

## Estimation of the standard enthalpies of formation of actinide mononitrides

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Actinide mononitrides ( $AnN$ ) are brittle, refractory materials of high melting point (usually  $>2000^\circ\text{C}$ ), which means they have potential for becoming good nuclear fuel and targets for fast reactors and for transmutation of minor actinide elements because of their advantageous thermal and neutronic properties [1, 2]. The thermodynamic properties of  $AnN$  are essential in fuel designs and evaluation of fuel behavior. The systematic understanding of the thermodynamic properties of  $AnN$  may promote advanced fuel technologies. The thermodynamic properties of some  $AnN$  have been measured [1–5], however, many are still unmeasured. A quantitative systematic study of the variation of thermodynamic properties of actinide mononitrides for the actinide series is still required. Such a systematic study would prove very useful, in order to predict the properties of those  $AnN$  that are difficult or impossible to measure experimentally.

Relationships linking thermodynamic properties of crystalline solids and aqueous cations are of considerable interest because they provide the possibility of predicting the thermodynamic data from the known properties of cations. Notably, Sverjensky and Molling have developed a linear free energy correlation model that correlates the standard formation free energy with the thermodynamics of corresponding metal cations [6, 7]. The empirically based Sverjensky equation, applicable to cations of any charge, radius or chemical type, has been a useful tool to calculate the formation free energy of isostructural intermetallic compounds from the known thermodynamic properties. Within an isostructural family of solids, the free energy change in going from one compositional endmember to another containing cations with the same (or similar) ionic radii is paralleled by the free energy change between the corresponding aqueous cations [1–4]. The relationship between the standard formation free energy and enthalpy of crystalline solid is  $\Delta G^0 = \Delta H^0 - T \Delta S^0$ . For the isostructural crystalline solids, we assume that formation enthalpy shows similar systematic variation as formation free energy, and we have successfully applied this approach for lanthanide chlorides and lanthanide oxides [8]. Accordingly, in this study, we estimate the standard enthalpies of formation of actinide mononitrides using a linear enthalpy model.

The  $AnN$ , which have the same  $NaCl$ -type face-centered cubic structure, crystallize in the rocksalt structure and, from a consideration of the lattice parameters of these compounds, the radius of the nitrogen

atom may be shown to be  $\sim 1.55 \text{ \AA}$  [9]. This is much too large for an uncharged interstitial nitrogen atom and approaches the size of an  $N^{3-}$  ion (Pauling radius  $1.71 \text{ \AA}$ ). Although, it is not correct to represent the  $AnN$  as purely ionic compounds  $An^{3+}N^{3-}$ , it seems clear that the compounds are highly ionic, and the  $PuN$  contains  $Pu^{3+}$  ions might be observed [3]. Regardless the real ionicity,  $An$  was treated as trivalent in this study in order to apply the linear enthalpy relationship.

With regard to the isostructural family of crystalline solids, the standard enthalpy of formation of  $AnN$ ,  $\Delta H_{f,AnN}^0$ , is paralleled by the free energy change between the corresponding aqueous actinide cations as [6–8, 10]

$$\Delta H_{f,AnN}^0 = \alpha \times \Delta G_{n,An^{3+}}^0 + \delta + \kappa \times \Delta S_{f,An^{3+}}^0 + \beta \times \gamma_{An^{3+}} \quad (1)$$

where  $\Delta G_{n,An^{3+}}^0$  is the standard non-solvation energy of cation  $An^{3+}$ ,  $\Delta S_{f,An^{3+}}^0$  the standard entropy of formation of aqueous cation  $An^{3+}$ ,  $\gamma_{An^{3+}}$  the crystallographic ionic radius of  $An^{3+}$ , and  $\alpha$ ,  $\delta$ ,  $\kappa$  and  $\beta$  are constants, which can be determined by a regression analysis from experimental data. Equation 1 can be rearranged as the following equation

$$\Delta H_{f,AnN}^0 - \kappa \times \Delta S_{f,An^{3+}}^0 - \beta \times \gamma_{An^{3+}} = \alpha \times \Delta G_{n,An^{3+}}^0 + \delta \quad (2)$$

According to Equation 2, we find that with the linear enthalpy correlation occurrence, a linear correlation should exist between  $(\Delta H_{f,AnN}^0 - \kappa \times \Delta S_{f,An^{3+}}^0 - \beta \times \gamma_{An^{3+}})$  and  $\Delta G_{n,An^{3+}}^0$ . This linear relationship can be used to determine the feasibility of the linear enthalpy correlation for actinide mononitrides.

