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# Determination of Standard Molar Enthalpy of Formation for the Coordination Compound $\text{Zn}(\text{His})\text{Cl}_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$ by an Isoperibol Solution–Reaction Calorimeter

You-Ying Di,<sup>†,‡</sup> Zhi-Cheng Tan,<sup>\*,†,‡</sup> Sheng-Li Gao,<sup>§</sup> and Shao-Xu Wang<sup>†</sup>

Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China, College of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, People's Republic of China, and Department of Chemistry, Northwest University, Xi'an 710069, People's Republic of China

An isoperibol solution–reaction calorimeter suitable for measuring molar enthalpies of solid–liquid and liquid–liquid interactions was constructed. The volume of calorimetric vessel made by transparent hard glass is about 100 cm<sup>3</sup>. Its energy equivalent is 0.48 kJ·K<sup>−1</sup> when containing 100 cm<sup>3</sup> of double distilled water. The thermal leakage modulus is  $2.7 \times 10^{-4} \text{ s}^{-1}$ . The time constant of the calorimeter is about 2.9 s. The precision of controlling and measuring the temperature is within  $\pm 0.001 \text{ K}$  and  $\pm 0.0001 \text{ K}$ , respectively. The performance of the calorimeter was tested by measuring the enthalpy of dissolution of KCl in double distilled water,  $\Delta_{\text{s}}H_{\text{m,KCl}}^{\circ} = (17\,547 \pm 13 \text{ J}\cdot\text{mol}^{-1})$  at  $T = (298.15 \pm 0.001) \text{ K}$ , and the measuring uncertainty was estimated to be within  $\pm 0.30\%$  by comparing our measured value with the reference. Molar enthalpies of dissolution of the  $\{\text{ZnCl}_2(\text{s}) + \text{L-His}(\text{s})\}$  mixture and the complex  $\text{Zn}(\text{His})\text{Cl}_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$  in 100 cm<sup>3</sup> of 2 mol·L<sup>−1</sup> HCl at  $T = (298.15 \pm 0.001) \text{ K}$  have been measured to be  $\Delta_{\text{d}}H_{\text{m,1}}^{\circ} = (26.419 \pm 0.019) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_{\text{d}}H_{\text{m,2}}^{\circ} = (11.862 \pm 0.009) \text{ kJ}\cdot\text{mol}^{-1}$ , respectively, by means of the isoperibol solution–reaction calorimeter. The standard molar enthalpy of formation of the complex  $\text{Zn}(\text{His})\text{Cl}_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$  has been derived to be  $\Delta_{\text{f}}H_{\text{m}}^{\circ} [\text{Zn}(\text{His})\text{Cl}_2 \cdot 1/2\text{H}_2\text{O}, \text{s}, 298.15 \text{ K}] = -(1010.1 \pm 2.3) \text{ kJ}\cdot\text{mol}^{-1}$  by the combination of the experimental values of enthalpies of dissolution with some auxiliary thermodynamic data through a designed Hess thermochemical cycle on the basis of a supposed chemical reaction.

## 1. Introduction

The isoperibol solution–reaction calorimetry is a universal technique widely used for the measurements of enthalpies of reaction, dissolution, dilution, mixing, adsorption, formation, and excess enthalpies<sup>1–10</sup> in a thermochemistry laboratory, which are involved in physical changes, chemical reactions, and living biochemical metabolisms evidently in the nature. The calorimetry is especially often applied to determine the standard molar enthalpies of formation of many important substances in industry and scientific research based on the data of enthalpies of dissolution or reaction and some auxiliary thermodynamic quantities. The datum of the standard molar enthalpy of formation plays an important role in theoretical study, application development, and industrial production of a compound as a basis of theoretical analysis. 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 highly sensible, precise, and computer-controlled isoperibol solution–reaction calorimeter suitable for investigating the systems of liquid–liquid and liquid–solid interactions is described in more detail on the basis of other commercial apparatus<sup>1–7</sup> and our previous works.<sup>8–10</sup> At the same time, the molar enthalpy of dissolution of KCl

in double distilled water at  $T = 298.15 \text{ K}$  has been measured so that the reliability of the calorimeter is confirmed.

