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MOLAR HEAT CAPACITIES AND STANDARD MOLAR ENTHALPY OF FORMATION OF 2-AMINO-5-METHYLPYRIDINE

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The heat capacities ($C_{p,m}$) of 2-amino-5-methylpyridine (AMP) were measured by a precision automated adiabatic calorimeter over the temperature range from 80 to 398 K. A solid–liquid phase transition was found in the range from 336 to 351 K with the peak heat capacity at 350.426 K. The melting temperature (T_m), the molar enthalpy ($\Delta_{fus}H_m^0$), and the molar entropy ($\Delta_{fus}S_m^0$) of fusion were determined to be 350.431±0.018 K, 18.108 kJ mol^{-1} and 51.676 J K^{-1} mol^{-1}, respectively. The mole fraction purity of the sample used was determined to be 0.99734 through the Van't Hoff equation. The thermodynamic functions (H_T–$H_{298.15}$ and S_T–$S_{298.15}$) were calculated. The molar energy of combustion and the standard molar enthalpy of combustion were determined, $\Delta U_c(C_6H_8N_2,cr)= -3500.15\pm1.51$ kJ mol^{-1} and $\Delta_c H_m^0(C_6H_8N_2,cr)= -3502.64\pm1.51$ kJ mol^{-1}, by means of a precision oxygen-bomb combustion calorimeter at T=298.15 K. The standard molar enthalpy of formation of the crystalline compound was derived, $\Delta_f H_m^0(C_6H_8N_2,cr)= -1.74\pm0.57$ kJ mol^{-1}.

Keywords: *2-amino-5-methylpyridine, low-temperature heat capacity, standard molar enthalpy of combustion, standard molar enthalpy of formation, thermodynamic function*

Introduction

2-amino-5-methylpyridine (AMP; molecular formula: $C_6H_8N_2$; CAS Registry No. 1603-41-4) is an important intermediate compound which is widely used in medicine, dye and pesticide industries. Its molecular structure is shown in Fig. 1.

As early as 1978, AMP was reported as initial materials, from which a new kind of anticoccidiostat was prepared [1]. At present, AMP is used widely since it has been successfully employed as a basic organic compound in a wide range of synthetic processes. In medicine area, AMP was used to synthesize medicine for treating or preventing diseases associated with e.g. anxiety, sleep disorders, insomnia and fibrosis [2–4]. In chemical synthesis, AMP was regarded as a kind of reactant, from which researchers can get some new compounds for further study [5–7]. However, the properties of AMP itself have received little attention, probably because it is common and even seems to count for little. During our literature search, only one paper [8] was found to be associated with its property-photoinduced amino-imino tautomerism. Therefore, in order to improve the process of chemical synthesis and increase understanding of the properties of this common but important compound, the study on thermodynamic properties of the substance is necessary.

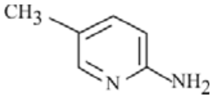

Fig. 1 The molecular structure of AMP

Heat capacity is one of the most fundamental thermodynamic properties of substances. In this paper, the low-temperature heat capacity of the organic compound over the temperature range (80 to 398 K) was measured by an automated adiabatic calorimeter. A solid–liquid phase transition was observed and the enthalpy and the entropy of the phase transition were determined based on the heat capacity measurements. The standard molar enthalpy of formation was determined by oxygen-bomb combustion calorimetry.

Experimental

Sample

The sample of AMP used in this study, which was purchased from ACROS ORGANICS Company, is colorless crystal. The labeled mole fraction purity is >99.0%.

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The sample was purified by recrystallizing it three times using ethanol with an analytical grade prior to the calorimetric experiments.

Instrumental methods

Adiabatic calorimetry

A precision automatic adiabatic calorimeter was applied to measure the heat capacities over the temperature range from 80 to 398 K. The calorimeter was established in the Thermochemistry Laboratory of Dalian Institute of Chemical Physics, Chinese Academy of Sciences. The principle and structure of the adiabatic calorimeter were described in detail elsewhere [9–11]. The sample amount used for the heat capacity measurements is 2.39777 g, equivalent to 22.173 mmol, based on a molar mass of 108.14 g mol^{-1}. The heating duration and temperature increment for each experimental heat capacity point was usually controlled to be about 10 min and (1 to 3 K), respectively, during the whole experimental process.

