

Prediction of thermodynamic properties of actinide and lanthanide compounds

LU Chunhai^{1,2,*} NI Shijun² SUN Ying¹ CHEN Wenkai³ ZHANG Chengjiang²

¹ Chengdu University of Technology, Chengdu 610059, China

² China Academy of Engineering Physics, P.O. Box 919-71, Mianyang 621900, China

³ Department of Chemistry, Fuzhou University, Fuzhou 350002, China

Abstract Several relationship models for thermodynamic functions of actinide and lanthanide compounds are built. The descriptors such as the difference of atomic radii between metal atoms and nonmetal atoms and the molecular mass are used in quantitative structure-activity/property relationships. The relative errors for entropy and heat capacity are less than 20% in the majority of gaseous compounds. Similar results are obtained from solid compounds.

Key words QSPR, Actinide, Lanthanide, Compound, Thermodynamics property

CLC numbers O614; 0642

1 Introduction

Actinide compounds are widely used in fields of nuclear science and technology. Uranium and plutonium oxides are fuel for nuclear reactor. And Actinide compounds are often used in radioactive sources^[1]. Lanthanide compounds are often substitute of actinide in research. And Gd₂O₃ is used to synthesize radioactive waste ceramic solidification^[2,3]. The measurements of enthalpy in formation of C-Sc₂O₃ and C-Y₂O₃ available in the literature were reviewed by Swamy *et al.*^[4]. The standard enthalpies of forming A-type R₂O₃ (R=La–Nd), B-type R₂O₃ (R=Sm–Gd), and C-type R₂O₃ (R=Tb–Lu) determined calorimetrically were reviewed, and the value of A-Pm₂O₃ was estimated, by Cordfunke and Konings^[5]. The enthalpies of forming C-type Pr₂O₃, Nd₂O₃, Sm₂O₃ and Eu₂O₃ were measured directly by solution calorimetry^[6]. In addition, enthalpy of C→B phase transition in Gd₂O₃ was measured by Kolitsch^[3] with differential scanning calorimetry, while corresponding enthalpies of B→A and A→H transformations were

determined by Barkhatov and co-workers with the use of an adiabatic boiling calorimeter^[6]. The same technique has been employed to measure the enthalpy of C→H phase transition in Y₂O₃, and the heat of fusion of C-Sc₂O₃ and H-Y₂O₃^[6]. Recently, the enthalpy of a solid-state phase transition and the enthalpy of fusion in Y₂O₃ has been re-measured using high-temperature DTA^[7]. Sheldon and Mulford^[8] have re-measured the emissivity of U(l), and calculated the concomitant corrections (which are appreciable) to the earlier measurements. Evaluations from literature data for NpO₂⁺ have been conducted by Kaszuba and Runde^[9]. Ogawa *et al.*^[10] have given an equation for $\Delta G(\text{PuN}, T)$, based on an assessment of the existing data. Ruello *et al.*^[11] determined heat capacity anomaly in UO₂ in the vicinity of 1300 K by high resolution X-ray and neutron powder diffraction studies.

The quantitative structure–activity (or structure–property) relationships (QSAR or QSPR) have been applied in chemistry and related research areas for many decades^[12]. Thermodynamic function of compounds is very important for research and

Supported by the National Key Laboratory Foundation of China (Grant No. : 9140C6601010804) and Sichuan Provincial Key Laboratory for Applied Nuclear Technology in Geology Foundation (Grant No. 27-7)

*Corresponding author. E-mail: luchhi@126.com

Received date: 2007-07-12

industrial applications in chemistry and chemical engineering. In recent years, many chemists have focused on studying quantitative structure-property relationships for compounds. While many compounds have well-known physical and chemical properties, as those compiled in databases of e.g. DIPPR^[13], there are still many compounds with little possibility to determine their properties.

Descriptors used in QSARs/QSPRs must encode a variety of physical and chemical properties to build reliable models. In this paper, we fit relationships among entropy, heat capacity, atomic radii, and molecular mass to obtain QSPRs. Energy of the highest occupied orbit and the lowest unoccupied orbit are often used as descriptors in QPSR studies^[14-17]. Gaussian 03 w^[18] was used in this work to calculate electronic properties of the molecules. However, electronic properties cannot improve QSPRs to predict thermodynamics properties. Therefore, we omit quantum chemistry calculation in order to save calculation cost and simplify the QSPR model.