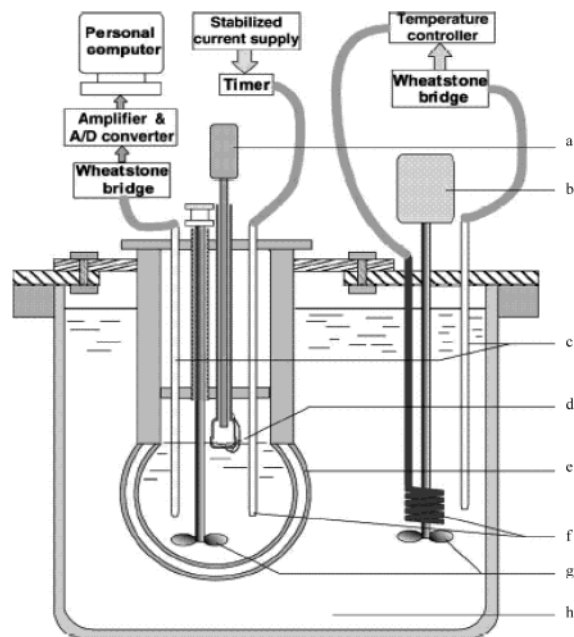
It is well known that zinc is one of the trace elements necessary for the human body, and  $\alpha$ -amino acids are the raw material which constitute the proteins demanded for the life activity. The complexes of zinc with L- $\alpha$ -amino acids have been considered to be one of the best zinc tonics because it has been verified experimentally that this kind of complex has a higher absorption ratio in the human body than that of other inorganic and organic weak-acid zinc tonics. These coordination compounds have vast application prospects in medicines, foodstuffs, and cosmetics as nutrient additives.<sup>11–12</sup> Sheng-Li Gao et al.<sup>13</sup> have investigated the coordination behavior between zinc salts and L- $\alpha$ -histidine (His) by the method of the semi-microphase equilibrium and successfully synthesized a series of coordination compounds of zinc salts with L- $\alpha$ -histidine from the mixture of water and acetone under the guidance of the ternary equilibrium phase diagrams. However, up to now, the data of the enthalpies of dissolution of these complexes in diluent acid solution and their standard molar enthalpies of formation have not been reported. As an important project of research program about the complexes of zinc with L- $\alpha$ -amino acids, in the present paper, the enthalpy of dissolution of the complex  $\text{Zn}(\text{His})\text{Cl}_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$  in diluent acid solution has been investigated by the homemade isoperibol solution calorimeter. Furthermore, the standard molar enthalpy of formation of the complex has been derived through a designed thermochemical cycle.

\* To whom correspondence may be addressed. Fax: +86-411-84691570. E-mail: tzc@dicp.ac.cn.

<sup>†</sup> Chinese Academy of Sciences.

<sup>‡</sup> Liaocheng University.

<sup>§</sup> Northwest University.



**Figure 1.** The schematic diagram of the isoperibol solution-reaction calorimeter: a, sampling stick; b, electric motor; c, thermistor probe; d, sampling cell; e, dewar vessel; f, electric heater; g, stirrer; h, water thermostat.

## 2. Experimental Section

**Samples.** KCl (AR) used for the calibration of the isoperibol calorimeter was provided from the National Institute of Standards and Technology, Standard Reference Material 1655. The labeled purity was  $>0.9990$  mass fraction. Chemical and elemental analysis indicated that its content was higher than 0.9999 mass fractions. It was dried under the temperature of  $T = (620-720)$  K for 16 h before the measurements were carried out.

