[Article]

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配位化合物 $\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$ ($\text{Met}=\text{L}-\alpha$ -蛋氨酸)的 低温热容及标准摩尔生成焓

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摘要: 利用精密绝热热量计测定了配合化合物 $\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$ ($\text{Met}=\text{L}-\alpha$ -蛋氨酸)在 78–371 K 温区的摩尔热容. 通过热容曲线解析, 得到了该配合物的起始脱水温度为 $T_0=325.10$ K. 将该温区的摩尔热容实验值用最小二乘法拟合得到了摩尔热容(C_p)对约化温度(T)的多项式方程, 由此计算得到了配合物的舒平热容值和热力学函数值. 基于设计的热化学循环, 选择 100 mL 2 mol·L⁻¹ HCl 溶液为量热溶剂, 利用等温环境溶解-反应热量计, 得到了 298.15 K 配合物的标准摩尔生成焓 $\Delta_f H_m^\circ[\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}, \text{s}] = -(1472.65 \pm 0.76) \text{ J} \cdot \text{mol}^{-1}$.

关键词: 绝热量热法; 热容; 标准摩尔生成焓; 溶解-反应量热法; $\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$

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Low Temperature Heat Capacities and Standard Molar Enthalpy of Formation of the Coordination Compound $\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$ ($\text{Met}=\text{L}-\alpha$ -Methionine)

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Abstract: Low temperature heat capacities of the compound $\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$ have been measured by a precision automated adiabatic calorimeter over the temperature range 78–371 K. The initial dehydration temperature of the coordination compound was determined to be $T_0=325.10$ K by analysis of the heat-capacity curve. The experimental values of the molar heat capacities in the temperature region have been fitted to a polynomial equation of heat capacities with the reduced temperature (X), [$X=f(T)$], by the least squares method. Smoothed heat capacities and thermodynamic functions relative to the standard reference temperature 298.15 K of the compound were derived from the fitted polynomial equation and listed at 5 K intervals. Using 100 mL of 2 mol·L⁻¹ HCl(aq) as calorimetric solvent, with an isoperibol solution-reaction calorimeter, the standard molar enthalpy of formation of the compound was determined to be $\Delta_f H_m^\circ[\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}, \text{s}] = -(1472.65 \pm 0.76) \text{ J} \cdot \text{mol}^{-1}$ by a designed thermochemical cycle.

Key Words: Adiabatic calorimetry; Heat capacity; Standard molar enthalpy of formation; Isoperibol solution-reaction calorimetry; $\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$

1 Introduction

It is well known that zinc as one of the trace elements plays an important role in the physical growth of human beings, especially in intelligence development. Many diseases result from

deficiency of zinc in the human body, such as dwarfism, hypertension, rheumatoid arthritis, sugar diabetes, and cardiovascular diseases, etc. The L- α -amino acids are indispensable nutrients in organisms and the basic units of the proteins necessary

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for life activity. Zinc compounds with L- α -amino acids are considered to be one of the most efficient zinc tonics because they have a higher absorption ratio in the human body than traditionally inorganic and organic weak-acid zinc tonics. Such zinc coordination compounds showed wide applications in medicine, foodstuff, animal feed, and cosmetic as nutrient additive.¹⁻³ Gao *et al.*⁴ has investigated the phase chemistry of the coordination behavior of zinc salts with L- α -methionine by the method of semi-micro phase equilibrium. The corresponding equilibrium phase diagram and refractive index diagram have been constructed from the compositions of saturated solutions and the data on refractive indices in ternary systems of Zn-Met-H₂O. The compound, Zn(Met)₃(NO₃)₂ · H₂O(s), was synthesized in water and acetone under the guidance of equilibrium phase diagram, characterized by means of Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis/differential thermal analysis (TG/DTA), and the initial dehydration temperature (T_b) of the solid compound was reported to be 323.15 K by thermogravimetry.

However, other important thermodynamic properties of the compound have not been reported in the literature so far. In continuation of our studies on the compounds of zinc with L- α -amino acid, the low temperature heat capacities over the temperature range 78–371 K and the standard molar enthalpy of formation of the title compound at $T=298.15$ K have been measured by adiabatic calorimetry and isoperibol solution-reaction calorimetry, respectively. The resulting data would provide more thermodynamic supports for the practical application of the compound.

