

STANDARD ENTHALPY OF FORMATION OF METAL (K, Ba, Li, Ca, Gd, Pb, Cu AND Zn) SALTS OF NTO

*Zihui Meng and Rongzu Hu**

Xian Modern Chemistry Research Institute, Xian 710061 Shaanxi, P. R. China

Abstract

From measurements of the enthalpy of solution of metal salts of 3-nitro-1,2,4-triazol-5-one (NTO) in water, the standard enthalpies of formation of $\text{KNTO}\cdot\text{H}_2\text{O}$, $\text{Ba}(\text{NTO})_2\cdot 3\text{H}_2\text{O}$, $\text{LiNTO}\cdot 2\text{H}_2\text{O}$, $\text{Ca}(\text{NTO})_2\cdot 4\text{H}_2\text{O}$ and $\text{Gd}(\text{NTO})_3\cdot 7\text{H}_2\text{O}$ were determined as $-(676.9\pm 2.6)$, $-(1627.0\pm 2.5)$, $-(966.6.3\pm 2.2)$, $-(1905.5\pm 4.4)$ and $-(3020.1\pm 6.4)$ $\text{kJ}\cdot\text{mol}^{-1}$, respectively. From measurements of the enthalpy of precipitation of $\text{KNTO}\cdot\text{H}_2\text{O}$ crystal with $\text{Pb}(\text{NO}_3)_2(\text{aq})$, $\text{CuSO}_4(\text{aq})$ and $\text{Zn}(\text{NO}_3)_2(\text{aq})$, the standard enthalpies of formation of $\text{Pb}(\text{NTO})_2\cdot\text{H}_2\text{O}$, $\text{Cu}(\text{NTO})_2\cdot 2\text{H}_2\text{O}$ and $\text{Zn}(\text{NTO})_2\cdot\text{H}_2\text{O}$ were determined as $-(247.4\pm 5.9)$, $-(712.1\pm 5.4)$ and $-(628.8\pm 5.7)$ $\text{kJ}\cdot\text{mol}^{-1}$, respectively.

Keywords: enthalpy of formation, enthalpy of reaction, enthalpy of solution, microcalorimetry, NTO salts

Introduction

The use of certain metal salts of 3-nitro-1,2,4-triazol-5-one (NTO) as energetic combustion catalysts in propellants has recently been proposed [1]. The standard enthalpies of formation of the silver, ammonium, sodium and potassium salts of NTO have been determined [2, 3]. The present paper reports the determination of the standard enthalpies of formation of the potassium salt monohydrate ($\text{KNTO}\cdot\text{H}_2\text{O}$), the barium salt trihydrate ($\text{Ba}(\text{NTO})_2\cdot 3\text{H}_2\text{O}$), the lithium salt dihydrate ($\text{LiNTO}\cdot 2\text{H}_2\text{O}$), the calcium salt tetrahydrate ($\text{Ca}(\text{NTO})_2\cdot 4\text{H}_2\text{O}$), the gadolinium salt heptahydrate ($\text{Gd}(\text{NTO})_3\cdot 7\text{H}_2\text{O}$), the lead salt monohydrate ($\text{Pb}(\text{NTO})_2\cdot\text{H}_2\text{O}$), the copper salt dihydrate ($\text{Cu}(\text{NTO})_2\cdot 2\text{H}_2\text{O}$) and the zinc salt monohydrate ($\text{Zn}(\text{NTO})_2\cdot\text{H}_2\text{O}$) of NTO by means of solution/reaction calorimetry.

* To whom correspondence should be addressed.

Experimental

Materials

The $\text{KNTO}\cdot\text{H}_2\text{O}$, $\text{Ba}(\text{NTO})_3\cdot 3\text{H}_2\text{O}$, $\text{LiNTO}\cdot 2\text{H}_2\text{O}$, $\text{Ca}(\text{NTO})_2\cdot 4\text{H}_2\text{O}$, $\text{Gd}(\text{NTO})_3\cdot 7\text{H}_2\text{O}$, $\text{Pb}(\text{NTO})_2\cdot \text{H}_2\text{O}$, $\text{Cu}(\text{NTO})_2\cdot 2\text{H}_2\text{O}$ and $\text{Zn}(\text{NTO})_2\cdot \text{H}_2\text{O}$ used in this work were prepared and recrystallized according to reported methods [4].

The results of chemical analysis and elemental analysis showed that these salts had the expected compositions and were pure enough for calorimetric experiments.

