

Comment on “A new equation of state based on Grover, Getting and Kennedy’s empirical relation between volume and bulk modulus. The high pressure thermodynamics of MgO” by M. H. G. Jacobs and H. A. J. Oonk, *Phys. Chem. Chem. Phys.*, 2000, 2, 2641

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This Comment discusses certain interesting implications of the new equation of state (EoS) proposed recently by Jacobs and Oonk (*Phys. Chem. Chem. Phys.*, 2000, 2, 2641). In essence, the physical significance of the temperature independent thermoelastic parameter ‘*b*’ appearing in their key equation is clarified by relating it to the more popular isothermal Anderson–Grüneisen parameter (δ_T). A novel quantification of the isobaric temperature dependence of δ_T is also established in this way. The similarity of the Jacobs–Oonk relation to the one proposed earlier by Tallon (*J. Phys. Chem. Solids*, 1980, 41, 837) is also pointed out. In addition it is shown that the validity of the Jacobs–Oonk relation for the temperature dependence of bulk modulus implies that the product of isothermal bulk modulus (B_T) and thermal expansivity (α_V) is temperature independent. Further, it also leads to an exponential scaling for the isothermal volume dependence of thermal expansivity.

The field of classical thermodynamics is considered at times to be a closed one, especially since the subject, in its entirety, is fully contained in the three basic laws that lay down the definitions of basic thermodynamic state functions and in the Maxwell identities, which serve to explore the synergy between them. Thus, it has emerged in recent times that innovations are hardly to be expected on the basic aspects of thermodynamics of condensed phases and further work would mainly be on elaborating the details. Nevertheless it is reassuring to note from the recent study of Jacobs and Oonk,¹ that if the concepts of thermodynamics are adroitly handled, it is still possible to obtain interesting revelations even about as complex a phenomenon as the equation of state at extreme conditions (see ref. 1). In their recent paper published in this journal, Jacobs and Oonk,¹ advanced a simple, thermodynamically self-consistent and empirical equation of state (EoS) that holds good over an extended range of pressure and temperature without giving rise to an instability. This EoS derives in turn from a linear scaling of the logarithmic bulk modulus with volume under constant pressure conditions. Besides being of considerable relevance in geothermal physics, this main empirical observation concerning the isobaric temperature dependence of bulk modulus has certain important and broad based thermodynamic implications to the general topic of equation of state itself. The purpose of the present Comment is to highlight these interesting and nontrivial consequences.

To begin with, let us recall the main relation proposed by Jacobs and Oonk¹ (see eqn. (1) of ref. 1)

$$V_T = V_0 + b \ln(K_T/K_0), \quad (1)$$

where V_T and V_0 are the actual and reference volumes pertaining to the actual and reference temperatures T and T_0 respectively. K_T and K_0 are likewise the actual and reference bulk modulus (inverse of compressibility) values. The parameter b is taken to be temperature independent. We adopt in

this paper a somewhat simpler nomenclature than that used in ref. 1. It should be remembered that expression (1) is essentially an isobar. It is similar in form to the one proposed earlier by Grover, Getting, and Kennedy (GGK),² for representing the isothermal volume dependence of compressibility. Thus, the original GGK relation is an isotherm. In their paper, Jacobs and Oonk¹ have assumed the validity of eqn. (1) to higher pressures as well, thus developing an apparently new equation of state for higher pressures. Let us now explore the thermodynamic consequences of this new EoS.

Differentiating eqn. (1) with respect to temperature at constant pressure, noting that K_0 and V_0 are to be treated as constants, we get

$$(\partial V_T / \partial T)_P = (b/K_T)(\partial K_T / \partial T)_P. \quad (2)$$

By substituting for $(\partial V_T / \partial T)_P$ in terms of volume thermal expansivity, α_V , we further simplify this relation to the following form

$$V_T \alpha_V = b(\partial \ln K_T / \partial T)_P. \quad (3)$$

Recalling at this point the definition of the isothermal Anderson–Grüneisen parameter (δ_T)³

$$\delta_T = -(\alpha_V)^{-1}(\partial \ln K_T / \partial T)_P, \quad (4)$$

We rewrite eqn. (3) as

$$V_T/b = (\alpha_V)^{-1}(\partial \ln K_T / \partial T)_P = -\delta_T. \quad (5)$$

