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Low-temperature heat capacity and standard molar enthalpy of formation of 9-fluorenemethanol ($C_{14}H_{12}O$)

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Abstract

Low-temperature heat capacities of the 9-fluorenemethanol ($C_{14}H_{12}O$) have been precisely measured with a small sample automatic adiabatic calorimeter over the temperature range between $T = 78$ K and $T = 390$ K. The solid–liquid phase transition of the compound has been observed to be $T_{\text{fus}} = (376.567 \pm 0.012)$ K from the heat-capacity measurements. The molar enthalpy and entropy of the melting of the substance were determined to be $\Delta_{\text{fus}}H_{\text{m}} = (26.273 \pm 0.013)\ \text{kJ} \cdot \text{mol}^{-1}$ and $\Delta_{\text{fus}}S_{\text{m}} = (69.770 \pm 0.035)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. The experimental values of molar heat capacities in solid and liquid regions have been fitted to two polynomial equations by the least squares method. The constant-volume energy and standard molar enthalpy of combustion of the compound have been determined, $\Delta_{\text{c}}U(C_{14}H_{12}O,\ \text{s}) = -(7125.56 \pm 4.62)\ \text{kJ} \cdot \text{mol}^{-1}$ and $\Delta_{\text{c}}H^{\circ}_{\text{m}}(C_{14}H_{12}O,\ \text{s}) = -(7131.76 \pm 4.62)\ \text{kJ} \cdot \text{mol}^{-1}$, by means of a homemade precision oxygen-bomb combustion calorimeter at $T = (298.15 \pm 0.001)$ K. The standard molar enthalpy of formation of the compound has been derived, $\Delta_{\text{f}}H^{\circ}_{\text{m}}(C_{14}H_{12}O,\ \text{s}) = -(92.36 \pm 0.97)\ \text{kJ} \cdot \text{mol}^{-1}$, from the standard molar enthalpy of combustion of the compound in combination with other auxiliary thermodynamic quantities through a Hess thermochemical cycle.

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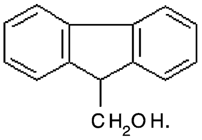
Keywords: 9-Fluorenemethanol; Adiabatic calorimetry; Low-temperature heat capacity; Enthalpy of fusion; Standard molar enthalpy of combustion; Standard molar enthalpy of formation

1. Introduction

The 9-fluorenemethanol (CAS No.: 24324-17-2) is an important chemical raw material and intermediate in the preparation of many medicines, germicides, herbicides, insecticides and growth regulator of plant. Especially, it is widely used to synthesize 9-fluorenemethyl chloroformic ester (abbreviated as Fmoc-Cl) and 9-fluorenemethyl-*N*-amber imino carbonate (abbreviated as Fmoc-OSU), which are the *N*-protecting reagents for the amino groups in many organic compounds as the intermediates and play an distinctive role in the synthesis of many polypeptide medicines. The molecular formula of 9-fluorenemethanol is $C_{14}H_{12}O$, the molar mass is $196.2482\ \text{g} \cdot \text{mol}^{-1}$ and the molecular structure is



The literature [1,2] has reported that the appearance of the compound is a white crystal with a needle-like shape and the melting point is $T = (375$ to $377)$ K. With the development of the pharmaceutical industry and the wide application of the polypeptides, many new fields in which the compound is involved are found and the demand for the 9-fluorenemethanol is greatly increased. However, up till now, the fundamental thermodynamic data of the compound have not been reported in the literature. For the purposes of further investigation and application of the substance, in the present work, low-temperature heat capacities over the temperature range between $T = 78$ K and $T = 390$ K and the standard molar enthalpies of combustion at $T = 298.15$ K were measured by adiabatic

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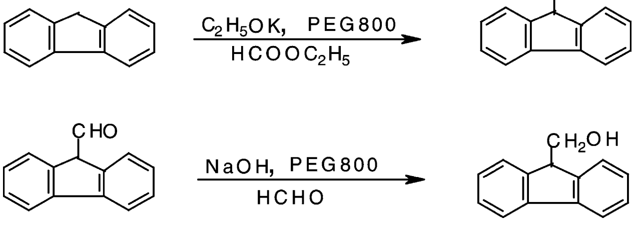
calorimetry and oxygen-bomb combustion calorimetry, respectively. The melting point, the enthalpy and entropy of fusion of the compound have been determined from the fractional melting method based on the results of the heat-capacity measurements.