$\text{Zn}(\text{His})\text{Cl}_2 \cdot 1/2\text{H}_2\text{O}(\text{s})$  is a white crystal. The sample used for the measurements was prepared by semi-microphase equilibrium method.<sup>13-14</sup> The solid complex obtained was put into a desiccator containing  $\text{P}_4\text{O}_{10}$  until the weight of the complex became constant. The results of chemical and elemental analysis, IR spectra, thermogravimetry-differential thermogravimetry, and X-ray diffraction have proved that the composition of the complex was  $\text{Zn}(\text{His})\text{Cl}_2 \cdot 1/2\text{H}_2\text{O}$ , as shown in ref 13. The purity of the complex determined by chemical analysis was higher than 0.9999 mass fractions (analytical error,  $\leq 0.002$  mass fraction).

**Isoperibol Solution-Reaction Calorimetry.** The isoperibol solution-reaction calorimeter consisted of a precision temperature-controlling system, the electric energy calibration system, the electric stirring system, the thermostatic bath made by transparent silicate glass, and the data processing system. The principle and structure of the calorimeter has been described in brief elsewhere.<sup>8-10</sup> The schematic diagram of the isoperibol solution-reaction calorimeter was shown in Figure 1.

The thermistor was adopted as the sensor for controlling temperature in the thermostatic bath. But the input signal of the modified high-precision temperature controller (model DWT-702, manufactured by Shanghai No. 6 Automated Instrumentation Works), which works in the proportional-integral-derivative mode, was not directly from the thermistor sensor but from the signal of a wheatstone resistance bridge used for temperature control. Water was used as the thermostatic medium. The standard resistance bridge consisted of a precision metal membrane resistance, a precision wire-wound resistance, and an adjustable

precision resistor. The electric heater used in the thermostatic bath was composed of two silicon-carbon bars connected in series with each other, which were surrounded by the stainless steel tube and placed in two opposite sides of the thermostatic bath. The total resistance of the heater was about  $80 \Omega$ . During whole experiment, the water thermostat was automatically maintained at  $T = (298.150 \pm 0.001)$  K by regulating an adjustable precision resistor in the wheatstone bridge. The ambient temperature of the laboratory in which the calorimeter was located must be kept between  $T = 288$  K and  $T = 293$  K and maintained steady. Any disturbances in the laboratory from air circulation, noise, and vibration were avoided. Experiments have demonstrated that the precision of temperature controlling of this kind of system can reach  $\pm 1 \times 10^{-3}$  K.

The calorimetric body consisted of the calorimetric chamber, the electric stirrer, the sampling system, the temperature measurement system, and the electric heater used for the purposes of electrical energy calibration and equilibration. The calorimetric chamber was a dewar glass and processed by transparent glass tube of about 55 mm in the inner diameter and about 200 mm in length. The effective volume of the calorimetric chamber was about  $100 \text{ cm}^3$ . A vacuum jacket evacuated to  $1 \times 10^{-3}$  Pa closely surrounded outside the calorimetric chamber so as to reduce the heat leakage from the air convection and heat conduction to a minimum level. The electric stirrer was made by hard glass bar that has an about 5 mm diameter. It was rotated with a motor at a rotation rate of about 200 r/min. A grinding fit between the stirring bar and its outer glass sleeve ensured a tight seal but allowed the stirrer to rotate smoothly. The volume of small sampling cell was about  $1.5 \text{ cm}^3$ . A grinding contact between it and its sleeve can ensure the tight sealing, and the sample does not deliquesce prior to carrying out the reaction. Two small rings were fixed vertically at the bottom of the sampling cell and on the sleeve, respectively. A segment of silicon-rubber string (about 0.8 mm in diameter) was tied to them. The long sampling stick in its sleeve was used to allow the sampling cell to fall into the calorimetric chamber. Such an arrangement can be used repeatedly. Measurements<sup>8-10</sup> for calorimetric standard substances (KCl) have demonstrated that such a sampling setup can completely ensure the accuracy and precision of measurement results. The measuring temperature system consisted of a similar wheatstone electric bridge to that of the controlling temperature system and another thermistor with large negative temperature coefficient of resistance. The thermistor thermometer was calibrated on the basis of ITS-90 by the Station of Low-temperature Metrology and Measurements, Academia Sinica. The thermistor had a nominal resistance of  $80 \text{ k}\Omega$  at  $T = 298.15$  K and constituted one of the four arms of the wheatstone bridge circuit. A data acquisition/switch unit (model 34970A, Agilent, USA) was used to determine the temperature of the solution in the chamber with an accuracy of 0.1 mK. The unbalanced voltage signal had a linear response to the change of temperature over the temperature range from 295 K to 310 K. The resistance value of the thermistor was changed with the temperature in the calorimetric chamber. This change was displayed on the Agilent data acquisition/switch unit (Agilent) in the form of the unbalanced voltage signal from the wheatstone electric bridge because the Agilent can turn this change of the resistance value of the thermistor into a voltage. The signal from the resistance bridge of measuring the temperature was amplified and automatically picked up by use of the Agilent and processed on line by a computer.

