ELSEVIER

Thermochimica Acta 275 (1996) 159–172

thermochimica acta

Thermochemical and thermodynamic properties of $M(NTO)_n$ and $M(NTO)_n \cdot mH_2O$

Hu Rongzu *, Meng Zihui, Kang Bing

Xian Modern Chemistry Research Institute, Xian 710065, Shaanxi, People's Republic of China

Received 11 January 1995; accepted 26 July 1995

Abstract

The enthalpies of solution in water of $M(NTO)_n \cdot mH_2O$ (M = metal, NTO = 3-nitro-1,2,4-triazol-5-one; M = Na, $n = m = 1$; M = La, Ce, Pr, Eu, Sm, $n = 3$, $m = 7$; M = Y, Yb, $n = 3$, $m = 6$; M = Dy, Tb, $n = 3$, $m = 5$; M = Nd, $n = 3$, $m = 8$; M = Co, Mn, Mg, $n = 2$, $m = 8$) have been measured calorimetrically at 298.15 K. By means of a thermochemical calculation, the standard enthalpies of formation for the above fourteen metal salt hydrates of NTO were obtained. With the help of the above-mentioned data, literature data and Kapustinskii's equation, the lattice energies, lattice enthalpies and standard enthalpies of formation for twenty $M(NTO)_n$ and the lattice energies, lattice enthalpies and standard enthalpies of dehydration were estimated for twenty $M(NTO)_n \cdot mH_2O$.

Keywords: Enthalpy of solution; Lattice energy; Lattice enthalpy; NTO salt; Standard enthalpy of dehydration; Standard enthalpy of formation

1. Introduction

$M(NTO)_n$ and $M(NTO)_n \cdot mH_2O$(NTO represents 3-nitro-1,2,4-triazol-5-one, M, metal) are energetic burning rate catalysts of propellants. As catalysts an understanding of their thermochemical and thermodynamic properties is very important. In the field of studying these properties, Finch et al. [1, 2] reported the standard enthalpies of formation of $M(NTO)_n$(M = NH_4, K, Na, Ag, $n = 1$). Zihui and Rongzu [3, 4] reported the results of enthalpies of solution in water of $M(NTO)_n \cdot mH_2O$ (M = K, $n = m = 1$; M = Li, $n = 1$, $m = 2$; M = Ba, $n = 2$, $m = 3$; M = Ca, $n = 2$, $m = 4$; M = Gd, $n = 3$,

* Corresponding author.

SSDI 0040-6031(95)02680-0

$m = 7$; M = Ni, $n = 2$, $m = 8$) and of enthalpies of precipitation of $KNTO \cdot H_2O$(cr) with $Pb(NO_3)_2$(aq), $CuSO_4$(aq) and $Zn(NO_3)_2$(aq), and of their standard enthalpies of formation. The values of the standard enthalpies of formation of the other metal salts and their hydrates of NTO have not yet been reported in the literature.

In continuation of our studies on thermochemical and thermodynamic properties of $M(NTO)_n$ and $M(NTO)_n \cdot mH_2O$, we now report results from the determination of the enthalpies of solution in water and standard enthalpies of formation of metal (Na, La, Ce, Pr, Eu, Nd, Y, Sm, Yb, Dy, Tb, Co, Mn, Mg) salt hydrates of NTO and the estimated results of some thermochemical and thermodynamic properties for twenty kinds of $M(NTO)_n$ and $M(NTO)_n \cdot mH_2O$.

2. Experimental

2.1. Materials

$M(NTO)_n \cdot mH_2O$ (M = Na, $n = m = 1$; M = La, Ce, Pr, Eu, Sm, $n = 3$, $m = 7$; M = Y, Yb, $n = 3$, $m = 6$; M = Dy, Tb, $n = 3$ $m = 5$; M = Nd, $n = 3$, $m = 8$; M = Co, Mn, Mg, $n = 2$, $m = 8$) used in this work were prepared and recrystallized according to reported methods [5–9]. Their structures were characterised by chemical analysis, molecular weight determination, IR, MS, NMR, TG–DTG techniques, X-ray powder diffraction and emission spectroscopic analyses. Their purities were more than 99.6%. These hydrates were sieved through a 160 mesh sifter and kept in a vacuum desiccator before use. The conductivity of deionized water used in the experiment was 5.48×10^{-8} S cm^{-1}.

2.2. Experimental equipment and conditions

All measurements were made using a Calvet microcalorimeter, type BT215 from Setaram, France, and operated at 298.15 ± 0.005 K.

The experimental precision and accuracy of enthalpies of solution were frequently checked by measurement of the enthalpies of solution ($\Delta_{sol}H^{\theta}_{\infty}$) of crystalline KCl in deionized water at 298.15 K. The experimental value of $\Delta_{sol}H^{\theta}_{\infty}$ of 17.217 ± 0.053 kJ mol^{-1} is an excellent accord with that of $\Delta_{sol}H^{\theta}_{\infty}$ of 17.234 kJ mol^{-1} reported in the literature [10]. This shows that the device of measuring the enthalpy of solution used in this work is reliable.