The oxygen-bomb combustion calorimeter is one of the basic devices necessary for some thermochemical research, especially useful for the determination of the combustion energies of some elements, organic compounds and metallorganics, etc. The combustion calorimetry is often applied to determine the standard molar enthalpies of formation of many important organic substances in industry and scientific research based on the data of enthalpies of combustion and some auxiliary thermodynamic quantities. The standard molar enthalpies of formation, together with the standard or specified entropy, are equally important data in determining any chemical equilibrium. In the present paper, a precise and computer-controlled isoperibol oxygen-bomb combustion calorimeter suitable for investigating combustion enthalpies of many novel compounds is described in more detail on the basis of other commercial apparatus [3–6] and our previous works [7,8]. The standard molar enthalpy of formation of the 9-fluorenemethanol has been derived from the combination of the result of the standard molar enthalpy of combustion with other auxiliary thermodynamic quantities.

2. Experimental

2.1. Sample synthesis and characterization

The 9-fluorenemethanol was prepared according to the procedure given in the literature [2]. The fluorene (A.R.) was chosen as the crude material, the potassium ethylate (A.R.) was used as the solid–liquid phase transfer catalyst and the ethyl formate (A.R.) as the solvent in the synthesis of the sample. The whole preparation was completed by the following two-step reactions:



The crude product was a pale yellow powder. It was recrystallized three times with petroleum ether of analytical grade. The final product was a white needle-like crystal. The melting point of the sample was determined to be $T = (376.3 \text{ to } 377.7)$ K with a microscopic melting point device (model: BY-1, Yazawa Co., Japan), and in agreement with that of the literature [1,2]. The actual purity of the sample was determined to be higher than 0.9990 mole fraction by HPLC (Shimadzu, model: LC-10AT, Japan) analysis and no impurity was detected. The elementary analysis (model: 1106, made in Italy) has indicated that the contents of C and H elements in the sample were 85.66% and 6.15%, respectively, which were identical with the theoretical contents of the H and C elements in the compound, 85.68% and 6.16%. The contents of the impurity elements were within the detection limit of the elementary analyzer. The IR (model: 260-10, made by HITACHI, Japan) showed characteristic absorption peaks at 3405, 3063, 2919, 2860, 1460, 1450, 1360, 1310, 1280, 1170, 1050, 1030, 1005, 930, 840, 750, 730, 720, 593, 530, 425 cm^{-1}. The ^{1}H NMR (model: Unity Plus 500, made by Varian Ltd., USA, $CDCl_3$) absorption peaks agreed with those of the literature [2].

2.2. Adiabatic calorimetry

A precision automatic adiabatic calorimeter was applied to measure the heat capacities over the temperature range between $T = 78$ K and $T = 390$ K. The calorimeter was established in Thermochemistry Laboratory of Dalian Institute of Chemical Physics, Chinese Academy of Sciences in PR China. The principle and structure of the adiabatic calorimeter were described in detail elsewhere [9–11]. Briefly, the calorimeter was mainly composed of a sample cell, a miniature platinum resistance thermometer, an electric heater, the inner and the outer adiabatic shields, two sets of six-junctions chromel–constantan thermopiles installed between the calorimetric cell and the inner shield and between the inner and outer shields, respectively, and a high vacuum can. The sample cell was made of gold-plated copper and had an inner volume of 0.006 dm^3. Four gold-plated copper vanes of 0.2 mm in thickness with a X-shape were placed into the cell to promote heat distribution in the sample cell. The miniature platinum resistance thermometer (IPRT No. 2, produced by Shanghai Institute of Industrial Automatic Meters, 16 mm in length, 1.6 mm in diameter and a nominal resistance of 100 Ω) was used to measure the temperature of the sample. The thermometer was calibrated on the basis of ITS-90 by the Station of Low-temperature Metrology and Measurements, Academia Sinica. The thermometer was inserted into the copper sheath which was silver-soldered closely at the bottom of the sample cell. The heater wire was bifilarly wound and fixed on the side surface of the cell. The lid of the cell with a copper capillary was sealed to the sample cell with adhesive after the sample was loaded. The air in the cell was evacuated and a small amount of helium gas (0.1 MPa) was introduced to enhance the heat transfer in the cell. The capillary was pinched off from the end away from the lid and soldered. The temperature differences between the sample cell and the inner shield and between the inner and outer shields were monitored by the two sets of thermopiles, and controlled by two sets of DWT-702 precision temperature controllers (manufactured by Shanghai No. 6 Automated Instrumentation Works). When the temperature of the sample cell increases due to heating, the differential thermocouples measure the temperature differences. This signal is used to control the heaters distributed on the walls of the inner and outer shields, respectively. Both shields were heated under the control of the signal and kept at the same temperatures as that of the sample cell. At the same time, the vacuum can where the sample cell housed was evacuated to be 10^{-3} Pa. In this way, the heat loss of the sample cell caused by the radiation and convection is greatly reduced. The sensitivity for the measurements of the electrical voltage through the heater of sample cell was $\pm 0.1\ \mu\mathrm{V}$. The electrical energy introduced into the sample cell and the equilibrium temperature of the cell after the energy input were automatically picked up by use of the Data Acquisition/Switch Unit (Model 34970A, Agilent, USA), and processed on line by a computer.