The values of  $\Delta G_{n,An^{3+}}^0$ ,  $\Delta S_{f,An^{3+}}^0$ , and  $\gamma_{An^{3+}}$  can be obtained from Ref. [6], as given in Table I. The experimentally derived standard enthalpies of formation of  $AnN$  at 1600 K were selected to fit Equation 1 with the properties of the trivalent aqueous cation,  $An^{3+}$ , in this study. The fitting result is shown in Fig. 1, where a linear correlation is clearly observed. The coefficients of  $\alpha = 2.327$ ,  $\delta = 6624.17 \text{ kJ/mol}$ ,  $\kappa = 5632.22 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}$ , and  $\beta = -6755.63 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{\AA}^{-1}$  were regressed. Accordingly, the currently unknown values of standard enthalpies of formation were calculated using

TABLE I Ionic radii, thermodynamic data for aqueous cations,  $An^{3+}$ , enthalpy of formation of  $AnN$  at 1600 K

An	$\gamma_{An^{3+}}$ (Å)	$An^{3+}$ , aqueous (kJ/mol)			$\Delta S_{f,An^{3+}}^0$ ( $J \cdot mol^{-1} \cdot K^{-1}$ )	$\Delta H_f^0$ (kJ/mol)	
		$\Delta G_{a,An^{3+}}^0$	$\Delta G_{f,An^{3+}}^0$	$\Delta G_{n,An^{3+}}^0$		Expt.	Calc.
Ac	1.12	-899	-609	290	-199	-	-1388
Th	1.08	-915	-339	576	-186	-378	-379
Pa	1.05	-927	-431	496	-183	-	-345
U	1.025	-937	-476	461	-190	-296	-296
Np	1.011	-943	-515	428	-185	-	-250
Pu	0.995	-950	-577	373	-190	-299	-299
Am	0.98	-956	-603	353	-199	-294	-294
Cm	0.97	-961	-594	367	-194	-	-167
Bk	0.955	-967	-578	389	-194	-	-13

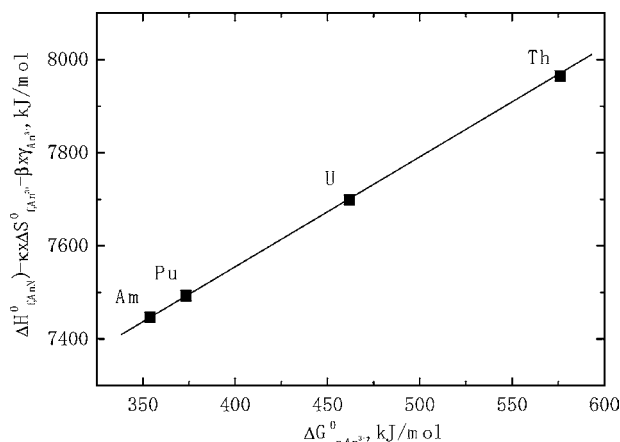


Figure 1 Linear enthalpy relationship of Equation 2 for the  $AnN$ .

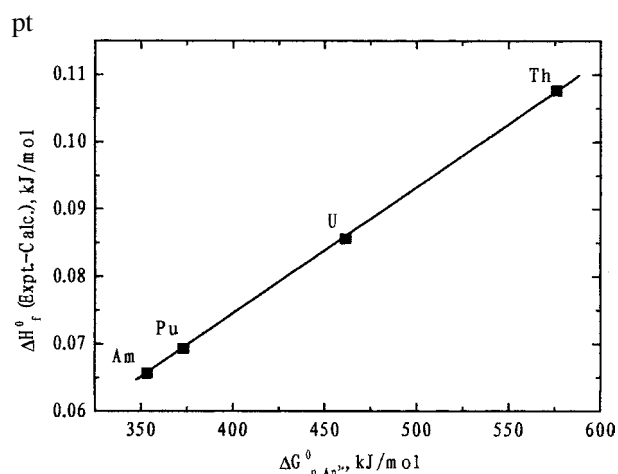


Figure 2 The discrepancy between calculated and experimental data of  $AnN$ .

Equation 1 together with the above regression coefficients, and other known parameters, as shown in Table I. The differences between experimental and calculated values of enthalpies of formation of the solids are given in Fig. 2. The calculated values and experimental data are in good agreement.

Although the predictions still need to be confirmed by experiments, and the physical meaning of coefficients  $\alpha$ ,  $\delta$ ,  $\kappa$  and  $\beta$  are not clear, the linear enthalpy correlation provides a useful tool for predicting unknown thermodynamic properties from a limited number of available data.

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