All salts were sieved through a 160 mesh sifter before experiments.

The conductivity of the deionized water used in the experiments was $5.48 \times 10^{-8} \text{ s}\cdot\text{cm}^{-1}$.

0.02502 M $\text{Pb}(\text{NO}_3)_2(\text{aq})$, 0.05607 M $\text{CuSO}_4(\text{aq})$ and 0.05204 M $\text{Zn}(\text{NO}_3)_2(\text{aq})$ were prepared by dissolving $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (AR, >99%), $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (AR, >99%) and $\text{Pb}(\text{NO}_3)_2$ (GR, 99.9%) in deionized water. All these reagents were commercial products of the Xian Chemical Reagent Factory.

Experimental equipment and conditions

All measurements were made with a Calvet microcalorimeter, type BT215 from SETARAM, France, and operated at $(298.15 \pm 0.005) \text{ K}$ as described previously [5].

The experimental precision and accuracy of enthalpies of solution were frequently checked by measurements of the enthalpies of solution of $\text{KCl}(\text{cr})$ in deionized water.

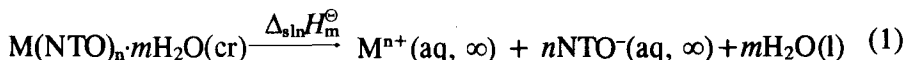
Results and discussion

Results on the enthalpies of solution of $\text{M}(\text{NTO})_n\cdot m\text{H}_2\text{O}(\text{cr})$ ($M=\text{K}$, $n=1$, $m=1$; $M=\text{Ba}$, $n=2$, $m=3$; $M=\text{Li}$, $n=1$, $m=2$; $M=\text{Ca}$, $n=2$, $m=4$; $M=\text{Gd}$, $n=3$, $m=7$) in deionized water at 298.15 K are reported in Tables 1–5, where $\Delta_{\text{soln}}H_m^\ominus$ denotes the enthalpy of solution in water of the NTO salt, m is the mass of the NTO salt, and r is the molar ratio $n(\text{H}_2\text{O})/n(\text{M}(\text{NTO})_n\cdot m\text{H}_2\text{O})$.

Results on the enthalpy $\Delta_r H_m^\ominus$ of precipitation of $\text{KNTO}\cdot\text{H}_2\text{O}$ with $\text{Pb}(\text{NO}_3)_2(\text{aq})$, $\text{CuSO}_4(\text{aq})$ and $\text{Zn}(\text{NO}_3)_2(\text{aq})$ at 298.15 K are reported in Tables 6–8, where m denotes the mass of $\text{KNTO}\cdot\text{H}_2\text{O}$ crystal.

Throughout this paper, the uncertainty intervals of the reported experimental results denote 99% confidence limits, calculated using Student's *t*-test with the appropriate number of degrees of freedom.

As the above salts were completely ionized in aqueous solution, and no solid residue was observed in the solution after calorimetry, the following equation holds:



The results for the solution reaction show a slight concentration dependence and the dilution of the final state in solution experiments; i.e. the values of r , is high enough to approximate closely to infinite dilution, and thus the following equation holds:

Table 1 Enthalpy of solution in water of $\text{KNTO} \cdot \text{H}_2\text{O}(\text{cr})$ at 298.15 K

m /mg	r	$\Delta_{\text{soln}}H_m^\ominus/\text{kJ} \cdot \text{mol}^{-1}$
7.284	13310	45.06
8.932	10800	43.61
9.147	10604	44.23
11.311	8539	44.68
12.403	7950	44.52
15.376	6292	45.32
16.601	5819	44.01
17.284	5589	44.01
20.176	4789	44.28
22.301	4340	43.78
25.505	3772	44.08
27.163	3554	44.94
29.778	3243	45.24
		Mean 44.41±0.48

$$\Delta_f H_m^\ominus(M(\text{NTO})_n \cdot m\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = \Delta_f H_m^\ominus(M^{n+}, \text{aq}, \infty) + n\Delta_f H_m^\ominus(\text{NTO}^-, \text{aq}, \infty) + m\Delta_f H_m^\ominus(\text{H}_2\text{O}, \text{l}) - \Delta_{\text{soln}}H_m^\ominus \quad (2)$$