To verify the accuracy of the calorimeter, the heat-capacity measurements of the reference standard material, α-Al_2O_3, were made over the temperature range $78 \leqslant (T/\mathrm{K}) \leqslant 400$. The sample mass used was 1.6382 g, which was equivalent to 0.0161 mol based on its molar mass, $M(Al_2O_3) = 101.9613\ \mathrm{g \cdot mol^{-1}}$. Deviations of the experimental results from those of the smoothed curve lie within ±0.2%, while the inaccuracy is within ±0.3%, as compared with those of the former National Bureau of Standards [12] over the whole temperature range.

Heat-capacity measurements were continuously and automatically carried out by means of the standard method of intermittently heating the sample and alternately measuring the temperature. The heating rate and temperature increments were generally controlled at (0.1 to 0.4) $\mathrm{K \cdot min^{-1}}$ and (1 to 4) K. The energy introduced into the sample cell was supplied by a d.c. voltage supplier with a stability of $5 \cdot 10^{-6}$. The heating duration was 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were always kept within (10^{-3} to 10^{-4}) $\mathrm{K \cdot min^{-1}}$ during the acquisition of all heat-capacity data. In order to obtain good adiabatic conditions between the calorimetric cell and its surroundings, the temperature difference between the calorimetric cell and the inner shield was automatically kept within 1 mK during the whole experiment. The data of heat capacities and corresponding equilibrium temperature have been corrected for heat exchange of the sample cell with its surroundings [9–11]. The sample mass used for calorimetric measurements was 2.0981 g, which was equivalent to 0.010691 mol in terms of its molar mass, $M = 196.2482\ \mathrm{g \cdot mol^{-1}}$.

2.3. Oxygen-bomb combustion calorimetry

The constant-volume energy of combustion of the sample was measured by means of a homemade precision oxygen-bomb combustion calorimeter. It was an isoperibolic macrocalorimeter with a static oxygen bomb and set up in our thermochemistry laboratory. The structure and principle of the calorimeter have been described previously in brief [7,8]. The schematic diagram of the isoperibol oxygen-bomb combustion calorimeter is shown in figure 1. It consisted of a static oxygen bomb, inner calorimetric vessel, outer thermostatic bath, platinum resistance thermometer, precision temperature controller, ignition system and temperature measurement system. The oxygen bomb was made from a special stainless steel with good heat conduction. The efficient volume of the bomb was about 0.3 $\mathrm{dm^3}$. Two stainless steel ignition electrodes of 0.8 cm in diameter were extended to the centre of the bomb downright from the lid of the bomb. The two ignition electrodes were installed in the lid of the bomb and linked with the ignition system. They had a good electrical insulation from the lid to eliminate the effect of the electric current of the ignition on the temperature measurements. Except for the two ignition electrodes, a filling-oxygen valve was also mounted in the lid. A small sample crucible of about 0.004 $\mathrm{dm^3}$ was hanged in the bomb by means of a horizontal ring. The ring was vertically fixed on one of the two stainless steel electrodes and in a good electric contact with the sample crucible. The second electrode was not directly coupled with the ring, but in a good electrical contact with the first electrode through the ignition nickel fuse. The nickel fuse in the form of the coil in its middle was tightly pressed on the sample after a pellet of sample was horizontally put in the sample crucible. The oxygen bomb was immersed in 2.850 $\mathrm{dm^3}$ of the deionized water contained in the inner calorimetric vessel during the whole combustion. The total mass of both inner calorimetric vessel and deionized water was 3900 g. The deionized water in the inner calorimetric vessel was stirred at a uniform rate of 150 rotations per minute so that heat released in the oxygen bomb was rapidly absorbed by the deionized water and the heat leakage from the inner calorimetric vessel to the surroundings was reduced to the minimum level during the combustion test.

The system of controlling the temperature was composed of a thermostatic bath, an electric stirrer, an electric heater, a precision temperature controller and a Cu 50 resistance thermometer. The thermostatic bath was made from the stainless steel plate of 5 mm in thickness, on the surface of which the thermal insulation paint was coated. The volume of the bath was about 60 $\mathrm{dm^3}$. The thermostatic medium is the distilled water to protect the inner calorimetric vessel from the corrosion. The Cu 50 resistance thermometer was used to measure