Measurement indicated that the precision of the temperature measurement system can reach  $\pm 1 \times 10^{-4}$  K at least and that the time constant of the calorimeter was about 3 s.

The system of electric energy calibration consisted of the electric heater and the precision power supply with stepwise constant currents. The electric heater was made by precision Karma wire of 0.12 mm in diameter, which was bifilarly wound on the surface of a porcelain bar of about 0.8 mm in diameter. The resistance change during the heating was less than 0.01%. A SKD-A coulomb meter was used as the precision power supply with stepwise constant currents, which was made by a scientific device factory, Wuhan University, People's Republic of China. It may display the Coulombian value by means of a photoelectric converter. It had a current precision of 0.02%. The timing system was calibrated by the international standard time; its timing precision was 0.01 s and the timing error was less than 0.001%. During each electrical energy calibration, the electrical current through the heater was set at  $I = 10.115$  mA, and the resistance of the electrical heater was  $R = 1017.2 \Omega$  at  $T = 298.15$  K.

It should be pointed out that Reynold's correction and Dickinson's method<sup>7</sup> (the equal area method) must be applied in the processing of all the original data so as to eliminate the effect of heat in the calorimetric chamber from stirring and friction and inevitable heat transfer between the calorimetric chamber and its surroundings on the measurement results. In addition, the necessary amount of sample needed for the calorimetric measurement was 0.2–0.8 g per experiment for the purpose of ensuring the measurement accuracy.

The temperature difference  $\Delta T_s$  between the beginning and end of the dissolution or reaction can be obtained from the analyses of a fore period of about 5 min, a main period of about 6–15 min, and an after period of about 5 min during all the measurements. It was directly proportional to the enthalpy of the reaction. When the temperature (voltage) during the after period has maintained stable, the electric energy calibration can be carried out based on the solution obtained from the chemical reaction or dissolution. The voltage change range of electric energy calibration ought to be the basically same as that during the reaction in order to ensure the accuracy of the measuring experiment. Similarly, the temperature difference  $\Delta T_e$  corresponding to the beginning and end of the electric energy calibration may be obtained from the analysis of the curve of voltage (mV) with time (min).

The reliability of the calorimeter was verified by measuring the dissolution enthalpy of KCl (calorimetrically primary standard) in double distilled water at  $T = 298.15$  K. The mean dissolution enthalpy was  $(17\,597 \pm 17)$  J·mol<sup>-1</sup> for KCl, which compared with corresponding published data,<sup>15</sup>  $(17\,536 \pm 3.4)$  J·mol<sup>-1</sup> for KCl.

### 3. Results and Discussion

**Enthalpy of Dissolution of KCl in Double Distilled Water.** According to the molar ratio of KCl to water,  $n_{\text{KCl}}:n_{\text{H}_2\text{O}} \approx 1:1110$ , a certain amount of KCl was dissolved in 100 mL double distilled water at  $T = (298.15 \pm 0.001)$  K. The average enthalpy of dissolution of KCl determined from the 6 tests was  $\Delta_s H_{\text{m,KCl}}^\circ = (17\,547 \pm 13)$  J·mol<sup>-1</sup>, as shown in Table 1. The literature value<sup>15</sup> of the enthalpy of dissolution of KCl under the same experimental conditions was  $\Delta_s H_{\text{m,KCl}}^\circ = (17\,536 \pm 3.4)$  J·mol<sup>-1</sup>. It showed that the error between the literature value and the measuring value was within  $\pm 0.3\%$ .

