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Determination of Heat Capacities and Thermodynamic Properties of 2-(Chloromethylthio)benzothiazole by an Adiabatic Calorimeter

**Mei-Han Wang,[†] Zhi-Cheng Tan,*[,†] Xiao-Hong Sun,[‡] Hong-Tao Zhang,[†] Bei-Ping Liu,[§]
Li-Xian Sun,[†] and Tao Zhang[†]**

Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,
Dalian 116023, China, College of Chemical Engineering, Northwest University, Xi'an 710069, China, and
Department of Chemistry, Hunan University of Arts and Science, Changde 415000, China

The molar heat capacities of 2-(chloromethylthio)benzothiazole (molecular formula $C_8H_6ClNS_2$, CA registry no. 28908-00-1) were measured with an adiabatic calorimeter in the temperature range between (80 and 350) K. The construction and procedures of the calorimeter were described in detail. The performance of the calorimetric apparatus was evaluated by heat capacity measurements on α-Al_2O_3. The deviation of experiment heat capacities from the corresponding smoothed values lies within ±0.3%, whereas the uncertainty is within ±0.5%, compared with that of the recommended reference data over the whole experimental temperature range. A fusion transition was found from the C_p-T curve of 2-(chloromethylthio)benzothiazole. The melting temperature and the molar enthalpy and entropy of fusion of the compound were determined to be $T_m = (315.11 \pm 0.04)$ K, $\Delta_{fus}H_m = (17.02 \pm 0.03)$ kJ·mol^{-1}, and $\Delta_{fus}S_m = (54.04 \pm 0.05)$ J·mol^{-1}·K^{-1}, respectively. The thermodynamic functions $(H_T - H_{298.15})$ and $(S_T - S_{298.15})$ were also derived from the heat capacity data. The molar fraction purity of the 2-(chloromethylthio)benzothiazole sample used in the present calorimetric study was determined to be 99.21 by fraction melting.

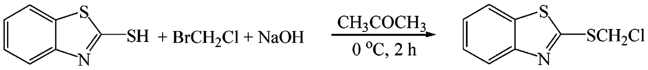
1. Introduction

Adiabatic calorimetry at low temperature is the classical method for heat capacity measurement, from which many other thermodynamic properties such as enthalpy, entropy, and Gibbs free energy can be calculated. These data are of significance in theoretical study, application development, and industrial production of a compound. In the present paper, a small-sample automated adiabatic calorimeter is described in more detail on the basis of our previous work.[1,2] At the same time, the heat capacities of the standard reference material α-Al_2O_3 were measured to demonstrate the accuracy of this calorimeter.

2-(Thiocyanomethylthio)benzothiazole (TCMTB) is a broad-spectrum fungicide that is used for soil and seed treatment against various diseases of field crops, certain vegetables, and ornamentals.[3] It is synthesized from 2-mercaptobenzothiazole (MBT). 2-(Chloromethylthio)benzothiazole is a very important intermediate in the synthesis process of TCMTB. Understanding the thermodynamic properties of this intermediate can improve the synthesis process of TCMTB. However, previous research has focused on the efficient synthesis of 2-(chloromethylthio)benzothiazole. The thermodynamic properties of this compound have not been studied as far as we know. In the present study, the low-temperature heat capacity has been measured in the temperature range from (80 to 350) K with a small-sample automated adiabatic calorimeter. The melting temperature and the molar enthalpy and entropy of fusion of the compound were determined.

2. Experimental Section

Samples. 2-(Chloromethylthio)benzothiazole was prepared according to the procedures given in the literature.[4] The process is



2-Mercaptobenzothiazole in acetone was mixed with bromochloromethane in a round-bottomed flask, and the reaction mixture was stirred for 10 min at room temperature. Sodium hydroxide was added slowly, and the temperature was kept at 0 °C for 2 h. The reaction mixture was allowed to reach room temperature, when excess acetone and bromochloromethane were removed. The resulting mixture was extracted with chloroform and washed with water. The organic layer was dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified by column chromatography on silica gel to yield the compound. Its melting point was determined to be (314 to 315) K with a microscopic melting-point device. The structure of the product was determined by IR and ^{1}H NMR. The IR (KBr) showed characteristic absorption peaks at 3100 (ph-H), 2920 (C−H), 1693 (C=C), 1457 (C=N), and 995 (C−S) cm^{-1}. The ^{1}H-NMR ($CDCl_3$) absorption peaks were detected at δ (5.336−5.387) × 10^{-6} (2H, s, CH_2) and (7.332−7.977) × 10^{-6} (4H, m, ph).