2 Computational method

According to thermodynamics^[19-22], entropy can be deduced by Eq.(1) from partition function and temperature:

$$S = Nk_B + Nk_B \ln \left(\frac{q(V, T)}{N} \right) + Nk_B T \left(\frac{\partial \ln q}{\partial T} \right)_V \quad (1)$$

With known molecular mass, Eq.(2) can be deduced from $n = N/N_A$ and $N_A k_B = R$ (where, $N=1$).

$$\begin{aligned} S &= R + R \ln(q(V, T)) + RT \left(\frac{\partial \ln q}{\partial T} \right)_V \\ &= R \ln(q(V, T)e) + RT \left(\frac{\partial \ln q}{\partial T} \right)_V \\ &= R \left(\ln(q_t q_e q_r q_v e) + T \left(\frac{\partial \ln q}{\partial T} \right)_V \right) \end{aligned} \quad (2)$$

Internal energy can be obtained from Eq.(3):

$$E = Nk_B T^2 \left(\frac{\partial \ln q}{\partial T} \right)_V \quad (3)$$

Finally, internal energy is used to obtain heat capacity at constant volume from Eq.(4):

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N,V} \quad (4)$$

These are basis to calculate thermodynamic properties for computational software^[19]. Molecular mass associates with thermodynamic properties of compounds. In this study, atomic radii and molecular mass were used to fit functions for thermodynamic properties of actinide and lanthanide compounds.

3 Result and discussion

3.1 Quantitative structure-property relationships

Data of molecular mass, atomic radii, entropy and heat capacity to fit QSPRs for thermodynamic properties are available in references. Table 1 shows the data to study QSPR for thermodynamic properties of actinide and lanthanide compounds. The median value is used, and the errors are omitted.

QSPRs for entropy and heat capacity were obtained with Eq.(5) and Eq.(6):

$$\lg S_{298.15K,S}^{\circ} = -5.42 + 5.093 \lg M - 0.806(\lg M)^2 + 5.748\Delta r - 30.143 (\Delta r)^2 \quad (5)$$

$$\lg Cp_{298.15K,S}^{\circ} = -26.16 + 19.169 \lg M - 3.3(\lg M)^2 + 14.711\Delta r - 60.139 (\Delta r)^2 \quad (6)$$

where M is molecular mass; Δr is difference between metal atomic radii and non-metal atomic radii.

3.2 Prediction for gaseous compounds

Table 2 shows results from Eq.(5) and Eq.(6). ReS and $ReCp$ are errors between experimental median and prediction. For a majority of actinide and lanthanide compounds, the relative errors (Fig. 1) are within 20%, which is satisfactory, as experimental error for UF and NpF are over 50%. Meanwhile, the equations can predict entropy and heat capacity of several actinide and lanthanide compounds that cannot be purified and synthesized. However, relative error for iodides is big. It means that the model shall be improved henceforth.

Table 1 Properties of uranium compounds^[23-25]

Compounds	$M/\text{g}\cdot\text{mol}^{-1}$	r_A/nm	r_B/nm	$S_{298.15\text{K}}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}$	$Cp_{298.15\text{K}}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}$	$\Delta H_{f298.15\text{K}}/\text{kJ}\cdot\text{mol}^{-1}$
UF	257.0	0.156	0.071	251.8	37.9	-47.0
UCl	273.5	0.156	0.099	265.9	43.2	187.0
UBr	317.9	0.156	0.114	278.5	44.5	245.0
UI	364.9	0.156	0.133	286.5	44.8	342.0
UF ₂	276.0	0.156	0.071	315.7	56.2	-540.0
UCl ₂	308.9	0.156	0.099	339.1	59.9	-155.0
UBr ₂	397.8	0.156	0.114	359.7	61.4	-40.0
UI ₂	491.8	0.156	0.133	376.5	61.9	103.0
UF ₃	295.0	0.156	0.071	347.5	76.2	-1065.0
UCl ₃	344.4	0.156	0.099	380.3	82.4	-523.0
UBr ₃	477.7	0.156	0.114	403.0	85.2	-371.0
UI ₃	618.7	0.156	0.133	431.2	86.0	-137.0
UF ₄	315.0	0.156	0.071	360.7	95.1	-1605.2
UCl ₄	379.8	0.156	0.099	409.3	103.5	-815.4
UBr ₄	557.6	0.156	0.114	451.9	106.9	-605.6
UI ₄	745.6	0.156	0.133	499.1	108.8	-518.3
UF ₆	352.0	0.156	0.071	376.3	129.4	-2148.6
UCl ₆	450.7	0.156	0.099	438.0	147.2	-985.5

