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NTO 负一价离子的水合焓 $\Delta_h H_m^\theta$(NTO$^-$)

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摘要：借助 $M(NTO)_n \cdot mH_2O$（M = La, Ce, Pr, Eu, Sm, Gd, $n=3$, $m=7$；M = Y, Yb, $n=3$, $m=6$；M = Dy, Tb, $n=3$, $m=5$；M = Nd, $n=3$, $m=8$）在水中的溶解焓 $\Delta_{sol}H_m^\theta$、晶格焓 ΔH_L^θ、晶格能 ΔU_L^θ 和标准生成焓 $\Delta_f H_m^\theta(M^{n+}, aq, \infty)$、$\Delta_f H_m^\theta(M^{n+}, g)$、$\Delta_f H_m^\theta(H_2O, g)$、$\Delta_f H_m^\theta(H_2O, l)$、$\Delta_f H_m^\theta(NTO^-, aq, \infty)$、$\Delta_f H_m^\theta(NTO^-, g)$ 以及 M^{n+} 的水合焓 $\Delta_h H_m^\theta(M^{n+})$ 的文献数据，估算了 NTO 负一价离子的水合焓 $\Delta_h H_m^\theta(NTO^-)$，结果显示，$\Delta_h H_m^\theta(NTO^-) = -(153.73 \pm 0.21)$ kJ·mol^{-1}。

关键词：物理化学；NTO 负离子；水合焓
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1　引　言

NTO 稀土金属配合物在水中的溶解焓来自 NTO 稀土配合物分子或离子(M^{3+}、NTO^-)的水合作用、分子和离子间的聚集和分散程度的变化。水合作用是水分子在离子(M^{3+}、NTO^-)周围作定向推列，形成稳定水合离子的过程，这个过程伴随一定能量的释放，该能量在数值上等于 NTO 稀土金属配合物正、负离子水合焓[$\Delta_h H_m^\theta(M^{n+})$、$\Delta_h H_m^\theta(NTO^-)$]之和[$\Delta_h H_m^\theta(M^{n+} + NTO^-)$]。其中，$\Delta_h H_m^\theta(NTO^-)$ 称 NTO 负离子的标准水合焓。该值，在实验上无法单独测得，只能通过热化学计算和水合焓的加和性原则算得。

2　方　法

由气态阴、阳离子[$NTO^-(g)$、$M^{n+}(g)$]和水分子形成晶体 $M(NTO)_n \cdot mH_2O(cr)$ 的反应式

$$M^{n+}(g) + nNTO^-(g) + mH_2O(g) \xrightarrow{\Delta H_L^\theta[M(NTO)_n \cdot mH_2O, cr]} M(NTO)_n \cdot mH_2O(cr) \quad (1)$$

和 298.15 K 下该晶体在水中的溶解反应式

$$M(NTO)_n \cdot mH_2O(cr) \xrightarrow{\Delta_{sol}H_m^\theta(M(NTO)_n \cdot mH_2O, cr), aq} M^{n+}(aq,\infty) + nNTO^-(aq,\infty) + mH_2O(l) \quad (2)$$

相加，得水合反应式

$$M^{n+}(g) + nNTO^-(g) + mH_2O(g) \xrightarrow{\Delta_h H_m^\theta(M^{n+} + NTO^- + H_2O), aq} M^{n+}(aq,\infty) + nNTO^-(aq,\infty) + mH_2O(l) \quad (3)$$

式中，$\Delta H_L^\theta[M(NTO)_n \cdot mH_2O, cr]$、$\Delta_{sol}H_m^\theta[M(NTO)_n \cdot mH_2O, cr]$ 和 $\Delta_h H_m^\theta(M^{n+} + NTO^- + H_2O)$ 分别为 $M(NTO)_n \cdot mH_2O$ 的晶格焓、在水中的溶解焓和水合焓。

由式(1)~(3)知

$$\Delta_h H_m^\theta(M^{n+} + NTO^- + H_2O) = \Delta H_L^\theta[M(NTO)_n \cdot mH_2O, cr] + \Delta_{sol}H_m^\theta[M(NTO)_n \cdot mH_2O, cr] \quad (4)$$

或

$$\Delta_h H_m^\theta(M^{n+} + NTO^- + H_2O) = \Delta U_L^\theta[M(NTO)_n \cdot mH_2O, cr] + \Delta nRT + \Delta_{sol}H_m^\theta[M(NTO)_n \cdot mH_2O, cr] \quad (5)$$