2 Experimental

2.1 Synthesis and characterization of the compound

ZnSO₄ · 7H₂O(s), NaNO₃(s), L- α -methionine(s), α -Al₂O₃(s), and HCl(aq) obtained from Shanghai Reagent Factory, China, were of analytical grade with purity prior to 99.50%. KCl(s) with 99.90% purity as Standard Reference Material 1655 was obtained from the National Institute of Standards and Technology. The solid compound, Zn(Met)₃(NO₃)₂ · H₂O(s) as white lumpy crystals, was prepared by a semi-micro phase equilibrium method.^{4,5} The solid compound obtained was kept in a desiccator containing P₄O₁₀. The results of chemical and elemental analyses, IR, TG/DTG, and XRD indicated that the compound was formulated as Zn(Met)₃(NO₃)₂ · H₂O(s). The purity of the compound was higher than 99.90% mass fraction (analytical uncertainty in mass fraction $\leq 0.20\%$).

2.2 Adiabatic calorimetry

A high-precision automatic adiabatic calorimeter was used to measure the heat capacities over the temperature range 78 K $\leq T \leq$ 371 K. The calorimeter was fabricated 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.^{6,7} Briefly, the calorimeter comprised a sample cell, a platinum re-

sistance thermometer, an electric heater, inner and outer adiabatic shields, two sets of six-junction chromel-constant thermopiles installed between the calorimetric cell and the inner shield and between the inner and outer shields, respectively, and a high vacuum can. The miniature platinum resistance thermometer (IPRT No.2, Shanghai Institute of Industrial Automatic Meters, 16 mm length, 1.6 mm 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, China. The electrical energy introduced into the sample cell and the equilibrium temperature of the cell after the energy input were automatically recorded with the Data Acquisition/Switch Unit (model 34970A, Agilent, USA), and processed online by a computer. To verify the accuracy of the calorimeter, the heat capacity of the reference standard material (α -Al₂O₃) was measured over the temperature range 78 K $\leq T \leq$ 373 K. The sample mass used was 1.6382 g, which was equivalent to 0.0161 mol based on its molar mass, $M(\text{Al}_2\text{O}_3)=101.9613$ g · mol⁻¹. The experimental molar heat capacities of α -Al₂O₃ were fitted by the least-squares method to a polynomial. Deviations of the experimental results from those of the smoothed curve lie within $\pm 0.2\%$, while the uncertainty is within 0.3%, when compared with the values given by the former National Bureau of Standards⁸ over the entire 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 controlled at 0.1–0.4 K · min⁻¹ and 1–3 K, respectively. The heating duration was 10 min, and the temperature drift rate of the sample cell measured during an equilibrium period was always kept within 10⁻³–10⁻⁴ K · min⁻¹ for acquisition of the heat capacity data. The data of heat capacities and corresponding equilibrium temperature have been corrected for heat exchange of the sample cell with its surroundings.^{6,7} The sample mass of Zn(Met)₃(NO₃)₂ · H₂O(s) used for the calorimetric measurement is 3.8993 g, which is equivalent to 0.00595 mol in terms of its molar mass, $M=655.0560$ g · mol⁻¹.

2.3 Isoperibol solution-reaction calorimetry

The isoperibol solution-reaction calorimeter is primarily consisted of a precision temperature controlling system, an electric energy calibration system, a calorimetric body, an electric stirring system, a thermostatic bath made from transparent silicate glass, a precision temperature measuring system and a data acquisition system. The principle and structure of the calorimeter have been described in detail elsewhere.⁹ The reliability of the calorimeter was verified initially by measuring the dissolution enthalpies of KCl (calorimetric primary standard) in doubly distilled water at $T=298.15$ K.⁹ The mean dissolution enthalpy was (17.547 $\pm$ 0.013) kJ · mol⁻¹ for KCl, which compares well with the corresponding published data, (17.536 $\pm$ 0.003) kJ · mol⁻¹.¹⁰ In all dissolution experiments, 100 mL of 2 mol · L⁻¹