Table 2 Predictions of S and Cp (in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) and relative error for actinide and lanthanide compounds

Compounds	M	r_A/nm	r_B/nm	Experiment ^[23-25]		Prediction		Relative error	
				S	Cp	S	Cp	ReS/%	ReCp/%
UF	257.0	0.156	0.071	251.8	37.9	277.7	48.6	10.3	28.2
UCl	273.5	0.156	0.099	265.9	43.2	271.9	39.7	2.3	-8.0
UBr	317.9	0.156	0.114	278.5	44.5	292.2	45.2	4.9	1.7
UI	364.9	0.156	0.133	286.5	44.8	284.6	39.6	-0.7	-11.7
UF ₂	276.0	0.156	0.071	315.7	56.2	302.1	60.9	-4.3	8.3
UCl ₂	308.9	0.156	0.099	339.1	59.9	311.8	56.7	-8.1	-5.4
UBr ₂	397.8	0.156	0.114	359.7	61.4	364.1	76.3	1.2	24.3
UI ₂	491.8	0.156	0.133	376.5	61.9	367.7	68.3	-2.3	10.4
UF ₃	295.0	0.156	0.071	347.5	76.2	325.9	74.1	-6.2	-2.7
UCl ₃	344.4	0.156	0.099	380.3	82.4	349.1	75.0	-8.2	-9.0
UBr ₃	477.7	0.156	0.114	403	85.2	424.5	105.1	5.3	23.3
UI ₃	618.7	0.156	0.133	431.2	86.0	429.2	87.4	-0.5	1.7
UF ₄	315.0	0.156	0.071	360.7	95.1	350.0	88.9	-3.0	-6.5
UCl ₄	379.8	0.156	0.099	409.3	103.5	383.9	93.8	-6.2	-9.4
UBr ₄	557.6	0.156	0.114	451.9	106.9	474.5	127.8	5.0	19.5
UI ₄	745.6	0.156	0.133	499.1	108.8	473.6	95.6	-5.1	-12.2
UF ₆	352.0	0.156	0.071	376.3	129.4	392.2	117.6	4.2	-9.1
UCl ₆	450.7	0.156	0.099	438.0	147.2	445.9	129.8	1.8	-11.8
NpF	256.0	0.155	0.071	251.0	33.8	276.0	47.5	10.0	40.5
NpF ₂	265.0	0.155	0.071	304.0	55.9	287.7	53.1	-5.4	-5.1

(To be continued in next page)

Table 2 (Continued)