3. Results and discussion

3.1. Enthalpy of solution in water of $M(NTO)_n \cdot mH_2O$

Results for the enthalpy of solution of $M(NTO)_n \cdot mH_2O$(cr) (M = Na, $n = m = 1$; M = La, Ce, Pr, Eu, Sm, $n = 3$, $m = 7$; M = Y, Yb, $n = 3$, $m = 6$; M = Dy, Tb, $n = 3$, $m = 5$; M = Nd, $n = 3$, $m = 8$; M = Co, Mn, Mg, $n = 2$, $m = 8$) in deionized water at 298.15 K are reported in Tables 1–14, where $\Delta_{sol}H^{\theta}_{m}$ denotes the enthalpy of solution in

Table 1
Enthalpy of solution in water of $NaNTO \cdot H_2O$(cr) at 298.15 K

m/mg	r'		$\Delta_{sol}H_m^\theta$/(kJ mol^{-1})
7.180	11833		30.29
8.130	10450		30.41
12.065	7042		30.65
13.534	6273		30.28
13.738	6184		30.08
16.025	5301		30.62
20.230	4241		30.38
		Mean	30.39 ± 0.28

Table 2
Enthalpy of solution in water of $La(NTO)_3 \cdot 7H_2O$(cr) at 298.15 K

m/mg	r'		$\Delta_{sol}H_m^\theta$/(kJ mol^{-1})
5.180	62900		41.35
5.940	54852		40.92
6.620	49218		40.72
7.550	43135		40.96
7.697	42331		40.96
9.161	35566		40.72
9.418	34596		41.02
10.018	32534		41.40
		Mean	41.01 ± 0.25

Table 3
Enthalpy of solution in water of $Ce(NTO)_3 \cdot 7H_2O$(cr) at 298.15 K

m/mg	r'		$\Delta_{sol}H_m^\theta$/(kJ mol^{-1})
4.780	68291		40.60
6.390	51085		41.13
7.285	44809		41.04
8.600	37957		40.80
9.470	34470		41.12
10.056	32461		40.63
10.950	29811		41.07
15.220	25386		40.72
18.510	17635		41.22
		Mean	40.93 ± 0.24

Table 4
Enthalpy of solution in water of $Pr(NTO)_3 \cdot 7H_2O$(cr) at 298.15 K

m/mg	r'		$\Delta_{sol}H_m^\theta$/(kJ mol^{-1})
11.247	29059		36.81
12.375	26410		37.85
14.300	22855		37.06
18.270	17888		37.13
19.760	16540		37.32
23.040	14181		37.00
24.760	13200		37.34
28.875	11319		36.88
30.430	10740		37.52
36.760	8891		37.76
		Mean	37.27 ± 0.36

Table 5
Enthalpy of solution in water of $Eu(NTO)_3 \cdot 7H_2O$(cr) at 298.15 K

m/mg	r'		$\Delta_{sol}H_m^\theta$/(kJ mol^{-1})
14.208	23391		43.38
15.350	21651		47.34
15.900	20902		48.25
17.180	19345		48.08
17.319	19190		47.98
17.504	18987		48.18
18.370	18092		48.44
18.470	17994		47.60
18.800	17678		47.79
		Mean	48.09 ± 0.29

Table 6
Enthalpy of solution in water of $Nd(NTO)_3 \cdot 8H_2O$(cr) at 298.15 K

m/mg	r'		$\Delta_{sol}H_m^\theta$/(kJ mol^{-1})
7.220	46744		38.67
11.891	28382		39.62
14.590	23132		39.73
15.002	22499		39.14
16.180	20858		39.03
16.376	20609		39.37
17.830	18928		38.73
19.000	17763		38.71
20.250	16666		39.15
20.630	16359		39.70
		Mean	39.15 ± 0.41

Table 7
Enthalpy of solution in water of $Y(NTO)_3 \cdot 6H_2O(cr)$ at 298.15 K

m/mg	r'		$\Delta_{sol}H^{\theta}_{m}$/(kJ mol^{-1})
12.460	23423		33.65
15.947	18301		34.13
22.830	12783		33.81
24.238	12041		34.38
29.520	9886		34.03
31.990	9120		34.00
32.340	9024		33.46
41.470	7038		33.74
		Mean	33.89 ± 0.38

Table 8
Enthalpy of solution in water of $Sm(NTO)_3 \cdot 7H_2O(cr)$ at 298.15 K

m/mg	r'		$\Delta_{sol}H^{\theta}_{m}$/(kJ mol^{-1})
12.560	26397		49.20
12.850	25801		49.74
14.440	22960		49.42
15.590	21267		49.64
15.640	21199		49.64
16.060	20644		49.94
24.620	13467		49.69
27.500	12056		49.83
33.790	9812		49.60
		Mean	49.63 ± 0.24