HCl was chosen as the calorimetric solvent for measuring the dissolution enthalpies of the mixtures $\{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s}) + 2\text{NaNO}_3(\text{s}) + 3\text{Met}(\text{s})\}$ and $\{\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s}) + \text{Na}_2\text{SO}_4(\text{s})\}$. The solid samples, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s})$, $\text{NaNO}_3(\text{s})$, and $\text{Met}(\text{s})$, were ground in an agate mortar into a fine powder. The solid compounds were weighed on parchment paper separately to avoid mixing before dissolution. The mixture of ~ 0.288 g of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s})$, ~ 0.171 g of $\text{NaNO}_3(\text{s})$, and ~ 0.450 g of $\text{Met}(\text{s})$ at a mole ratio of $n(\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}):n(\text{NaNO}_3):n(\text{Met})=1:2:3$ was dissolved in 100 mL of $2 \text{ mol} \cdot \text{L}^{-1}$ HCl solution at $T=298.15$ K. The final solution obtained was designated as solution A. The solids, $\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$ and $\text{Na}_2\text{SO}_4(\text{s})$, were ground into a fine powder and dried in a vacuum drying oven in order to remove additional adsorbed water. The solid compounds were weighed on parchment paper separately to avoid mixing before dissolution. The dissolution enthalpy of the mixture of ~ 0.65 g of $\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$ and ~ 0.14 g of $\text{Na}_2\text{SO}_4(\text{s})$ at a mole ratio of $n(\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}):n(\text{Na}_2\text{SO}_4)=1:1$ in 100 mL of $2 \text{ mol} \cdot \text{L}^{-1}$ HCl solution was determined under the same conditions as mentioned above. The final solution obtained was named as solution A'. Finally, the UV/Vis spectra and the data of the refractive indices were used to confirm whether solution A was in the same thermodynamic state as that of solution A'. The results indicate that chemical components and physicochemical properties of solution A are consistent with those of solution A'.

3 Results and discussion

3.1 Low-temperature heat capacities

The structure of the coordination compound is shown to be stable over the temperature range 78–325 K, as shown in Table 1 and Fig.1. No phase change, association nor thermal decomposition is seen to occur. However, at temperatures above 325 K, the heat capacity curve rises steeply. The phenomenon is associated with the dehydration or thermal decomposition of the compound, as shown by TG analysis.⁴ In addition, the initial dehydration temperature (T_D) has been obtained by analysis of the heat capacity curve. Two sections of the heat capacity curves, i.e., 78–325 K and 326–371 K are extrapolated linearly. The intersection point of these two straight lines is the initial decomposition temperature, $T_D=325.10$ K (Fig.1). TG analysis shows the initial dehydration temperature of 323.15 K, the final dehydration temperature of 458.15 K and the mass loss of 2.79%. The mass loss is identical with the percentage of the water molecule in the coordination compound (the theoretical mass loss during dehydration is 2.75%). The initial dehydration temperature obtained from TG analysis is in agreement with that from the heat capacity curve. The main reason for the difference (1.90 K) between the two results is that the sample surface adsorbed moisture from the air during TG measurement. The surface adsorbed water removed prior to crystal water in the sample, which reduces the initial dehydration temperature and increases the actual mass loss of the sample. Howev-

Table 1 Experimental molar heat capacities of the compound $\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$ (molar mass $M=655.056 \text{ g} \cdot \text{mol}^{-1}$)

