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Thermodynamics of enthalpy, volume and bulk modulus in α-Pu

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ABSTRACT

The thermodynamic interrelationship between thermal and elastic properties at constant pressure has been studied from the point of view of an empirical linear relation between adiabatic bulk modulus (B_S) and enthalpy increment (ΔH). A thermodynamic analysis of this linear scaling suggests several possible simple relations for expressing the isobaric temperature dependence of various thermal quantities. These approximations invoke one or more thermoelastic quantities such as Grüneisen, and Anderson–Grüneisen parameters. The proposed B_S–ΔH linear relation together with the auxiliary thermoelastic relations deduced thereof constitute a self-consistent thermodynamic framework which will be useful in a critical appraisal of the internal consistency of diverse sources of thermal and elastic property data. The applicability of this framework is highlighted by modelling the available experimental data on thermal and elastic properties of α-plutonium. In particular, a successful prediction of its molar volume could be made from the recent experimental data on bulk modulus and assessed information on enthalpy increment.

1. Introduction

A rigorous thermodynamic description of condensed phases in terms of pressure (P), volume (V) and temperature (T) coordinates, namely the equation of state (EoS) suggests that there must exist certain well-defined interrelationship between thermal and elastic properties, especially with regard to their temperature and pressure dependencies [1,2]. A good example to illustrate this point is the relatively temperature independent nature of the Grüneisen parameter γ_G, which contains rather implicitly the compensating or synergetic influence of temperature on different thermal and elastic quantities, such as volume thermal expansivity (α_V), molar specific heat (C_P), molar volume (V) and adiabatic bulk modulus (B_S) [3]. In a similar context, it also emerges from basic thermodynamic principles that the isothermal pressure dependence of volume thermal expansivity $(\partial\alpha_V/\partial P)_T$, is identically related to the isobaric temperature variation of bulk modulus $(\partial B_T/\partial T)_P$ [2]. In reality, it is possible to establish different linkages or approximations connecting the temperature and or pressure dependencies of different thermodynamic quantities [4–6]. Despite such theoretical possibilities, it is not always easy to decipher the existence of a particular thermodynamic linkage entirely from first principles [1]. This is so, because the measured thermal and elastic quantities often take *apparently* diverse functional representations with regard to their temperature and pressure variations [1,6]. However, the experimental data on many thermophysical quantities of condensed phases, in particular their pressure and temperature variations, when taken and analysed together, reveal certain surprisingly simple relations over a reasonable range of temperature and or pressure [6–14]. Although appearing empirical at first sight, such experimentally deduced correlations reflect certain underlying physical basis, which if correctly identified and exploited judiciously can lead to a versatile thermodynamic framework that will help the cause of a self-consistent interpolation *cum* prediction of thermal quantities from limited, inhomogeneous or even partial data sets [10,11]. It is with this intent that we analyse in this study the thermodynamic implications of a linear relationship connecting molar volume (V) with enthalpy increment ($H_T - H_0$) and bulk modulus under constant pressure conditions. The practical utility of some of the thermodynamic relations developed from this linear correlation is demonstrated by taking on α-plutonium as the case study material.

2. Theoretical development

The starting point of our analysis is the following linear relation which is essentially identical to the proposed originally by Anderson [6,12], for characterising the relative variation of adiabatic bulk modulus (B_S) with respect to the corresponding enthalpy increment ($H_T - H_0$) under constant pressure.

$$B_S = B_0 - \xi_S(H_T - H_0). \tag{1}$$

In the above expression, B_S and B_0 stand respectively for the adiabatic bulk modulus values at temperatures T and T_0 respectively. T_0 is an appropriately chosen reference temperature. $H_T - H_0$

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represents the corresponding incremental enthalpy, with H_0 being the enthalpy at the reference temperature. ξ_S is assumed to be a temperature independent thermoelastic constant as a first order approximation. A detailed discussion on the physics of this expression, especially the nearly temperature independent nature of ξ_S is deferred to another section in this paper. In what follows, the attention is focused on enlisting some of the important thermodynamic implications of this approximation. Eq. (1) can be rewritten as follows.

$$H_T = H_0 + (B_0/\xi_S)\{1-(B_S/B_0)\}. \tag{2}$$

Now, the temperature dependent bulk modulus ratio $B_S(T)/B_0$, may be expressed in terms of the corresponding ratio (V_T/V_0), of molar volume by appealing to the concept of temperature independent adiabatic Anderson–Grüneisen parameter, δ_S [6,13]. Thus one may write,

$$B_S/B_0 = (V_T/V_0)^{-\delta_S}. \tag{3}$$

The Anderson–Grüneisen parameter δ_S is given by the following expression [6,13]

$$\delta_S = -(1/\alpha_V B_S)\times(\partial B_S/\partial T)_P = -(\partial\ln B_S/\partial\ln V)_P. \tag{4}$$

It may be remarked at this juncture that Eq. (3) also follows from the earlier theoretical analysis of Grüneisen [14], nevertheless in the present study we retain the popular terminology of denoting δ_S after Anderson [6,13]. The negative sign on the right-hand side of Eq. (4) stands for the fact that as the volume increases with increasing temperature at constant pressure, the bulk modulus suffers a concomitant decrease, so that the derivative $(\partial\ln {}_S/\partial\ln\,)_P$ takes a negative value and δ_S in turn turns out to be a positive quantity. Substituting for B_S/B_0 from Eq. (3) into (2), we obtain the following relation connecting directly the enthalpy with molar volume.

