

## Determination of the Specific Heat Capacity of RE(Et<sub>2</sub>dtc)<sub>3</sub>(phen) by Microcalorimetry

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A calculation formula for determining the specific heat capacity of solid compound with an improved RD496-III microcalorimeter was derived. The calorimetric constant and precision determined by the Joule effect were  $(63.901 \pm 0.030) \mu\text{V/mW}$  and 0.3% at 298.15 K, respectively, and the total disequilibrium heat has been measured by the Peltier effect. The specific heat capacities of two standard substances (benchmark benzoic acid and  $\alpha\text{-Al}_2\text{O}_3$ ) were obtained with this microcalorimeter, and the differences between their calculated values and literature values were less than 0.4%. Similarly, the specific heat capacities of thirteen solid complexes, RE(Et<sub>2</sub>dtc)<sub>3</sub>(phen) (RE=La, Pr, Nd, Sm—Lu, Et<sub>2</sub>dtc: diethyldithiocarbamate ion, phen: 1,10-phenanthroline) were gained, and their total deviations were within 1.0%. These values were plotted against the atomic numbers of rare-earth, which presents tripartite effect, suggesting a certain amount of covalent character in the bond of RE<sup>3+</sup> and ligands, according to Nephelauxetic effect of 4f electrons of rare earth ions.

**Keywords** microcalorimetry, disequilibrium heat, solid complex, specific heat capacity

### Introduction

The solid complexes containing lanthanide-sulfur bond have high performance of biology and frictional properties.<sup>1-4</sup> The vast investigations have been reported on preparations, characterizations and structures of these compounds,<sup>5-9</sup> which are meaningful for explaining the bonding characteristic of rare earth elements and expanding the application of these complexes. To our interests, these complexes were the precursors for preparing lanthanide sulfide.<sup>10,11</sup> The complexes of NaEt<sub>2</sub>dtc•3H<sub>2</sub>O and *o*-phen•H<sub>2</sub>O have been reported to react with rare earth compounds in literature.<sup>12</sup> In Ref. 13, the crystal structure and spectroscopy properties of Eu(Et<sub>2</sub>dtc)<sub>3</sub>(phen) have been documented. In our laboratory, the thermochemistry of Nd(Et<sub>2</sub>dtc)<sub>3</sub>(phen)<sup>14</sup> and Tb(Et<sub>2</sub>dtc)<sub>3</sub>(phen)<sup>15</sup> have been studied. The structures of these complexes were studied by IR spectra, the enthalpy changes of formation reaction were measured with a microcalorimeter, the constant-volume combustion energies were determined using a precise rotating bomb calorimeter, and the standard molar formation enthalpies were calculated. These data can interpret the preparation and characterizations of these complexes

from the thermodynamic point of view. However, the specific heat capacity data of these complexes were rarely reported in literatures.

The specific heat capacity is one of essential thermodynamic data for substance, important to many theoretic researches in physics and chemistry field, and the relevant engineering technologic design of energies and materials. The low temperature adiabatic calorimeter system for measuring the specific heat capacities of substance has been built by Tan,<sup>16-18</sup> and a great deal of specific heat capacity and thermodynamic data were obtained. Hu<sup>19,20</sup> determined the room-temperature specific heat capacities for some energetic materials by an RD496-II microcalorimeter. In this paper, the specific heat capacities of the title complexes RE(Et<sub>2</sub>dtc)<sub>3</sub>(phen) (RE=La, Pr, Nd, Sm—Lu) were determined on an improved RD496-III microcalorimeter, and the results were satisfied.

### Experimental

#### Derivation of formula of specific heat capacity

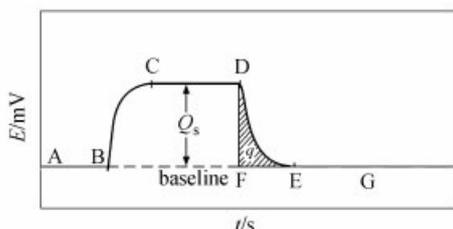
The specific heat capacity of a substance can be de-

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terminated according to the principle showed in Figure 1, where AG is the baseline, at time B the Peltier current begins to generate heat, during CD a new homeostasis state is formed with  $Q_s$  to be the amount of heat flux under the steady-state condition, at the point D the Peltier current is cut, at time E the system comes back to the original state of baseline,  $q$  is the integral area of the shadow part in the figure to represent the whole disequilibrium heat.