Automated Adiabatic Calorimeter. The adiabatic calorimeter consisted of a sample cell, inner and outer adiabatic shields, vacuum can, and Dewar vessel. The cross-sectional diagram of the adiabatic calorimeter is shown in Figure 1.

The sample cell was made of thin-walled gold-plated copper and had an inner volume of 6 cm^3. Four L-shaped

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* Corresponding author. E-mail: tzc@dicp.ac.cn. Tel: +86-411-84379199. Fax: +86-411-84691570.

[†] Dalian Institute of Chemical Physics.

[‡] Northwest University.

[§] Hunan University of Arts and Science.

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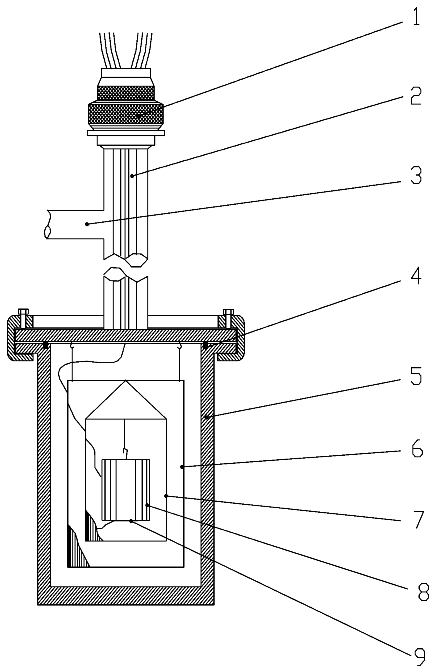

Figure 1. Cross-sectional diagram of the adiabatic calorimeter: 1, sealing junction unit; 2, vacuum tube; 3, to high-vacuum system; 4, fuse gasket; 5, vacuum can; 6, outer adiabatic shield; 7, inner adiabatic shield; 8, sample cell; 9, platinum resistance thermometer.

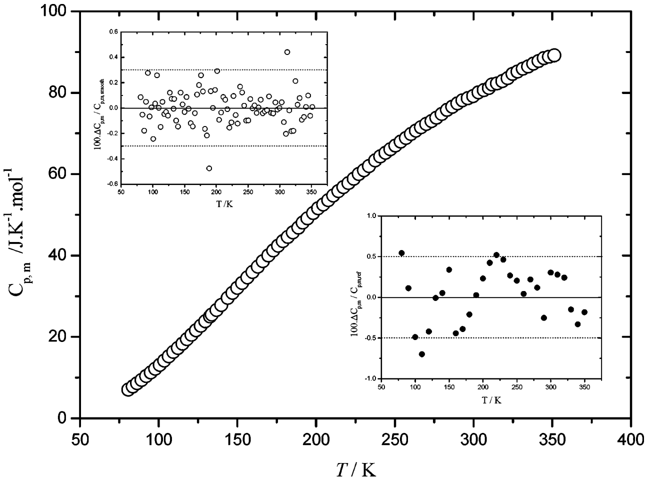

Figure 2. Molar heat capacities of the standard reference material α-Al_2O_3: inset ○, deviation of the measured molar heat capacities from the smoothed curves; inset ●, plot of deviations 100$\Delta C_{p,m}/C_{p,m,ref}$ of the measured values, where $\Delta C_{p,m}$ is the difference between the measured values and the reference values; $C_{p,m,ref}$ is the molar heat capacity reported by Archer.[5]

0.10-mm-thick radial gold-plated copper vanes were placed in the cell to shorten the thermal equilibrium time. A 5-m-long copper capillary was welded at the center of the lid for the introduction of helium gas into the sample cell. The lid was sealed to the main body of the cell with special epoxy adhesive (epoxy resine/curing agent = 5/1). After 0.1 MPa helium exchanging gas was introduced into the cell, the capillary was pinched off, and the resultant fracture was soldered with a small amount of solder to ensure the sealing of the cell.

