



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

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ARTICLE INFO

Article history:

Received 17 May 2010

Accepted 31 October 2010

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.

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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.

$$B_S = B_0 - \xi_S(H_T - H_0). \quad (1)$$

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.

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

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,

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

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

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

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 $(\partial \ln B_S/\partial \ln V)_P$ 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.

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

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 ($T \geq \theta_D$), 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].

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

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

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

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.

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

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

$$A = (1 + \delta_S)/V_T = (1 + \delta_0)/V_0, \quad (9)$$

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.

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

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

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

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].

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

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,

$$(\partial B_S/\partial T)_P = -\xi_S C_P. \quad (13)$$

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]

$$\gamma_G = \alpha_V B_S V / C_P, \quad (14)$$

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

$$\xi_S = \gamma_G \delta_S / V. \quad (15)$$

Note that in the above formulation of ξ_S , we have not assumed the temperature independence of either γ_G or δ_S . In fact, their individual temperature sensitivities are implicitly subsumed or compensated in the overall nearly temperature independent nature of ξ_S . In this sense, ξ_S represents a higher order thermoelastic quantity. It must further be added that in general the temperature sensitivities of γ_G and δ_S in themselves are generally small, and besides are formidable issues to be resolved on a rigorous thermodynamic basis. Nevertheless, in proposing an empirical linear scaling relation between two thermal properties, such as Eq. (1), the intricacies of the temperature variations of two complex thermoelastic parameters like γ_G and δ_S are adequately taken care of. In hindsight, this is one of the remarkable advantages of the linear scaling approximation given in Eq. (1).

As the first simplifying step, the temperature dependence of both γ_G and δ_S may be set to zero [15,19]. Such an approximation may be valid only at high temperatures ($T > \theta_D$). Under such case, one can estimate ξ_S as

$$\xi_0 = \gamma_0 \delta_0 / V_0. \quad (16)$$

The other important point to note from Eq. (16) is that by substituting for $\xi_0 = \gamma_0 \delta_0 / V_0$ in Eq. (8), we can further simplify the enthalpy dependence of molar volume in the following manner.

$$H_T = H_0 + (B_0 / \gamma_0)(V_T - V_0). \quad (17)$$

The above linear approximation suggests that $(\partial H / \partial V)_P = (B_S / \gamma_G)$, is another nearly temperature independent composite quantity. In what follows, we present an illustrative application of the thermodynamic framework developed in this study by estimating the thermal properties of α -plutonium.

4. A case study on α -plutonium

A study on α -plutonium is interesting on two counts. In the first, it is rather difficult to carry out extensive experimentation on plutonium and its alloys on account of its highly radioactive and self-damaging nature [20]. Secondly, a fundamental understanding of the physics of plutonium is indeed a challenging task, as it is one of a delicate balance between a typically delocalised versus localised descriptions of the dynamics of bonding electrons [21]. It is believed that the physicochemical characteristics of α -Pu, the first among the six allotropes, must in some way derive from this intricate physics. Notwithstanding the experimental difficulties, a fair amount of experimental information on thermal and physical properties exist for α -plutonium [22–33]. Thanks to the availability of fairly pure α -Pu with reasonable mass in the recent past, some of its physical properties have been redetermined [34–37]. Recently, Ledbetter et al. [37] have accurately determined the temperature variation of the elastic properties of α -Pu by resonant ultrasound spectroscopy in the temperature range of 18 to about 385 K, thus offering a complete set of values for most part of the existence domain of α -Pu. The interesting part of their work is the finding that notwithstanding the subtleties of f -electron physics, the measured temperature dependence of the adiabatic bulk modulus can be adequately characterised by the classical Varshni's model, as given below [38].

$$B_S(T) = B_S(0) - s / [\exp(\theta_E / T) - 1]. \quad (18)$$

In the above expression, s is a temperature independent constant and θ_E is the characteristic Einstein temperature. Strictly speaking they are to be treated as fit-constants. However, as shown by Ledbetter [18], the above model may be derived by assuming the Einstein single oscillator model of specific heat, besides implicitly invoking the *ansatz* that $(\partial B_S / \partial T)_P = -\xi_S C_P$. In fact, it can be shown that within the spirit of the linear correlation between enthalpy

and bulk modulus (Eq. (1)), the constant s is given by the relation [18]

$$s = (3R\theta_E)\xi_S, \quad (19)$$

and the slope $(\partial B_S / \partial T)_P$ by the expression

$$(\partial B_S / \partial T)_P = -\{s / \theta_E \times 1 / 3R\} C_P. \quad (20)$$