**Figure 1** Schematic thermogram of measurement of the heat capacity of solid.

To measure the specific heat capacities of the samples, the empty cell (Eq. 1, system 1), the cell containing the test sample (Eq. 2, system 2), the cell containing the first standard substance (Eq. 3, system 3) and the cell containing the second standard substance (Eq. 4, system 4) were heated by the same Peltier current with the microcalorimeter, and then the endothermic equations were obtained:

$$q_0 = a\theta \quad (1, \text{system 1})$$

$$q = (a + mc)\theta \quad (2, \text{system 2})$$

$$q_1 = (a + m_1c_1)\theta \quad (3, \text{system 3})$$

$$q_2 = (a + m_2c_2)\theta \quad (4, \text{system 4})$$

where  $q_0$ ,  $q$ ,  $q_1$  and  $q_2$  are the heat amounts of thermal disequilibrium (J) as the curve returns to baseline after the Peltier current of the four systems above is cut,  $a$  is the apparent heat capacity ( $\text{J}\cdot\text{K}^{-1}$ ) of the empty cell,  $\theta$  is the equilibrium temperature (K) of calorimeter at homeostasis state,  $m$ ,  $m_1$  and  $m_2$  are the mass values (g) of the test samples, the first standard substance and the second standard one respectively,  $c$ ,  $c_1$  and  $c_2$  are the specific heat capacities ( $\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ ) of these samples, respectively.

Combining Eqs. 1–4, the following equation can be reached:

$$c = [(q - q_0)/2m][m_1c_1/(q_1 - q_0) + m_2c_2/(q_2 - q_0)] \quad (5)$$

Provided the specific heat capacities  $c_1$  and  $c_2$  of the two standard substances are available, the specific heat capacity  $c$ , calibrated by these standard substances, of the test sample can be calculated according to Eq. 5.

## Reagents

The complexes studied in this paper were prepared with the same procedure in literature<sup>14,15</sup>. KCl, spectrum grade, the purity of which is beyond 99.99% (Shanghai

No. 1 Reagent Factory), was used after it was dried under 900 °C for 8 h. Benchmark benzoic acid of 99.999% purity (Chengdu Chemical Reagent Factory) was sublimated three times and stored in vacuum before use.  $\alpha\text{-Al}_2\text{O}_3$ , spectrum grade with the purity >99.99% (Shanghai No.1 Reagent Factory), could be used after drying under 1900 °C for 2 h, making all the samples transformed into a phase confirmed by XPS results.

## Calorimetric apparatus and experimental conditions

The experiment was performed by an RD496-III type microcalorimeter.<sup>21</sup> The calorimetric constant of the calorimeter was  $(63.901 \pm 0.030) \mu\text{V}/\text{mW}$ , measured by the Joule effect at 298.15 K before experiment. The solution enthalpy of KCl in deionized water was determined at 298.15 K with the value of  $(17.238 \pm 0.048) \text{kJ}\cdot\text{mol}^{-1}$ , close to the literature value of  $(17.241 \pm 0.018) \text{kJ}\cdot\text{mol}^{-1}$ ,<sup>22</sup> to show that the calorimetric system was reliable. In the calorimetric experiment, the solid sample was loaded into a 15 mL sample cell and the reference cell with the same size was empty. The experimental system was heated till thermal equilibrium, and the thermal curve was recorded.