Table 1. Experimental Molar Heat Capacity of 2-(Chloromethylthio)benzothiazole (M = 215.72 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}
80.927	102.3	204.068	193.3	314.911	30 686
84.537	106.6	207.197	196.3	314.938	10 748
88.029	110.9	210.320	198.5	316.595	328.2
91.402	114.0	213.413	200.5	320.288	330.2
94.665	118.9	216.476	202.5	323.952	331.6
97.853	122.4	219.498	203.4	327.473	334.4
100.970	124.9	222.480	205.3	330.940	335.8
104.023	127.4	225.406	206.9	334.437	337.4
107.005	129.9	228.251	208.2	337.976	340.2
109.957	132.3	231.007	210.1	341.562	342.7
112.836	135.0	233.737	213.4	345.165	345.4
115.690	137.0	236.448	215.3	348.805	348.3
118.496	140.1	239.123	217.0		
121.273	141.4	241.718	218.9		
124.012	144.0	244.352	221.0		
126.719	146.3	247.031	222.4		
129.395	148.7	249.689	224.2		
132.041	150.4	252.315	225.6		
134.665	152.4	254.916	227.4		
137.259	154.1	257.491	228.6		
139.831	155.6	260.864	230.5		
142.374	157.4	265.095	232.4		
145.381	159.2	269.256	234.1		
148.830	161.3	273.680	236.1		
152.246	163.4	278.043	238.1		
155.625	165.2	282.062	240.7		
158.969	167.1	286.072	242.2		
162.291	168.8	290.054	244.5		
165.584	170.2	293.901	246.6		
168.862	172.2	297.722	249.5		
172.121	174.3	301.512	252.5		
175.363	176.9	305.286	255.1		
178.588	179.2	308.964	287.7		
181.801	180.3	312.217	473.7		
185.005	182.0	314.078	2010		
188.201	184.3	314.600	6220		
191.385	186.0	314.772	9563		
194.562	187.3	314.863	15 715		
197.730	189.0	314.884	45 693		
200.904	191.1	314.907	82 597		

An Ω-shaped sheath was silver soldered at the bottom of the cell so that a miniature platinum resistance thermometer could be inserted. The thermometer (IPRT no. 2, produced by the Shanghai Institute of Industrial Automatic Meter, 16 mm long, 1.6 mm in diameter, nominal resistance of 100 Ω) was calibrated on the basis of ITS-90 by the Station of Low-Temperature Metrology and Measurements, Academic Sinica. The resistance of the thermometer was measured with a 7½ digit nanovolt/micro ohm meter, 34420A Agilent. The temperature of the sample was calculated by the computer according to the relationship between resistance and temperature. A heater (Karma wire of 0.12 mm diameter, 105 Ω) was wound bifilarly on the surface of the cell and was covered with aluminum-plated Dacron film. The electrical energy introduced into the sample cell was supplied by a regulated dc power supply (MATRIX-MPS-3002L-1) with a stability of 5 ppm and was automatically picked up by the data acquisition/switch unit, 34970A Agilent.

The sample cell is surrounded by inner and outer adiabatic shields, which are made of chromium-plated copper. Each adiabatic shield consists of three parts: the upper lid, the lower bottom, and the cylindrical main body. Manganin heating wires are wound evenly on these three parts so that the adiabatic shields have a uniform temperature distribution. Two sets of chromel-copel (Ni-55%, Cu-45%) thermocouples were mounted between the sample cell and the inner shield and between the inner shield and the outer shield, respectively. Each set of thermopiles consists of six thermocouples so that the thermal emf is 171 μV·K^{-1} at 80 K and 390 μV·K^{-1} at 300 K. The thermal emf signal was transferred to a temperature controller (Lake Shore

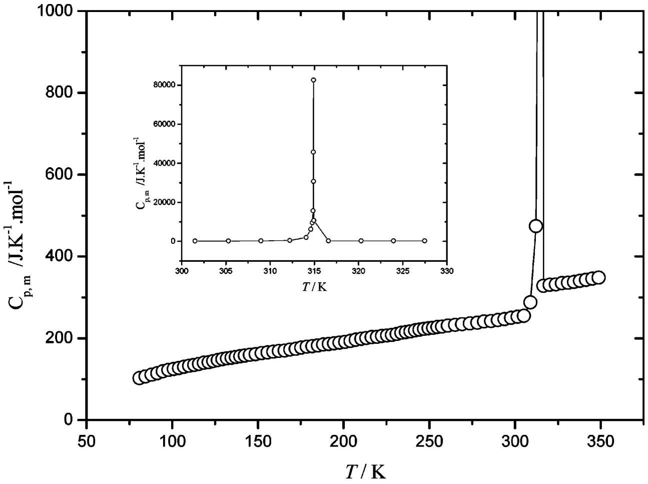

Figure 3. Experimental molar heat capacity $C_{p,\mathrm{m}}$ of 2-(chloromethylthio)benzothiazole as a function of temperature (T).

340) to control the temperature of the two shields. When the adiabatic circuits were operating, the temperature difference between the sample cell and the inner shield was ≤ 0.5 mK during the entire experimental process. The temperature drift of the sample cell could be controlled within 2×10^{-6} K·s^{-1} under this shield control condition.