By substituting the mean of the $\Delta_{\text{soln}}H_m^\ominus$ values in Tables 1–5 and the reported values $\Delta_f H_m^\ominus(\text{NTO}^-, \text{aq}, \infty) = -(94.3 \pm 2.1) \text{ kJ} \cdot \text{mol}^{-1}$ [2], $\Delta_f H_m^\ominus(\text{H}_2\text{O}, \text{l}) = -285.83 \text{ kJ} \cdot \text{mol}^{-1}$ [6], $\Delta_f H_m^\ominus(\text{K}^+, \text{aq}, \infty) = -252.38 \text{ kJ} \cdot \text{mol}^{-1}$ [6], $\Delta_f H_m^\ominus(\text{Ba}^{2+}, \text{aq}, \infty) = -537.64 \text{ kJ} \cdot \text{mol}^{-1}$ [6], $\Delta_f H_m^\ominus(\text{Li}^+, \text{aq}, \infty) = -278.48 \text{ kJ} \cdot \text{mol}^{-1}$ [6], $\Delta_f H_m^\ominus(\text{Ca}^{2+}, \text{aq}, \infty) = -542.83 \text{ kJ} \cdot \text{mol}^{-1}$ [6], and $\Delta_f H_m^\ominus(\text{Gd}^{3+}, \text{aq}, \infty) = -686.18 \text{ kJ} \cdot \text{mol}^{-1}$ [6], into Eq. (2), the following values were obtained:

$$\Delta_f H_m^\ominus(\text{KNTO} \cdot \text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(676.9 \pm 2.6) \text{ kJ} \cdot \text{mol}^{-1}$$

Table 2 Enthalpy of solution in water of Ba(NTO)₂·3H₂O(cr) at 298.15 K

<i>m</i> /mg	<i>r</i>	$\Delta_{\text{slp}}H_m^\ominus/\text{kJ}\cdot\text{mol}^{-1}$
5.30	79638	43.65
6.594	66942	43.53
6.433	65137	43.21
9.312	47443	43.20
10.242	43033	43.01
12.176	36335	43.39
15.152	29026	42.91
15.388	28681	43.01
15.450	31764	44.00
Mean 43.32±0.39		

Table 3 Enthalpy of solution in water of LiNTO·2H₂O(cr) at 298.15 K

<i>m</i> /mg	<i>r</i>	$\Delta_{\text{slp}}H_m^\ominus/\text{kJ}\cdot\text{mol}^{-1}$
2.534	26969	22.00
2.640	25936	22.00
4.791	16407	22.09
6.596	10560	22.17
6.892	9808	22.31
7.315	9225	22.16
8.740	7626	22.02
10.000	6696	22.12
10.041	6749	22.20
10.030	6684	22.30
11.022	6207	22.26
13.034	6135	22.14
10.970	6142	22.20
11.965	5686	22.25
11.954	5674	22.68
11.952	5697	22.02
Mean 22.16±0.08		

$$\Delta_f H_m^\ominus(\text{Ba}(\text{NTO})_2 \cdot 3\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(1627.0 \pm 2.5) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^\ominus(\text{LiNTO} \cdot 2\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(966.6 \pm 2.2) \text{ kJ}\cdot\text{mol}^{-1}$$

Table 4 Enthalpy of solution in water of $\text{Ca}(\text{NTO})_2 \cdot 4\text{H}_2\text{O}(\text{cr})$ at 298.15 K

m /mg	r	$\Delta_{\text{soln}}H_m^\ominus/\text{kJ}\cdot\text{mol}^{-1}$
6.081	28548	31.24
9.442	19371	30.90
10.606	16359	30.84
16.935	10237	30.89
19.112	9075	30.33
21.536	8057	30.56
23.538	7361	31.07
27.060	6413	31.02
30.359	5713	30.43
35.360	4908	30.68
39.371	4406	30.73
45.352	3826	30.49
51.107	3394	30.70
55.288	3135	30.90
66.290	2616	30.30
		Mean 30.74±0.21

Table 5 Enthalpy of solution in water of $\text{Gd}(\text{NTO})_3 \cdot 7\text{H}_2\text{O}(\text{cr})$ at 298.15 K

m /mg	r	$\Delta_{\text{soln}}H_m^\ominus/\text{kJ}\cdot\text{mol}^{-1}$
2.560	135832	50.20
5.841	59507	50.21
6.522	53316	50.11
6.738	51631	49.94
8.259	42280	50.33
8.700	39997	50.19
9.434	46843	50.29
13.229	27557	50.12
14.440	24123	50.03
		Mean 50.19±0.13

$$\Delta_f H_m^\ominus(\text{Ca}(\text{NTO})_2 \cdot 4\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(1905.5 \pm 4.4) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^\ominus(\text{Gd}(\text{NTO})_3 \cdot 7\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(3020.1 \pm 6.4) \text{ kJ}\cdot\text{mol}^{-1}$$

