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估算正负离子标准水合焓的一种简易方法

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摘要: 提出了一个估算正负离子标准水合焓 $\Delta_h H_m^\theta(M^{n\pm})$ 的简易公式。$\Delta_h H_m^\theta(M^{n\pm})$ 的计算值与报道值相对误差在 8% 以内。用所建立的计算式预估了一些已知 $\Delta_h H_m^\theta(M^{n\pm})$ 和 $\Delta_f H_m^\theta(M^{n\pm}, aq, \infty)$ 或 $\Delta_f H_m^\theta(M^{n\pm}, g)$ 值的气态正负离子的标准生成焓 $\Delta_f H_m^\theta(M^{n\pm}, g)$ 和正负水合离子的标准生成焓 $\Delta_f H_m^\theta(M^{n\pm}, aq, \infty)$。

关键词: 物理化学; 正离子; 负离子; 水合焓; 标准生成焓
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在文献[1-2]中,我们先后报道了气态 NTO 负离子的标准生成焓 $\Delta_f H_m^\theta(NTO^-, g)$ 和 NTO 负离子的标准水合焓 $\Delta_h H_m^\theta(NTO^-)$。为了验证所得 $\Delta_f H_m^\theta(NTO^-, g)$ 和 $\Delta_h H_m^\theta(NTO^-)$ 值的可靠性,我们对数据: NTO 水合离子的标准生成焓 $\Delta_f H_m^\theta(NTO^-, aq, \infty) = -(94 \pm 2.1)\ kJ \cdot mol^{-1}$[3]、$\Delta_f H_m^\theta(NTO^-, g) = -374.30\ kJ \cdot mol^{-1}$、$\Delta_h H_m^\theta(NTO^-) = -153.73\ kJ \cdot mol^{-1}$ 和离子价 $n = -1$,进行了关联,建立了经验式:

$$-\Delta_h H_m^\theta(NTO^-) = -\Delta_f H_m^\theta(NTO^-, aq, \infty) + \Delta_f H_m^\theta(NTO^-, g) - 433.73\, n \qquad (1)$$

并将式(1)改写成通式:

$$-\Delta_h H_m^\theta(M^{n\pm}) = -\Delta_f H_m^\theta(M^{n\pm}, aq, \infty) + \Delta_f H_m^\theta(M^{n\pm}, g) - 433.73\, n \qquad (2)$$

将该通式用于由 $\Delta_f H_m^\theta(M^{n\pm}, aq, \infty)$ 和 $\Delta_f H_m^\theta(M^{n\pm}, g)$ 估算其它正负离子的标准水合焓 $\Delta_h H_m^\theta(M^{n\pm})$,结果如表 1 所示,或通过 $\Delta_h H_m^\theta(M^{n\pm})$ 和式(2)右端前二项中的一项,估算右端前二项中的另一项值,结果如表 2 所示。

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表 1　用方程(2)和取自文献[4]的 $\Delta_f H_m^\theta(M^{n\pm}, g)$ 和 $\Delta_f H_m^\theta(M^{n\pm}, aq, \infty)$ 算得的 $\Delta_h H_m^\theta(M^{n\pm})$ 值

Table 1　The calculated values of the hydrous enthalpy of $M^{n\pm}$ obtained by Eq. (2) and the standard enthalpy of formation of $M^{n\pm}(aq, \infty)$ and $M^{n\pm}(g)$ taken from Reference[4]