The sample cell and the adiabatic shields were housed in the high-vacuum can to eliminate convection heat transfer. During the heat capacity measurements, the vacuum can was evacuated to (10^{-3} to 10^{-4}) Pa by means of a combined rotational mechanical pump and oil diffusion pump (Edwards, model -NXK333000). A Dewar vessel filled with liquid nitrogen was used to cool the sample cell down to 78 K.

Prior to heat capacity measurements of the sample, the reliability of the calorimetric apparatus was verified by heat capacity measurements of the standard reference material, synthetic sapphire (α-Al_2O_3, SRM 720).

3. Results and Discussion

Heat Capacity of α-Al_2O_3. The experimental molar heat capacities of the reference standard material α-Al_2O_3 are plotted in Figure 2 in the sequence of the temperature increment. The deviations of the measured values from the smoothed curves lie within ±0.3%, whereas the measuring uncertainty, $100\Delta C_{p,\mathrm{m}}/C_{p,\mathrm{m,ref}}$, is within ±0.5% over the whole temperature range, where $\Delta C_{p,\mathrm{m}}$ is the difference between the measured values and the reference values and $C_{p,\mathrm{m,ref}}$ is the molar heat capacity reported by Archer.[5]

Heat Capacity of 2-(Chloromethylthio)benzothiazole. Heat capacity measurements are listed in Table 1 and plotted in Figure 3. The heat capacities of the sample increase with temperature in a smooth and continuous manner without any thermal anomaly in the range from (80 to 305) K, which means that the compound is stable in this range. However, a thermal anomaly was observed in the temperature range between (305 and 316) K. The thermal anomaly can be ascribed to a solid–liquid-phase transition according to the previous melting-point measurement. The temperature of the phase transition (T_m) was determined to be 315.11 K from the melting curve obtained by observing the equilibrium temperatures and the melted fractions of sample.

The experimental molar heat capacities were fit to the following polynomial equations in reduced temperature (X) by a least-squares method.

Table 2. Calculated Thermodynamic Functions of 2-(Chloromethylthio)benzothiazole

T/K	$C_{p,\mathrm{m}}$/J·K^{-1}·mol^{-1}	$(H_T - H_{298.15})$/kJ·mol^{-1}	$(S_T - S_{298.15})$/J·K^{-1}·mol^{-1}
		Crystal	
80	100.1	−40.07	−221.4
85	107.0	−39.55	−215.1
90	113.2	−39.00	−208.8
95	118.8	−38.42	−202.6
100	124.1	−37.82	−196.3
105	128.9	−37.18	−190.2
110	133.3	−36.53	−184.1
115	137.4	−35.85	−178.1
120	141.3	−35.15	−172.2
125	145.0	−34.44	−166.3
130	148.5	−33.70	−160.6
135	151.8	−32.95	−154.9
140	155.1	−32.19	−149.3
145	158.2	−31.40	−143.8
150	161.3	−30.60	−138.4
155	164.3	−29.79	−133.0
160	167.3	−28.96	−127.8
165	170.3	−28.12	−122.6
170	173.3	−27.26	−117.4
175	176.4	−26.38	−112.4
180	179.4	−25.49	−107.3
185	182.4	−24.59	−102.4
190	185.5	−23.67	−97.49
195	188.6	−22.73	−92.64
200	191.7	−21.78	−87.83
205	194.8	−20.82	−83.06
210	198.0	−19.83	−78.33
215	201.2	−18.84	−73.64
220	204.3	−17.82	−68.98
225	207.5	−16.79	−64.36
230	210.7	−15.75	−59.76
235	213.8	−14.69	−55.20
240	217.0	−13.61	−50.66
245	220.1	−12.52	−46.15
250	223.1	−11.41	−41.67
255	226.2	−10.29	−37.22
260	229.1	−9.148	−32.79
265	232.1	−7.995	−28.40
270	234.9	−6.828	−24.03
275	237.7	−5.646	−19.69
280	240.5	−4.451	−15.39
285	243.1	−3.242	−11.11
290	245.7	−2.020	−6.863
295	248.3	−0.7845	−2.644
298.15	249.8	0	0
300	250.8	0.4631	1.548
305	253.2	1.723	5.715
		Liquid	
315	327.4	18.74	59.76
320	330.0	20.38	64.93
325	332.5	22.04	70.07
330	335.3	23.71	75.17
335	338.2	25.39	80.23
340	341.5	27.09	85.26
345	345.2	28.81	90.28
350	349.4	30.55	95.27

For the solid phase over the temperature range of (80 to 305) K, $C_{p,\mathrm{m}}/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 187.04 + 69.572X + 5.9225X^2 - 1.5483X^3 - 16.303X^4 + 8.4965X^5$, where $X = \{(T/\mathrm{K}) - 192.5\}/112.5$ and T is the absolute temperature. The correlation coefficient of the fitted curve is $R^2 = 0.9996$. The deviations of experimental results from the smoothed curve lie within ±0.6%.