T/K	$C_{p,m}$ ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)	T/K	$C_{p,m}$ ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)	T/K	$C_{p,m}$ ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)
78.110	138.751	156.622	269.588	284.954	440.420
79.528	141.929	158.151	272.076	288.070	444.685
81.525	147.193	159.834	274.652	291.051	452.028
84.113	152.236	161.517	276.073	294.099	458.662
86.560	156.411	163.046	278.383	296.945	466.005
88.931	161.564	164.653	280.959	299.722	471.691
91.302	166.805	166.259	282.381	302.501	477.850
93.521	171.957	167.865	283.625	305.074	484.483
95.815	177.021	169.395	285.401	307.513	490.406
97.957	181.463	172.454	289.044	309.749	495.617
100.098	185.372	176.661	294.285	311.984	505.567
102.239	189.902	180.638	298.371	314.288	511.726
104.305	194.611	184.615	302.014	316.319	517.649
106.370	197.631	188.593	306.633	319.165	526.177
108.435	201.273	192.340	310.719	321.536	540.628
110.424	203.849	196.241	315.694	323.975	554.368
112.336	206.871	199.989	319.692	326.414	571.187
114.325	210.335	203.737	322.890	328.853	586.823
116.237	213.977	207.485	327.865	331.224	611.934
118.073	217.264	211.079	331.329	333.663	635.149
119.985	220.284	214.751	334.705	335.981	661.016
121.897	223.394	218.422	338.969	338.352	684.927
123.733	225.703	221.941	343.322	340.645	702.932
125.568	228.368	225.459	347.498	342.941	724.312
127.404	230.678	228.977	351.939	345.236	744.004
129.087	232.544	232.419	356.204	347.531	760.601
130.922	235.386	235.861	360.290	349.749	774.386
132.758	236.808	239.303	364.466	351.891	787.607
134.517	240.095	242.515	368.463	353.955	798.579
136.276	241.960	245.881	372.735	356.021	810.675
138.035	244.092	249.169	377.791	358.009	821.928
139.795	246.402	252.611	382.588	359.845	830.367
141.554	248.534	255.977	387.563	361.604	838.807
143.159	251.110	259.189	391.472	363.287	847.587
144.919	252.443	262.555	395.469	364.816	853.509
146.602	254.575	265.844	401.895	366.040	858.898
148.285	257.240	269.132	407.447	367.417	863.636
149.891	260.349	272.345	413.740	368.411	867.723
151.573	262.837	275.557	420.477	370.017	872.935
153.256	264.880	278.693	427.658	371.701	877.139
154.939	267.012	281.829	434.987		

er, during the adiabatic calorimetric measurements, when the sample is put into the sample cell, the air pressure within the sample cell is vacuumed to below 100 Pa with a vacuum pump to prevent moisture from being adsorbed on the surface of the sample. Then, about 100 kPa of high purity helium is filled in the sample cell to increase the rate of heat conduction of sample cell during low temperature heat capacity measurements and also to reduce the time to reach thermal equilibrium. The

Fig.1 Plot of heat capacity ($C_{p,m}$) against temperature (T) for $\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$

sample cell was sealed by soldering. In the temperature range of 78–325 K, the rise in heat capacity curve is steady. However, at 326–371 K, the curve rises very steeply, indicating that the compound is decomposed into another substance. The experimental points in the temperature range of 78–325 K are fitted by the least-squares method, and a polynomial equation of experimental molar heat capacities ($C_{p,m}$)/(J·K⁻¹·mol⁻¹) versus the reduced temperature (X), $X=f(T)=[T-(T_1+T_2)/2]/[(T_1-T_2)/2]$ where $T_1=325$ K and $T_2=78$ K, is obtained (Eq.(1)).

$$C_{p,m}=320.683+137.917X+7.567X^2+45.893X^3+9.619X^4+23.068X^5+7.318X^6 \quad (1)$$

where $X=(T-201.5)/123.5$. The standard deviations of experimental molar heat capacities from the smoothed heat capacities calculated by the polynomial equation are within $\pm 0.3\%$ except for some points around the lower and upper temperature. In addition, Fig.1 shows that a slow process of dehydration occurs after 325 K rather than an obvious peak of dehydration. There are two possible reasons for this phenomenon. On the one hand, the crystal water possesses a large percentage in the compound; while on the other hand, the mass of the sample is large. Since the sample cell is sealed during the entire calorimetric experiment, once the dehydration occurs, the speed of dehydration should accelerate with the temperature rising. Meanwhile, the rate of the dehydration is also inhibited as a result of the rapid increase of vapor pressure of the water in the sample cell.

