三聚氰胺的生成焓、热容和熵

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摘要: 通过多种热化学方法研究了三聚氰胺的热力学性质. 首先用氧弹式燃烧热量计测定了三聚氰胺在298.15 K 时的燃烧热, 根据燃烧热结果, 计算出三聚氰胺的标准摩尔燃烧焓和标准摩尔生成焓, 分别为: $\Delta_c H_m^\ominus = (-2455.17 \pm 4.65) \text{ kJ} \cdot \text{mol}^{-1}$; $\Delta_f H_m^\ominus = (-763.38 \pm 5.16) \text{ kJ} \cdot \text{mol}^{-1}$. 然后根据键焓与燃烧焓之间的关系, 估算出三聚氰胺中的 C $\approx$ N(此键介于单键与双键之间)键能为 $458.30 \text{ kJ} \cdot \text{mol}^{-1}$, 此值介于碳氮单键键能和双键键能之间. 通过绝热热量计测定了三聚氰胺从 80 到 385 K 的低温热容. 根据热容值, 计算了此温度区间的标准摩尔生成焓, 其与温度呈线性关系. 另外, 三聚氰胺的热稳定性也用热重-差示扫描量热(TG-DSC)法进行了分析, 确定其分解的 DSC 曲线的峰顶温度为 603.37 K.

关键词: 热容; 三聚氰胺; 燃烧热; 绝热热量计

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Enthalpy of Formation, Heat Capacity and Entropy of Melamine

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Abstract: The thermodynamic properties of melamine were studied by multiple thermochemical methods. A bomb combustion calorimeter was used to determine the combustion heat of melamine at 298.15 K. According to the results, we calculated the standard molar enthalpy of combustion and standard molar enthalpy of formation of melamine: $\Delta_c H_m^\ominus = (-2455.17 \pm 4.65) \text{ kJ} \cdot \text{mol}^{-1}$; $\Delta_f H_m^\ominus = (-763.38 \pm 5.16) \text{ kJ} \cdot \text{mol}^{-1}$. The bond enthalpy of C $\approx$ N (between single bond and double bond) in melamine was then estimated to be $458.30 \text{ kJ} \cdot \text{mol}^{-1}$ according to the relationship between bond enthalpy and combustion enthalpy. This value is larger than that of C—N but smaller than that of C=N. Heat capacity measurements were carried out in a small sample adiabatic calorimeter from 80 to 385 K. We obtained $\Delta_f H_m^\ominus$ at different temperatures between 80 and 385 K using the heat capacity data. Through calculation with the values of heat capacity, the relationship between the standard molar enthalpy of formation and temperature is also presented as a functional equation. We also measured the thermal stability of melamine by the thermogravimetry-differential scanning calorimetry (TG-DSC) technique, which showed a thermal decomposition peak at 603.37 K for the DSC curve.

Key Words: Heat capacity; Melamine; Combustion heat; Adiabatic calorimeter

Melamine (molecular structure: Fig.1; formula: $\text{C}_3\text{H}_6\text{N}_6$; molecular mass: $126.12 \text{ g} \cdot \text{mol}^{-1}$) is an organic base and a trimer of cyanamide, with a 1,3,5-triazine skeleton. Like cyanamide, it

contains 66% (mass fraction) nitrogen and, if mixed with resins, has fire retardant properties due to its release of nitrogen gas when burned or charred, and has several other industrial uses^[1-5].

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Fig.1 Structure diagram of melamine

Melamine is also a metabolite of cyromazine, a pesticide^[6]. Melamine is combined with formaldehyde to produce melamine resin, a very durable thermosetting plastic used in Formica, and melamine foam, a polymeric cleaning product^[7]. Melamine also enters the fabrication of melamine poly-sulfonate used as super plasticizer for making high-resistance concrete^[8]. The use of melamine as fertilizer for crops had been envisaged during the 1950s and 1960s because of its high nitrogen content.

Melamine is sometimes illegally added to food products in order to increase the apparent protein content. Standard test, such as the Kjeldahl and Dumas tests, estimate protein levels by measuring the nitrogen content^[9-11], so they can be misled by adding nitrogen-rich compounds such as melamine. In September 2008, several companies were implicated in a scandal involving milk infant formula which had been adulterated with melamine, leading to kidney stones and other renal failure, especially among young children.

Because the thermodynamics of a compound is involved in the quantitative studies on the energetic, these parameters are very important for the quantum chemistry, computer-aided molecular designs of drugs and new materials, and biochemical reactions. As a common compound, melamine has caused the shock in the field of food safety. However, the mechanism how melamine becomes kidney stones in body is not very clear. One possible reason is that melamine combines with cyanuric acid to form melamine cyanurate, then settled in renal^[12-15]. So there is a need for studying the thermodynamic parameters of melamine to calculate the thermodynamic properties of the reaction involved with melamine in body. In the present study, an adiabatic calorimeter was used to determine the heat capacity of melamine in the temperature range from 80 to 385 K. Besides, we tried to measure the standard molar enthalpy of formation of melamine by combustion heat at 298.15 K. Thermal analysis technique was used to evaluate the heat stability of melamine.