No.	$M^{n\pm}$	$\Delta_f H_m^\theta(M^{n\pm}, g)$ /kJ·mol^{-1}	$\Delta_f H_m^\theta(M^{n\pm}, aq, \infty)$ /kJ·mol^{-1}	$-\Delta_h H_m^\theta(M^{n\pm})$/kJ·mol^{-1} Calc.	$-\Delta_h H_m^\theta(M^{n\pm})$/kJ·mol^{-1} Ref.[5]	error /%
1	Ag^+	1019.2	105.6	479.9	473	-1.5
2	Al^{3+}	5484.0	-531.4	4714.1	4665	-1.1
3	Ba^{2+}	1660.5	-537.6	1330.6	1305	-2.0
4	Be^{2+}	2993.2	-382.8	2508.6	2494	-0.6
5	Cd^{2+}	2623.5	-75.9	1832.0	1807	-1.4
6	Ce^{3+}	3963.9	-696.2	3358.9	3337	-0.7
7	Cr^{2+}	2653.5	-143.5	1929.5		
8	Co^{2+}	2841.6	-58.2	2032.3	1996	-1.8
9	Co^{3+}	6080.1	92.0	4686.9		
10	Cu^+	1090.1	71.7	584.7	593	1.4
11	Cu^{2+}	3054.0	64.8	2121.8	2100	-1.0
12	Eu^{2+}	1820.0	-527.2	1479.8		
13	Ga^{3+}	5815.8	-211.7	4726.3		
14	H^+	1536.2	0	1102.5	1091	-1.1
15	In^{3+}	5345.3	-104.6	4148.7		
16	Fe^{2+}	2752.2	-89.1	1973.9		
17	Fe^{3+}	5714.9	-48.5	4462.3	4430	-0.7
18	La^{3+}	3904.5	-707.1	3310.4	3296	-0.4
19	Pb^{2+}	2373.4	-1.7	1507.6	1481	-1.8
20	Mg^{2+}	2348.5	-466.9	1947.9	1921	-1.4
21	Mn^{2+}	2519.2	-220.7	1872.5	1841	-1.7
22	Hg^{2+}	2890.4	171.1	1851.8	1824	-1.5
23	Ni^{2+}	2930.1	-54.0	2116.7	2105	-0.6
24	Pd^{2+}	3069.4	149.0	2053.0	1989	-3.2
25	Pr^{3+}	4002.0	-704.6	3405.4	3405	0
26	Ra^{2+}	1659.8	-527.6	1319.9		
27	Sr^{2+}	1790.6	-545.8	1468.9	1443	-1.8
28	Tl^+	777.7	5.4	338.7		
29	Tl^{3+}	5639.2	196.7	4141.4		
30	Th^{4+}	7016.6	-769.0	6050.7		
31	Tm^{3+}	4297.0	-697.9	3693.7	3650	-1.2
32	Sn^{2+}	2431.1	-8.8	1572.4	1556	-1.1
33	Yb^{3+}	4381.9	-674.5	3755.2	3740	-0.4
34	Zn^{2+}	2782.7	-153.9	2069.2	2046	-1.1
35	Br^-	-233.9	-121.5	321.4	348	7.6
36	Cl^-	-246.0	-167.2	354.9	378	6.1
37	F^-	-270.7	-332.6	495.7	524	5.4
38	I^-	-196.7	-55.2	292.3	308	5.1

表 2　用方程(2)和 $\Delta_h H^\theta_m(M^{n\pm})$、$\Delta_f H^\theta_m(M^{n\pm},aq,\infty)$或 $\Delta_f H^\theta_m(M^{n\pm},g)$算得的 $\Delta_f H^\theta_m(M^{n\pm},aq,\infty)$和 $\Delta_f H^\theta_m(M^{n\pm},g)$值

Table 2　The values of $\Delta_f H^\theta_m(M^{n\pm},aq,\infty)$ and $\Delta_f H^\theta_m(M^{n\pm},g)$ obtained by Eq.(2) and $\Delta_h H^\theta_m(M^{n\pm})$, $\Delta_f H^\theta_m(M^{n\pm},aq,\infty)$ or $\Delta_f H^\theta_m(M^{n\pm},g)$ taken from Ref.[4,5]