**Table 1. Enthalpy of Solution of KCl in Double Distilled Water at  $T = 298.15$  K<sup>a</sup>**

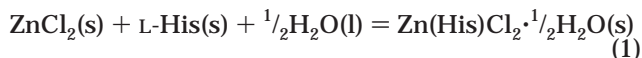
no.	$W/\text{g}$	$\Delta E_s/\text{mV}$	$\Delta E_e/\text{mV}$	$t_e/\text{s}$	$Q_s/\text{J}$	$\Delta_s H_{\text{m,KCl}}^\circ/\text{J}\cdot\text{mol}^{-1}$
1	0.3728	6.618 2	6.593 1	841.8	87.939	17 585
2	0.3733	6.650 1	6.667 2	847.6	87.980	17 570
3	0.3731	6.641 9	6.682 1	848.2	87.743	17 532
4	0.3726	6.574 1	6.619 3	845.9	87.434	17 494
5	0.3730	6.638 2	6.694 2	851.5	87.871	17 562
6	0.3729	6.619 6	6.567 9	836.3	87.721	17 537
avg						$\Delta_s H_{\text{m,KCl}}^\circ/\text{J}\cdot\text{mol}^{-1} = (17\,547 \pm 13)$

$$^a M_{\text{KCl}} = 74.55 \text{ g}\cdot\text{mol}^{-1}.$$

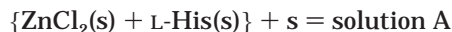
**Table 2. Enthalpy of Solution of the Mixture  $\{\text{ZnCl}_2(\text{s}) + \text{L-His}(\text{s})\}$  at a Molar Ratio of  $n(\text{ZnCl}_2):n(\text{L-His}) = 1:1$  in 100 mL of 2 mol·L<sup>-1</sup> HCl at  $T = 298.15$  K**

no.	$W_{\text{ZnCl}_2(\text{s})}/\text{g}$	$W_{\text{L-His}(\text{s})}/\text{g}$	$\Delta E_s/\text{mV}$	$\Delta E_e/\text{mV}$	$t/\text{s}$	$Q_s/\text{J}$	$\Delta_d H_{\text{m,1}}^\circ/\text{J}\cdot\text{mol}^{-1}$
1	0.218 3	0.248 1	4.271 7	3.820 4	364.2	42.380	26 460
2	0.218 6	0.248 7	4.303 1	3.867 6	365.5	42.321	26 387
3	0.218 4	0.248 5	4.299 4	3.844 2	364.4	42.414	26 469
4	0.218 8	0.249 0	4.315 5	3.881 4	366.4	42.396	26 410
5	0.218 4	0.248 6	4.299 3	3.891 8	367.2	42.216	26 346
6	0.218 7	0.248 8	4.300 1	3.859 8	365.9	42.423	26 439
avg							$\Delta_d H_{\text{m,1}}^\circ/\text{J}\cdot\text{mol}^{-1} = (26\,419 \pm 19)$

**Enthalpy of Dissolution of  $\{\text{ZnCl}_2(\text{s}) + \text{L-His}(\text{s})\}$  in 2 mol·L<sup>-1</sup> HCl.** The complex  $\text{Zn}(\text{His})\text{Cl}_2 \cdot 1/2 \text{H}_2\text{O}(\text{s})$  was supposed to be the product in the following reaction



