

Study of Pressure Derivatives of Bulk Modulus

Abstract

Thermodynamic properties of solids under high pressure and high temperature can be understood by investigating an adequate form of EOS [1, 2, 3]. An equation of state can be used to determine the bulk modulus K and its variation with pressure and temperature [4-8]. The isothermal bulk modulus (K) can be determined from an isothermal equation of state representing relation between pressure and volume at fixed temperature.

Keywords: Equations of state, Bulk Modulus, Pressure Derivative.

Introduction

In the field of high pressure thermodynamics the interest of industries and scientists has always been taking a significant space. It is very obvious that materials undergo strong structural and chemical changes when subjected to high pressure. This is due to rearrangement of chemical bonding and basis of the material. This study can be made in two very clear ways, one of them is theoretical and other one is experimental, both of which are complementary of each other. Pressure derivatives are important tools too meet with our purpose.

Objectives of the Study

High pressure is a very active field of research and one whose ramifications affect many scientific and technological fields, from astrophysics and geophysics to materials physics and the food industry. From the fundamental view, the behavior of materials at high pressure is still poorly understood, and the usual textbook chemistry rules that apply to zero-pressure chemistry are essentially useless when molecules and materials are subjected. Calculated data (elastic moduli, longitudinal and shear velocities, thermal expansion and conduction, heat capacities, Grüneisen parameters, transition pressures, Clapeyron slopes, etc.) are very helpful in the interpretation of experimental data and in the construction of models of the Earth's interior. In order to describe the thermodynamic state of a system, certain variables are required.

Review of Literature

The thermodynamic state of a solid can be specified by its pressure (P), volume (V) and temperature (T). Out of these three variables P , V and T only two are independent variables and the third may be considered as the function of the remaining two. The relationship between the pressure P , the volume V and absolute temperature T for the substance is known as its equation of state (EOS). Thermodynamic properties of solids under high pressure and high temperature can be understood by investigating an adequate form of EOS. An equation of state can be used to determine the bulk modulus K and its variation with pressure and temperature [12-14]. These equations can in principle be derived from the knowledge of interatomic potentials for solids. Phenomenological forms of equation of state can also be derived by considering some particular relationship for the pressure dependence and temperature dependence of bulk modulus. The isothermal bulk modulus (K) can be determined from an isothermal equation of state representing relation between pressure and volume at fixed temperature. There exist a number of such equations obtained by various investigations [15].

An isobaric equation is that in which a relation takes place between volume and temperature at a constant pressure. In the field of high-pressure thermodynamics of solids many equations of states have been studied but Murnaghan's and Birch-Murnaghan's equations of state play a vast role in this field. But these equations of state are required to be modified by introduction of higher order terms if we want to study the relation at higher temperature and pressure. The principle of Birch-Murnaghan's Equation of State is based on Euler's theory while



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Murnaghn's Equation of State is based on linear dependence of bulk modulus on pressure.

As we know that short range force constant are dependent of volume, a process has been developed to get an equation of state for ionic solids using the theory of potentials inside ionic materials. In this process the formula for isothermal bulk modulus and its derivatives with respect to pressure are also developed for NaCl upto 30GPa[9].The results are compared with the available experimental data. The variation of the pressure derivative of bulk modulus with pressure has also been studied using the formulation recently developed by Stacey.

Concept and Hypothesis

In this study, we have presented the formulations used and numerical analysis for various solids. The results obtained in present study are discussed and compared with available experimental data. We study pressure-volume relationship using different equations of state for NaCl and MgO. This provides an opportunity for testing various equation of state corresponding to a wide range of compressions. In the present study, we consider eight equations of state(1-8). Reliable values of compressions (V/V₀) have been obtained by Birch for NaCl at different pressures by making a careful analysis of experimental measurements.This provides an opportunity for testing various equation of state corresponding to a wide range of compressions.These equations of state yield following relationships between pressure P and compression.