C_P is given by the Einstein approximation [3]

$$C_P = 3R(\theta_E / T)^2 \exp(\theta_E / T) / [\exp(\theta_E / T) - 1]^2. \quad (21)$$

In Fig. 1, we present the linear correlation observed between the experimental values of enthalpy [39] and adiabatic bulk modulus [37]. The slope ξ_S , of the best-fit line is found to be $2.3 \times 10^6 \text{ mol m}^{-3}$. This experimental value for ξ_S compares rather well with the theoretically estimated value of $2.85 \times 10^6 \text{ mol m}^{-3}$. At this point, it is instructive to make a mention of the dimension and approximate magnitude of ξ_S . From Eq. (15), it emerges that ξ_S , shares an inverse dimensional relationship with molar volume V , since both γ_G and δ_S are dimensionless quantities. If volume is expressed on a molar basis, then ξ_S takes the dimension of mol m^{-3} . Further, if we set the value of the composite product $\gamma_G \times \delta_S$ to be within the range 26–30, which is probable for α -plutonium from the point of view of its current thermophysical property estimates, then the magnitude of ξ_S is approximately about $30/V$. In the present study the theoretical estimate of ξ_S , is obtained from Eq. (19) using Varshni's model fit parameters, namely $s = 11.3 \text{ GPa}$ and $\theta_E = 158.8 \text{ K}$. In fact, using this latter theoretical value of $2.85 \times 10^6 \text{ mol m}^{-3}$ for ξ_S , and making a back calculation of enthalpy in terms of experimental B_S data using Eq. (1), it is found that the calculated values are within $\pm 5\%$ of the assessed experimental data [39]. This is reflected in Fig. 2, where the original experimental and back calculated enthalpy values are compared for α -plutonium. Although, we could not estimate the uncertainty associated with the theoretical estimate of the thermoelastic constant ξ_S (the corresponding uncertainty in the empirical fit parameters s and θ_E are not known), it appears that experimental enthalpy values are generally no better than $\pm 5\%$ level of accuracy [30]. As a further cross check, one can also estimate ξ_S , using the definition given in Eq. (16) in terms of γ_0 , δ_0 and V_0 . Taking the required data for α -plutonium ($\gamma_0 = 2.87$ (extrapolated), $\delta_0 = 8.91$, $V_0 = 11.712 \times 10^{-06} \text{ m}^3 \text{ mol}^{-1}$) from the theoretical analysis of Wallace [40], a value of 2.18×10^6 has been deduced for ξ_0 . It is again noteworthy that this value is fairly close to 2.3×10^6 , that is obtained from the slope of the straight-line fit that is given in Fig. 1. In summary, it may be noted that notwithstanding the uncertainties inherent of the

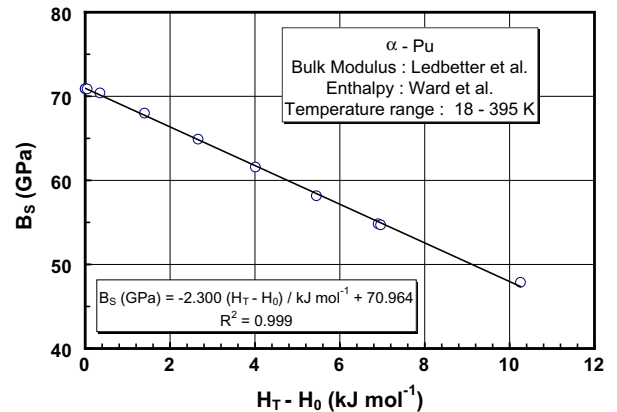


Fig. 1. The linear relationship between adiabatic bulk modulus B_S and enthalpy increment ΔH , for α -plutonium, as suggested by Eq. (1) is graphically demonstrated.

