

Thermodynamic analysis of light-actinide elements

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Abstract

The thermophysical properties of the alpha phases of the light actinide elements Th, U, Np and Pu were analysed. For each of the analysed elements, the Gibbs free-energy was modelled by an explicit function of temperature T and pressure P over the whole relevant T – P range, in a manner compatible with the CALPHAD (Calculation of Alloy Phase Diagrams) method. Several adjustable model-parameters were fitted to available experimental results. The model is based on a new semi-empirical equation of state, which interpolates with Thomas–Fermi type models for the volume and with the Dulong–Petit value for the heat capacity, at extreme pressures.

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1. Introduction

In order to enable reliable interpolations and extrapolations of thermophysical properties, it is desirable to fit the available experimental data to consistent thermodynamic models. One common type of models is based on the Mie–Grüneisen equation of state (EOS). For many purposes, the use of the Mie–Grüneisen EOS is cumbersome, since it is written in terms of temperature and volume (T, V) whereas in most experiments the controlled variables are temperature and pressure (T, P). A different approach is outlined by Eq. (1):

$$G(T, P) = G(T, P_0) + \int_{P_0}^P V dP, \quad (1)$$

where G is the Gibbs free energy and P_0 is the reference pressure (usually 1 atm). The first term in Eq. (1) is the Gibbs free energy along the reference isobar, which is determined by thermochemical measurements, i.e. the isobaric heat capacity. The second term represents the isothermal change of G with pressure. Thermodynamic models of this type were used to couple thermophysical properties with phase-equilibrium calculations in conjunction with the CALPHAD (Calculation of Alloy Phase Diagrams) method [1–3]. However, the formalism outlined in Eq. (1) suffers from several difficulties. For the expression for G to remain explicit, an EOS of the form $V(T, P)$ is required. For this reason most workers used the Murnaghan EOS which, however, is limited in its range of application to $P < B_0/2$ [4], where B_0 is the zero-pressure bulk modulus. A second difficulty lies in the temperature-dependence of the EOS. For example, Jacobs and Oonk [5] have shown that isothermal EOS with temperature-dependent parameters are prone to predict negative thermal expansion at high pressures, even for closed packed substances. Finally, at high pressure, a phase may become stable outside the temperature range,

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at which it is stable at ambient pressure. Thus, in order to calculate high-pressure phase equilibria, $G(T, P_0)$ has to be extrapolated outside the measured range. Although the extrapolation itself may not be tested directly, it may affect the predicted high-pressure thermal properties. The existing methods of heat-capacity extrapolation [6] were not constructed in view of such effects.

In the present contribution, we employ a new scheme for the analysis of thermophysical properties. The scheme includes a new $V(T, P)$ EOS and a new method for the evaluation of $G(T, P_0)$. As will be shown in the next section, the new EOS is an interpolation between the low-pressure behaviour and Thomas–Fermi type models at very high pressures. It may be integrated to yield an explicit, analytic expression of $G(T, P)$ and is valid to high pressures, $P > B_0$. The consistency of the model is improved by invoking the assumption that at high pressure, and above the Debye temperature, the heat capacity tends to the Dulong–Petit value of $3R$, as implied by physically motivated models for the heat capacity [7,8]. By use of this assumption, $G(T, P_0)$ is related to the EOS. The new model is applied to the analysis of the properties of the light actinide elements Th, U, Np and Pu.

2. The model

The volume $V(T, P)$ may be written as a sum of two terms:

$$V(T, P) = V(T_0, P) + V_{th}(T, P), \quad (2)$$

where T_0 is a reference temperature and $V_{th}(T, P)$ will be called ‘Thermal volume’. The function $V(T_0, P)$ describes the isothermal compression at the reference temperature. We suggest that $V(T_0, P)$ may be written as a sum:

$$V = \sum_{n=2}^5 c_n \cdot f_n(V_0, B_0, B'_0, P), \quad (3)$$

where f_n are functions of the pressure, that also depend on the material parameters: V_0, B_0, B'_0 that are the reference molar volume, the bulk modulus and its pressure derivative at (T_0, P_0) . f_n are given by

$$f_n(V_0, B_0, B'_0, P) = V_0 \cdot \left[1 - a_n + a_n \cdot \left(1 + \frac{n}{3a_n} \cdot \frac{P}{B_0} \right)^{\frac{1}{n}} \right]^{-3}, \quad (4)$$

where $a_n = (n - 1) \cdot (3B'_0 - 1)^{-1}$.