式中，$\Delta U_L^\theta[M(NTO)_n \cdot mH_2O, cr]$ 为 $M(NTO)_n \cdot mH_2O$ 的晶格能；$\Delta n = -(1 + n + m)$；R 为通用气体常数；$T = 298.15$ K。

由式(3)知

$$\Delta_h H_m^\theta(M^{n+} + NTO^- + H_2O) = \Delta_f H_m^\theta(M^{n+}, aq, \infty) + n\Delta_f H_m^\theta(NTO^-, aq, \infty) + m\Delta_f H_m^\theta(H_2O, l) - \Delta_f H_m^\theta(M^{n+}, g) - n\Delta_f H_m^\theta(NTO^-, g) - m\Delta_f H_m^\theta(H_2O, g) \quad (6)$$

由水合反应

$$M^{n+}(g) + nNTO^-(g) \xrightarrow{\Delta_h H_m^\theta(M^{n+} + NTO^-), aq} M^{n+}(aq,\infty) + nNTO^-(aq,\infty) \quad (7)$$

知

$$\Delta_h H_m^\theta(M^{n+} + NTO^-) = \Delta_f H_m^\theta(M^{n+}, aq, \infty) + n\Delta_f H_m^\theta(NTO^-, aq, \infty) - \Delta_f H_m^\theta(M^{n+}, g) - n\Delta_f H_m^\theta(NTO^-, g) \quad (8)$$

由加和性原则，知

$$\Delta_h H_m^\theta(M^{n+} + NTO^-) = \Delta_h H_m^\theta(M^{n+}) + n\Delta_h H_m^\theta(NTO^-) \quad (9)$$

由式(6)减式(8)，得

$$\Delta_h H_m^\theta(M^{n+} + NTO^- + H_2O) = \Delta_f H_m^\theta(M^{n+} + NTO^-) +$$

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$$m\Delta_f H_m^\theta(H_2O,l) - m\Delta_f H_m^\theta(H_2O,g) \quad (10)$$

由式(8),知

$$\Delta_h H_m^\theta(NTO^-) = [\Delta_h H_m^\theta(M^{n+}+NTO^-) - \Delta_h H_m^\theta(M^{n+})]/n \quad (11)$$

上述各式中,$\Delta_f H_m^\theta$ 为标准生成焓。

一旦从热化学实验知 $\Delta_{sol} H_m^\theta[M(NTO)_n \cdot mH_2O,cr]$,由热化学计算得 $\Delta H_L^\theta[M(NTO)_n \cdot mH_2O,cr]$、$\Delta_h H_m^\theta(M^{n+}+NTO^-+H_2O)$、$\Delta_h H_m^\theta(M^{n+}+NTO^-)$、$\Delta U_L^\theta[M(NTO)_n \cdot mH_2O,cr]$,从热化学手册中查得 $\Delta_h H_m^\theta(M^{n+})$、$\Delta_f H_m^\theta(M^{n+},aq,\infty)$、$\Delta_f H_m^\theta(M^{n+},g)$、$\Delta_f H_m^\theta(NTO^-,g)$、$\Delta_f H_m^\theta(NTO^-,aq,\infty)$、$\Delta_f H_m^\theta(H_2O,l)$、$\Delta_f H_m^\theta(H_2O,g)$,就可从方程(4)[或(5)]、(10)和(11)或方程(8)和(11)算得 NTO 负一价离子的水合焓 $\Delta_h H_m^\theta(NTO^-)$。

3 结 果

应用上述方法,处理表 1 中的热化学数据,算得 NTO 稀土金属配合物正、负离子的水合焓 $\Delta_h H_m^\theta(M^{n+}+NTO^-)$和 NTO^-的水合焓 $\Delta_h H_m^\theta(NTO^-)$,结果如表 1 所示,后者取平均值,得 $\Delta_h H_m^\theta(NTO^-) = -(153.73 \pm 0.21)$ kJ·mol^{-1}。

表 1 M^{n+}和 NTO^-的水合焓,$M^{n+}(aq,\infty)$、$M^{n+}(g)$、$NTO^-(aq,\infty)$、$NTO^-(g)$、$H_2O(l)$和 $H_2O(g)$ 标准生成焓及 $M(NTO)_n \cdot mH_2O$ 的晶格焓、水中的溶解焓和晶格能