Table 2 Smoothed heat capacities and thermodynamic functions of the compound $\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$

T/K	$C_{p,m}$ (J·K ⁻¹ ·mol ⁻¹)	$[H_T-H_{298.15\text{K}}]$ (J·mol ⁻¹)	$[S_T-S_{298.15\text{K}}]$ (J·K ⁻¹ ·mol ⁻¹)	$[G_T-G_{298.15\text{K}}]$ (J·mol ⁻¹)
298.15	467.307	0	0	0
300	472.001	868.766	2.9039	-2.42011
305	485.409	3261.59	10.811	-35.5119
310	499.978	5724.24	18.815	-108.306
315	515.842	8262.82	26.935	-221.735
320	533.151	10884.1	35.189	-376.381
325	552.066	13595.8	43.595	-572.405

3.2 Smoothed heat capacities and thermodynamic functions of the sample

The smoothed values of molar heat capacities and thermodynamic functions of the compound, $\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$ are derived according to the following thermodynamic equations (Eqs.(2)–(4)).

$$H_T - H_{298.15\text{K}} = \int_{298.15}^T C_{p,m} dT \quad (2)$$

$$S_T - S_{298.15\text{K}} = \int_{298.15}^T C_{p,m} T^{-1} dT \quad (3)$$

$$G_T - G_{298.15\text{K}} = \int_{298.15}^T C_{p,m} dT - T \int_{298.15}^T C_{p,m} T^{-1} dT \quad (4)$$

The fitted polynomial values of the molar heat capacities and fundamental thermodynamic functions of the sample relative to the standard reference temperature, 298.15 K at an interval of 5 K, are given in Table 2.

3.3 Dissolution enthalpies of the mixtures $\{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s}) + 2\text{NaNO}_3(\text{s}) + 3\text{Met}(\text{s})\}$ and $\{\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s}) + \text{Na}_2\text{SO}_4(\text{s})\}$

The compound, $\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$, is one of the products in the following reaction (Eq.(5)).

The enthalpy change of the proposed reaction above and standard molar enthalpy of formation of the compound $\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$ are determined by a designed thermochemical cycle using the experimental data of isoperibol calorimetry and other thermodynamic data.

If “s”=calorimetric solvent, 2 mol·L⁻¹ HCl(aq), the dissolution process of the mixture of reactants in reaction (5) is expressed as $\{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s}) + 2\text{NaNO}_3(\text{s}) + 3\text{Met}(\text{s})\} + \text{“s”}$ to give solution A.

Table 3 Dissolution enthalpy of $\{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s}) + 2\text{NaNO}_3(\text{s}) + 3\text{Met}(\text{s})\}$ mixture at a mole ratio of $n(\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}):n(\text{NaNO}_3):n(\text{Met})=1:2:3$ in 100 mL 2 mol·L⁻¹ HCl solution at 298.15 K

No.	$W_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}}/\text{g}$	$W_{\text{NaNO}_3}/\text{g}$	W_{Met}/g	$\Delta E_c/\text{mV}$	$\Delta E_s/\text{mV}$	t/s	Q_s/J	$\Delta_d H_{m,1}^0/(\text{kJ} \cdot \text{mol}^{-1})$
1	0.2876	0.1700	0.4477	3.2295	3.2536	623.46	64.405	64.397
2	0.2885	0.1705	0.4491	3.2272	3.2719	634.46	65.129	64.917
3	0.2892	0.1710	0.4502	3.2612	3.2769	628.26	65.072	64.704
4	0.2891	0.1709	0.4500	3.2185	3.2758	634.11	64.840	64.495
5	0.2886	0.1706	0.4493	3.2272	3.2659	629.85	64.773	64.540

$$\Delta_d H_{m,1}^0 (\text{avg.}) = (64.611 \pm 0.091) \text{ kJ} \cdot \text{mol}^{-1}$$

W : mass of the sample; ΔE_c : voltage change during electric calibration; ΔE_s : voltage change during dissolution of the sample; t : heating time during electric calibration; Q_s : heat effect during dissolution of the sample; $\Delta_d H_{m,1}^0$: molar enthalpy of dissolution, $\Delta_d H_{m,1}^0 = (\Delta E_s / \Delta E_c) \cdot F R t \cdot (M/W)$; R : the resistance of the heater in the reaction chamber ($R=1017.2 \Omega$ at $T=298.15 \text{ K}$); I : the current through heater during electric calibration ($I=10.115 \text{ mA}$); M : molar weight of the sample. $I=10.115 \text{ mA}$, $R=1017.2 \Omega$