1 Experimental

1.1 Materials

Anhydrous melamine (solid) was bought from Bodi Chemical Corporation of Tianjin and its purity was above 99.5%. Its molecular structure is shown in Fig.1.

1.2 Methods

1.2.1 Measurement of enthalpy of combustion

The combustion heat of melamine was measured by Bomb Combustion Calorimeter (Changsha Instrumental, SF-GR3500, China). The temperature of the water thermostat was maintained

at $T=298.15$ K. The water temperature in the caloritube was subsequently adjusted to be lower than that of the water thermostat. A known amount of twice distilled water was added into the calorimeter. When the sample was placed in the crucible fixed on the support in the bomb, the Ni wire was fixed in the bomb. After the bomb was filled with 2.4 MPa oxygen gas, it was sealed. Before the calorimetric test, the calorimeter was set up well. It was important to keep up a constant temperature change rate in the calorimeter at the beginning of the experiment. In the early period of the experiment, the magnitudes of the temperature were recorded *vs* time typically with one entry every 5 s. Then the sample was ignited until the main period of the combustion reaction was finished. In the later period of the experiment, the magnitudes of the temperature were recorded in the early period of the experiment. After the experiment was accomplished, the final products of the combustion reaction were analyzed. The change of temperature was recorded. The analysis methods have been discussed in the literature^[16]. The analytical results of the final solution showed that the combustion reactions were complete. Neither carbon deposits nor carbon monoxide was formed during the combustion reactions. The amount of NO_x in the final gas was insignificant. The NIST standard reference material, benzoic acid, was used to calibrate the combustion calorimeter^[17].

1.2.2 Measurement of molar heat capacity of melamine

The heat capacity measurement was carried out in a small sample adiabatic calorimeter over the temperature range from 80 to 385 K. The adiabatic calorimeter was constructed in the Dalian Institute of Chemical Physics, Chinese Academy of Sciences, the detailed description of which has been described in the literature^[18-21]. Before the experiment, the molar heat capacities of synthetic sapphire (Al_2O_3 , standard reference material 720, National Institute of Standards and Technology) were measured in the same temperature range to verify the reliability of the adiabatic calorimeter. The deviations of the experimental results from the recommended values of NIST were within $\pm 0.5\%$ from 80 to 385 K.

1.2.3 Thermal stability of melamine determined by TG-DSC

The TG-DSC instrument (NETZSCH STA 449 C) was run under sub-ambient temperature conditions. The sample chamber was purged with dry nitrogen at $10 \text{ mL} \cdot \text{min}^{-1}$. The heating rate was $10 \text{ K} \cdot \text{min}^{-1}$, and the temperature range was from room temperature to 773 K.

2 Results and discussion

The constant-volume energy of combustion of melamine, $\Delta_c U_m^\ominus$, was $-(2451.45 \pm 4.65) \text{ kJ} \cdot \text{mol}^{-1}$, which was determined by a combustion calorimeter for five times. The standard molar enthalpy of combustion of melamine, $\Delta_c H_m^\ominus$, refers to the combustion enthalpy change of the following ideal combustion reaction at $T=298.15$ K and $p=101.325$ kPa.

The standard molar enthalpy of combustion of melamine was

Table 1 The estimation of molar enthalpy of combustion of melamine by bond enthalpies

Bond of reactant	Number	Average bond enthalpy (kJ·mol ⁻¹)	Bond of product	Number	Average bond enthalpy (kJ·mol ⁻¹)
C≈N	6	$\Delta_b H_{C\approx N}^\ominus$	C=O(CO ₂)	3×2=6	799
C—N	3	293	O—H(H ₂ O)	3×2=6	463
O=O(O ₂)	4.5	495	N≡N(N ₂)	3	954.4
N—H	6	354			

$\Delta_c H_m^\ominus = \sum (\text{bond enthalpies of bonds broken}) - \sum (\text{bond enthalpies of bonds formed}) = 5230.5 + 6\Delta_b H_{C\approx N}^\ominus - 10435.2 = -2455.17 \text{ kJ}\cdot\text{mol}^{-1}$; $\Delta_b H_{C\approx N}^\ominus = 458.3 \text{ kJ}\cdot\text{mol}^{-1}$

calculated from the constant-volume energy of combustion at $T=298.15 \text{ K}$ by the following equation:

$\Delta_c H_m^\ominus = \Delta_c U_m^\ominus + \Delta(pV) = \Delta_c U_m^\ominus + \Delta n \cdot RT$

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

where n is the total amount (in mol) of gas present as products or reactants, $\Delta n = -1.5 \text{ mol}$, $R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, $T = 298.15 \text{ K}$. We could obtain the standard molar enthalpy of reaction, $\Delta_c H_m^\ominus = (-2455.17 \pm 4.65) \text{ kJ}\cdot\text{mol}^{-1}$. With the standard enthalpy of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ at 298.15 K , the standard molar enthalpy of formation of melamine could be obtained, $\Delta_f H_m^\ominus = (-763.38 \pm$

$5.16) \text{ kJ}\cdot\text{mol}^{-1}$.