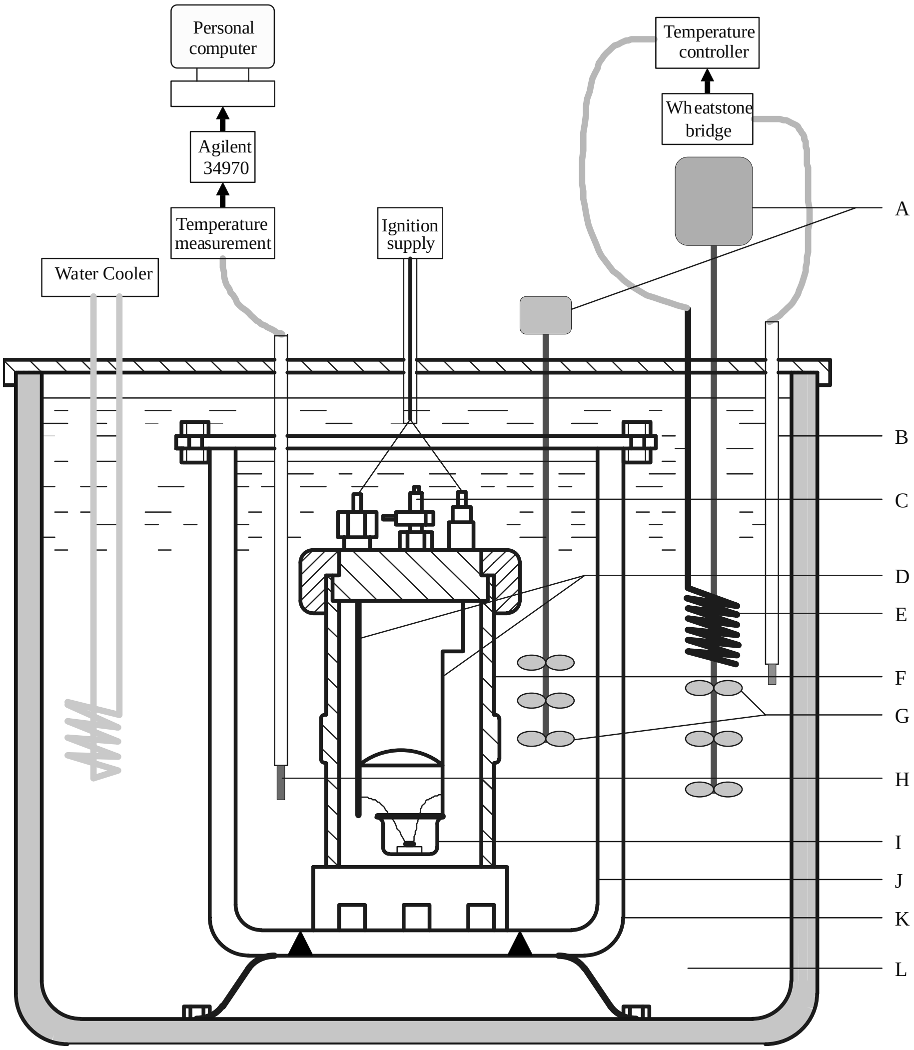


FIGURE 1. The schematic diagram of an isoperibol oxygen-bomb combustion calorimeter (A – electric motor; B – Cu 50 resistance thermometer; C – oxygen-filling valve; D – ignition electrodes; E – heater; F – oxygen bomb; G – stirrers; H – Pt resistance thermometer; I – sample crucible; J – inner calorimetric vessel; K – thermal shield; L – water thermostat).

the temperature of the water in thermostatic bath. The inner calorimetric vessel was located at the centre of the outer thermostatic bath and completely immersed in the thermostatic water of the outer bath. The oxygen bomb was put in the centre of the inner calorimetric vessel. There was an air jacket of 2.5 cm in thickness between the inner calorimetric vessel and the outer thermostatic bath so as to increase the thermal insulation of the calorimetric system. The temperature of the water in the outer thermostatic bath was controlled by means of a precision temperature controller (model: AL-708, made in Yuguang institute of electronic technology, Xiamen, PR China). The Cu 50 thermometer and the electric heater were linked with the temperature controller through a precision electric bridge. The thermostatic water was stirred by an electric stirrer at a rate of 240 rotations per minute. Measurements have shown that the precision of controlling the temperature for the thermostatic system can at least reach ±0.001 K.

The temperature measurement system consisted of a precision platinum resistance thermometer and a Data Acquisition/Switch Unit (Model 34970A, Agilent, USA). The temperature of the water in the inner calorimetric vessel of the calorimeter was measured by the precision platinum resistance thermometer (PTΦ 5× 40, 40 mm in length, 5 mm in diameter; $R_0 = 196.9865\Omega$, made by the Instrument Manufacture Co. of Yunnan, PR China). The thermometer was calibrated on the basis of ITS-90 by the National Institute of Metrology (NIM). The thermometer was linked in four leads with two interfaces of the Agilent Data Acquisition/Switch Unit to measure the temperatures of the calorimetric system through a program on line by a personnel computer.