## Results and discussion

### Composition of the complexes

The results of the composition analyses for the complexes are showed in Table 1, which were identified as a general formula of  $\text{RE}(\text{Et}_2\text{dtc})_3(\text{phen})$ . The characterization of  $\text{RE}(\text{Et}_2\text{dtc})_3(\text{phen})$  was referred to the Ref. 14. The purities of the compounds were 99.99%, checked by an HP-1100 type high performance liquid chromatography analyzer, adopting the solvent  $\text{CH}_2\text{Cl}_2$ , the rinsing reagent  $\text{CH}_2\text{Cl}_2$  and the column contra-phase carbon-18.

### Specific heat capacities of the empty cell and the standard substances

The specific heat capacities of the empty cell and the standard substances were determined according to the method above and listed in Table 2 with standard deviation  $\text{SD} = \sqrt{\sum(x_i - \bar{x})^2 / (n - 1)}$ . The measurement precisions were in the range of  $1.7 \times 10^{-3}$ – $2.2 \times 10^{-3}$  and all the measurement accuracies of the two standard samples were  $4 \times 10^{-3}$ .

### Specific heat capacities of complexes

The heat of disequilibrium for the complexes was measured by the method above 6 times for each sample, and their specific heat capacities were calculated from the data in Table 2 by Eq. 5 and presented in Table 3.

The specific heat capacities  $C$  of the complexes were plotted against the atomic numbers of lanthanide  $Z_{\text{RE}}$  (Figure 2), which presents an obvious tripartite effect, suggesting existence of certain covalent character in the bond of  $\text{RE}^{3+}$  and ligands, according to Nephelauxetic effect of 4f electrons of rare earth ions.

From the curves in Figure 2, the specific heat capacities for the two unstudied complexes of the same

series Ce(Et<sub>2</sub>dtc)<sub>3</sub>(phen) and Pm(Et<sub>2</sub>dtc)<sub>3</sub>(phen) can be estimated to be 108 and 72 J•mol<sup>-1</sup>•K<sup>-1</sup>, respectively.

**Table 1** Analytical results related to the compositions of the complexes<sup>a</sup>

RE	RE/%	C/%	N/%	S/%	H/%
La	18.21 (18.18)	42.53 (42.45)	9.09 (9.17)	25.07 (25.18)	4.87 (5.01)
Pr	18.30 (18.40)	42.23 (42.36)	9.10 (9.14)	25.07 (25.12)	4.79 (5.00)
Nd	18.59 (18.75)	42.08 (42.16)	9.01 (9.10)	24.87 (25.01)	4.69 (4.98)
Sm	19.42 (19.39)	41.81 (41.82)	9.00 (9.03)	24.79 (24.81)	4.97 (4.94)
Eu	19.57 (19.56)	41.72 (41.74)	9.04 (9.01)	24.77 (24.76)	4.89 (4.93)
Gd	20.12 (20.10)	41.44 (41.46)	8.97 (8.95)	24.56 (24.59)	4.91 (4.90)
Tb	20.28 (20.27)	41.29 (41.37)	8.99 (8.93)	24.52 (24.54)	4.92 (4.89)
Dy	20.85 (20.63)	40.77 (41.18)	8.80 (8.89)	24.89 (24.43)	4.68 (4.86)
Ho	20.99 (20.88)	40.82 (41.05)	8.81 (8.86)	24.82 (24.36)	4.57 (4.67)
Er	20.28 (21.11)	41.29 (40.93)	8.99 (8.84)	24.52 (24.27)	4.92 (4.83)
Tm	21.10 (21.28)	40.67 (40.85)	8.89 (8.82)	24.32 (24.23)	4.76 (4.82)
Yb	21.47 (21.68)	40.81 (40.64)	8.85 (8.78)	24.18 (24.11)	4.68 (4.80)
Lu	22.01 (21.87)	40.65 (40.54)	8.64 (8.75)	24.10 (24.05)	4.64 (4.79)

<sup>a</sup>RE<sup>3+</sup> was determined with EDTA by complexometric titration. C, H, N and S analyses were carried out with an instrument of Vario EL-III CHNOS made in German. The data in brackets are calculated values.