Prior to the heat capacity measurements of the sample, the reliability of the calorimetric apparatus was verified by heat capacity measurements of the reference standard material, α-Al_2O_3. The deviations of our experimental values from those of the smoothed curve lie within ±0.2%, while the uncertainty is within ±0.3%, as compared with the recommended values reported by Archer [12] of NIST in the temperature range from 80 to 405 K.

Oxygen bomb combustion calorimetry

The constant-volume enthalpy of combustion of the sample was measured by means of a precision oxygen bomb combustion calorimeter, which is an isoperibolic calorimeter with a static oxygen bomb. The calorimeter was set up in our thermochemistry laboratory and the structure and the procedure of work of the calorimeter have been described previously in detail [13, 14].

The sample (about 0.6 g) was pressed into pellets and put in a small sample crucible (about 0.004 dm^3), which was suspended in the bomb (about 0.3 dm^3), and burned under an oxygen pressure of 3.00 MPa ignited by a nickel fuse of about 16 cm length. The purity of the oxygen used in the combustion was of 'research grade', with mole fraction 0.99998. The real energy of combustion of the nickel fuse (Q_{Ni}) was calculated from the formula, $Q_{\mathrm{Ni}}/J=2.929\Delta L$, in which ΔL/cm was the length of the combusted nickel wire. The amount of the aqueous nitric acid produced by oxidation of traces of nitrogen, which were contained in the oxygen bomb, was determined by the neutral acid-base titration with a 0.05892 mol dm^{-3} of sodium hydroxide solution by using the phenolphthalein as the indicator. The energy correction for the formation of the aqueous nitric acid in the combustion was based on the molar energy of formation of HNO_3(aq) from N_2(g), O_2(g) and H_2O(l), $\Delta_c U^{\circ}_{\mathrm{m}}$ is 59.87 kJ mol^{-1} for 0.1 mol dm^{-3} of HNO_3(aq) [15].

Results and discussion

Heat capacity

The experimental molar heat capacities obtained by the adiabatic calorimeter over the temperature range from 80 to 398 K are shown in Fig. 2 and tabulated in Table 1. From Fig. 2, it can be seen that in the two ranges of T=80 to 336 K and T=351 to 398 K the heat capacities of the sample increase in a smooth and continuous manner, respectively; and no phase transition or thermal anomaly occurred. Therefore, the sample is stable in the above temperature range. However, a thermal anomaly was observed in the temperature range from 336 to 351 K with the peak temperature 350.426 K. The thermal anomaly can be ascribed to a solid–liquid phase transition according to its melting point.

The values of experimental heat capacities can be fitted to the following polynomial equations by least square method:

For the solid phase over the temperature range 80 to 336 K:

$$C_{p,m}/\mathrm{J\ K^{-1}\ mol^{-1}} = 104.46283 + 50.8611X - 14.84607X^2 + 0.09571X^3 + 12.7139X^4 \quad (1)$$

where X is the reduced temperature $X=[T-(T_{\max}+T_{\min})/2]/[(T_{\max}-T_{\min})/2]$, T the experimental temperature, thus, in the solid state (80 to 336 K), $X=[(T/\mathrm{K})-208]/128$, $T_{\max}$ is the upper limit (336 K) and $T_{\min}$ is the lower limit (80 K) of the above temperature region. The correlation coefficient of the fitting is R^2=0.9964.

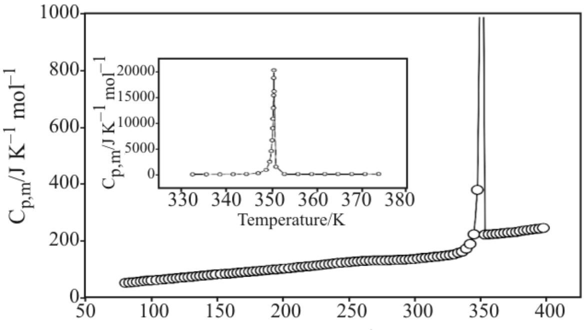

Fig. 2 Experimental molar heat capacity $C_{p,m}$ of AMP as a function of temperature

For the liquid phase over the temperature range 351 to 398 K:

$$C_{p,m}/\text{J K}^{-1}\text{ mol}^{-1} = 228.2934 + 13.57702X + 4.97008X^2 - 1.24714X^3 - 2.40173X^4 \tag{2}$$

where X is the reduced temperature, X=[(T/K)–374.5]/23.5. The correlation coefficient of the fitted curve is R^2=0.9984.