(a) Tait's Equation of state

$$P = \frac{K_0}{K_0^1} \left[\left(\exp(K_0^1 + 1) \left(1 - \frac{V}{V_0} \right) \right) - 1 \right] \dots\dots\dots(1)$$

(b) Born – Mie Equation of state

$$P = \frac{3K_0}{3K_0^1 - 8} \left(\left(\frac{V}{V_0} \right)^{4/3 - K_0^1} - \left(\frac{V}{V_0} \right)^{-4/3} \right) \dots\dots\dots(2)$$

(c) Brennan – Stacey Equation of state

$$P = \frac{3K_0 \left(\frac{V}{V_0} \right)^{-4/3}}{(3K_0^1 - 5)} \left[\left[\exp \left(\frac{3K_0^1 - 5}{3} \right) \left(1 - \frac{V}{V_0} \right) \right] - 1 \right] \dots\dots\dots(3)$$

(d) Shanker *et al* Equation of state

Where $y = 1 - \frac{V}{V_0}$ and $t = K_0^1 - 8/3$ $\dots\dots\dots(4)$

(e) Vinet *et al* Equation of state

$$P = \frac{3K_0 \left(1 - \frac{V}{V_0} \right)^{-1/3}}{\left(\frac{V}{V_0} \right)^{2/3}} \exp \left[\frac{3}{2} \left(K_0^1 - 1 \right) \left(1 - \frac{V}{V_0} \right) \right] \dots\dots\dots(5)$$

(f) Birch – Murnaghan equation of state

$$P = \frac{3K_0}{2} \left(\left(\frac{V}{V_0} \right)^{-7/3} - \left(\frac{V}{V_0} \right)^{-5/3} \right) \dots\dots\dots(6)$$

(g) Born-Mayer equation of state

$$P = \frac{3K_0}{\sigma - 2} \left[\left(\frac{V}{V_0} \right)^{-2/3} \exp \left\{ \sigma \left(1 - \left(\frac{V}{V_0} \right)^{-1/3} - \left(\frac{V}{V_0} \right)^{-4/3} \right) \right\} \right] \dots\dots\dots(7)$$

(h) Murnaghan's Equation of State

$$P = \frac{K_0}{K_0^1} \left\{ \left(\frac{V}{V_0} \right)^{-K_0^1} - 1 \right\} \dots\dots\dots(8)$$

As we know that the compressibility of any material gives the information about its crystal

Remarking An Analisation

structure we will have to develop a relation between bulk modulus and pressure derivatives. Expressions for isothermal bulk modulus are obtained using the relationship $K_T = -V (dP/dV)_T$. The corresponding expressions are

(a) Tait's equation of state

$$K = K_0 \frac{V}{V_0} \left[\left(\exp(K_0^1 + 1) \left(1 - \frac{V}{V_0} \right) \right) \right] \dots\dots\dots(9)$$

(b) Born – Mie equation of state

$$K = K_0 \left(\left(\frac{V}{V_0} \right)^{4/3 - K_0^1} + \frac{4}{3} P \right) \dots\dots\dots(10)$$

(c) Brennan – Stacey equation of state

$$K = K_0 \left(\frac{V}{V_0} \right)^{1/3} \left[\left[\exp \left(K_0^1 - \frac{5}{3} \right) \left(1 - \frac{V}{V_0} \right) \right] + \frac{4}{3} P \right] \dots\dots\dots(11)$$

(d) Shanker *et al* Equation of state

$$K = K_0 \left(\frac{V}{V_0} \right)^{1/3} \exp \left[\left(K_0^1 - \frac{5}{3} \right) \left(1 - \frac{V}{V_0} \right) \right] + \frac{4}{3} P \dots\dots\dots(12)$$

(e) Vinet *et al* equation of state

$$K = Kx^2 [1 + (\eta x + 1)(1 - x)] \exp \{ \eta(1 - x) \} \dots\dots\dots(13)$$

Where $x = \left(\frac{V}{V_0} \right)^{1/3}$ and $\eta = \frac{3}{2} (K_0^1 - 1)$

(f) Birch – Murnaghan equation of state

$$K = \frac{1}{5} K_0 (7X^{-7} - 5X^{-5}) + \frac{3}{8} K_0 (K_0^1 - 4) (9X^{-9} - 14X^{-7} + 5X^{-5}) \dots\dots\dots(14)$$

(g) Murnaghan equation of state

$$K = K_0 \left(\frac{V}{V_0} \right)^{-K_0^1} \dots\dots\dots(15)$$

Research Design

Shanker *et al* [9] obtained three sets of equations of for pressure P, isothermal bulk modulus K and its pressure derivatives dK/dP and d²K/dP² corresponding to three functions for the short-range force constant given by equations.