The coefficients c_n in Eq. (3) also depend on material properties, but should not be considered as additional adjustable parameters. These coefficients are normalized to give $1 = \sum_{n=2}^5 c_n$ in order that $V(T_0, P_0) = V_0$, and are chosen so that Eq. (3) interpolates smoothly with the Thomas–Fermi type models [9]. In the present work,

Table 1
Model-parameters for light actinide elements and references to experimental data

Element	Parameter	References												
		H_0 [J/mol]	S_0 [J K ⁻¹ /mol]	V_0 [cc/mol]	B_0 [GPa]	B'_0	α_0 [K ⁻¹]	α_1 [K ⁻²]	$\frac{\delta_0}{B'_0}$	c_2	c_3	c_4	c_5	
Th		-11 011	16.43	19.785	57	3.5	3.1×10^{-5}	2.8×10^{-9}	1 ^a	0.30008	0.26079	-2.4831	2.9223	[14–17]
U		-18 952	-13.307	12.495	108	5.8	4.4×10^{-5}	5.3×10^{-9}	1.4	0.04263	0.35308	-0.4429	1.0473	[17–22]
Np		-33 112	-60.821	11.574	118	6.6	7.9×10^{-5}	5×10^{-9}	1 ^a	-0.04	0.61617	-0.4886	0.91240	[17,23,24]
Pu		-21 821	-22.932	12.04	45	15	14×10^{-5}	10^{-9}	1 ^a	-0.3383	1.6875	-1.0176	0.66848	[17,25–28]

^a Held constant during the fitting procedure.

the calculation by Kalitkin and Kuzmina [10] was used. The functional form for the thermal volume V_{th} is selected so that the following conditions are fulfilled:

$$\frac{\partial V_{\text{th}}}{\partial T} \geq 0, \quad \frac{\partial^2 V_{\text{th}}}{\partial T^2} \geq 0, \quad \int_{P_0}^{P=\infty} V_{\text{th}}(T, P), dP < \infty, \quad (5)$$

where the first condition means positive thermal expansion and the second implies that the heat capacity decreases monotonously as pressure increases. The third condition means that the decrease of the thermal volume is rapid enough, so that in compression, its contribution to the Gibbs free energy, converges to a finite value at extreme pressure. We found that the following form fulfills the above requirements:

$$V_{\text{th}}(T, P) = V_0 \cdot \left[1 - b_m + b_m \cdot \left(1 - \frac{m}{3b_m} \cdot A(T) + \frac{m}{3b_m} \cdot \frac{P}{B_0} \right)^{\frac{1}{m}} \right]^{-3} - V_0 \cdot \left[1 - b_m + b_m \cdot \left(1 + \frac{m}{3b_m} \cdot \frac{P}{B_0} \right)^{\frac{1}{m}} \right]^{-3}, \quad (6)$$

m is an integer. We found that $m = 3$, suits several materials. $b_m = (m - 1) \cdot (3\delta_0 - 1)^{-1}$ where δ_0 is an adjustable parameter that may be identified with the Anderson–

Gruneisen parameter at (T_0, P_0) [11]. In many cases it may be assumed that $\delta_0 = B_0'$. Above the Debye temperature, $A(T) = \alpha_0 \cdot T + \alpha_1 \cdot T^2 - \alpha_0 \cdot T_0 - \alpha_1 \cdot T_0^2$ where α_0 and α_1 are adjustable parameters. α_0 may be identified with the thermal expansion coefficient at (T_0, P_0) . Now, if it is assumed, that at extreme pressures the heat capacity tends to the Dulong–Petit value of $3R$, it is possible to derive the relation between $G(T, P_0)$ and the EOS [8]:

$$G(T, P_0) = H_0 - T \cdot S_0 + 3R \cdot T \cdot \ln \left(\frac{T_0}{T} \right) + 3R \cdot (T - T_0) - \int_{P_0}^{P=\infty} V_{\text{th}}(T, P) dP, \quad (7)$$

where S_0 and H_0 are constants that may be set to yield the conventional values of enthalpy and entropy at standard conditions.