The correction of the temperature rise (ς) was obtained from the following formula [13,14]:

$$\varsigma = \left(\frac{V_n - V_0}{\theta_n - \theta_0}\right) \cdot \left(\frac{T_0 + T_f}{2} + \sum_{T_0}^{T_f} T_i - n\theta_n\right) + nV_n$$

in which V_n/K · min^{-1} is the temperature drift rate in the final period; V_0/K · min^{-1}, the temperature drift rate in the initial period; θ_n/K, the average temperature of the calorimeter during the final period; θ_0/K, the average temperature of the calorimeter during the initial period; T_0/K, the last reading of the temperatures in the initial period; T_f/K, the first reading of the temperatures in the final period; n, the number of readings for the reaction or main period; the corrected temperature rise of the combustion or reaction is: $\Delta T = (T_f - T_0) + \varsigma$.

The ignition system was composed of a transformer and an electric switch. The voltage of the transformer used in the ignition was set at about 25 V. The length of the ignition nickel wire used in each of combustion tests was about 16 cm. The resistance of the ignition nickel fuse was about 7 Ω. The electric energy for the ignition was determined from the change in potential difference across a capacitor when discharged through the nickel wire to be 0.89 J.

The sample was pressed into pellets of (0.6 to 1.0) g for each combustion and burned under an oxygen pressure of 3.01 MPa in the presence of 0.001 dm^3 of distilled water in the bomb to ensure equilibrium in the final state after the combustion. The purity of the oxygen used in the experiment was of research grade, mole fraction 0.99998. The mass of the sample has been calibrated from the air buoyancy on the basis of the determination of the density for a pellet of the sample. At the $T = (298.15 \pm 0.001)$ K, the differential quotient of the constant-volume energy of combustion with the oxygen pressure, $(\partial U/\partial P)_T$, for these solids was assumed to be -0.21 J · g^{-1} · MPa^{-1}, a typical value for organic solids. The standard energy of combustion of the nickel fuse for ignition has been determined previously to be $\Delta_c U°/\mathrm{J \cdot cm^{-1}} = 2.929$. The real energy of combustion of the nickel fuse (Q_{Ni}) was calculated from the formula, $Q_{Ni}/\mathrm{J} = 2.929 \cdot \Delta L$, in which ΔL/cm was the length of the combusted nickel wire. The correction for the energy of formation of aqueous nitric acid, produced by oxidation of a trace of nitrogen contained in the oxygen bomb, was determined by the neutral titration with a 0.1000 mol · dm^{-3} of sodium hydroxide solution by using the methyl orange as the indicator. The heat of formation of the aqueous nitric acid in the oxygen bomb can be derived from the equation, $Q_{HNO_3}/\mathrm{J} = 59.8 \cdot N \cdot V$, in which N/mol · dm^{-3} is the concentration of the sodium hydroxide solution and V/cm^3 is the volume of the consumed sodium hydroxide solution, based on the molar energy of formation of HNO_3(aq) from N_2(g), O_2(g) and H_2O(l), $\Delta_f H^\circ_m = 59.8$ kJ · mol^{-1} [5,6], for 0.1 mol · dm^{-3} of HNO_3(aq).

The measurement was composed of initial (10 min), combustion (15 min) and final (10 min) periods. The data acquisition starts automatically when the temperature of the calorimeter reached the equilibrium point of controlling the temperature at $T = (298.15 \pm 0.001)$ K. In each period, all the voltage values across the platinum resistance thermometer and the standard resistance ($R_N = 100.053\Omega$) connected in series with the thermometer, E_p and E_N were collected at the same time at the interval of 30 s by using the Agilent Data Acquisition/Switch Unit, and the corresponding temperatures were calculated on line according to the calibrated parameters of the thermometer by a personnel computer. The sample was ignited at 600 s from the start of data acquisition. After each run, the combustion products were analyzed mainly for carbon dioxide by the Rossini method [15]. No soot was observed in the sample crucible after combustion experiments of the 9-fluorenemethanol. Qualitative tests for CO with indicator tubes were negative within the limits of their sensitivity {mole fraction x (CO) $< 1 \cdot 10^{-6}$}.

The energy equivalent, ε_{calor}, of the calorimeter has been determined from 10 combustion experiments using about 0.7 g of NIST 39i benzoic acid with a certified massic energy of combustion under experimental conditions of $\Delta_c U = -(26434 \pm 3)$ J · g^{-1} to be: $\varepsilon_{calor} = (13572.22 \pm 0.98)$ J · K^{-1}. The uncertainty of the results was the standard deviation of the mean value from the respective measurements.