Or equivalently, the temperature independent parameter b appearing in eqn. (1) can now be given in terms of the isothermal Anderson–Grüneisen parameter and thermodynamic volume. Thus,

$$(V_T/\delta_T) = -b. \quad (6)$$

In view of eqn. (6), the original relation proposed by Jacobs and Oonk (eqn. (1)) can be recast in the following manner.

$$K_T = K_0 \exp(-\delta_T \Delta V/V_T) \quad (7)$$

Where, $\Delta V = V_T - V_0$ is the volume dilation. It is instructive to note at this stage, another similar relation proposed by Tallon⁴ for the purpose of scaling the isobaric volume dependence of bulk modulus. Tallon's relation can be written as⁴

$$K_T = K_0 \exp\{-g_K(\Delta V/V_0)\}, \quad (8)$$

where $g_K = -V_0 (\partial \ln K_T / \partial V_T)_P$, is again a temperature independent parameter. Comparing eqns. (7) and (8), it is evident that $g_K = (V_0/V_T)\delta_T$. Further, since $(V_T/\delta_T) = -b$, from eqn. (6), we can clearly see that $g_K = -V_0/b = V_0 \delta_T/V_T$. In other words, the parameter b is given by the relation,

$$b = (\partial \ln K_T / \partial V_T)_P^{-1}. \quad (9)$$

Thus, it is gratifying to note that eqn. (1) proposed by Jacobs and Oonk is very much in tune with that proposed by Tallon, although, these two approaches start from different premises. In addition, the parameter b can be shown to possess interesting links with the thermal Grüneisen parameter, γ_G . This is explained below.

Let us start with the definitions of the isothermal Anderson–Grüneisen parameter (δ_T) and the thermal Grüneisen parameter (γ_G).

$$\delta_T = -\{1/(\alpha_V K_T)\}(\partial K_T / \partial T)_P. \quad (10)$$

$$\gamma_G = \alpha_V K_T V_T / C_V. \quad (11)$$

From eqns. (10) and (11), the following relation can be deduced after some algebraic manipulations

$$V_T/\delta_T = -\gamma_G C_V (\partial K_T / \partial T)_P^{-1}. \quad (12)$$

Since $b = -V_T/\delta_T$ (*vide* eqn. (6)) it emerges that

$$b = \gamma_G C_V / (\partial K_T / \partial T)_P. \quad (13)$$

Eqn. (13) can be employed to provide an alternate and useful definition of the Anderson–Grüneisen parameter. Thus, we can write for δ_T the following expression

$$\delta_T = -(V_T/(\gamma_G C_V))(\partial K_T / \partial T)_P. \quad (14)$$

It can be inferred from eqn. (14) that the temperature variation of δ_T is decided in turn by the temperature dependencies of two distinct quantities, namely $\gamma_G C_V/V_T$ and $(\partial K_T / \partial T)_P$. A compensating influence of these two can give rise to a temperature independent δ_T . For a solid such as MgO, the quantity $(\partial K_T / \partial T)_P$ (evaluated from the data provided in Table 1 of ref. 1) takes a constant value of about -3×10^7 Pa K⁻¹ in the temperature range 300–1800 K. Thus, it emerges from eqn. (14) that if δ_T were to remain temperature independent, the product $(\alpha_V B_T)$ must be temperature insensitive. This approximation is reasonably obeyed by MgO for temperatures exceeding 1000 K. This will be discussed further at a latter point in this paper.