3. Application

The adjustable parameters of the new scheme were fitted to available experimental data on the light actinides. The values of the fitted parameters and references to the experimental data are given in Table 1. Some calculations done with our model for α -U, are illustrated in Fig. 1. In Fig. 1(a) and (b), the calculated molar volume

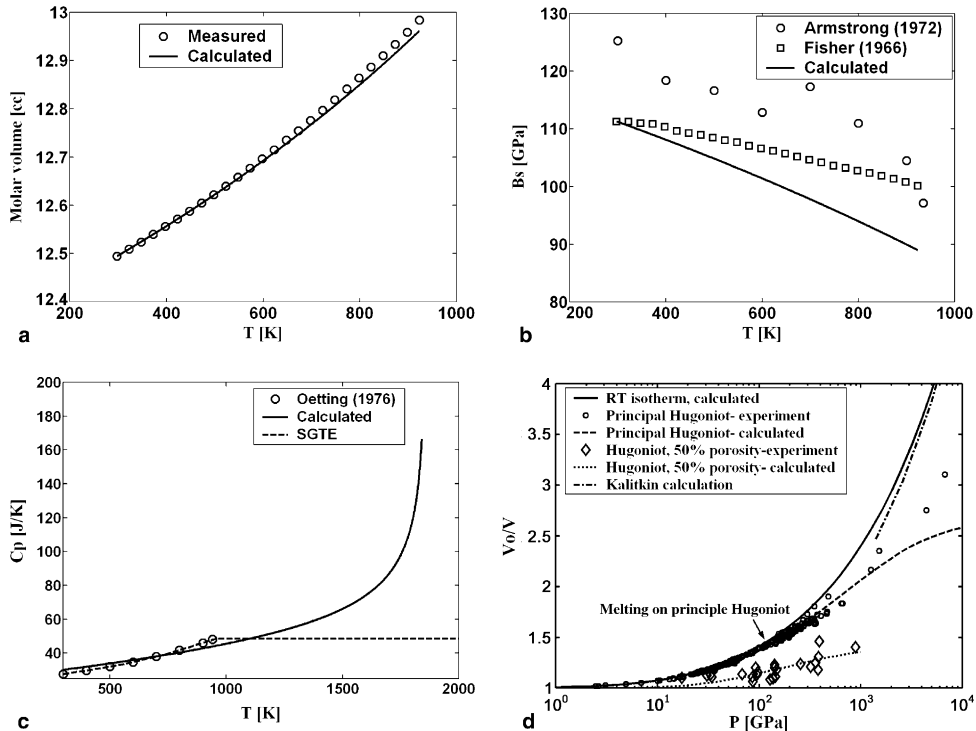


Fig. 1. Properties of U. (a) Molar volume at atmospheric pressure. (b) Adiabatic bulk modulus at atmospheric pressure. (c) Isobaric heat capacity of the α phase at atmospheric pressure, with extrapolation to high temperatures. (d) Room temperature isotherm and V – P relation along the Hugoniot.

and the adiabatic bulk modulus, are compared with experimental results for ambient pressure. The fit may be regarded as satisfactory, allowing for the small number of the adjustable parameters. In Fig. 1(c), the isobaric heat capacity of α -U at ambient pressure, calculated by the new model, is compared with the currently used thermodynamic database (SGTE) [6]. Although U transforms from α to β at 942 K, the extrapolation of the heat capacity of the α phase to higher temperatures is required for calculation of high-pressure phase equilibria, as discussed in Section 1. While in the SGTE database it is assumed that at high temperatures the heat capacity of solid phases is equal to the heat capacity of the liquid, the new model results in a very different extrapolation [8]. This difference should result, via Eq. (1), in different predictions for the properties of α -U at elevated temperatures and pressures. As suggested by Fernández Guillermet [12], we compared the model predictions with experimental Hugoniot data for Th and U [13]. Even though the Hugoniot data was not used in fitting the model parameters, and although most of the Hugoniot lies in the liquid range of stability, the calculated Hugoniot is found to be in surprisingly good agreement with experiment, as may be seen in Fig. 1(d) (for U). While the good agreement between the calculated and measured Hugoniot is not an ultimate proof for the correctness of the new EOS, it may still be viewed as a partial check of its validity.

4. Conclusion

A new scheme was applied to the analysis of the thermophysical properties of light actinide elements in their alpha phases, which allows consistent evaluation of various properties. Thus, more reliable interpolations and extrapolations are made possible. The new scheme is compatible with the CALPHAD method. Thus, it may be used for calculation of high-pressure phase equilibria, when the new scheme will be extended to other phases, including the liquid. Such an extension is currently in preparation.

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