A thermochemical cycle using the experimental data of isoperibol solution calorimetry was designed on the basis of the above reaction, and a reaction scheme was used to derive the standard molar enthalpy of formation of the complex  $\text{Zn}(\text{His})\text{Cl}_2 \cdot 1/2 \text{H}_2\text{O}(\text{s})$  according to the cycle. In all these measurements, 2 mol·L<sup>-1</sup> HCl and its solution were chosen as the calorimetric solvents for measuring the dissolution enthalpies of the reactants and products in the reaction 1. The  $\text{ZnCl}_2(\text{s})$  and  $\text{L-His}(\text{s})$  were ground within an agate mortar into fine powder. About 0.466 g of  $\text{ZnCl}_2(\text{s})$  and  $\text{L-His}(\text{s})$  mixture at a mole ratio of  $n(\text{ZnCl}_2):n(\text{L-His}) = 1:1$  was dissolved in 100 mL of 2 mol·L<sup>-1</sup> HCl at  $T = 298.15$  K. The detailed results obtained from six tests have been listed in Table 2. If "s" = calorimetric solvent of 100 mL of 2 mol·L<sup>-1</sup> HCl, then

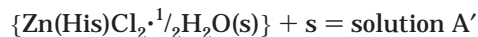


The dissolution of  $\{1/2 \text{H}_2\text{O}(\text{l})\}$  for one of reactants of the reaction 1 in the solution A can be shown as

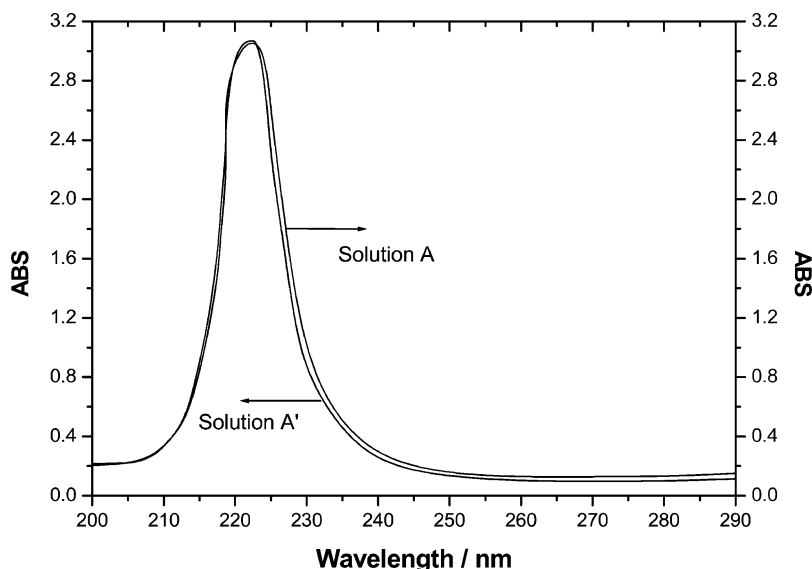


The enthalpy of the process ( $\Delta_d H_{\text{m,2}}^\circ$ ) was within the scope of experimental error, cannot be detected, and may be omitted because the amount of  $\text{H}_2\text{O}(\text{l})$  is only about 0.014 mL, much less than a drop of water according to the stoichiometric number of  $\text{H}_2\text{O}(\text{l})$  in the reaction.

**Enthalpy of Dissolution of  $\{\text{Zn}(\text{His})\text{Cl}_2 \cdot 1/2 \text{H}_2\text{O}(\text{s})\}$  in 2 mol·L<sup>-1</sup> HCl.** The  $\text{Zn}(\text{His})\text{Cl}_2 \cdot 1/2 \text{H}_2\text{O}(\text{s})$  was also ground within an agate mortar into fine powder. About 0.48 g of  $\text{Zn}(\text{His})\text{Cl}_2 \cdot 1/2 \text{H}_2\text{O}(\text{s})$  was dissolved in 100 mL of 2 mol·L<sup>-1</sup> HCl at  $T = 298.15$  K. The detailed results obtained from six tests have been listed in Table 3. If "s" = calorimetric solvent of 100 mL of 2 mol·L<sup>-1</sup> HCl, then







**Figure 2.** Plot of absorbance from the UV-vis spectrum of solution A and solution A' against wavelength. Solution A and solution A' were obtained from the dissolutions of the reactants and products in reaction 1, which occurred in 2 mol·L<sup>-1</sup> HCl and was diluted 1:20.