Table 9
Enthalpy of solution in water of $Yb(NTO)_3 \cdot 6H_2O(cr)$ at 298.15 K

m/mg	r'		$\Delta_{sol}H^{\theta}_{m}$/(kJ mol^{-1})
7.355	45395		36.21
8.900	37514		36.58
13.130	25429		36.20
17.310	19288		36.19
17.390	19199		36.59
17.850	18705		36.48
23.580	14159		36.08
23.640	14123		36.15
		Mean	36.31 ± 0.25

Table 10
Enthalpy of solution in water of $Dy(NTO)_3 \cdot 5H_2O(cr)$ at 298.15 K

m/mg	r'	$\Delta_{sol}H_m^\theta$/(kJ mol^{-1})
9.180	34186	41.63
11.580	27600	41.24
13.200	24213	41.21
13.645	23423	41.31
14.570	21956	41.71
14.830	21552	41.56
19.600	16307	41.59
22.692	14085	41.31
25.070	12748	41.62
	Mean	41.46 ± 0.22

Table 11
Enthalpy of solution in water of $Tb(NTO)_3 \cdot 5H_2O(cr)$ at 298.15 K

m/mg	r'	$\Delta_{sol}H_m^\theta$/(kJ mol^{-1})
9.150	34736	42.17
10.370	30649	41.94
12.250	25945	42.35
12.763	24903	42.12
12.820	24792	41.94
13.340	23825	42.10
15.200	20910	42.09
15.876	20020	42.29
24.165	13152	42.20
	Mean	42.14 ± 0.17

Table 12
Enthalpy of solution in water of $Co(NTO)_2 \cdot 8H_2O(cr)$ at 298.15 K

m/mg	r'	$\Delta_{sol}H_m^\theta$/(kJ mol^{-1})
4.835	47651	61.42
5.570	41363	61.09
5.780	39860	61.39
6.990	32960	61.35
8.180	28165	61.48
9.380	24562	61.11
9.428	24437	61.60
12.000	19199	60.91
12.660	18190	61.72
	Mean	61.34 ± 0.26

Table 13
Enthalpy of solution in water of $Mn(NTO)_2 \cdot 8H_2O(cr)$ at 298.15 K

m/mg	r'		$\Delta_{sol}H_m^\theta$/(kJ mol^{-1})
9.360	24401		64.26
10.570	21608		64.04
10.900	20954		64.08
11.280	20248		63.49
11.950	19113		63.39
12.770	17886		63.14
13.400	17045		63.35
13.800	16550		63.62
		Mean	63.68 ± 0.48

Table 14
Enthalpy of solution in water of $Mg(NTO)_2 \cdot 8H_2O(cr)$ at 298.15 K

m/mg	r'		$\Delta_{sol}H_m^\theta$/(kJ mol^{-1})
1.680	126843		60.43
1.930	110413		60.31
2.400	88791		60.01
3.230	66974		60.66
3.450	61756		60.91
3.810	55494		60.61
4.375	48708		60.35
5.510	38675		60.71
6.140	34706		60.38
		Mean	60.49 ± 0.30

water of the salt of NTO, m is the mass of the salt of NTO, r' is the molar ratio $n(H_2O)/n(M(NTO)_n \cdot mH_2O)$. Throughout this paper uncertainty intervals of reported experimental results denote 99% confidence limits, calculated using Student's t-test at the appropriate number of degrees of freedom.

Because above-mentioned metal salt hydrates of NTO completely ionized in aqueous solution, their ionization processes can be represented as

$$M(NTO)_n \cdot mH_2O(cr) \xrightarrow{\Delta_{sol}H_m^\theta} M^{n+}(aq, \infty) + nNTO^-(aq, \infty) + mH_2O(l) \quad (1)$$

In process (1), the greater values of r' were used. Therefore, the mean of $\Delta_{sol}H_m^\theta$ in Tables 1–14 can be considered at infinite dilution.

3.2. *Standard enthalpy of formation of* $M(NTO)_n \cdot mH_2O(cr)$, $\Delta_f H_m^\theta[M(NTO)_n \cdot mH_2O, cr, 298.15\,K]$