Table 1 The hydrous enthalpy for M^{n+} and NTO^-, standard enthalpy of formation for $M^{n+}(aq,\infty)$, $M^{n+}(g)$, $NTO^-(aq,\infty)$, $NTO^-(g)$, $H_2O(l)$ and $H_2O(g)$, and lattice enthalpy, enthalpy of solution in water and lattice energy for $M(NTO)_n \cdot mH_2O$[1-3]

$M(NTO)_n \cdot mH_2O$	A[4]	B	C	D	E	F	G				H
							route 1	route 2	route 3	mean	
$Y(NTO)_3 \cdot 6H_2O$	-3583	-723.41	4215.4	-4395.08	33.89 ± 0.38	-4370.28	-4097.13 ± 0.38	-4097.12 ± 0.38	-4098.81 ± 6.3	-4097.69 ± 2.11	-171.56 ± 0.70
$La(NTO)_3 \cdot 7H_2O$	-3296	-707.10	3904.5	-4120.36	41.01 ± 0.25	-4093.08	-3771.28 ± 0.25	-3771.27 ± 0.25	-3771.60 ± 6.3	-3771.38 ± 2.10	-158.46 ± 0.70
$Ce(NTO)_3 \cdot 7H_2O$	-3337	-696.22	3963.9	-4168.86	40.93 ± 0.24	-4141.58	-3819.86 ± 0.24	-3819.85 ± 0.24	-3820.12 ± 6.3	-3819.94 ± 2.10	-160.98 ± 0.70
$Pr(NTO)_3 \cdot 7H_2O$	-3405	-704.59	4002.0	-4211.66	37.27 ± 0.36	-4184.38	-3866.32 ± 0.36	-3866.31 ± 0.36	-3866.59 ± 6.3	-3866.41 ± 2.11	-153.80 ± 0.70
$Nd(NTO)_3 \cdot 8H_2O$	-3420	-696.22	4041.3	-4288.44	39.15 ± 0.41	-4258.68	-3897.21 ± 0.41	-3897.20 ± 0.41	-3897.52 ± 6.3	-3897.31 ± 2.11	-159.10 ± 0.70
$Sm(NTO)_3 \cdot 7H_2O$	-3500	-691.62	4095.3	-4304.36	49.63 ± 0.24	-4277.08	-3946.66 ± 0.24	-3946.65 ± 0.24	-3946.92 ± 6.3	-3946.74 ± 2.10	-148.91 ± 0.70
$Eu(NTO)_3 \cdot 7H_2O$	-3600	-605.00	4230.9	-4352.06	48.09 ± 0.29	-4324.78	-3995.90 ± 0.29	-3995.89 ± 0.29	-3995.90 ± 6.3	-3995.90 ± 2.10	-131.97 ± 0.70
$Gd(NTO)_3 \cdot 7H_2O$	-3470	-686.18	4165.6	-4370.06	50.19 ± 0.13	-4342.78	-4011.80 ± 0.13	-4011.79 ± 0.13	-4011.78 ± 6.3	-4011.79 ± 2.10	-180.60 ± 0.70
$Tb(NTO)_3 \cdot 5H_2O$	-3540	-682.83	4197.0	-4302.00	42.14 ± 0.17	-4289.68	-4039.81 ± 0.17	-4049.80 ± 0.17	-4039.83 ± 6.3	-4043.15 ± 2.10	-167.72 ± 0.70
$Dy(NTO)_3 \cdot 5H_2O$	-3750	-698.73	4206.6	-4326.80	41.46 ± 0.22	-4314.48	-4065.29 ± 0.22	-4075.28 ± 0.22	-4065.33 ± 6.3	-4068.63 ± 2.10	-106.21 ± 0.70
$Yb(NTO)_3 \cdot 6H_2O$	-3740	-674.46	4318.9	-4516.38	36.31 ± 0.25	-4491.58	-4216.01 ± 0.25	-4216.00 ± 0.25	-4153.36 ± 6.3	-4195.12 ± 2.10	-151.71 ± 0.70
										mean	-153.73 ± 0.21

Note: A is $\Delta_h H_m^\theta(M^{n+})$, kJ·mol^{-1}; B is $\Delta_f H_m^\theta(M^{n+},aq,\infty)$, kJ·mol^{-1}; C is $\Delta_f H_m^\theta(M^{n+},g)$, kJ·mol^{-1}; D is $\Delta H_L^\theta[M(NTO)_n \cdot mH_2O,cr]$, kJ·mol^{-1}; E is $\Delta_{sol} H_m^\theta[M(NTO)_n \cdot mH_2O,cr]$, kJ·mol^{-1}; F is $\Delta U_L^\theta[M(NTO)_n \cdot mH_2O,cr]$, kJ·mol^{-1}; G is $\Delta_h H_m^\theta(M^{n+}+NTO^-)$, kJ·mol^{-1}; H is $\Delta_h H_m^\theta(NTO^-)$, kJ·mol^{-1}.