Table 6 Enthalpy of precipitation of KNTO·H₂O(cr) with 0.02502 M Pb(NO₃)₂(aq) at 298.15 K

<i>m</i> /mg	$\Delta_r H_{m1}^{\ominus}$ /kJ·mol ⁻¹
4.381	83.45
5.482	82.37
7.064	83.36
8.248	81.86
9.567	82.61
11.500	81.81
12.740	82.34
12.794	82.45
19.179	81.61
Mean 82.43±0.72	

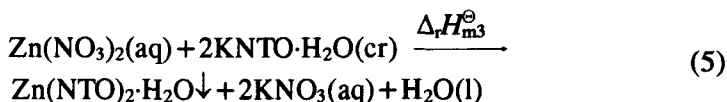
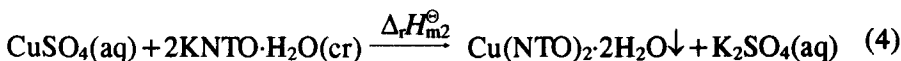
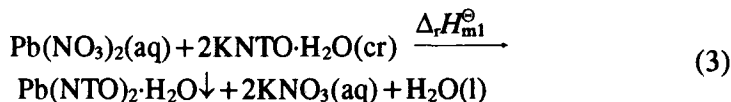
Table 7 Enthalpy of precipitation of KNTO·H₂O(cr) with 0.05607 M CuSO₄(aq) at 298.15 K

<i>m</i> /mg	$\Delta_r H_{m2}^{\ominus}$ /kJ·mol ⁻¹
12.150	72.38
13.949	72.20
20.711	72.18
22.322	72.02
22.756	72.33
25.050	72.14
Mean 72.20±0.21	

Table 8 Enthalpy of precipitation of KNTO·H₂O(cr) with 0.02504 M Zn(NO₃)₂(aq) at 298.15 K

<i>m</i> /mg	$\Delta_r H_{m3}^{\ominus}$ /kJ·mol ⁻¹
13.410	88.35
15.142	88.73
16.100	88.47
17.494	87.76
18.258	88.05
19.046	88.13
23.345	87.58
24.034	87.87
26.260	89.11
Mean 88.30±0.53	

According to precipitation reactions 3–5 for $\text{KNTO}\cdot\text{H}_2\text{O}(\text{cr})$ with $\text{Pb}(\text{NO}_3)_2(\text{aq})$, $\text{CuSO}_4(\text{aq})$ and $\text{Zn}(\text{NO}_3)_2(\text{aq})$:



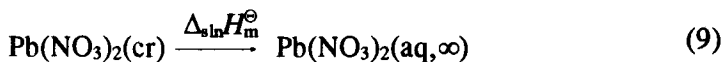
and Eqs 6–8, deduced from reactions 3–5:

$$\Delta_f H_m^\ominus \text{Pb}(\text{NTO})_2\cdot\text{H}_2\text{O}(\text{cr}) = \Delta_r H_{m1}^\ominus + \Delta_f H_m^\ominus \text{Pb}(\text{NO}_3)_2(\text{aq}) + 2\Delta_f H_m^\ominus \text{KNTO}\cdot\text{H}_2\text{O}(\text{cr}) - 2\Delta_f H_m^\ominus \text{KNO}_3(\text{aq}) - \Delta_f H_m^\ominus \text{H}_2\text{O}(\text{l}) \quad (6)$$

$$\Delta_f H_m^\ominus \text{Cu}(\text{NTO})_2\cdot 2\text{H}_2\text{O}(\text{cr}) = \Delta_r H_{m2}^\ominus + \Delta_f H_m^\ominus \text{CuSO}_4(\text{aq}) + 2\Delta_f H_m^\ominus \text{KNTO}\cdot\text{H}_2\text{O}(\text{cr}) - \Delta_f H_m^\ominus \text{K}_2\text{SO}_4(\text{aq}) \quad (7)$$