The enthalpy of combustion reaction of melamine could also be estimated by the average bond enthalpies without considering the intermolecular forces^[22-24]. $\Delta_c H_m^\ominus = \sum (\text{bond enthalpies of bonds broken}) - \sum (\text{bond enthalpies of bonds formed})$. Because the melamine is of aromaticity, the bond of $\text{C} \approx \text{N}$ on the ring is equivalent. The bond enthalpy of $\text{C} \approx \text{N}$ could be calculated from the molar enthalpy of combustion of melamine. The process of calculation was shown in Table 1. The bond enthalpy of $\text{C} \approx \text{N}$ is $458.30 \text{ kJ}\cdot\text{mol}^{-1}$. The reported bond enthalpies for $\text{C}—\text{N}$ and

Table 2 Calculated thermodynamic data of melamine

T/K	$C_{p,m}$ ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)	$(\Delta_c H_{m,298.15\text{ K}}^\ominus - \Delta_c H_{m,T}^\ominus)$ ($\text{kJ}\cdot\text{mol}^{-1}$)	$(S_{m,298.15\text{ K}}^\ominus - S_{m,T}^\ominus)$ ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)	$\Delta_c H_{m,T}^\ominus$ ($\text{kJ}\cdot\text{mol}^{-1}$)	T/K	$C_{p,m}$ ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)	$(\Delta_c H_{m,298.15\text{ K}}^\ominus - \Delta_c H_{m,T}^\ominus)$ ($\text{kJ}\cdot\text{mol}^{-1}$)	$(S_{m,298.15\text{ K}}^\ominus - S_{m,T}^\ominus)$ ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)	$\Delta_c H_{m,T}^\ominus$ ($\text{kJ}\cdot\text{mol}^{-1}$)
80	41.462	-20.781	-110.067	-784.161	240	121.531	-7.880	-29.296	-771.260
85	43.851	-20.568	-107.482	-783.948	245	124.041	-7.266	-26.762	-770.646
90	46.316	-20.342	-104.903	-783.722	250	126.514	-6.639	-24.231	-770.019
95	48.808	-20.105	-102.330	-783.485	255	128.952	-6.000	-21.699	-769.380
100	51.294	-19.854	-99.762	-783.234	260	131.356	-5.350	-19.172	-768.730
105	53.755	-19.592	-97.199	-782.972	265	133.728	-4.687	-16.646	-768.067
110	56.182	-19.317	-94.644	-782.697	270	136.072	-4.012	-14.124	-767.392
115	58.573	-19.030	-92.096	-782.410	275	138.392	-3.326	-11.605	-766.706
120	60.931	-18.731	-89.555	-782.111	280	140.691	-2.629	-9.091	-766.009
125	63.265	-18.421	-87.022	-781.801	285	142.975	-1.919	-6.581	-765.299
130	65.583	-18.098	-84.497	-781.478	290	145.247	-1.199	-4.075	-764.579
135	67.897	-17.765	-81.978	-781.145	295	147.511	-0.467	-1.574	-763.847
140	70.217	-17.419	-79.466	-780.799	298.15	148.935	0.000	0.000	-763.380
145	72.553	-17.063	-76.961	-780.443	300	149.770	0.276	0.924	-763.104
150	74.914	-16.694	-74.460	-780.074	305	152.024	1.030	3.417	-762.349
155	77.306	-16.313	-71.963	-779.693	310	154.275	1.797	5.906	-761.584
160	79.735	-15.921	-69.469	-779.301	315	156.522	2.574	8.392	-760.807
165	82.203	-15.516	-66.977	-778.896	320	158.762	3.362	10.874	-760.018
170	84.712	-15.099	-64.485	-778.479	325	160.992	4.161	13.353	-759.219
175	87.261	-14.669	-61.993	-778.049	330	163.205	4.972	15.828	-758.408
180	89.846	-14.226	-59.498	-777.606	335	165.396	5.793	18.299	-757.587
185	92.464	-13.770	-57.001	-777.15	340	167.557	6.626	20.766	-756.755
190	95.109	-13.301	-54.501	-776.681	345	169.680	7.469	23.229	-755.911
195	97.775	-12.819	-51.997	-776.199	350	171.758	8.322	25.686	-755.058
200	100.454	-12.324	-49.489	-775.704	355	173.784	9.186	28.138	-754.194
205	103.139	-11.815	-46.977	-775.195	360	175.755	10.060	30.583	-753.320
210	105.823	-11.292	-44.461	-774.672	365	177.670	10.944	33.019	-752.436
215	108.498	-10.756	-41.940	-774.136	370	179.536	11.837	35.449	-751.543
220	111.157	-10.207	-39.416	-773.587	375	181.364	12.739	37.869	-750.641
225	113.795	-9.645	-36.889	-773.025	380	183.178	13.650	40.283	-749.730
230	116.406	-9.069	-34.359	-772.449	385	185.012	14.571	42.689	-748.809
235	118.985	-8.481	-31.828	-771.861