3. Results and discussion

3.1. Heat capacity

All heat-capacity experimental results, listed in table 1 and plotted in figure 2, showed that the structure of the compound was stable: no phase change occurred in the solid phase, nor did association or thermal decomposition occur in the liquid phase ($T < 390$ K). The experimental values of the heat capacities have been fitted to polynomial equations by means of the least squares method.

For the solid phase

$$C_{p,m}/\mathrm{J \cdot K^{-1} \cdot mol^{-1}} = 188.364 + 128.923X - 15.187X^2 - 30.653X^3 + 53.622X^4 + 51.590X^5 - 4.7824X^6,$$

where $X = (T - 220.5)/142.5$. The above equation is valid in the temperature range from $T = 78$ K to $T = 363$ K, with an uncertainty of ±0.50%.

For the liquid phase

$$C_{p,m}/\mathrm{J \cdot K^{-1} \cdot mol^{-1}} = 439.958 + 24.319X + 1.4348X^2 - 1.3644X^3 - 3.2919X^4,$$

TABLE 1
Experimental molar heat capacities of the 9-fluorenemethanol ($M = 196.2482\ \mathrm{g \cdot mol^{-1}}$) ($R = 8.314472\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$)[a]

T/K	$C_{\mathrm{p,m}}$/R	T/K	$C_{\mathrm{p,m}}$/R	T/K	$C_{\mathrm{p,m}}$/R
78.503	8.9715	184.317	18.652	273.684	28.274
79.899	9.0972	186.346	18.842	276.768	28.559
82.262	9.2874	188.375	19.056	280.827	28.922
84.642	9.4944	190.323	19.248	284.155	29.269
85.940	9.5937	192.271	19.455	287.888	29.637
87.239	9.7056	194.219	19.659	291.216	29.905
88.538	9.8260	196.168	19.849	294.463	30.316
89.836	9.9486	198.116	20.089	297.547	30.679
91.054	10.034	200.064	20.256	300.713	31.061
92.271	10.143	201.931	20.462	303.797	31.457
93.814	10.277	203.879	20.699	306.963	31.901
95.682	10.444	205.745	20.927	310.047	32.279
97.466	10.626	207.694	21.141	313.051	32.725
99.252	10.775	209.561	21.386	316.135	33.137
101.038	10.921	211.427	21.597	319.219	33.596
102.742	11.066	213.213	21.808	322.223	34.039
104.447	11.220	215.079	22.039	325.226	34.579
106.151	11.351	216.947	22.256	328.229	35.196
107.775	11.493	218.732	22.431	331.151	35.830
110.047	11.713	220.518	22.659	334.073	36.476
112.807	11.949	222.385	22.905	336.995	37.093
115.567	12.159	224.171	23.139	339.836	37.794
118.245	12.397	225.956	23.362	342.677	38.496
120.843	12.635	227.661	23.551	345.437	39.268
123.441	12.888	229.447	23.773	348.034	39.965
126.038	13.157	231.151	23.946	350.713	40.726
128.554	13.363	232.856	24.185	353.311	41.462
131.071	13.585	234.642	24.391	355.989	42.231
133.505	13.759	236.346	24.518	358.586	42.976
135.941	14.013	238.051	24.724	360.941	43.667
138.375	14.219	239.755	24.912	363.781	45.345
140.729	14.462	241.459	25.105	366.622	50.364
143.083	14.665	243.083	25.262	369.301	66.446
145.437	14.853	244.706	25.405	371.898	94.727
147.791	15.102	246.411	25.533	374.008	157.64
150.063	15.307	248.116	25.706	375.307	377.43
152.336	15.546	249.739	25.866	375.956	890.43
154.609	15.740	251.362	26.041	376.281	1793.8
156.801	15.930	253.067	26.246	376.362	3882.9
158.992	16.144	254.691	26.421	376.444	4331.9
161.184	16.368	256.314	26.561	376.536	4417.4
163.375	16.552	257.937	26.672	376.545	4429.8
165.567	16.746	259.560	26.849	376.606	2318.9
167.677	16.960	261.184	26.975	377.174	729.28
169.869	17.162	262.726	27.150	378.409	50.199
171.979	17.352	264.349	27.291	379.627	50.758
174.089	17.557	265.973	27.466	381.412	51.751
176.119	17.779	267.596	27.626	383.586	52.704
178.229	17.986	269.138	27.798	385.714	53.719
180.258	18.195	270.681	27.956	387.581	54.671
182.288	18.434	272.142	28.116	389.692	55.376

[a] Obtained from [16].

where $X = (T - 384)/6$. This equation applies to the temperature range from $T = 378$ K to $T = 390$ K, with an uncertainty of ±0.20%.

Figure 3 gives the plot of relative deviations of the experimental heat capacity values, $C_{\mathrm{p,m}}$(Expt), from the fitted heat-capacity values, $C_{\mathrm{p,m}}$(fit), against the absolute temperature. It is seen from figure 3 that relative deviations of most experimental points are within ±0.50% except for several points around upper and lower limits of the temperature range in the solid phase.