Table 1 Experimental molar heat capacity of AMP (M=108.14 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}
80.513	49.212	198.008	99.045	317.284	142.540
83.511	50.378	200.954	99.845	320.304	143.996
86.517	51.747	204.623	101.388	323.217	145.676
89.418	53.115	208.253	102.993	326.332	147.692
92.264	54.935	211.187	105.222	329.415	149.983
95.036	56.690	214.168	106.059	332.520	155.003
97.745	57.680	217.120	107.508	335.553	159.219
100.386	58.335	220.052	108.447	338.530	169.836
103.964	59.389	223.019	109.774	341.465	186.191
107.696	60.671	226.026	110.939	344.386	220.165
110.634	62.231	228.985	112.664	346.976	376.724
113.601	63.582	231.949	114.690	348.697	1024.178
116.553	64.901	234.961	116.104	349.507	2608.985
119.493	66.262	237.956	117.404	349.862	4653.035
122.463	67.385	240.913	119.238	350.052	6737.467
125.424	68.562	244.452	120.309	350.166	9067.023
128.382	69.752	248.019	121.953	350.246	10859.332
131.335	70.946	250.990	123.080	350.309	12968.417
134.287	72.679	253.929	124.653	350.360	15383.194
137.237	73.823	256.833	125.316	350.393	18724.452
140.186	75.019	259.796	126.157	350.426	20236.324
143.135	76.680	262.807	126.921	350.458	16170.161
146.086	78.163	265.795	127.304	350.850	1650.785
149.038	79.632	268.763	127.954	352.753	219.182
152.850	80.594	271.704	128.068	355.739	220.309
156.670	81.664	274.753	128.399	358.723	221.180
159.608	82.390	277.859	128.947	361.636	222.513
162.520	83.363	280.937	129.597	364.527	223.500
165.458	85.035	283.986	129.941	367.550	224.941
168.425	86.209	287.005	130.285	370.482	226.100
171.366	87.353	289.993	130.935	373.469	227.280
174.288	88.611	292.960	131.489	376.442	228.850
177.234	89.871	295.914	132.213	379.410	231.704
180.211	91.338	298.941	133.117	382.351	233.872
183.166	92.736	302.021	135.015	385.290	235.452
186.102	93.760	305.096	136.761	388.233	237.286
189.062	95.167	308.159	137.937	391.171	239.225
192.057	96.457	311.212	139.361	394.093	240.702
195.037	97.130	314.253	141.077	397.011	243.070

Melting temperature, enthalpy and entropy of fusion

The standard molar enthalpy and entropy of fusion $\Delta_{\text{fus}}H^0_{\text{m}}$ and $\Delta_{\text{fus}}S^0_{\text{m}}$ of the sample were derived according to the following Eqs (3) and (4):

$$\Delta_{\text{fus}}H^0_{\text{m}} = \\ = \frac{Q - n\int_{T_i}^{T_m} C_{p(S)}\mathrm{d}T - n\int_{T_m}^{T_f} C_{p(L)}\mathrm{d}T - \int_{T_i}^{T_f} \overline{C}_0\mathrm{d}T}{n} \qquad (3)$$

$$\Delta_{\text{fus}}S^0_{\text{m}} = \frac{\Delta_{\text{fus}}H^0_{\text{m}}}{T_{\text{m}}} \qquad (4)$$

where T_{i} is the temperature that is slightly below the starting melting temperature and T_{f} is the temperature slightly higher than that of the transition completion; Q is the total energy introduced into the sample cell from T_{i} to T_{f}; $\overline{C}_0$ is the heat capacity of the sample cell from T_{i} to T_{f}; $C_{\text{p(S)}}$ is the heat capacity of the sample in solid phase from T_{i} to T_{m}; $C_{\text{p(L)}}$ is 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: T_{m}=350.431±0.018 K, $\Delta_{\text{fus}}H^0_{\text{m}}$=18.108 kJ mol^{-1} and $\Delta_{\text{fus}}S^0_{\text{m}}$=51.676 J K^{-1} mol^{-1}.