Compounds	<i>M</i>	<i>r_A</i> /nm	<i>r_B</i> /nm	Experiment ^[23-25]		Prediction		Relative error	
				<i>S</i>	<i>C_p</i>	<i>S</i>	<i>C_p</i>	Re <i>S</i> /%	Re <i>C_p</i> /%
NpCl ₃	343.4	0.155	0.099	362.8	78.5	346.3	73.1	-4.6	-6.8
NpF ₄	303.0	0.155	0.071	369.8	95.3	335.1	79.1	-9.4	-17.0
NpCl ₄	378.9	0.155	0.099	423.0	105.0	380.9	91.6	-10.0	-12.8
NpF ₆	341.0	0.155	0.071	376.6	129.1	379.4	107.9	0.7	-16.4
PuF	258.1	0.160	0.071	251.0	33.5	280.4	51.2	11.7	52.8
PuF ₂	277.1	0.160	0.071	297.0	51.5	304.9	64.0	2.7	24.3
PuF ₃	296.1	0.160	0.071	336.1	72.2	328.7	77.9	-2.2	7.8
PuCl ₃	345.5	0.160	0.099	368.6	78.5	357.3	81.0	-3.1	3.3
PuBr ₃	478.8	0.160	0.114	423.0	81.5	437.5	115.0	3.4	41.1
PuF ₄	315.1	0.160	0.071	359.0	92.4	351.7	92.5	-2.0	0.1
PuCl ₄	381.2	0.160	0.099	409.0	103.4	393.0	101.4	-3.9	-1.9
PuF ₆	353.1	0.160	0.071	368.9	129.3	395.2	123.2	7.1	-4.7
AmF ₃	300.1	0.174	0.071	330.4	72.2	333.2	89.6	0.8	24.1
AmF ₄	319.1	0.174	0.071	154.1	—	356.0	106.0	131.0	—
LaF ₃	195.9	0.274	0.057	321.9	72.7	70.3	6.3	-78.2	-91.3
LaBr ₃	378.6	0.274	0.112	383.7	80.0	311.4	135.2	-18.8	68.9
LaI ₃	519.6	0.274	0.132	412.8	81.6	473.4	272.9	14.7	234.5
LaS	171.0	0.274	0.109	256.6	34.4	115.2	9.5	-55.1	-72.3
LaSe	217.9	0.274	0.255	263.0	35.7	151.4	7.5	-42.4	-78.9
LaTe	266.5	0.274	0.142	270.8	36.2	266.1	65.3	-1.7	80.4
PrF ₃	197.9	0.267	0.057	339.4	72.4	80.0	7.8	-76.4	-89.2
PrCl ₃	247.3	0.267	0.097	374.0	78.4	181.2	37.8	-51.5	-51.8
PrBr ₃	380.6	0.267	0.112	401.2	80.0	332.7	146.7	-17.1	83.3
PrI ₃	521.6	0.267	0.132	430.9	81.6	495.0	282.9	14.9	246.9
NdF ₃	201.2	0.264	0.057	115.5	72.2	85.8	9.0	-25.7	-87.5
NdCl ₃	250.6	0.264	0.097	144.0	78.3	190.0	41.1	32.0	-47.5
NdBr ₃	384.0	0.264	0.112	215.1	80.2	343.7	153.3	59.8	91.3
NdI ₃	525.0	0.264	0.132	430.6	81.6	505.2	287.8	17.3	252.7
NdS	176.3	0.264	0.109	264.7	34.3	131.9	12.1	-50.2	-64.7
SmF ₃	207.4	0.259	0.057	335.1	73.6	96.4	11.4	-71.2	-84.6
SmCl ₂	221.3	0.259	0.097	315.6	51.6	170.2	28.1	-46.1	-45.5
SmS	182.4	0.259	0.109	267.8	34.3	144.2	14.6	-46.1	-57.4
SmSe	229.3	0.259	0.255	278.4	35.2	136.0	5.7	-51.2	-83.7
EuF ₃	209.0	0.256	0.057	328.4	81.5	101.8	12.5	-69.0	-84.7
EuBr ₂	311.8	0.256	0.112	337.3	60.7	295.9	98.2	-12.3	61.9
EuS	184.0	0.256	0.109	272.1	35.1	149.3	15.5	-45.1	-55.8
GdCl ₃	263.6	0.254	0.097	371.5	78.2	221.5	54.1	-40.4	-30.8
GdBr ₃	397.0	0.254	0.112	398.9	79.9	380.6	175.9	-4.6	120.1
GdI ₃	538.0	0.254	0.132	427.6	81.5	537.0	300.1	25.6	268.3
TbF ₃	215.9	0.251	0.057	339.8	71.5	114.1	15.7	-66.4	-78.1
DyF ₃	219.5	0.249	0.057	341.1	71.3	119.8	17.3	-64.9	-75.7
DyCl ₃	268.9	0.249	0.097	379.9	78.2	236.2	60.2	-37.8	-23.0
DyBr ₃	402.2	0.249	0.112	404.1	79.9	397.2	184.9	-1.7	131.4
DyI ₃	543.2	0.249	0.132	432.5	81.5	549.7	302.3	27.1	270.9
HoF ₃	221.9	0.247	0.057	342.3	71.2	124.9	18.8	-63.5	-73.7

(To be continued in next page)

Table 2 (Continued)

Compounds	M	r_A/nm	r_B/nm	Experiment ^[23-25]		Prediction		Relative error	
				S	C_p	S	C_p	ReS/%	ReCp/%
HoCl ₃	271.3	0.247	0.097	363.6	78.2	242.5	62.9	-33.3	-19.5
ErF ₃	224.3	0.245	0.057	340.1	71.0	129.9	20.2	-61.8	-71.5
ErCl ₃	273.6	0.245	0.097	363.6	78.1	248.6	65.6	-31.6	-16.1
ErBr ₃	407.0	0.245	0.112	403.5	79.8	410.3	191.9	1.7	140.4
ErI ₃	548.0	0.245	0.132	431.6	81.5	559.1	302.7	29.5	271.7
TmF ₃	225.9	0.242	0.057	339.4	70.9	136.2	21.9	-59.9	-69.1
TmCl ₃	275.3	0.242	0.097	364.6	78.1	255.7	68.2	-29.9	-12.7
TmBr ₃	408.6	0.242	0.112	401.2	79.8	418.0	194.9	4.2	144.2
TmI ₃	549.6	0.242	0.132	429.8	81.4	564.0	301.0	31.2	269.7
YbF ₃	230.0	0.24	0.057	326.8	70.8	142.9	24.2	-56.3	-65.8
YbCl ₃	279.4	0.24	0.097	370.0	78.1	263.7	72.2	-28.7	-7.6
LuF ₃	232.0	0.225	0.057	315.4	70.6	170.7	31.1	-45.9	-56.0
LuCl ₃	281.3	0.225	0.097	352.5	78.1	288.9	77.8	-18.0	-0.3

