Prediction of thermodynamic properties of actinide and lanthanide compounds

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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; O642

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 Gd_2O_3 is used to synthesize radioactive waste ceramic solidification[2,3]. The measurements of enthalpy in formation of C-Sc_2O_3 and C-Y_2O_3 available in the literature were reviewed by Swamy *et al.*[4]. The standard enthalpies of forming A-type R_2O_3 (R=La–Nd), B-type R_2O_3 (R=Sm–Gd), and C-type R_2O_3 (R=Tb–Lu) determined calorimetrically were reviewed, and the value of A-Pm_2O_3 was estimated, by Cordfunke and Konings[5]. The enthalpies of forming C-type Pr_2O_3, Nd_2O_3, Sm_2O_3 and Eu_2O_3 were measured directly by solution calorimetry[6]. In addition, enthalpy of C→B phase transition in Gd_2O_3 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 Y_2O_3, and the heat of fusion of C-Sc_2O_3 and H-Y_2O_3[6]. Recently, the enthalpy of a solid-state phase transition and the enthalpy of fusion in Y_2O_3 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 NpO_2^+ have been conducted by Kaszuba and Runde[9]. Ogawa *et al* [10] have given an equation for $\Delta G(PuN, T)$, based on an assessment of the existing data. Ruello *et al*[11] determined heat capacity anomaly in UO_2 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

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 educed 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 educed from $n=N/N_A$ and $N_A k_B = R$ (where, $N=1$).

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

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):

$$\lg S^0_{298.15K,S} = -5.42 + 5.093 \lg M - 0.806(\lg M)^2 + 5.748\Delta r - 30.143 (\Delta r)^2 \quad (5)$$

$$\lg Cp^0_{298.15K,S} = -26.16 + 19.169 \lg M - 3.3(\lg M)^2 + 14.711\Delta r - 60.139 (\Delta r)^2 \quad (6)$$

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.