Thermodynamic functions of AMP

The thermodynamic functions relative to the reference temperature 298.15 K were calculated in the temperature range 80 to 336 and 351 to 398 K with an interval of 5 K, using the polynomial equation for heat capacity and thermodynamic relationships as follows:

Before melting of the sample,

$$H_{\text{T}} - H_{298.15\text{ K}} = \int_{298.15}^{T} C_{\text{p,m}}(\text{s})\mathrm{d}T \qquad (5)$$

$$S_{\text{T}} - S_{298.15\text{ K}} = \int_{298.15}^{T} C_{\text{p,m}}(\text{s})/T\mathrm{d}T \qquad (6)$$

After melting of the sample,

$$H_{\text{T}} - H_{298.15\text{ K}} = \\ = \int_{298.15}^{T_{\text{m}}} C_{\text{p,m}}(\text{s})\mathrm{d}T + \Delta_{\text{fus}}H_{\text{m}} + \int_{T_{\text{f}}}^{T} C_{\text{p,m}}(l)\mathrm{d}T \qquad (7)$$

$$S_{\text{T}} - S_{298.15\text{ K}} = \\ = \int_{298.15}^{T_{\text{i}}} \frac{C_{\text{p,m}}(\text{s})}{T}\mathrm{d}T + \frac{\Delta_{\text{fus}}H_{\text{m}}}{T_{\text{m}}} + \int_{T_{\text{f}}}^{T} \frac{C_{\text{p,m}}(l)}{T}\mathrm{d}T \qquad (8)$$

Table 2 Calculated thermodynamic function data of AMP

T/K	$C_{\text{p,m}}$/ J K^{-1} mol^{-1}	H_{T}–$H_{298.15\text{ K}}$/ kJ mol^{-1}	S_{T}–$S_{298.15\text{ K}}$/ J K^{-1} mol^{-1}
80	51.374	–20.674	–112.140
95	52.635	–20.414	–108.989
90	54.066	–20.147	–105.940
95	55.648	–19.873	–102.975
100	57.366	–19.590	–100.078
105	59.203	–19.299	–97.235
110	61.145	–18.998	–94.336
115	63.178	–18.687	–91.673
120	65.288	–18.366	–88.940
125	67.462	–18.034	–86.231
130	69.688	–17.691	–83.542
135	71.955	–17.337	–80.869
140	74.251	–16.972	–78.211
145	76.568	–16.595	–75.565
150	78.895	–16.206	–72.930
155	81.225	–15.806	–70.305
160	83.549	–15.394	–67.689
165	85.860	–14.970	–65.083
170	88.151	–14.535	–62.486
175	90.418	–14.089	–59.898
180	92.655	–13.631	–57.319
185	94.857	–13.162	–54.750
190	97.022	–12.683	–52.192
195	99.145	–12.192	–49.644
200	101.226	–11.691	–47.107
205	103.263	–11.180	–44.582
210	105.254	–10.659	–42.070
215	107.200	–10.127	–39.570
220	109.102	–9.587	–37.084
225	110.960	–9.036	–34.611
230	112.778	–8.477	–32.152
235	114.557	–7.909	–29.708
240	116.301	–7.332	–27.277
245	118.015	–6.746	–24.861
250	119.704	–6.151	–22.460
255	121.373	–5.549	–20.073
260	123.028	–4.938	–17.700
265	124.676	–4.318	–15.341
270	126.326	–3.691	–12.995
275	127.986	–3.055	–10.662
280	129.665	–2.411	–8.340
285	131.372	–1.758	–6.030
290	133.119	–1.097	–3.730
295	134.917	–0.427	–1.439
298.15	136.082	0.000	0.000

Table 2 Continued

T/K	$C_{p,m}$/ J K^{-1} mol^{-1}	H_T–$H_{298.15\,K}$/ kJ mol^{-1}	S_T–$S_{298.15\,K}$/ J K^{-1} mol^{-1}
300	136.778	0.252	0.844
305	138.715	0.941	3.121
310	140.741	1.640	5.393
315	142.869	2.349	7.662
320	145.117	3.069	9.929
325	147.497	3.800	12.198
330	150.028	4.544	14.469
335	152.726	5.301	16.745
340	Phase change	–	–
345	Phase change	–	–
350	Phase change	–	–
355	220.023	25.264	73.700
360	221.753	27.440	79.786
365	223.635	29.671	85.939
370	225.881	31.958	92.163
375	228.585	34.306	98.466
380	231.720	36.718	104.856
385	235.145	39.198	111.338
390	238.598	41.746	117.915
395	241.701	44.365	124.587

The values of thermodynamic function H_T–$H_{298.15}$ and S_T–$S_{298.15}$ are listed in Table 2.