By substituting the mean of $\Delta_{sol} H_m^\theta$ listed in Tables 1–14 and the reported values of $\Delta_f H_m^\theta(NTO^-, aq, \infty)$ of $-(94.3 \pm 2.1)$ kJ mol^{-1} [2], $\Delta_f H_m^\theta(H_2O)$ of -285.83 kJ mol^{-1} [11], $\Delta_f H_m^\theta(Na^+, aq, \infty)$ of -240.12 kJ mol^{-1} [11], $\Delta_f H_m^\theta(La^{3+}, aq, \infty)$ of -707.10 kJ mol^{-1} [11], $\Delta_f H_m^\theta(Ce^{3+}, aq, \infty)$ of -696.22 kJ mol^{-1} [11], $\Delta_f H_m^\theta(Pr^{3+}, aq, \infty)$ of -704.59 kJ mol^{-1} [11], $\Delta_f H_m^\theta(Eu^{3+}, aq, \infty)$ of -605.0 kJ mol^{-1} [11], $\Delta_f H_m^\theta(Nd^{3+}, aq, \infty)$ of -696.22 kJ mol^{-1} [11], $\Delta_f H_m^\theta(Y^{3+}, aq, \infty)$ of -723.41 kJ mol^{-1} [11], $\Delta_f H_m^\theta(Sm^{3+}, aq, \infty)$ of -691.62 kJ mol^{-1} [11], $\Delta_f H_m^\theta(Yb^{3+}, aq, \infty)$ of -674.46 kJ mol^{-1} [11], $\Delta_f H_m^\theta(Dy^{3+}, aq, \infty)$ of -698.73 kJ mol^{-1} [11], $\Delta_f H_m^\theta(Tb^{3+}, aq, \infty)$ of -682.83 kJ mol^{-1} [11], $\Delta_f H_m^\theta(Co^{2+}, aq, \infty)$ of -58.16 kJ mol^{-1} [11], $\Delta_f H_m^\theta(Mn^{2+}, aq, \infty)$ of -220.75 kJ mol^{-1} [11] and $\Delta_f H_m^\theta(Mg^{2+}, aq, \infty)$ of -466.85 kJ mol^{-1} [11], into Eq. (2),

$$\Delta_f H_m^\theta(M(NTO)_n \cdot mH_2O, cr, 298.15\,K) = \Delta_f H_m^\theta(M^{n+}, aq, \infty) + n\Delta_f H_m^\theta(NTO^-, aq, \infty) + m\Delta_f H_m^\theta(H_2O, l) - \Delta_{sol} H_m^\theta \quad (2)$$

the following values were obtained:

$$\Delta_f H_m^\theta(NaNTO \cdot H_2O, cr, 298.15\,K) = -(650.6 \pm 2.4)\ \text{kJ mol}^{-1}$$

$$\Delta_f H_m^\theta(La(NTO)_3 \cdot 7H_2O, cr, 298.15\,K) = -(3031.8 \pm 6.6)\ \text{kJ mol}^{-1}$$

$$\Delta_f H_m^\theta(Ce(NTO)_3 \cdot 7H_2O, cr, 298.15\,K) = -(3020.6 \pm 6.5)\ \text{kJ mol}^{-1}$$

$$\Delta_f H_m^\theta(Pr(NTO)_3 \cdot 7H_2O, cr, 298.15\,K) = -(3025.6 \pm 6.7)\ \text{kJ mol}^{-1}$$

$$\Delta_f H_m^\theta(Eu(NTO)_3 \cdot 7H_2O, cr, 298.15\,K) = -(2936.8 \pm 6.6)\ \text{kJ mol}^{-1}$$

$$\Delta_f H_m^\theta(Nd(NTO)_3 \cdot 8H_2O, cr, 298.15\,K) = -(3304.9 \pm 6.7)\ \text{kJ mol}^{-1}$$

$$\Delta_f H_m^\theta(Y(NTO)_3 \cdot 6H_2O, cr, 298.15\,K) = -(2755.2 \pm 6.7)\ \text{kJ mol}^{-1}$$

$$\Delta_f H_m^\theta(Sm(NTO)_3 \cdot 7H_2O, cr, 298.15\,K) = -(3025.0 \pm 6.5)\ \text{kJ mol}^{-1}$$

$$\Delta_f H_m^\theta(Yb(NTO)_3 \cdot 6H_2O, cr, 298.15\,K) = -(2708.6 \pm 6.6)\ \text{kJ mol}^{-1}$$

$$\Delta_f H_m^\theta(Dy(NTO)_3 \cdot 5H_2O, cr, 298.15\,K) = -(2452.2 \pm 6.5)\ \text{kJ mol}^{-1}$$

$$\Delta_f H_m^\theta(Tb(NTO)_3 \cdot 5H_2O, cr, 298.15\,K) = -(2437.0 \pm 6.5)\ \text{kJ mol}^{-1}$$

$$\Delta_f H_m^\theta(Co(NTO)_2 \cdot 8H_2O, cr, 298.15\,K) = -(2594.7 \pm 4.5)\ \text{kJ mol}^{-1}$$

$$\Delta_f H_m^\theta(Mn(NTO)_2 \cdot 8H_2O, cr, 298.15\,K) = -(2759.7 \pm 4.7)\ \text{kJ mol}^{-1}$$

$$\Delta_f H_m^\theta(Mg(NTO)_2 \cdot 8H_2O, cr, 298.15\,K) = -(3002.6 \pm 4.5)\ \text{kJ mol}^{-1}$$