**Table 3.** Enthalpy of Dissolution of Zn(His)Cl<sub>2</sub>·1/2H<sub>2</sub>O(s) in 100 mL of 2 mol·L<sup>-1</sup> HCl at T = 298.15 K<sup>a</sup>

no.	W/g	ΔE <sub>m</sub> /mV	ΔE <sub>e</sub> /mV	t/s	Q <sub>e</sub> /J	Δ <sub>d</sub> H <sub>m,3</sub> <sup>0</sup> /J·mol <sup>-1</sup>
1	0.481 2	2.717 2	2.814 3	189.4	19.031	11 883
2	0.481 6	2.721 4	2.796 8	187.3	18.967	11 833
3	0.481 4	2.724 6	2.852 2	191.1	18.998	11 857
4	0.481 7	2.735 1	2.819 6	188.8	19.060	11 888
5	0.481 3	2.723 2	2.780 4	186.5	19.010	11 867
6	0.481 0	2.713 5	2.748 1	184.6	18.970	11 849
avg						Δ <sub>d</sub> H <sub>m,3</sub> <sup>0</sup> /J·mol <sup>-1</sup> = (11 862 ± 9)

$$^a M_{\text{Zn(His)Cl}_2 \cdot 1/2\text{H}_2\text{O(s)}} = 300.46 \text{ g}\cdot\text{mol}^{-1}.$$

**Table 4.** Reaction Scheme Used to Determine the Standard Molar Formation Enthalpy of the Zn(His)Cl<sub>2</sub>·1/2H<sub>2</sub>O(s) at T = 298.15 K<sup>a</sup>

no.	reaction scheme	Δ <sub>r</sub> H <sub>m</sub> <sup>0</sup> or Δ <sub>d</sub> H <sub>m</sub> <sup>0</sup> ± σ <sub>a</sub> (kJ·mol <sup>-1</sup> )
1	{ZnCl <sub>2</sub> (s) and His(s)} + s = solution A	(26.419 ± 0.019) (ΔH <sub>1</sub> )
2	solution A + {1/2H <sub>2</sub> O(l)} = solution A'	0 (ΔH <sub>2</sub> )
3	{Zn(His)Cl <sub>2</sub> ·1/2H <sub>2</sub> O(s)} + s = solution A'	(11.862 ± 0.009) (ΔH <sub>3</sub> )
4	Zn(s) + Cl <sub>2</sub> (g) = ZnCl <sub>2</sub> (s)	-415.05 (ΔH <sub>4</sub> )
5	6C(s) + 3/2N <sub>2</sub> (g) + O <sub>2</sub> (g) + 9/2H <sub>2</sub> (g) = His(s)	-(466.70 ± 2.30) (ΔH <sub>5</sub> )
6	1/2O <sub>2</sub> (g) + H <sub>2</sub> (g) = H <sub>2</sub> O(l)	-(285.83 ± 0.04) (ΔH <sub>6</sub> )
7	Zn(s) + Cl <sub>2</sub> (g) + 5/4O <sub>2</sub> (g) + 3/2N <sub>2</sub> (g) + 6C(s) + 5H <sub>2</sub> (g) = Zn(His)Cl <sub>2</sub> ·1/2H <sub>2</sub> O(s)	-(101.0 ± 2.3) (ΔH <sub>7</sub> )

<sup>a</sup> In which "s" is the calorimetric solvent, 2 mol·L<sup>-3</sup> HCl; σ<sub>a</sub> = (Σ<sub>i=1</sub><sup>6</sup> (x<sub>i</sub> -  $\bar{x}$ )<sup>2</sup>/n(n-1))<sup>1/2</sup>, in which n is the experimental number, x<sub>i</sub> is a single value in a set of dissolution measurements, and  $\bar{x}$  is the mean value of a set of measurement results.