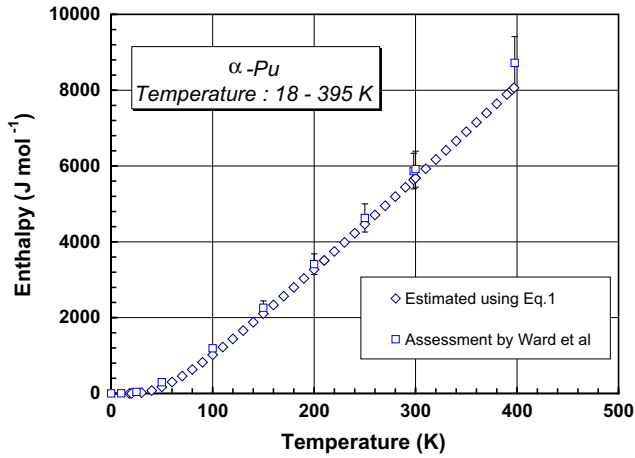


Fig. 2. The calculated and assessed experimental enthalpy values for α -plutonium are compared as a function of temperature.

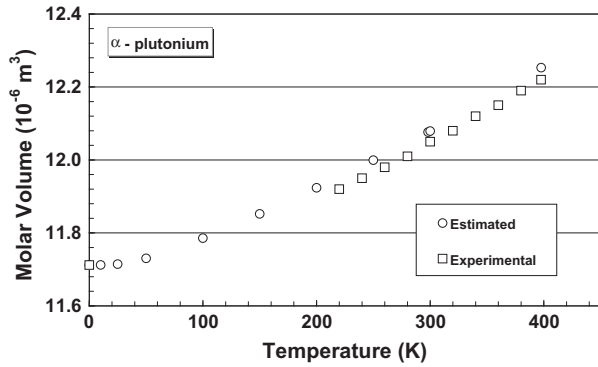


Fig. 3. Comparison of experimental and calculated molar volume variation as a function of temperature is graphically illustrated.

experimental data, there is a genuine linear correlation between bulk modulus and enthalpy (Eq. (1)) for α -plutonium.

In the next step, we attempt to estimate the temperature variation of molar volume using experimental enthalpy data. Among various approximations developed in this study, we chose the simplest of approximations given by Eq. (17). The values of $V_0 = 11.712 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$, $\gamma_0 = 2.87$ and $B_0 = 54.4 \text{ GPa}$, needed for this purpose are taken respectively from the tabulation of Wallace [40], who in turn has considered in his analysis the extensive compilation of the experimental data by Wick [26], and Ledbetter et al. [37]. In Fig. 3, the estimated and experimental values of molar volume as a function of temperature are compared. As can be seen from this figure, the estimated values are only slightly higher than the experimental estimates. In view of the uncertainty that is invariably associated with lattice parameter measurements, and also considering the fact that Eq. (17) is basically a linear approximation, this level of agreement can be considered as good.

5. Discussion

A study on the interrelationship between thermophysical quantities is in fact not new. In all probability, the early and a well-noted thermodynamic treatment of the interrelationship between thermal and elastic quantities had been provided by Grüneisen himself [14]. By proposing a temperature independent parameter γ_G (Eq. (14)), he had issued a compact statement with regard to the compensating influence of temperature on (α_V/C_P) vis a vis

the product $(B_S V)$. In a recent study, we further probed this topic of interrelationship between thermal and elastic properties from the standpoint of one of the Grüneisen hypotheses, namely the ratio $\lambda = \alpha_V/C_P$, is temperature insensitive [10,41]. When viewed in a broader perspective, this assumption translates into following relation between molar volume and enthalpy at constant pressure [10].

$$V_T = V_0 \exp(\lambda_0 \Delta H). \quad (22)$$

λ_0 is the value of the α_V/C_P ratio at the reference temperature [10]. If in the above approximation, we further assume that $\exp(\lambda_0 \Delta H) \approx (1 + \lambda_0 \Delta H)$, then we recover a linear relation connecting V_T with ΔH .