Purity determination of the sample

Adiabatic calorimetry provides an accurate way for determining the purity of a substance in the fusion region of solid–liquid phase transition. Here, we suppose that the impurity resolves ideally in the liquid phase of the sample and does not resolve at all in the solid phase. The total amount of impurities does not exceed a couple of mole%. According to the ideal solution law, the relation between the mole fraction N (N<<1) of a small amount of impurities in the sample and its melting point depression is as follows:

$$N=\frac{\Delta_{\text{fus}}H^{0}_{\text{m}}(T_0-T_1)}{RT_0^2} \tag{9}$$

where T_0 is the melting temperature of an absolutely pure substance; T_1 is the melting temperature of the given sample; $\Delta_{\text{fus}}H^{0}_{\text{m}}$ is the standard molar enthalpy of fusion of the sample; and R is the gas constant. As for the liquid solution formed by a part of the sample melted, given that N' is the mole fraction of the impurities and T is the melting temperature of the solution, then N' can be obtained by

$$N'=\frac{\Delta_{\text{fus}}H^{0}_{\text{m}}(T_0-T)}{RT_0^2} \tag{10}$$

If it is assumed that the impurities are solid-insoluble and all of the impurities are transferred completely into the liquid phase when the melting started, the relative amount of the sample in the liquid phase will be increasingly more in the process of the melting; on the other hand, since the total amount of the impurities remains constant, the mole fraction of the impurities in the liquid phase will gradually decrease. Given: F is the ratio of the amount of the sample in the liquid phase to the total amount of the sample, then

$$F=\frac{q}{Q} \tag{11}$$

where F is also designated as the fraction melted, its value being the ratio of the heat required to melt a part of the sample q to the total heat required to melt the whole sample Q. The heat q introduced into the sample can be measured by the adiabatic calorimeter, and $Q=n\Delta_{\text{fus}}H^{0}_{\text{m}}$. Obviously, F is inversely proportional to the mole fraction of the impurities in the liquid phase; that is

$$N'=\frac{1}{F}N \tag{12}$$

Substituting Eqs (7) and (8) into (10), we can get

$$T_0-T=\frac{1}{F}(T_0-T_1) \tag{13}$$

Equation (11) suggests that the relationship between the equilibrium melting temperature T and the re-

Table 3 Experimental values of melted fraction (F) and equilibrium temperature (T) of AMP

q/J	F	1/F	T/K
31.406	0.0782	12.7845	346.976
58.407	0.1455	6.8743	348.697
90.198	0.2246	4.4514	349.507
123.732	0.3082	3.2450	349.862
158.059	0.3937	2.5402	350.052
192.735	0.4800	2.0832	350.166
227.589	0.5668	1.7642	350.246
262.565	0.6539	1.5292	350.309
297.727	0.7415	1.3486	350.360
332.897	0.8291	1.2061	350.393
368.059	0.9167	1.0909	350.426

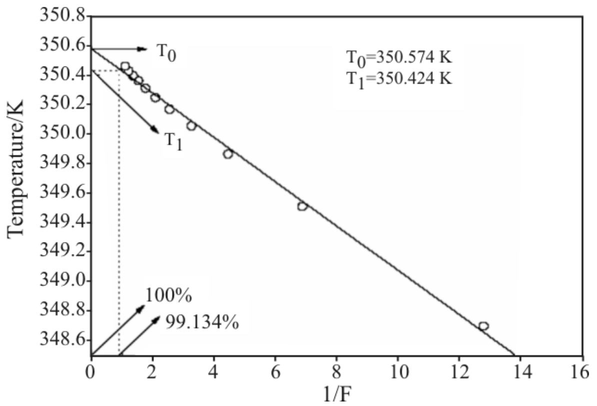

Fig. 3 Melting curve (*T vs.* 1/*F*) of AMP

ciprocal of melting fraction 1/*F* is linear. By plotting *T vs.* 1/*F* and extrapolating the straight line to 1/*F*=1 and 1/*F*=0, T_1 and T_0 can be derived. The results are tabulated in Table 3 and plotted in Fig. 3, where T_1=350.424 and T_0=350.574 K are obtained. The melting temperature (T_1=350.424 K) agrees well with that (T_m= 350.431±0.018 K) obtained from the heat capacity measurements as described earlier. From Eq. (7), *N*=0.00266 mole is evaluated. The mole fraction purity of the sample is 1–*N*= 99.734%.