Proceeding further, it is also possible to express the temperature dependence of δ_T in an elegant manner starting from eqn. (6) in the following fashion.

$$(\partial \delta_T / \partial T)_P = -(1/b)(\partial V_T / \partial T)_P. \quad (15)$$

Or,

$$(\partial \delta_T / \partial V)_P = -(1/b). \quad (16)$$

Eqn. (16), which is based on the validity of eqn. (1), serves to estimate the isobaric volume dependence of δ_T purely from the corresponding data on bulk modulus temperature variation. Finally, we wish to point out that the validity of eqn. (1) has interesting implications for the pressure dependence of volume thermal expansivity as well. From basic thermodynamics, the following thermodynamic identity can be established.³

$$(\partial K_T / \partial T)_P = K_T^2 (\partial \alpha_V / \partial P)_T. \quad (17)$$

Substituting from eqn. (17) for $(\partial K_T / \partial T)_P$ in eqn. (13), we get after some simplifying steps

$$b = -\{(\gamma_G C_V)/(K_T^2)\}(\partial \alpha_V / \partial P)_T^{-1}. \quad (18)$$

This can further be simplified by substituting the definition of the thermal Grüneisen parameter (γ_G) as given in eqn. (11). Thus we obtain

$$b = -(\partial \ln \alpha_V / \partial V)_T^{-1}. \quad (19)$$

Integrating eqn. (19) along an isotherm and assuming the parameter b to be pressure independent (an assumption invoked by Jacobs and Oonk) yields,

$$\alpha_V(P) = \alpha_V(0) \exp\{-(V_P - V_0)/b\} \quad (20)$$

where, V_P is the volume at pressure P , and V_0 is the corresponding volume at zero external pressure. It is interesting to note that eqn. (20) is the thermal expansivity analogue of the original GGK relation.

Finally, it may be of interest to note that the validity of the Jacobs–Oonk relation (eqn. (1)) implies the temperature independence of the product of thermal expansivity and bulk modulus ($\alpha_V K_T$). The proof is relatively straightforward and proceeds as follows.

Assuming that $\alpha_V K_T = k$ is temperature independent, then we can write the following relation by starting from the definition of δ_T

$$\delta_T/V = -(\partial \ln B_T / \partial V)_P. \quad (21)$$

Comparing this relation with the definition of b in (eqn. 6), we have

$$1/b = (\partial \ln B_T / \partial V)_P. \quad (22)$$

Integrating eqn. (22) with the assumption that b is temperature independent, we get back Jacobs–Oonk relation (eqn. (1)). The thermodynamic consequences of the temperature independence of $(\alpha_V K_T)$ have been analysed by us recently.⁵ More importantly, it turns out that the intrinsic temperature dependence of K_T (at constant volume), namely $(\partial K_T / \partial T)_V$ happens to be zero. This, in turn, suggests that K_T is a function of only volume, and not temperature *per se*. This limitation may not be readily apparent from a plot of V_T vs. $\ln(K_T/K_0)$. But, if one were to compare the estimated δ_T values using eqn. (6) with the actual experimental ones as given by eqn. (10), the limitation becomes strikingly evident. This is illustrated for MgO in Fig. 1. The required data for this figure is taken from Table 1 of ref. 1. It is clear from Fig. 1

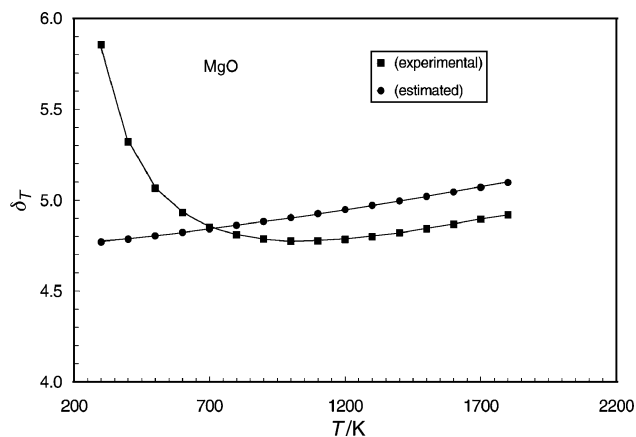


Fig. 1 Temperature dependence of the isothermal Anderson–Grüneisen parameter (δ_T) for MgO obtained from the experimental data (taken from Table 1 of ref. 1) is compared with the estimated ones using eqn. (6). Note that the experimental δ_T is reasonably temperature independent from about 1000–1800 K, while the estimated ones, assuming the constancy of ‘ b ’ (eqn. (1)) shows a mild increase with temperature. Also, notice their contrasting behaviours at low temperatures.