No.	$M^{n\pm}$	$\Delta_f H^\theta_m(M^{n\pm},g)$ /kJ·mol^{-1}	$\Delta_f H^\theta_m(M^{n\pm},aq,\infty)$ /kJ·mol^{-1}	$-\Delta_h H^\theta_m(M^{n\pm})$ /kJ·mol^{-1}
1	BF_4^-	-1734.6	-1574.9	274
2	BrO_3^-	-151.8	-67.1	349
3	CO_3^{2-}	-230.6	-677.1	1314
4	HCO_3^-	-745.7	-692.0	380
5	CNO^-	-257.8	-146.0	322
6	CNS^-	-47.3	76.4	310
7	ClO_3^-	-618.6	-99.2	348
8	CrO_4^{2-}	-645.6	-881.2	1103
9	Dy^{3+}	1750.1	-698.7	3750
10	Er^{3+}	4145.8	-705.4	3550
11	Eu^{3+}	4296.2	-605.0	3600
12	HF_2^-	-615.7	-649.9	468
13	Gd^{3+}	4085.0	-686.2	3470
14	Ho^{3+}	4196.2	-705.0	3600
15	OH^-	-316.7	-230.0	347
16	IO_3^-	-329.1	-221.3	326
17	Lu^{3+}	4165.9	-665.3	3530
18	Nd^{3+}	4025.0	-696.2	3420
19	NO_2^-	-133.3	-104.6	405
20	NO_3^-	-1194.5	-207.4	314
21	NH_4^+	608.2	-132.5	307
22	K^+	503.4	-252.4	322
23	Sm^{3+}	4109.6	-691.6	3500
24	Sc^{3+}	4584.0	-614.2	3897
25	SO_4^{2-}	-717.7	-909.3	1059
26	Tb^{3+}	4158.4	-682.8	3540
27	Y^{3+}	4160.8	-723.4	3583
28	Ca^{2+}	1925.5	-543.9	1602
29	Cs^+	458.0	-239.8	264
30	Li^+	679.6	-273.2	519
31	N^{3+}	9327.8	7674.7	352
32	Pr^{4+}	7765.5	-409.4	6440
33	Rb^+	490.1	-236.6	293
34	Sm^{2+}	1832.6	-543.9	1509
35	Na^+	609.0	-233.8	409
36	Yb^{2+}	1944.7	-526.7	1604

Note: The values of $\Delta_f H^\theta_m(M^{n\pm},g)$ for No. 1 to 27 and $\Delta_f H^\theta_m(M^{n\pm},aq,\infty)$ for No. 28 to 36 are obtained by Eq.(2).

表 1 和表 2 结果表明：

(1) 由式(2)估算的 38 种离子的 $\Delta_h H^\theta_m(M^{n\pm})$值与文献报道值[5]相对误差在 8% 以内。说明：式(1)中系数 433.73 kJ·mol^{-1}值在误差范围内可信，逆向印证 $\Delta_h H^\theta_m(NTO^-) = -153.73$ kJ·mol^{-1}，$\Delta_f H^\theta_m(NTO^-,g) = -374.30$ kJ·mol^{-1}在极大程度上是可取的。

(2) $\Delta_h H^\theta_m(M^{n\pm})$、$\Delta_f H^\theta_m(M^{n\pm},aq,\infty)$、$\Delta_f H^\theta_m(M^{n\pm},g)$和 n 间的关系，可以用式(2)定量描述。

(3) 推断用式(2)估算的未见文献报道的 36 种离子的 $\Delta_f H^\theta_m(M^{n\pm},aq,\infty)$或 $\Delta_f H^\theta_m(M^{n\pm},g)$值，在一定程度上可信。

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A Simple Method of Estimating the Standard Hydrous Enthalpy of Cation and Anion

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Abstract: A simple formula of estimating the standard hydrous enthalpy of cation and anion, $\Delta_h H^\theta_m(M^{n\pm})$ was presented. The errors between calculated and reported values of $\Delta_h H^\theta_m(M^{n\pm})$ was within 8%. The standard enthalpies of formation of cations and anions with known $\Delta_h H^\theta_m(M^{n\pm})$ and $\Delta_f H^\theta_m(M^{n\pm},aq,\infty)$ or $\Delta_f H^\theta_m(M^{n\pm},g)$, $\Delta_f H^\theta_m(M^{n\pm},g)$ or $\Delta_f H^\theta_m(M^{n\pm},aq,\infty)$ were estimated by the formula established.

Key words: physical chemistry; cation; anion; hydrous ion; hydrous enthalpy; standard enthalpy of formation