For the liquid phase over the temperature range of (316 to 349) K, $C_{p,\mathrm{m}}/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 336.7 + 9.7291X + 1.5184X^2 + 0.5627X^3$, where $X = \{(T/\mathrm{K}) - 332.5\}/16.5$ and $R^2 = 0.9981$. The deviations of the experimental results from the smoothed curve lie within ±0.3%.

Thermodynamic Functions of 2-(Chloromethylthio)benzothiazole. The molar enthalpy and molar entropy of

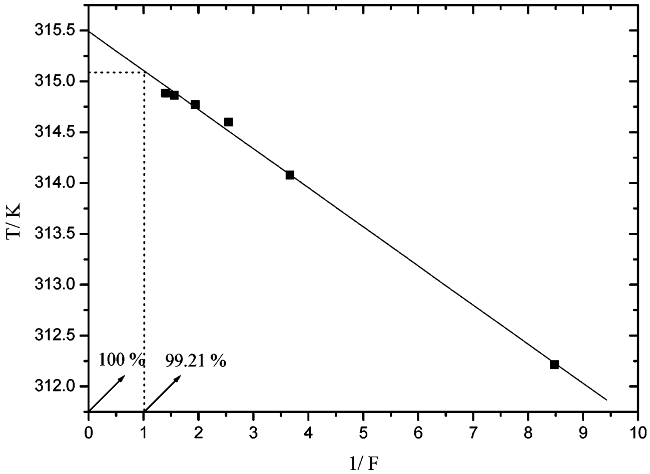

Figure 4. Plot of temperature versus reciprocal of the fraction melted during the melting process of 2-(chloromethylthio)benzothiazole.

Table 3. Observed Equilibrium Temperature (*T*) and Fraction Melted (*F*) during the Melting Process

$F = q/Q$	$1/F$	T/K
0.1179	8.478	312.22
0.2727	3.667	314.08
0.3925	2.548	314.60
0.5151	1.941	314.77
0.6399	1.563	314.86
0.7122	1.404	314.88

fusion of the compound were determined to be (17.02 ± 0.03) kJ·mol^{-1} and (54.04 ± 0.05) J·K^{-1}·mol^{-1}, respectively, from the following equations.[6,7]

$$\Delta H_m = \frac{Q - n\int_{T_i}^{T_m} C_{p,m}(s)\,dT - n\int_{T_m}^{T_f} C_{p,m}(l)\,dT - n\int_{T_i}^{T_f} C_p(0)\,dT}{n}$$

$$\Delta S_m = \frac{\Delta H_m}{T}$$

where T_i is a temperature slightly lower than the initial melting temperature, T_f a temperature slightly higher than the final melting temperature, Q the total energy introduced into the sample cell from T_i to T_f, $C_p(0)$ is the heat capacity of the sample cell from T_i to T_f, $C_{p,m}(s)$ is the heat capacity of the sample in the solid phase from T_i to T_m, $C_{p,m}(l)$ is the heat capacity of the sample in the liquid phase from T_m to T_f, and n is the 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 results are listed in Table 2.

Adiabatic calorimetry provides an accurate way of determining the purity of a substance. The purity of a sample can be evaluated from the observed melting curve.[8] If the liquid solution formed in the premelting region is ideal and thus obeys Raoult's law, then the following expressions can be used to calculate the purity of the sample:

$$x_2 = \frac{\Delta H_m (T_0 - T_1)}{R T_0^2} \qquad F = \frac{q}{Q} \qquad T_0 - T = \frac{T_0 - T_1}{F}$$

where F is the fraction of sample melted, ΔH_m is the molar enthalpy of fusion, T_0 is the triple-point temperature of the pure substance, T_1 is the triple-point temperature of the given sample, and x_2 is the mole fraction of impurity in the liquid solution. The plots of T against $1/F$ in the melting process are shown in Figure 4. T_0 is the temperature when $1/F$ equals 0, and T_1 is equivalent to the temperature when $1/F$ is 1. From Figure 4, T_0 and T_1 are found to be 315.49 K and 315.11 K, respectively. Thus $x_2 = 0.79$ mol % can be calculated, and the purity of the 2-(chloromethylthio)benzothiazole sample studied in the present calorimetric experiment amounts to $1 - x_2 = 99.21$ mol % (Table 3).

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