3.3. Standard enthalpy of formation of $NTO^-(g)$, $\Delta_f H_m^\theta(NTO^-, g)$

Assuming that $\Delta H_L^\theta(MNTO, cr)$ is the lattice enthalpy in forming the crystal MNTO from $M^+(g)$ and $NTO^-(g)$ at 298.15 K

$$M^+(g) + NTO^-(g) \xrightarrow{\Delta H_L^\theta(MNTO, cr)} MNTO(cr) \tag{3}$$

the equation for calculating the standard enthalpy of formation, $\Delta_f H_m^\theta(NTO^-, g)$, of gaseous anion $NTO^-(g)$ may be expressed as

$$\begin{aligned}\Delta_f H_m^\theta(NTO^-, g) &= \Delta_f H_m^\theta(MNTO, cr, 298.15\,K) \\ &\quad - \Delta_f H_m^\theta(M^+, g) - \Delta H_L^\theta(MNTO, cr) \\ &= \Delta_f H_m^\theta(MNTO, cr, 298.15\,K) - \Delta_f H_m^\theta(M^+, g) \\ &\quad - \Delta U_L^\theta(MNTO, cr) - \Delta nRT \end{aligned} \tag{4}$$

where $\Delta H_L^\theta(MNTO, cr) = \Delta U_L^\theta(MNTO, cr) + \Delta nRT$ and $\Delta U_L^\theta(MNTO, cr)$ is the crystal lattice energy.

By substituting the following three sets of initial data into Eq. (4)

for $NH_4NTO(cr)$, $\Delta_f H_m^\theta(NH_4NTO, cr) = -269.9$ kJ mol^{-1} [1]; $\Delta_f H_m^\theta(NH_4^+, g) = 619$ kJ mol^{-1} [10]; $\Delta U_L^\theta(NH_4NTO, cr) = -512$ kJ mol^{-1} [1]; $\Delta n = -2$; $RT = 2.5$ kJ mol^{-1}.
for $KNTO(cr)$, $\Delta_f H_m^\theta(KNTO, cr) = -385.1$ kJ mol^{-1} [2]; $\Delta_f H_m^\theta(K^+, g) = 514.30$ kJ mol^{-1} [10]; $\Delta U_L^\theta(KNTO, cr) = -550$ kJ mol^{-1} [1]; $\Delta n = -2$; $RT = 2.5$ kJ mol^{-1}.
for $NaNTO(cr)$, $\Delta_f H_m^\theta(NaNTO, cr) = -362.6$ kJ mol^{-1} [2]; $\Delta_f H_m^\theta(Na^+, g) = 608.98$ kJ mol^{-1} [10]; $\Delta U_L^\theta(NaNTO, cr) = -560$ kJ mol^{-1} [1]; $\Delta n = -2$; $RT = 2.5$ kJ mol^{-1}.

the mean of $\Delta_f H_m^\theta(NTO^-, g)$ of -374.3 kJ mol^{-1} is obtained.

3.4. Lattice energy of $M(NTO)_n(cr)$, $\Delta U_L^\theta[M(NTO)_n, cr]$

Values of $\Delta U_L^\theta[M(NTO)_n, cr]$ are calculated using Kapustinskii's equation [4]:

$$\Delta U_L^\theta = 1201.6 \frac{\eta_1 \eta_2 \Sigma n'}{r_1 + r_2}\left(1 - \frac{0.345}{r_1 + r_2}\right) \text{kJ mol}^{-1} \tag{6}$$

where η_1 and η_2 are the moduli of the anion and cation charges; n' is the number of ions in the molecule; r_1 and r_2 are the radii of anion and cation in Å. For $M(NTO)_n(cr)$, $\eta_1 = \eta_{NTO} = 1$; $\eta_2 = \eta_{M^{n+}} = n$; $n' = n(M^{n+} + nNTO^-) = 1 + n$; $r_1 = r(NTO^-, g) = 2.5$ Å [1]; $r_2 = r(M^{n+}, g)$, these values are taken from Ref. [12].

The results of the calculation are given in Table 15, from which it is seen that the values of $-\Delta U_{L(M(NTO)_3)}^\theta$, increase with increasing the atomic number of the elements in the lanthanide series. The magnitude of the lattice energy of $Y(NTO)_3$ falls between those of $Tb(NTO)_3$ and $Dy(NTO)_3$. It has been proved once again that Yttrium belongs to the group of heavy rare earth elements.

Table 15
The lattice energy, lattice enthalpy and standard enthalpy of formation for $M(NTO)_n$(cr)