3.2. Melting point, molar enthalpy and entropy of fusion

Pre-melting occurred owing to the presence of impurities in the sample. The measurements of the melting point and the molar entropy of fusion of the sample

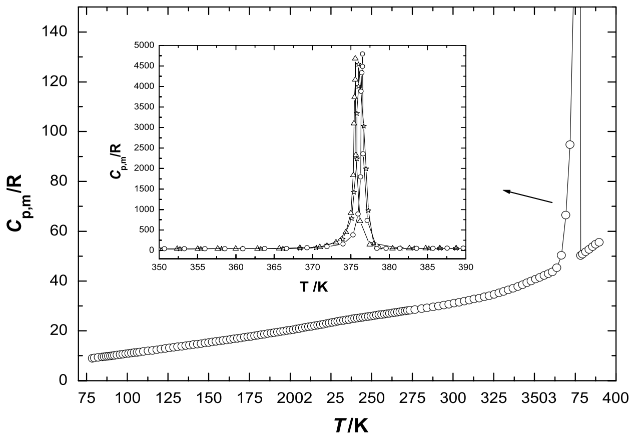


FIGURE 2. The plot of experimental molar heat capacities ($C_{p,m}/R$) of 9-fluorenemethanol against the temperature (T) ("○", the first series of heat capacity measurements; "△", the second series of heat capacity measurements; "*", the third series of heat capacity measurements).

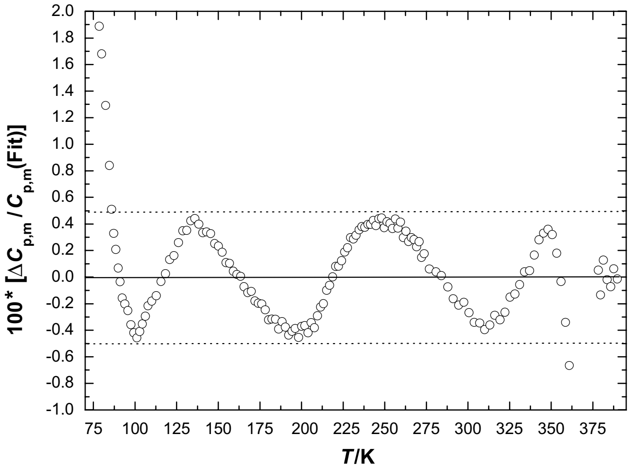


FIGURE 3. The plot of relative deviations of the fitted heat-capacity values [$C_{p,m}$(fit)] from the experimental heat capacity values [$C_{p,m}$(Expt)] against the absolute temperature. {$\Delta C_{p,m} = [C_{p,m}(\mathrm{fit}) - C_{p,m}(\mathrm{Expt})]$}.

were done as follows: the temperatures for the start of the pre-melting and for complete melting were determined. Between these two temperatures the m.p. was determined by successive approximation through stepwise heating. Then, by heating the sample from a temperature slightly lower than the initial melting temperature to a temperature slightly higher than the final melting temperature, the enthalpy of the sample was evaluated. The enthalpy used to heat the empty sample container and the sample itself (solid or liquid) was subtracted from the total amount of heat introduced to the sample and container during the whole fusion, the melting enthalpy of the sample can be obtained, as described in the literature [11].

Three series of heat-capacity experiments in the fusion region of the compound were carried out so that the reversibility and repeatability of the fusion region were verified. Before each series of measurements, the sample was cooled from $T = 390$ K to $T = 300$ K using different cooling rates. In the first series, the sample was quenched into liquid nitrogen (about 20 $\mathrm{K\cdot min^{-1}}$); in the second series, the sample was naturally cooled (about 0.5 $\mathrm{K\cdot min^{-1}}$); and in the third series, the ice-water was used as coolant (about 5 $\mathrm{K\cdot min^{-1}}$). The results of the three series of repeated experiments are plotted in the inset to figure 1 and also given in table 2. It can be seen from figure 1 that the phase transition is reversible and repeatable, no supercooling and other thermal anomaly was caused by the different cooling rates.

The melting temperature T_{fus} of the sample was calculated from an equation based on the heat capacity in the fusion region, as described in the literature [11]. The molar enthalpy of fusion $\Delta_{fus}H_m$ was determined following the method described in the literature [11]. The molar entropy of fusion, using $\Delta_{fus}S_m = \Delta_{fus}H_m/T_{fus}$, was calculated.

The results of T_{fus}, $\Delta_{fus}H_m$ and $\Delta_{fus}S_m$ of the sample obtained from the three series of repeated heat-capacity measurements are listed in table 2.

