
403.3	4.44	10.5	Zhang *et al*. [6]
402.40	7.518	18.68	present work
403.14	7.96	19.75	DSC

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