$M(NTO)_n$	$\Delta_f H_m^\theta(M^{n+}, g)$[6]/(kJ mol^{-1})	$r(M^{n+}, g)$/Å	$-\Delta U_L^\theta$/(kJ mol^{-1})	$-\Delta H_L^\theta$/(kJ mol^{-1})	$-\Delta_f H_m^\theta$[$M(NTO)_n$, cr]/(kJ mol^{-1})
LiNTO	679.57	0.60	689.0	694.0	388.7
NaNTO	608.98	0.95	626.9	613.9	397.2
KNTO	514.30	1.33	571.0	575.9	435.9
$Mg(NTO)_2$	2348.5	0.65	2038	2046	446.1
$Ca(NTO)_2$	1925.9	0.99	1862	1869	691.7
$Mn(NTO)_2$	2519.2	0.80	1956	1964	193.6
$Co(NTO)_2$	2841.6	0.74	1988	1996	97.0
$Cu(NTO)_2$	3054.0	0.72	1999	2007	−298.4
$Zn(NTO)_2$	2782.7	0.74	1988	1996	−38.1
$Y(NTO)_3$	4215.4[a]	0.93	3781	3791	698.5
$La(NTO)_3$	3904.5(57)[b]	1.061	3657	3667	885.4
$Ce(NTO)_3$	3963.9(58)	1.034	3682	3692	851.0
$Pr(NTO)_3$	4002.0(59)	1.013	3702	3711	831.9
$Nd(NTO)_3$	4041.3[a](60)	0.995	3719	3728	809.6
$Sm(NTO)_3$	4095.3[a](62)	0.964	3748	3758	785.6
$Eu(NTO)_3$	4230.9[a](63)	0.950	3762	3772	664.0
$Gd(NTO)_3$	4165.6[a](64)	0.938	3773	3783	740.3
$Tb(NTO)_3$	4197.0[a](65)	0.923	3788	3798	723.9
$Dy(NTO)_3$	4206.6[a](66)	0.908	3803	3813	729.3
$Yb(NTO)_3$	4318.9(70)	0.858	3853	3863	604.0

[a] Cited from Ref. [12].

[b] The data in parentheses are the atomic numbers of the elements in the lanthanide series.

3.5. *Lattice enthalpy of* $M(NTO)_n(cr)$, ΔH_L^θ [$M(NTO)_n$, cr]

These values are calculated according to the process (7) and relationship (8):

$$M^+(g) + nNTO^-(g) \xrightarrow{\Delta H_L^\theta[M(NTO)_n, cr]} M(NTO)_n(cr) \quad (7)$$

and

$$\Delta H_L^\theta[M(NTO)_n, cr] = \Delta U_L^\theta[M(NTO)_n, cr] + \Delta nRT \quad (8)$$

where $\Delta n = -(n+1)$; $RT = 2.5\ kJ\ mol^{-1}$.

The results of the calculations are shown in Table 15.

3.6. *Standard enthalpy of formation of* $M(NTO)_n(cr)$, $\Delta_f H_m^\theta[M(NTO)_n, cr, 298.15\ K]$

These values are calculated by using the process (7) and Eq. (9):

$$\Delta_f H_m^\theta[M(NTO)_n, cr, 298.15\ K] = \Delta_f H_m^\theta(M^{n+}, g) + n\Delta_f H_m^\theta(NTO^-, g) + \Delta H_L^\theta[M(NTO)_n, cr] \quad (9)$$

where values of $\Delta_f H_m^\theta(M^{n+}, g)$ are taken from Refs. [2, 12].

The results of the calculations are shown in Table 15. Two plots of $-\Delta U_L^\theta[M(NTO)_n, cr]$, $-\Delta H_L^\theta[M(NTO)_n, cr]$, $-\Delta_f H_m^\theta[M(NTO)_n, cr]$ against the atomic numbers (Z) and ionic radii (r) of elements in the lanthanide series are shown in Fig. 1. Six straight lines in Fig. 1 can be described using the six expressions:

$$\Delta U_L^\theta[M(NTO)_n, cr] = -2840 - 14.55Z,\ R' = -0.9941$$

$$\Delta H_L^\theta[M(NTO)_n, cr] = -2837 - 14.77Z,\ R' = -0.9955$$

$$\Delta_f H_m^\theta[M(NTO)_n, cr] = -1873 + 17.57Z,\ R' = 0.9865 \text{ (except Eu and Yb)}$$

$$\Delta U_L^\theta[M(NTO)_n, cr] = -4664 + 950.6r,\ R' = 0.9983$$

$$\Delta H_L^\theta[M(NTO)_n, cr] = -4689 + 964.8r,\ R' = 0.9998$$

$$\Delta_f H_m^\theta[M(NTO)_n, cr] = 266.5 - 1083r,\ R' = -0.9920 \text{ (except Eu and Yb)}$$

3.7. *Lattice enthalpy and energy of* $M(NTO)_n \cdot mH_2O(cr)$, $\Delta H_L^\theta[M(NTO)_n \cdot mH_2O, cr]$, $\Delta U_L^\theta[M(NTO)_n \cdot mH_2O, cr]$

Setting ΔH_L^θ [$M(NTO)_n \cdot mH_2O$, cr] as the lattice enthalpy in forming the crystal $M(NTO)_n \cdot mH_2O$ from $M^{n+}(g)$, $NTO^-(g)$ and $H_2O(g)$ at 298.15 K and ΔU_L^θ [$M(NTO)_n \cdot mH_2O$, cr] as the crystal lattice energy

$$M^{n+}(g) + nNTO^-(g) + mH_2O(g) \xrightarrow{\Delta H_L^\theta[M(NTO)_n \cdot mH_2O, cr]} M(NTO)_n \cdot mH_2O(cr) \quad (10)$$