Energy of combustion, standard molar enthalpy of combustion, and standard enthalpy of formation

The constant-volume combustion energy can be calculated from the equation:

$$\Delta_c U = (\varepsilon_{calor}\Delta T - Q_{Ni} - Q_{HNO_3})M/W \qquad (14)$$

where ε_{calor} is the energy equivalent of the oxygen bomb calorimeter; ΔT is the corrected temperature rise; *M* is the molar mass of the sample; *W* is the mass of the sample. The results calculated by the equation are listed in Table 4.

The standard molar enthalpy of combustion of the organic compound, $\Delta_c H_m^0$, referred to the combustion enthalpy change of the following reaction at *T*=298.15 K and p^o=100 kPa based on the definition of the combustion enthalpy of the organic compound:

$$C_6H_8N_2(cr) + 8O_2(g) = 6CO_2(g) + \\ +4H_2O(l) + N_2(g) \qquad (15)$$

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

$$\Delta_c H_m^0 = \Delta_c U_m^0 + \Delta nRT \qquad (16)$$

$$\Delta n = \sum n_i \text{ (products, g)} - \sum n_i \text{ (reactants, g)} \qquad (17)$$

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 organic compound was $\Delta_c H_m^0$ = –3502.64±1.51 kJ mol^{-1}.

The standard molar enthalpy of formation, $\Delta_f H_m^0$, was calculated by a designed Hess thermochemical cycle according to the Eq. (13) as follows:

$$\Delta_f H_m^0(C_6H_8N_2,cr) = [6\Delta_f H_m^0(CO_2,g) + \\ + 4\Delta_f H_m^0(H_2O,l)] - \Delta_c H_m^0(C_6H_8N_2,cr) \qquad (18)$$

In the above equation, the standard molar enthalpies of formation of CO_2(g) and H_2O(l), recommended by CODATA [16], $\Delta_f H_m^0(CO_2,g)$= –393.51±0.13 kJ mol^{-1}, and $\Delta_f H_m^0(H_2O,l)$= –285.83±0.04 kJ mol^{-1}, were employed in the calculation of $\Delta_f H_m^0(C_6H_8N_2,cr)$ values. Based on these val-

Table 4 Experimental results of constant-volume combustion energy for AMP

No.	Sample mass m/g	Heat value of nickel wire Q_{Ni}/J	Heat value of nitric acid Q_N/J	Corrected temp. rise ΔT/K	Combustion energies ΔU_C/kJ mol^{-1}
1	0.60622	36.024	72.162	1.3966	3493.58
2	0.60630	38.953	70.364	1.4012	3504.54
3	0.60038	40.710	66.345	1.3869	3503.05
4	0.61755	38.660	69.377	1.4243	3497.87
5	0.60719	40.125	61.092	1.3983	3493.62
6	0.60721	38.660	62.714	1.4016	3501.59
7	0.58720	39.246	61.798	1.3553	3500.87
8	0.61319	41.296	72.585	1.4182	3506.63
9	0.61040	39.832	69.553	1.4087	3499.69
Average ΔU_c=$(\overline{\Delta U_c} \pm \sigma_a)^a$ = –3500.15±1.51 kJ mol^{-1}					

$^a\sigma_a = \sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 / n(n-1)}$, in which *n* is the number of experimental determinations (*n*=9); x_i a single value of combustion energies; $\bar{x}$ is the mean value of combustion energies ues and the standard molar enthalpy of combustion, the standard molar enthalpy of formation of AMP could be calculated: $\Delta_f H_m^0(C_6H_8N_2,cr)=-1.74\pm0.57\ kJ\ mol^{-1}$.

Conclusions

The heat capacities of AMP were measured in the temperature range from 80 to 398 K by a high-precision automated adiabatic calorimeter. From the results of heat capacity experiment, the thermodynamic properties of fusion were completely studied, and the thermodynamic functions $(H_T-H_{298.15})$ and $(S_T-S_{298.15})$ were derived in the range from 80 to 390 K with temperature intervals of 5 K. The melting temperature T_m, the standard molar enthalpy $\Delta_{fus}H_m^0$ and the entropy $\Delta_{fus}S_m^0$ of fusion were determined to be 350.431±0.018 K, 18.108 kJ mol^{-1} and 51.676 J K^{-1} mol^{-1}, respectively. The chemical purity was calculated to be 0.99734 mol fraction according to the Van't Hoff equation. The standard molar enthalpy of formation of AMP was derived to be -1.74 ± 0.57 kJ mol^{-1} with a precision oxygen bomb combustion calorimeter.

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