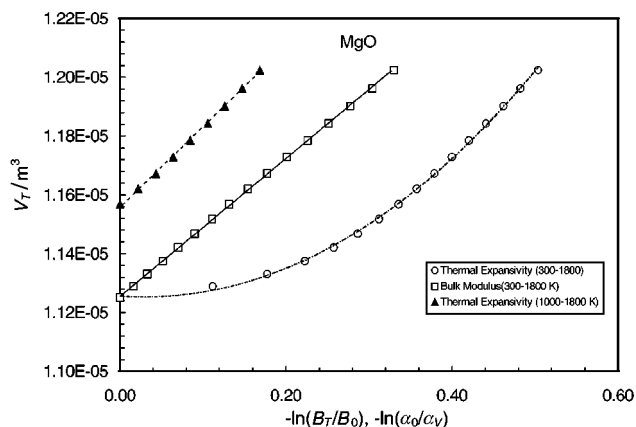


Fig. 2 The isobaric volume dependencies of logarithmically scaled bulk modulus $\ln(B_T/B_0)$, and volume thermal expansivity $\ln(\alpha_0/\alpha_T)$, for MgO are graphically portrayed. In view of the contrasting variations of bulk modulus and thermal expansivity with temperature, we choose to plot $\ln(\alpha_0/\alpha_T)$ rather than $\ln(\alpha_T/\alpha_0)$. Note the non-linearity in the lower curve when thermal expansivity data from 300 to 1800 K are considered. However, when the reference temperature is changed from 1000 to 1800 K, the same data exhibit a clear linear behaviour. This discrepancy is, however, not readily apparent from the corresponding bulk modulus data.

that notwithstanding the uncertainties in the input data, the experimental δ_T values, after an initial rapid fall, are fairly constant and somewhat linear with temperature in the range 1000 to 1800 K. On the other hand, the δ_T values estimated *vide* eqn. (6) show a mild, but definitely increasing trend in the entire temperature range. The reason for this discrepancy is that for a solid such as MgO, the assumption that $(\alpha_V K_T)$ is a temperature independent constant, is reasonably obeyed only for temperatures exceeding 1000 K.³ Although the exact values of δ_T are known to be very sensitive to the uncertainties in the input data, we have not estimated in this study the error limits for the experimental δ_T vs. T curve, especially since we have used the internally consistent and optimised

data listed by Jacobs and Oonk¹ to demonstrate our view point. It is however useful to note that the experimental values of δ_T obtained in this study reveal a similar qualitative trend with those obtained by Anderson.³

Further, in view of the fact that the strict validity of the Jacobs–Oonk relation is linked with the temperature insensitivity of the product $(\alpha_V K_T)$, we amplify this point by plotting for MgO, the V_T vs. $\ln(\alpha_0/\alpha_T)$ data in the temperature range 300 to 1800 K. The resulting curve, as depicted in Fig. 2, is non-linear in the low-temperature ($300 \text{ K} \leq T \leq 1000 \text{ K}$) regime. However, by shifting the reference temperature T_0 slightly above θ_D , the Debye temperature, and thereby ensuring the apparent temperature insensitivity of $\alpha_V B_T$, this limitation can be overcome. This is demonstrated in the upper curve of Fig. 2. As already noted, this aspect of eqn. (1) is not readily apparent from the corresponding V_T vs. $\ln(K_T/K_0)$ curve.

Thus, the fact emerges that eqn. (1) is basically a good high-temperature approximation to the actual state of affairs. However, its adaptation to lower temperatures must be viewed with caution.

Finally, it remains to be pointed out that as for the validity of the relation $K' = -V_T/b$, (eqn. (24) of ref. 1) is concerned, it is clear from eqn. (6) of the present paper, that only under special circumstances in which the pressure derivative of bulk modulus K' equals δ_T , this relation holds good. This again is an outcome of the fact that the validity of the Jacobs–Oonk bulk modulus relation is intimately linked to the condition, $(\partial K_T/\partial T)_V = 0$.

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