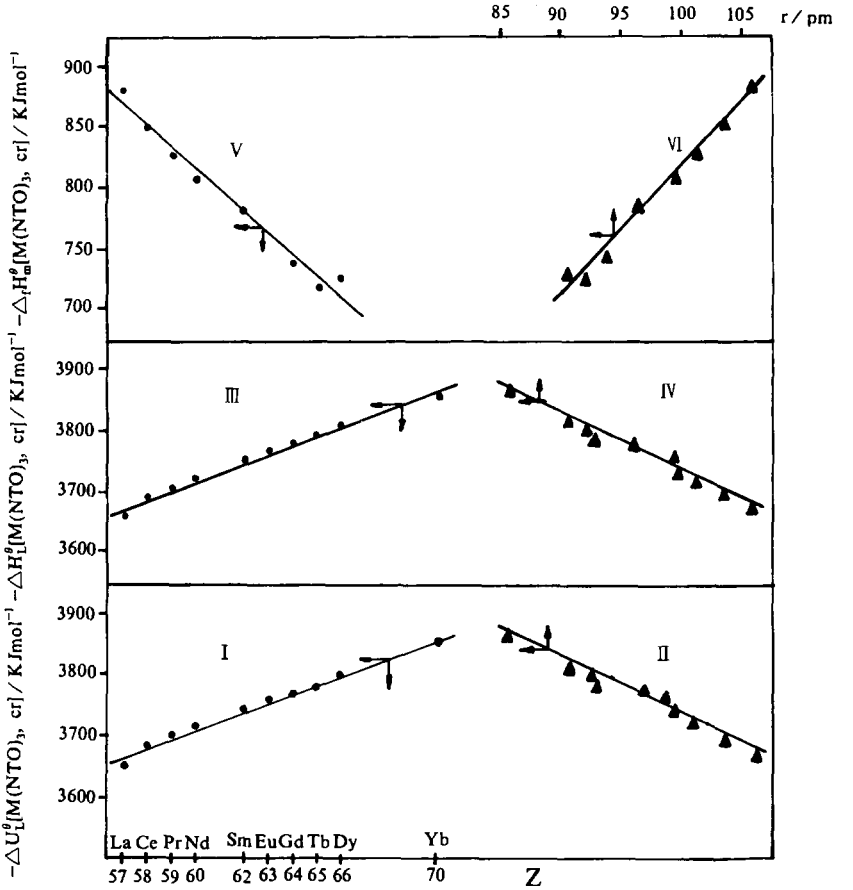

Fig. 1. A plot of $-\Delta U_L^\theta$[M(NTO)$_3$, cr], $-\Delta H_L^\theta$[M(NTO)$_3$, cr] and $-\Delta_f H_m^\theta$[M(NTO)$_3$, cr] values vs. the values of Z and r of elements in the lanthanide series.

we have

$$\Delta H_L^\theta[\mathrm{M(NTO)}_n\cdot m\mathrm{H_2O}, \mathrm{cr}] = \Delta_f H_m^\theta[\mathrm{M(NTO)}_n\cdot m\mathrm{H_2O}, \mathrm{cr}, 298.15\,\mathrm{K}] - \Delta_f H_m^\theta(\mathrm{M}^{n+}, \mathrm{g}) - n\Delta_f H_m^\theta(\mathrm{NTO}^-, \mathrm{g}) - m\Delta_f H_m^\theta(\mathrm{H_2O}, \mathrm{g}) \quad (11)$$

and

$$\Delta U_L^\theta[\mathrm{M(NTO)}_n\cdot m\mathrm{H_2O}, \mathrm{cr}] = \Delta H_L^\theta[\mathrm{M(NTO)}_n\cdot m\mathrm{H_2O}, \mathrm{cr}] - \Delta nRT \quad (12)$$

where $\Delta_f H_m^\theta(\mathrm{H_2O}, \mathrm{g}) = -241.82\ \mathrm{kJ\ mol^{-1}}$ [10]; $\Delta n = -(m+n+1)$; $RT = 2.5\ \mathrm{kJ\ mol^{-1}}$.

By substituting the above-mentioned data into Eqs. (11) and (12), the values of $\Delta H_L^\theta[M(NTO)_n \cdot mH_2O, cr]$ and $\Delta U_L^\theta[M(NTO)_n \cdot mH_2O, cr]$ in Table 16 are obtained.

3.8. Standard enthalpy of dehydration of $M(NTO)_n \cdot mH_2O(cr)$, $\Delta H_d^\theta[M(NTO)_n \cdot mH_2O, cr]$

These values were calculated according to process (13) and Eq. (14).

$$M(NTO)_n \cdot mH_2O \xrightarrow{\Delta H_d^\theta[M(NTO)_n \cdot mH_2O, cr]} M(NTO)_n(cr) + mH_2O(l) \quad (13)$$

and

$$\Delta H_d^\theta[M(NTO)_n \cdot mH_2O, cr] = \Delta_f H_m^\theta[M(NTO)_n, cr, 298.15\,K] + m\Delta_f H_m^\theta(H_2O, l) - \Delta_f H_m^\theta[M(NTO)_n \cdot mH_2O, cr. 298.15\,K] \quad (14)$$

where $\Delta_f H_m^\theta(H_2O, l) = -285.83\,kJ\,mol^{-1}$ [10].