$$H_T = H_0 + (B_0/\xi_S)\{1-(V_T/V_0)^{-\delta_S}\}. \tag{5}$$

It is useful to recall that apart from invoking the validity of Eq. (1), the only other assumption that has gone into deriving Eq. (5) is the temperature independent nature of δ_S. Following the example of nearly temperature independent thermal Grüneisen parameter, γ_G [15], it is often assumed that at high temperatures ($T \geqslant \theta_D$), δ_S is only *mildly* temperature sensitive and that for all practical purposes, a nearly temperature independent constant value δ_0 may be used in Eq. (5) [6,13]. On the contrary, it is also possible to improve the technical sophistication of this simple approximation (Eq. (5)), by taking recourse to some models that characterise the temperature variation of $\delta_S(T)$ itself. It may be inferred from Eq. (4) that models for the temperature variation of δ_S translate effectively into models that account for the isobaric volume variation of bulk modulus [6,11,13]. Thus for example, we may invoke the following empirical relation proposed recently by Jacobs and Oonk for expressing the isobaric volume dependence of bulk modulus [9].

$$B_S/B_0 = \exp\{-\delta_0[(V_T-V_0)/V_0]\}, \tag{6}$$

Using Eq. (6) in Eq. (2), we may derive

$$H_T = H_0 + (B_0/\xi_S)\{1-\exp(-\delta_0[(V_T-V_0)/V_0])\}. \tag{7}$$

Incidentally, it must be mentioned that Eq. (6) presupposes the fact that in place of temperature independent δ_S, the composite quantity (δ_S/V) is taken as temperature independent [16]. Since the argument inside the exponential function on the right-hand side of Eq. (7) is rather small, that is, $\delta_0[(V_T-V_0)/V_0] \ll 1$, we may approximate the exponential function as a series expansion in $(V_T - V_0/V_0)$ and retaining only the linear term in such an expansion, we obtain after some algebraic manipulation, the following linear correlation between enthalpy and molar volume.

$$H_T = H_0 + (B_0\delta_0/V_0\xi_S)(V_T-V_0). \tag{8}$$

It is clear that Eq. (8) is a less sophisticated approximation than Eq. (7); nevertheless it is a simple and useful one.

Alternately, one may also adopt the Chopelas and Boehler approximation for expressing the volume dependence of δ_S [17]. In this approximation, a composite quantity A, defined by the following expression

$$A = (1+\delta_S)/V_T = (1+\delta_0)/V_0, \tag{9}$$

is taken to be temperature independent. That is in place of (δ_S/V), the composite quantity $(1+\delta_S)/V_T$ is assumed to be temperature independent. With this assumption, the corresponding expression for the isobaric volume dependence of bulk modulus takes the following form.

$$B_S/B_0 = (V_T/V_0)\exp\{-A(V_T-V_0)\}. \tag{10}$$

Substituting for B_S/B_0 from Eq. (10) in (2), we get the following fourth approximation connecting enthalpy variation with volume.

$$H_T = H_0 + (B_0/\xi_S)\times\{1-(V_T/V_0)\exp[-A(V_T-V_0)]\}. \tag{11}$$

2.1. Estimation of thermoelastic constants δ_S and ξ_S from standard values of reference temperature thermal properties

The expressions given in (5), (7), (8), and (11) provide for a ready estimation of enthalpy from molar volume data, if values of B_0, V_0, ξ_S and δ_0 are known. Of these, B_0 and V_0 are standard quantities corresponding to the reference temperature T_0. Reliable estimates these quantities may be considered as readily available input for many materials. Additionally, the values of thermoelastic constants ξ_S and δ_0 need to be known at the reference temperature. As evident from the definition of δ_S *vide* Eq. (4), δ_0 is determined, if the temperature derivative of bulk modulus $(\partial B_S/\partial T)_0$ and volume thermal expansivity (α_0) at the reference temperature (T_0) are known. For a good number of materials, the bulk modulus data may be available over a small range of temperature in the low to moderate temperature region. But in general, the extensive availability of temperature dependent elastic property data is still rather scarce for many solids of practical interest. If information regarding $(\partial B_S/\partial T)_0$ is lacking for a solid of specific interest, we may employ the following relation suggested by Ledbetter for obtaining a first order estimate of this quantity [18].

$$(\partial B_S/\partial T)_P = -(\alpha_V B_S)\delta_S = -(C_P\gamma_G/V)\delta_S = -3R\gamma_G(\gamma_G+1)/V. \tag{12}$$

The above relation gives basically the high temperature constant limit value of $(\partial B_S/\partial T)_P$. It is useful to recall that γ_G is the Grüneisen parameter. Thus after defining all the quantities, the only remaining thermoelastic parameter that remains to be explained in detail is ξ_S. This point is addressed in the following section.

3. Physical meaning of ξ_S

Upon differentiating Eq. (1) with respect to temperature, we get,

$$(\partial B_S/\partial T)_P = -\xi_S C_P. \tag{13}$$

Now, by substituting for $(\partial B_S/\partial T)_P$ in the above expression in terms of δ_S from Eq. (4) and in addition, employing the following definition of the thermal Grüneisen parameter γ_G [3,6]

$$\gamma_G = \alpha_V B_S V/C_P, \tag{14}$$

in effectively replacing the product of thermal expansivity and bulk modulus $(\alpha_V B_S)$, we finally arrive at the following expression for ξ_S

$$\xi_S = \gamma_G\delta_S/V. \tag{15}$$