Table 4 Dissolution enthalpy of $\{\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s}) + \text{Na}_2\text{SO}_4(\text{s})\}$ mixture at a mole ratio of $n(\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}):n(\text{Na}_2\text{SO}_4)=1:1$ in 100 mL 2 mol·L⁻¹ HCl solution at 298.15 K

No.	$W_{\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}}/\text{g}$	$W_{\text{Na}_2\text{SO}_4}/\text{g}$	$\Delta E_c/\text{mV}$	$\Delta E_r/\text{mV}$	t_e/s	Q_c/J	$\Delta_d H_{m,2}^0/(\text{kJ} \cdot \text{mol}^{-1})$
1	0.6551	0.1422	2.3646	2.4096	465.77	47.569	47.563
2	0.6572	0.1426	2.5546	2.5750	463.97	47.905	47.749
3	0.6588	0.1430	2.3228	2.3962	476.38	48.060	47.788
4	0.6586	0.1429	2.4939	2.5367	467.75	47.859	47.604
5	0.6574	0.1427	2.5255	2.5738	468.51	47.844	47.672
$\Delta_d H_{m,2}^0(\text{avg.})=(47.675 \pm 0.042) \text{ kJ} \cdot \text{mol}^{-1}$							

Table 5 Reaction scheme used to determine the standard molar enthalpy of formation of $\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$ at 298.15 K

No.	Reaction	$(\Delta_d H_m^0 \text{ or } \Delta_d H_m^0 \pm \sigma_r)/(\text{kJ} \cdot \text{mol}^{-1})$	Enthalpy change of reaction
1	$\{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s}) + 2\text{NaNO}_3(\text{s}) + 3\text{Met}(\text{s})\} + "s" = \text{solution A}$	(64.611 ± 0.091)	ΔH_1
2	$\{\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s}) + \text{Na}_2\text{SO}_4(\text{s})\} + "s" = \text{solution A}'$	(47.675 ± 0.042)	ΔH_2
3	$\text{solution A}' + \{6\text{H}_2\text{O}(\text{l})\} = \text{solution A}$	0	ΔH_3
4	$\text{Na}(\text{s}) + (1/2)\text{N}_2(\text{g}) + (3/2)\text{O}_2(\text{g}) = \text{NaNO}_3(\text{s})$	-466.24	ΔH_4
5	$\text{Zn}(\text{s}) + \text{S}(\text{s}) + (11/2)\text{O}_2(\text{g}) + 7\text{H}_2(\text{g}) = \text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s})$	-3077.75	ΔH_5
6	$5\text{C}(\text{s}) + 1/2\text{N}_2(\text{g}) + \text{O}_2(\text{g}) + 11/2\text{H}_2(\text{g}) + \text{S}(\text{s}) = \text{Met}(\text{s})$	$-(577.50 \pm 0.70)$	ΔH_6
7	$2\text{Na}(\text{s}) + \text{S}(\text{s}) + 2\text{O}_2 = \text{Na}_2\text{SO}_4(\text{s})$	-1383.16	ΔH_7
8	$\text{H}_2(\text{g}) + (1/2)\text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{l})$	$-(285.830 \pm 0.042)$	ΔH_8
9	$\text{Zn}(\text{s}) + 15\text{C}(\text{s}) + (35/2)\text{H}_2(\text{g}) + (13/2)\text{O}_2(\text{g}) + (3/2)\text{N}_2(\text{g}) = \text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$	$-(2292.44 \pm 11.12)$	ΔH_9