Fig.2 Experimental molar heat capacity $C_{p,m}$ of melamine versus temperature

C=N are 293 and 615 kJ·mol⁻¹ [23]. It can be seen that the bond enthalpy of C≈N in melamine molecules is larger than that of single bond C—N and less than that of double bond C=N.

The heat capacities of melamine were measured with the adiabatic calorimeter over the temperature range from 80 to 385 K. The result is shown in Fig.2. The differences between 298.15 K and other temperatures for the formation enthalpy and entropy ($\Delta_f H_{m,298.15\text{ K}}^\ominus - \Delta_f H_{m,T}^\ominus$) and ($S_{m,298.15\text{ K}}^\ominus - S_{m,T}^\ominus$) were presented in Table 2. The temperature increment for each experimental point was about 3 K in the whole temperature range. No phase transition was observed in this temperature region. The data of the molar heat capacities of melamine between 80 and 385 K are very close to a straight line and can be represented by the following equation with a correlation coefficient of 0.9994.

$$C_{p,m} = 3.61 + 0.483T$$

According to the value of $\Delta_f H_m^\ominus$, the standard molar enthalpy of formation for melamine in the temperature range from 80 to 385 K can be calculated, which is shown in Table 2. To estimate the enthalpy of combustion of melamine with a wide range of temperature, the following recycle of thermo-chemistry was designed.

According to data in Refs.[25,26], it can be known that $C_{p,m}(\text{CO}_2) = 44.22 + 8.79 \times 10^{-3}T - 8.62 \times 10^{-5}T^2$, $C_{p,m}(\text{O}_2) = 29.96 + 4.18 \times 10^{-3}T - 1.67 \times 10^{-5}T^2$, $C_{p,m}(\text{H}_2\text{O}) = 75.48$, $C_{p,m}(\text{N}_2) = 28.58 + 3.76 \times 10^{-3}T - 0.56 \times 10^{-6}T^2$.

$$\Delta_c H_{m,T}^\ominus = \Delta_c H_{m,298.15\text{ K}}^\ominus + \Delta H_1 + \Delta H_2$$

$$= \Delta_c H_{m,298.15\text{ K}}^\ominus + \int_{298.15}^T \Delta C_{p,m} dT$$

$$= \Delta_c H_{m,298.15\text{ K}}^\ominus + \int_{298.15}^T (306.41 - 0.49T -$$

$$1.68 \times 10^{-6}T^2 - 1.84 \times 10^{-9}T^3) dT$$

$$\Delta_c H_m^\ominus = -2455.17 + \frac{306.41T - 0.245T^2 - 0.56T^3 + 1.84 \times 10^{-6}T^4}{1000}$$

The TG-DTA measurements were carried out in N₂ atmo-

Fig.3 TG-DSC results of melamine from 323 to 773 K

sphere. The TG-DSC results are presented in Fig.3. It can be seen from the mass-loss curve that most of the activities occur from 495.15 to 607.15 K in a single step. No residue was found in the crucible after the experiment was completed. An obvious peak was observed from the DSC curve. The peak was associated with heat decomposition of melamine. Between room temperature and 603.37 K, no phase transition was observed.

3 Conclusions

The thermodynamic properties of melamine were studied by combination of several thermal chemistry technique, including the standard molar enthalpy of formation and the heat capacity over the temperature range from 80 to 385 K. From the data, it can be seen that the value of the standard molar enthalpy of formation is high, which means that melamine is a very stable compound. There is a linear relationship between the molar heat capacities of melamine and temperature from 80 to 385 K. Besides, according to the relation between the combustion enthalpy and the bond enthalpy, the bond enthalpy of C≈N in melamine was estimated. The value is smaller than that of C—N and larger than that of C=N, which can be attributed to the tension of C≈N in cyclic melamine molecule. By providing the fundamental thermodynamics of melamine, this study is insightful to understanding the biological effect of melamine *in vivo*.

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