**Table 2** Data of the disequilibrium heat (mJ) and heat capability of the empty cell and the standard substances at 298.15 K

	The empty cell	Standard $\alpha$ -Al <sub>2</sub> O <sub>3</sub> (literature)	Sublimed benzoic acid (literature)
<i>q</i> (1)	4453.908	4959.916	6088.611
<i>q</i> (2)	4444.543	4962.776	6080.422
<i>q</i> (3)	4432.133	4977.771	6094.207
<i>q</i> (4)	4447.035	4984.568	6098.640
<i>q</i> (5)	4438.165	4967.144	6075.115
<i>q</i> (6)	4450.647	4983.760	6073.035
<i>q</i> (Mean $\pm$ SD)	4444.405 $\pm$ 3.610	4972.656 $\pm$ 4.824	6085.005 $\pm$ 4.672
Precision	1.816 $\times 10^{-3}$	2.169 $\times 10^{-3}$	1.717 $\times 10^{-3}$
Specific heat capacity <i>C</i> /(J•mol <sup>-1</sup> •K <sup>-1</sup> )	—	78.707 $\pm$ 2.927 (79.03 <sup>22</sup> )	145.923 $\pm$ 0.562 (145.327 <sup>23</sup> )

**Table 3** Data of the specific heat capacities of the complexes at 298.15 K

RE	<i>M</i> /g	<i>q</i> (mean $\pm$ SD)/mJ	<i>C</i> (mean $\pm$ SD)/(J•K•mol <sup>-1</sup> )
La	5.61862	6016.940 $\pm$ 4.797	112.16 $\pm$ 0.54
Pr	3.23058	5238.163 $\pm$ 4.604	98.46 $\pm$ 0.91
Nd	1.74031	4815.092 $\pm$ 5.507	85.36 $\pm$ 1.891
Sm	2.97107	4873.839 $\pm$ 6.388	57.92 $\pm$ 1.24
Eu	2.50203	4901.127 $\pm$ 6.644	73.15 $\pm$ 1.51
Gd	1.36054	4620.261 $\pm$ 5.503	51.80 $\pm$ 2.28
Tb	2.53219	4849.371 $\pm$ 6.134	64.09 $\pm$ 1.41
Dy	2.05819	5003.055 $\pm$ 5.630	108.78 $\pm$ 1.62
Ho	1.08107	4640.693 $\pm$ 5.835	72.76 $\pm$ 3.17
Er	1.14687	4667.328 $\pm$ 4.710	77.90 $\pm$ 2.59
Tm	2.14869	4887.161 $\pm$ 5.863	82.58 $\pm$ 1.60
Yb	1.89654	4853.002 $\pm$ 5.534	86.34 $\pm$ 1.74
Lu	2.36987	4942.512 $\pm$ 5.958	82.23 $\pm$ 1.47

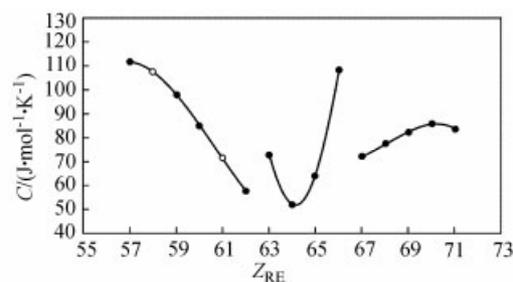


Figure 2 Special heat capacities of complexes against  $Z_{RE}$ .

## Conclusions

(1) The method of measuring the specific heat capacities of solid samples by the improved RD496-III type microcalorimeter has become more convenient, concise and reliable than that of RD496-II.

(2) The calculated values of the specific heat capacities for two standard substances (benzoic acid and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) at 298.15 K were close to the reference ones with the difference less than 0.4%, which testified the reliability of the experiment.

(3) The specific heat capacities  $C$  of the complexes against the atomic numbers of lanthanide  $Z_{RE}$  present an obvious tripartite effect, which witnesses the existence of certain covalent character in the bond of RE<sup>3+</sup> and ligands, according to Nephelauxetic effect of 4f electrons of rare earth ions.

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