Route 1 is Eqs. (4),(10); Route 2 is Eqs. (5),(10); Route 3 is Eqs. (6),(10) or (8).

$\Delta_f H_m^\theta(NTO^-,aq,\infty) = -(94.3 \pm 2.1)$ kJ·mol^{-1}, $\Delta_f H_m^\theta(NTO^-,g) = -374.30$ kJ·mol^{-1}, $\Delta_f H_m^\theta(H_2O,l) = -285.83$ kJ·mol^{-1}, $\Delta_f H_m^\theta(H_2O,g) = -241.82$ kJ·mol^{-1}, cited from References [1-3].

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Deformation Analysis of Free Loading Propellant in Storage

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Abstract: Three-dimentional viscoelastic large deformation incremental constitutive equation was derived based on Total Lagrangian method. From materials property testing of composite modified double base (CMDB) propellant by dynamic mechanical analyzer (DMA), deformation, equivalent von mises stress and strain of free loading propellant in storage were obtained. The results show that the subsidence magnitude of solid propellant in the axis direction is about 0.16 mm. Outer diameter increases 0.04 mm and inner diameter is nearly unchanged. Stress between solid propellant and binder is about 11.8 kPa, which will not lead to dewetting. Balanceable time of the free loading propellant in long-term storage is about half a year. Thus the deformation of the free loading propellant grains in storage can be deduced by that of propellant stored for more than half a year.

Key words: aerospace propulsion theory and engineering; free loading propellant; storage; viscoelasticity; dynamic mechanical analyzer (DMA)

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The Hydrous Enthalpy of NTO^-

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Abstract: Based on the literature data of the enthalpies of solution in water, $\Delta_{sol}H_m^\theta$, lattice enthalpy, ΔH_L^θ, lattice energy, ΔU_L^θ for the complexes of the lanthanidi metals with 3-nitro-1,2,4-triazol-5-one (NTO), $M(NTO)_n \cdot mH_2O$ (M = La, Ce, Pr, Eu, Sm, Gd, $n=3, m=7$; M = Y, Yb, $n=3, m=6$; M = Dy, Tb, $n=3, m=5$; M = Nd, $n=3, m=8$), standard enthalpies of formation, $\Delta_f H_m^\theta(M^{n+}, aq, \infty)$, $\Delta_f H_m^\theta(M^{n+}, g)$, $\Delta_f H_m^\theta(H_2O, g)$, $\Delta_f H_m^\theta(H_2O, l)$, $\Delta_f H_m^\theta(NTO^-, aq, \infty)$, $\Delta_f H_m^\theta(NTO^-, g)$ and hydrous enthalpy of M^{n+}, $\Delta_h H_m^\theta(M^{n+})$, the hydrous enthalpy of NTO^-, $\Delta_h H_m^\theta(NTO^-)$ was estimated as $-(153.73 \pm 0.21)$ kJ · mol^{-1}.

Key words: physical chemistry; NTO^-; hydrous enthalpy

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斯蒂芬酸在 DMF 中的热化学和热动力学性质研究

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摘要: 应用微热量热仪测定了斯蒂芬酸(TNR)在溶剂 *N*,*N*-二甲基甲酰胺(DMF)中不同浓度(b)时的溶解焓,用计算机拟合的方法求得计算该物质溶解焓($\Delta_{sol}H$)的经验公式($\Delta_{sol}H = -14.392 - 988.6b + 34.992b^{1/2}$)。由此得到了该物质的标准摩尔溶解焓($\Delta_{sol}H_m^\theta = -14.392$ kJ · mol^{-1}),并分别推导出了 TNR 的相对表观摩尔焓、相对偏摩尔焓以及配合物的稀释焓的经验公式。同时,对 TNR 溶液反应的动力学进行了研究,通过分析热流对时间的曲线图,确定了该溶解反应的速率常数为 1.632×10^{-3} s^{-1},反应级数为 0.6158。

关键词: 物理化学; 热化学性质; 热动力学性质; 斯蒂芬酸 (TNR); 微热量热法

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