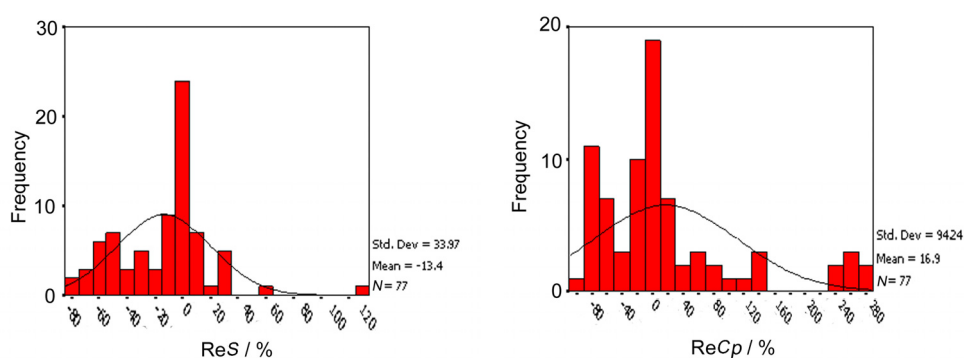


Fig.1 Distribution of relative error for prediction of ReS (entropy) and ReCp (heat capacity).

3.3 Prediction for solid compounds

QSPRs for thermodynamic properties of solid actinide and lanthanide compounds were deduced from cerium compounds according to the above method, and Eq.(7) and Eq.(8) were obtained.

$$\lg S_{298.15K,S} = -5.985 + 5.45 \lg M - 0.899(\lg M)^2 + 1.095\Delta r - 3.583(\Delta r)^2 \quad (7)$$

$$\lg C_{p298.15K,S} = -4.656 + 3.509 \lg M - 0.551(\lg M)^2 + 14.475\Delta r - 38.702(\Delta r)^2 \quad (8)$$

Thermodynamic properties of solid actinide and lanthanide compounds are predicted and relative errors for most actinide and lanthanide compounds are within 20%, too (Fig. 2).

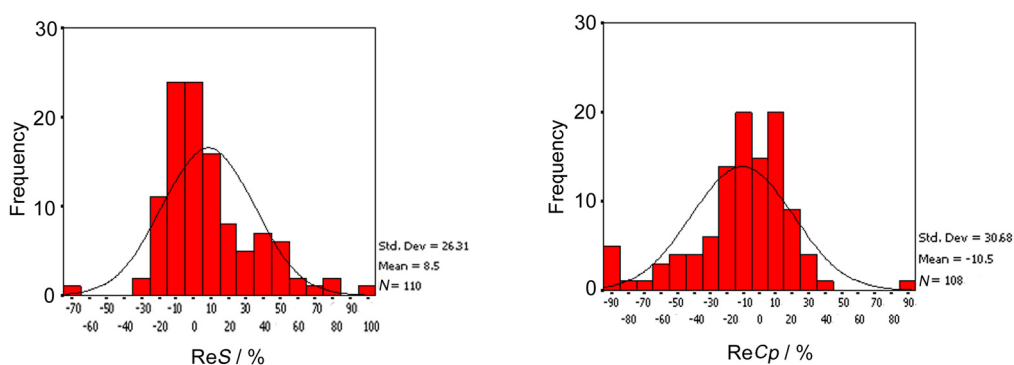


Fig. 2 Distribution of relative error for prediction of ReS (entropy) and ReCp (heat capacity).