3.3. Constant-volume combustion energy, standard molar enthalpy of combustion and standard molar enthalpy of formation

The method for determining the constant-volume combustion energy of the sample was the same as that used in the calibration of the calorimeter with benzoic acid. The constant-volume combustion energy of the sample can be calculated from the equation

$$\Delta_c U/\mathrm{J\cdot mol^{-1}} = (\varepsilon_{calor}\cdot \Delta T - Q_{Ni} - Q_{HNO_3})\cdot M/W$$

in which $\varepsilon_{calor}/\mathrm{J\cdot K^{-1}}$ was the energy equivalent of the oxygen-bomb calorimeter; ΔT/K, the corrected temperature rise; $M/\mathrm{g\cdot mol^{-1}}$, the molar mass of the sample; W/g, the mass of the sample.

TABLE 2
The results of melting of the compound obtained from three series of heat capacity measurements

Thermodynamic properties	Series 1, x_1	Series 2, x_2	Series 3, x_3	$(\bar{x} \pm \sigma_a)^a$
T_{fus}/K	376.545	376.586	376.569	376.567 ± 0.012
$\Delta_{fus}H_m/(\mathrm{kJ\cdot mol^{-1}})$	26.251	26.299	26.268	26.273 ± 0.013
$\Delta_{fus}S_m/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$	69.715	69.835	69.756	69.770 ± 0.035

[a] $\sigma_a = \sqrt{\sum_{i=1}^{3}(x_1 - \bar{x})^2/n(n-1)}$, in which n is the experimental number; x_i, a single value in a set of dissolution measurements; $\bar{x}$, the mean value of a set of measurement results.

TABLE 3
The experimental results of the combustion energies of the compound obtained from the oxygen-bomb combustion calorimetry at $T = 298.15$ K

No.	Sample mass m/g	Heat value of nickel wire Q_{Ni}/J	Heat value of nitric acid Q_N/J	Corrected temperature rise ΔT/K	Combustion energies $-\Delta U_c/(\mathrm{kJ \cdot mol^{-1}})$
1	0.9212	39.5388	49.4139	2.4789	7135.18
2	0.8922	38.9530	43.2372	2.3981	7127.73
3	0.9016	39.2459	47.3550	2.4228	7125.65
4	0.8882	40.1246	45.2961	2.3878	7128.33
5	0.9155	38.0744	48.6703	2.4543	7108.52
6	0.9088	39.2459	46.6423	2.4429	7127.93
Avg. $\Delta U_c = -(7125.56 \pm 4.62)$ kJ · mol^{-1}					

The calculated results of the constant-volume combustion energy of the sample were listed in table 3.

The standard molar enthalpy of combustion of the sample, $\Delta_c H_m^\circ$, was the combustion enthalpy change of the following reaction at $T = 298.15$ K and $P^0 = 100$ kPa based on the definition of the combustion enthalpy about the organic compound

$$C_{14}H_{12}O(s) + 33/2O_2(g) = 14CO_2(g) + 6H_2O(l). \quad (1)$$

The standard molar enthalpies of combustion can be derived from the constant-volume combustion energy by means of the following formula:

$$\Delta_c H_m^\circ = \Delta_c U_m + \Delta n \cdot RT,$$

$$\Delta n = \sum n_i(\text{products, g}) - \sum n_i(\text{reactants, g}),$$

where $\sum n_i$ was the total molar amount of the gases in products or reactants. The calculated standard molar enthalpy of combustion of the sample was: $\Delta_c H_m^\circ = -(7131.76 \pm 4.62)$ kJ · mol^{-1}.

The standard molar enthalpy of formation of the compound, $\Delta_f H_m^\circ$, was calculated by a designed Hess thermochemical cycle according to the reaction (1) as follows:

$$\Delta_f H_m^\circ(C_{14}H_{12}O, s) = [14\Delta_f H_m^\circ(CO_2, g) + 6\Delta_f H_m^\circ(H_2O, l)] - \Delta_c H_m^\circ(C_{14}H_{12}O, s).$$

In the above formula, the standard molar enthalpies of formation of CO_2(g) and H_2O(l), recommended by *CODATA* [17,18], $\Delta_f H_m^\circ(CO_2,g) = -(393.51 \pm 0.13)$ kJ · mol^{-1} and $\Delta_f H_m^\circ(H_2O,l) = -(285.83 \pm 0.04)$ kJ · mol^{-1}, were employed in the calculation of $\Delta_f H_m^\circ$ ($C_{14}H_{12}O$,s) values. The standard molar enthalpy of formation of the compound can be derived based on these values and standard molar enthalpy of combustion of the substance to be: $\Delta_f H_m^\circ$ ($C_{14}H_{12}O$,s) = –(92.36 ± 0.97) kJ · mol^{-1}.

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