**Standard Molar Enthalpy of Formation of the Complex Zn(His)Cl<sub>2</sub>·1/2H<sub>2</sub>O(s).** Enthalpy change (Δ<sub>r</sub>H<sub>m</sub>) of reaction 1 can be calculated from dissolution enthalpies of {ZnCl<sub>2</sub>(s) + L-His(s)} (Δ<sub>d</sub>H<sub>m,1</sub><sup>0</sup>) and {Zn(His)Cl<sub>2</sub>·1/2H<sub>2</sub>O(s)} (Δ<sub>d</sub>H<sub>m,2</sub><sup>0</sup>) in accordance with Hess's law and the above designed thermochemical cycle by means of the following equation

$$\Delta_r H_m = (\Delta_d H_{m,1}^0 + \Delta_d H_{m,2}^0) - \Delta_d H_{m,3}^0 = (14.557 \pm 0.021) \text{ kJ}\cdot\text{mol}^{-1}$$

A reaction scheme applied to derive the standard molar enthalpy of formation of Zn(His)Cl<sub>2</sub>·1/2H<sub>2</sub>O(s) was given in Table 4. The enthalpy change of reaction 1 was combined

with some auxiliary thermodynamic data: Δ<sub>f</sub>H<sub>m</sub><sup>0</sup>[ZnCl<sub>2</sub>, s] = -415.050 kJ·mol<sup>-1</sup>,<sup>16</sup> Δ<sub>f</sub>H<sub>m</sub><sup>0</sup>[H<sub>2</sub>O, l] = -(285.830 ± 0.042) kJ·mol<sup>-1</sup>,<sup>17</sup> Δ<sub>f</sub>H<sub>m</sub><sup>0</sup>[His, s] = -466.70 ± 2.30 kJ·mol<sup>-1</sup><sup>18</sup> to calculate the standard molar enthalpy of formation of Zn(His)Cl<sub>2</sub>·1/2H<sub>2</sub>O(s) as follows

$$\begin{aligned} \Delta_f H_m^0[\text{Zn(His)Cl}_2 \cdot 1/2\text{H}_2\text{O, s}] &= \Delta H_7 = (\Delta H_1 + \Delta H_2 - \\ &\quad \Delta H_3) + (\Delta H_4 + \Delta H_5 + 1/2\Delta H_6) = \Delta_r H_m + \\ &\quad (\Delta_f H_m^0[\text{ZnCl}_2, \text{s}] + \Delta_f H_m^0[\text{L-His, s}] + 1/2\Delta_f H_m^0[\text{H}_2\text{O, l}]) = \\ &\quad -(1010.1 \pm 2.3) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

in which ΔH<sub>1</sub> ~ ΔH<sub>6</sub> were the enthalpy changes of the corresponding reactions in Table 4.

In this paper, solution A obtained from the dissolution of reactants in the reaction 1 was in thermodynamic equivalent states to solution A' from dissolution of products in the reaction, which has been confirmed by UV-vis spectroscopy and the refractive indices of two solutions (A and A'). The measured values of refractive indices were (1.3599 ± 0.0006) for solution A and (1.3596 ± 0.0005) for solution A'. The absorbance of UV spectroscopy was shown in Figure 2. The UV-vis spectrum and the value of the refractive index of solution A obtained agree with those of solution A'. No difference in the structure and chemical composition of the two solutions appeared. These results demonstrated that chemical components and physical-chemistry properties of solution A were consistent with those of solution A'. As a result, the designed thermochemical cycle is reasonable and reliable and can be used to calculate the standard molar enthalpy of formation of the complex Zn(His)Cl<sub>2</sub>·1/2H<sub>2</sub>O(s).

The equilibrium constant (K) and the yield of the chemical reaction in which the complex Zn(His)Cl<sub>2</sub>·1/2H<sub>2</sub>O(s) is involved can be determined based on the standard molar enthalpies of formation and the specified entropies of the reactants and products of the reaction used in industry. In addition, histidine is one of the L-α-amino acids necessitated in the human body. Good coordination behavior of zinc salts with other amino acids take place due to the existence of the amino group. The standard molar enthalpies of formation of other complexes of zinc salts with L-α-amino acids can be determined by using the same method as that applied in the paper.

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