Table 3 Properties of cerium compounds^[23]

Compounds	$M / \text{g}\cdot\text{mol}^{-1}$	r_A / nm	r_B / nm	$S_{298.15\text{K}} / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}$	$C_{p,298.15\text{K}} / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}$
CeH ₂	142.1	0.27	0.079	55.8	40.9
CeF ₃	197.1	0.27	0.057	115.3	85.3
CeCl ₃	246.5	0.27	0.097	149.8	95.9
CeBr ₃	379.8	0.27	0.112	182.0	101.7
CeI ₃	520.8	0.27	0.132	214.6	102.5
Ce ₂ O ₃	328.2	0.27	0.065	150.6	109.8
CeO _{1.72}	167.6	0.27	0.065	69.0	55.8
CeO ₂	172.1	0.27	0.065	62.3	61.5
CeS	172.2	0.27	0.109	78.2	50.0
Ce ₃ S ₄	548.6	0.27	0.109	255.2	180.0
Ce ₂ S ₃	376.4	0.27	0.109	180.3	128.7
CeTe	267.7	0.27	0.142	97.9	36.1
CeN	154.2	0.27	0.075	44.4	40.4
Ce ₂ C ₃	316.3	0.27	0.091	173.6	103.3
CeC ₂	164.1	0.27	0.091	90.0	61.0
CeSi	168.2	0.27	0.146	100.8	69.8
CeB ₆	205.0	0.27	0.117	74.1	103.3

4 Conclusion

In this paper, the quantitative structure- property relationships for thermodynamic properties are given. The relationships for entropy and heat capacity for actinide and lanthanide compounds only depend on two parameters: atomic radii and molecular mass. Comparing experimental results, the relative error for majority of predicted results for actinide and lanthanide compounds is not more than 20%, which is satisfactory.

References

- Grossmann R, Maier HJ, Szerypo J, *et al.* Nucl Instr Meth in Phys Res A, 2008, **590**: 122–125.
- King W D, Wilmarth W R, Hobbs D T, *et al.* J Alloys Compd, 2008, **458**: 158–160.
- Kutty KV G, Asuvathraman R, Madhavan R R, *et al.* J Phys Chem Solids, 2005, **66**: 596–601.
- Swamy V, Seifert HJ, Aldinger F. J Alloys Compd, 1998, **269**: 201–207.
- Cordfunke E, Konings R. Thermochim Acta, 2001, **375**: 65–79.
- Zinkevich M. Progress in Materials Science, 2007, **52**: 597–647.
- Navrotsky A, Benoist L, Lefebvre H. J Am Ceram Soc, 2005, **88**: 2942–2944.
- Sheldon RI, Mulford RNR. J Nucl Mater, 1991, **185**: 297–298.
- Kaszuba JP, Runde W. Environ Sci Technol, 1999, **33**: 4427–4433.
- Ogawa T, Kobayashi F, Sato T, *et al.* J Alloys Compd, 1998, **271–273**: 347–354.
- Ruello P, Desgranges L, Baldinozzi G, *et al.* Journal of Physics and Chemistry of Solids. 2005, **66**(5): 823–831.
- Maran U, Sild S, Kahn I, *et al.* Future Generation Computer Systems, 2007, **23**: 76–83.
- Liu S, Cai S, Cao C, *et al.* J Chem Inf Comput Sci, 2000, **40**: 1337–1348.
- Dyckjaer JD, Jonsdottir SO. Industrial and Engineering Chemistry Research, 2003, **42**: 4241–4259.
- Beck B, Breindl A, Clark T. Journal of Chemical Information and Computer Sciences. 2000, **40**: 1046–1051.
- Chalk AJ, Beck B, Clark T. Journal of Chemical Information and Computer Sciences, 2001, **41**: 457–462.
- Chen J, Peijnenburg WJGM, Quan X, *et al.* Chemosphere, 2000, **40**: 1319–1326.
- Frisch MJ, Trucks GW, Schlegel HB, *et al.* Gaussian 03. Revision B.01. Pittsburgh PA: Gaussian, Inc., 2003.
- Ochterski JW. Thermochemistry in Gaussian Accessed. Gaussian, Inc., 2000.

-
- | | |
|---|--|
| <p>20 Tang Y. Statistic mechanics and its application in physical chemistry. Beijing: Science Press, 1964.</p> <p>21 Liu G, Dai S. Application of chemical statistic mechanics. Beijing: Science Press, 2001.</p> <p>22 Yang H L, Wang Z D, Huang Y P, <i>et al.</i> Journal Wuhan University of Technology, Materials Science Edition, 2004, 19: 41-43.</p> | <p>23 Liang Y, Che Y. Handbook for inorganic thermodynamic data. Shenyang: Northeast University Press, 1993.</p> <p>24 Lemire RJ. Chemical thermodynamics of neptunium and plutonium. New York: Elsevier, 2001.</p> <p>25 Guillaumont R. Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium. New York: Elsevier, 2003.</p> |
|---|--|