The results of the calculation are given in Table 16.

Table 16
The standard enthalpy of formation, lattice enthalpy, lattice energy and standard enthalpy of dehydration for $M(NTO)_n \cdot mH_2O$

$M(NTO)_n \cdot mH_2O$	$-\Delta_f H_m^\theta$/(kJ mol^{-1})	$-\Delta H_L^\theta$/(kJ mol^{-1})	$-\Delta U_L^\theta$/(kJ mol^{-1})	ΔH_d^θ/(kJ mol^{-1})
$LiNTO \cdot 2H_2O$	966.6 ± 2.2 [a]	788.13	778.21	6.21
$NaNTO \cdot H_2O$	650.6 ± 2.4	643.36	635.92	2.17
$KNTO \cdot H_2O$	676.9 ± 2.6 [a]	574.98	567.54	5.97
$Mg(NTO)_2 \cdot 8H_2O$	3002.6 ± 4.5	2667.74	2640.46	269.86
$Ca(NTO)_2 \cdot 4H_2O$	1905.5 ± 4.4 [a]	2115.32	2097.96	70.48
$Mn(NTO)_2 \cdot 8H_2O$	2759.7 ± 4.7	2595.54	2568.26	279.66
$Co(NTO)_2 \cdot 8H_2O$	2594.7 ± 4.5	2752.94	2725.66	211.06
$Cu(NTO)_2 \cdot 2H_2O$	712.1 ± 5.4 [a]	2533.66	2521.26	438.84
$Zn(NTO)_2 \cdot H_2O$	628.8 ± 5.7 [a]	2420.88	2410.96	381.07
$Y(NTO)_3 \cdot 6H_2O$	2755.2 ± 6.7	4395.08	4370.28	340.32
$La(NTO)_3 \cdot 7H_2O$	3031.8 ± 6.6	4120.36	4093.08	145.59
$Ce(NTO)_3 \cdot 7H_2O$	3020.9 ± 6.5	4168.86	4141.58	169.09
$Pr(NTO)_3 \cdot 7H_2O$	3025.6 ± 6.7	4211.66	4184.38	192.89
$Nd(NTO)_3 \cdot 8H_2O$	3304.9 ± 6.7	4288.44	4258.68	208.66
$Sm(NTO)_3 \cdot 7H_2O$	3025.0 ± 6.5	4304.36	4277.08	238.59
$Eu(NTO)_3 \cdot 7H_2O$	2936.8 ± 6.6	4352.06	4324.78	271.99
$Gd(NTO)_3 \cdot 7H_2O$	3020.1 ± 6.4 [a]	4370.06	4342.78	278.99
$Tb(NTO)_3 \cdot 5H_2O$	2437.0 ± 6.5	4302	4289.68	283.95
$Dy(NTO)_3 \cdot 5H_2O$	2452.2 ± 6.5	4326.8	4314.48	293.75
$Yb(NTO)_3 \cdot 6H_2O$	2708.6 ± 6.6	4516.38	4491.58	389.62

[a] Cited from Ref. [3]

References

[1] A. Finch, P.J. Gardner, A.J. Head and H.S. Majdi, Thermochim. Acta, 213 (1993) 17–22.
[2] A. Finch, P.J. Gardner, A.J. Head and H.S. Majdi, J. Chem. Thermodyn., 23(12) (1991) 1169–1173.
[3] Meng Zihui and Hu Rongzu, J. Therm. Anal., 45(1–2) (1995) 79–86.
[4] Hu Rongzu and Meng Zihui, Proc. 3rd Beijing Int. Symp. Pyrotechnics and Explos., Beijing, China, 1995, Beijing Institute of Technology Press, Beijing, 1995, pp. 160–166.
[5] Zhang Tonglai, Hu Rongzu, Liang Yanjun and Li Fuping, J. Therm. Anal., 39 (1993) 827–847
[6] Zhang Tonglai, Hu Rongzu and Li Fuping, Thermochim. Acta, 244 (1994) 185–194.
[7] Zhang Tonglai, Hu Rongzu and Li Fuping, 9th Symp. Chem. Problems Connected with the Stability of Explos., Margretetorp, Sweden, 1993, p. 259–265.
[8] Xie Yi, Hu Rongzu, Zhang Tonglai and Li Fuping, J. Therm. Anal. 39 (1993) 41–51.
[9] Zhang Tonglai, Hu Rongzu and Li Fuping, Energ. Mater. 1(4) (1993) 827–847 (in Chinese).
[10] R.C. Weast, CRC Handbook of Chemistry and Physics, 70th edn, CRC Press Inc., Boca Raton, FL, 1989, D–122.
[11] R.C. Weast, CRC Handbook of Chemistry and Physics, 63rd edn, CRC Press Inc, Boca Raton, FL, 1982–1983, D 52–95.
[12] Yi Jinzhi and Sun Tongshan, personal communication, 1995.