$$\Delta_f H_m^\ominus \text{Zn}(\text{NTO})_2\cdot\text{H}_2\text{O}(\text{cr}) = \Delta_r H_{m3}^\ominus + 2\Delta_f H_m^\ominus \text{KNTO}\cdot\text{H}_2\text{O}(\text{cr}) + \Delta_f H_m^\ominus \text{Zn}(\text{NO}_3)_2(\text{aq}) - 2\Delta_f H_m^\ominus \text{KNO}_3(\text{aq}) - \Delta_f H_m^\ominus \text{H}_2\text{O}(\text{l}) \quad (8)$$

the enthalpies of formation of $\text{Pb}(\text{NTO})_2\cdot\text{H}_2\text{O}(\text{cr})$, $\text{Cu}(\text{NTO})_2\cdot 2\text{H}_2\text{O}(\text{cr})$ and $\text{Zn}(\text{NTO})_2\cdot\text{H}_2\text{O}(\text{cr})$ may be obtained from the values of $\Delta_r H_m^\ominus$ in Tables 6–8, $\Delta_f H_m^\ominus \text{KNTO}\cdot\text{H}_2\text{O}(\text{cr}) = -676.9 \pm 2.6 \text{ kJ}\cdot\text{mol}^{-1}$, obtained in this work, $\Delta_f H_m^\ominus (\text{KNO}_3, \text{aq}, \infty) = -459.74 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H_m^\ominus (\text{H}_2\text{O}, \text{l}) = -285.83 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H_m^\ominus (\text{CuSO}_4, \text{aq}, \infty) = -844.50 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H_m^\ominus (\text{K}_2\text{SO}_4, \text{aq}, \infty) = -1414.0 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H_m^\ominus (\text{Zn}(\text{NO}_3)_2, \text{aq}, \infty) = -568.60 \text{ kJ}\cdot\text{mol}^{-1}$, taken from reference [6], and $\Delta_f H_m^\ominus (\text{Pb}(\text{NO}_3)_2, \text{aq}, \infty) = -181.3 \text{ kJ}\cdot\text{mol}^{-1}$, obtained from reaction (9):



and the values of $\Delta_f H_m^\ominus (\text{Pb}(\text{NO}_3)_2, \text{cr}) = -219.0 \text{ kJ}\cdot\text{mol}^{-1}$, taken from reference [7], and $\Delta_{\text{sln}} H_m^\ominus = 37.7 \text{ kJ}\cdot\text{mol}^{-1}$, from reference [8].

The following values are obtained:

$$\Delta_f H_m^\ominus (\text{Pb}(\text{NTO})_2\cdot\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(247.4 \pm 5.9) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^\ominus (\text{Cu}(\text{NTO})_2\cdot 2\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(712.1 \pm 5.4) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^\ominus(\text{Zn}(\text{NTO})_2 \cdot \text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(628.8 \pm 5.7) \text{ kJ} \cdot \text{mol}^{-1}$$

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Zusammenfassung — Ausgehend von den Lösungsenthalpien der Metallsalze von 3-Nitro-1,2,4-Triazol-5-on (NTO) in Wasser wurden die Standard-Bildungsenthalpien von $\text{KNTO} \cdot \text{H}_2\text{O}$, $\text{Ba}(\text{NTO})_2 \cdot 3\text{H}_2\text{O}$, $\text{LiNTO} \cdot 2\text{H}_2\text{O}$, $\text{Ca}(\text{NTO})_2 \cdot 4\text{H}_2\text{O}$ und $\text{Gd}(\text{NTO})_3 \cdot 7\text{H}_2\text{O}$ mit $-(676.9 \pm 2.6)$, $-(1627.0 \pm 2.5)$, $-(966.6 \pm 2.2)$, $-(1905.5 \pm 4.4)$ und $-(3020.1 \pm 6.4)$ kJ/mol ermittelt. Aus Messungen der Präzipitationenthalpie von $\text{KNTO} \cdot \text{H}_2\text{O}$ -Kristallen mit $\text{Pb}(\text{NO}_3)_2(\text{aq})$, $\text{CuSO}_4(\text{aq})$ und $\text{Zn}(\text{NO}_3)_2(\text{aq})$ wurden die Standard-Bildungsenthalpien von $\text{Pb}(\text{NTO})_2 \cdot \text{H}_2\text{O}$, $\text{Cu}(\text{NTO})_2 \cdot 2\text{H}_2\text{O}$ und von $\text{Zn}(\text{NTO})_2 \cdot \text{H}_2\text{O}$ mit $-(247.4 \pm 5.9)$, $-(712.1 \pm 5.4)$ und mit $-(628.8 \pm 5.7)$ kJ/mol ermittelt.