The experimental results of the process are listed in Table 3. The dissolution process of the products, $\{\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s}) + \text{Na}_2\text{SO}_4(\text{s})\}$, in reaction (5) may be expressed as $\{\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s}) + \text{Na}_2\text{SO}_4(\text{s})\} + "s"$ to give solution A'. The results of the dissolution experiments are shown in Table 4. solution A' + $\{6\text{H}_2\text{O}(\text{l})\} = \text{solution A}$. The enthalpy of dissolution of $\{6\text{H}_2\text{O}(\text{l})\}$ ($\Delta_d H_{m,3}$) as one of the products in reaction (5) in the solvent is within the range of experimental error, and may be omitted since the amount of $\text{H}_2\text{O}(\text{l})$ is very small according to the stoichiometric number of $\text{H}_2\text{O}(\text{l})$ in reaction (5), i.e., $\Delta_d H_{m,3} = 0 \text{ kJ} \cdot \text{mol}^{-1}$. The enthalpy change of reaction (5), $\Delta_d H_{m,5}$, can be calculated in accordance with the designed thermochemical cycle above and experimental results are listed in Tables 3 and 4 by the following equation: $\Delta_d H_{m,10} = \Delta_d H_{m,1} - (\Delta_d H_{m,2}^0 + \Delta_d H_{m,3}^0) = (16.936 \pm 0.100) \text{ kJ} \cdot \text{mol}^{-1}$.

In order to obtain the standard molar enthalpy of formation of the compound $\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$, a reaction scheme is arranged and given in Table 5. The enthalpy change of reaction (5) obtained from experimental values of the dissolution enthalpies of $\{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s}) + 2\text{NaNO}_3(\text{s}) + 3\text{Met}(\text{s})\}$ and $\{\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s}) + \text{Na}_2\text{SO}_4(\text{s})\}$ in 100 mL of 2 mol·L⁻¹ hydrochloric acid combined with some auxiliary thermodynamic data:^{11–14} $\Delta_f H_m^0[\text{Na}_2\text{SO}_4, \text{s}] = -1383.16 \text{ kJ} \cdot \text{mol}^{-1}$,¹¹ $\Delta_f H_m^0[\text{NaNO}_3, \text{s}] = -466.24 \text{ kJ} \cdot \text{mol}^{-1}$,¹² $\Delta_f H_m^0[\text{Met}, \text{s}] = -(577.50 \pm 0.70) \text{ kJ} \cdot \text{mol}^{-1}$,¹³ $\Delta_f H_m^0[\text{H}_2\text{O}, \text{l}, 298.15 \text{ K}] = -(285.83 \pm 0.04) \text{ kJ} \cdot \text{mol}^{-1}$,¹⁴ have been used to calculate the standard molar enthalpy of formation of the compound $\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$ as follows:

$$\begin{aligned} \Delta_f H_m^0[\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}, \text{s}] \\ &= \Delta H_9 \\ &= \Delta H_1 - (\Delta H_2 + \Delta H_3) + (2\Delta H_4 + \Delta H_5 + 3\Delta H_6 - \Delta H_7 - 6\Delta H_8) \\ &= \Delta_d H_{m,10} + 2\Delta_f H_m^0(\text{NaNO}_3, \text{s}) + \Delta_f H_m^0(\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}, \text{s}) + \\ &\quad 3\Delta_f H_m^0(\text{Met}, \text{s}) - \Delta_f H_m^0(\text{Na}_2\text{SO}_4, \text{s}) - 6\Delta_f H_m^0(\text{H}_2\text{O}, \text{l}) \end{aligned}$$

$$= -(2292.44 \pm 11.12) \text{ J} \cdot \text{mol}^{-1}$$

where ΔH_1 to ΔH_9 are the molar enthalpy changes of the corresponding reactions in Table 5. The results of UV/Vis spectrum and refractive index are important for checking the differences of the structure and composition for the two solutions. In the present study, all the reactants and products of reaction (5) can be easily dissolved in the selected solvent. The measured values of the refractive indices of solution A and solution A' are 1.3882 ± 0.0004 and 1.3880 ± 0.0005 , respectively. The results of UV/Vis spectrum and the data of the refractive indices of solution A obtained are in agreement with those of solution A'. These results have demonstrated that the solutions A and A' are same, and the designed Hess thermochemical cycle can be used reliably to derive the standard molar enthalpy of formation of the compound $\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$.

4 Conclusions

In summary, as for the compound $\text{Zn}(\text{Met})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}(\text{s})$, low temperature heat capacities have been measured by a precision automated adiabatic calorimeter over the temperature range 78–371 K. The thermodynamic functions of dehydration, the enthalpy, entropy and Gibbs free energy are obtained. In addition, the standard molar enthalpy of formation of the compound is also determined from the enthalpies of dissolution of the reactants and products and other thermodynamic data by a Hess thermochemical cycle.

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