That is,

$$V_T = V_0 + \lambda_0 V_0 \Delta H. \quad (23)$$

It is instructive to note the similarity between Eqs. (23) and (17). In other words, the present linear approximation can be traced to Grüneisen's exponential relationship (Eq. (22)). In Fig. 4, the graphical depiction of the linear correlation between enthalpy and molar volume in case of α -plutonium is portrayed.

It emerges from the comparison of these two linear relations (Eqs. (17) and (23)) that $\lambda_0 V_0 = \gamma_0/B_0$, which otherwise also follows from the definition of γ_0 , as given in Eq. (14). By making use of this fact in the thermodynamic definition of $\xi_0 = \gamma_0 \delta_0/V_0$, we obtain

$$\xi_0 = \lambda_0 \delta_0 B_0. \quad (24)$$

In view of the above, Eq. (1) may now be rewritten in the following equivalent form.

$$B_S = B_0(1 - \lambda_0 \delta_0 \Delta H). \quad (25)$$

The other important point with regard to the applicability of the approximations developed in this study is concerned with the true constancy of various thermoelastic parameters invoked for the purpose. As a general remark, it may be said that all thermoelastic quantities are in principle sensitive to temperature variation and a rigorous theoretical quantification of this dependency is indeed difficult. It is generally found that for many solids, and for temperatures exceeding the Debye characteristic temperature, $T \gg \theta_D$, the temperature variation of thermoelastic quantities may be considered as negligible. It is in this light, that the proposition of a second order thermoelastic parameter like ξ_S , which implicitly incorporates the temperature dependence of primary or first order thermoelastic quantities, such as γ_G , λ , and δ_S assumes practical significance. As amply demonstrated by the results obtained for α -plutonium, the self-consistency of approximations suggested in this study is quite obvious. In this sense, the invocation of a constant ξ_S can offer fairly

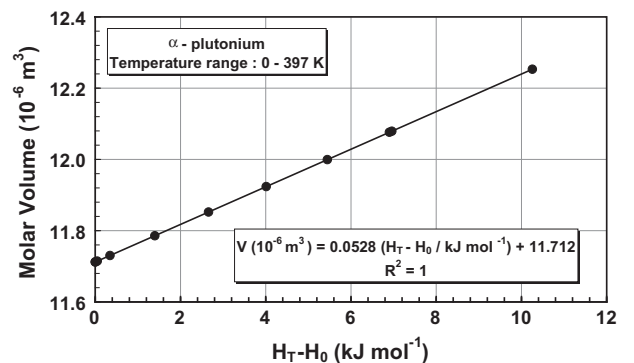


Fig. 4. The linear approximation between molar volume and enthalpy increment for α -plutonium, as suggested by Eq. (17) is graphically demonstrated.

reliable predictions for molar volume from bulk modulus data or *vice versa*. Further, it may also be said that in proposing empirical correlations like Eqs. (1), (17), (23) involving measurable thermodynamic quantities, a consistent description of the interrelationship between them has also been enabled. This fact will be of use in analysing the internal thermodynamic consistency among diverse data sets. The other point that must be kept in mind while using the approximations derived in this study is with regard to the onset of phase transformations. For obvious reasons, the various thermodynamic quantities suffer continuous or discontinuous changes in the domain of phase transformations and as a result of this, the temperature independent character of various thermoelastic parameters is lost in the phase transition region. In view of this, the validity of the thermoelastic relations suggested in this study is lost, when the system under study evinces phase instability.

6. Conclusions

A comprehensive thermodynamic analysis of the linear isobaric relationship between bulk modulus and enthalpy has been presented. By invoking a hierarchy of approximations for representing the volume dependence of bulk modulus, a set of self-consistent relations connecting molar volume and enthalpy increment has been deduced. The applicability of the thermodynamic framework derived in this study has been demonstrated in case of α -plutonium by successfully predicting its molar volume as a function of temperature using enthalpy data.

Acknowledgements

The authors thank Dr. Baldev Raj, Dr. T. Jayakumar and Dr. M. Vijayalakshmi, for their encouragement and sustained support during the course of this study. The comments of the reviewer are very much helpful in enhancing the clarity of presentation. This paper is dedicated to the fond memories of Prof. P. Ramachandra Rao, with whom one of the authors (S.R.) have spent many a wonderful time in discussing the nuances of classical thermodynamics.

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