$$f \left(\frac{V}{V_0} \right) = \left(\frac{V}{V_0} \right)^{-m} \dots\dots\dots(16)$$

$$f \left(\frac{V}{V_0} \right) = \exp \left\{ -k \left(\frac{V}{V_0} \right) \right\} \dots\dots\dots(17)$$

And

$$f \left(\frac{V}{V_0} \right) = \frac{1}{V} \exp \left\{ -t \left(\frac{V}{V_0} \right) \right\} \dots\dots\dots(18)$$

Where, t is a constant. For the purpose of numerical analysis, we have choosenn the Nacl crystal. The P=V data for the solid are also available upto pressure of 30 G Pa [10]. This pressure yields a big compression range as it is significantly higher than the value of isothermal bulk modulus for Nacl. For making the comparison meaningful we have used the ultrasonic experimental values for input parameters K₀=23.84 G Pa and K₀¹=5.35 for Nacl as reported by Spetzler *et al* [11] and recommended by Anderson [16]. The same values of K₀ and K₀¹ have been used for each set of equations with out any adjustments for fitting.

Remarking An Analisation

First, we have calculated the pressure corresponding to selected values of compression V/V_0 as tabulated by Birch [17] using equations

$$P = \frac{3K_0}{3K_0^1 - 8} \left[\left(\frac{V}{V_0} \right)^{\frac{4}{3} - K_0^1} - \left(\frac{V}{V_0} \right)^{-\frac{4}{3}} \right] \dots\dots\dots(19)$$

$$P = \frac{3K_0 (V/V_0)^{-4/3}}{3K_0^1 - 5} \left[\left[\exp \frac{3K_0^1 - 5}{3} \left(1 - \frac{V}{V_0} \right) - 1 \right] \right] \dots\dots\dots(20)$$

$$P = K_0 \left(\frac{V}{V_0} \right)^{-4/3} \left[\left(1 - \frac{1}{t} + \frac{y}{t^2} \right) (\exp(ty) - 1) + y \left(1 + y - \frac{y}{t} \right) \exp(ty) \right] \dots\dots\dots(21)$$

Where $t = K_0^1 - 8/3$

And $y = 1 - \frac{V}{V_0}$

The results are compared in Table (1). Values of isothermal bulk modulus K have been calculated from equations

$$K = K_0 \left(\frac{V}{V_0} \right)^{-m-1/3} + \frac{4}{3}P \dots\dots\dots(22)$$

$$K = K_0 \left(\frac{V}{V_0} \right)^{-1/3} \exp \left\{ \left(K_0^1 - \frac{5}{3} \right) \left(1 - \frac{V}{V_0} \right) \right\} + \frac{4}{3}P \dots\dots\dots(23)$$

$$K = K_0 \left(\frac{V}{V_0} \right)^{-4/3} \exp \left\{ \left(K_0^1 - \frac{8}{3} \right) \left(1 - \frac{V}{V_0} \right) \right\} + \frac{4}{3}P \dots\dots\dots(24)$$

Using the values of P and V/V_0 corresponding to equations (4), (5) and (6) respectively, Values of dK/dP are then calculated from equations

$$\frac{dK}{dP} = \left(1 - \frac{4P}{3K} \right) \left(K \frac{V}{V_0} + \frac{5}{3} \right) + \frac{16P}{9K} \dots\dots\dots(25)$$

$$\frac{dK}{dP} = \left(1 - \frac{4P}{3K} \right) \left\{ \left(K_0^1 - \frac{8}{3} \right) \frac{V}{V_0} + \frac{8}{3} \right\} + \frac{16P}{9K} \dots\dots\dots(26)$$

$$\frac{dK}{dP} = \left(1 - \frac{4P}{3K} \right) \left\{ \left(K_0^1 - \frac{8}{3} \right) \frac{V}{V_0} + \frac{8}{3} \right\} + \frac{16P}{9K} \dots\dots\dots(27)$$

Using the corresponding values of P, V/V_0 and K. The results are reported in Tables 2 and 3.

Table – 1
Values of pressure P (GPa) for NaCl crystal calculated from Eqs. (4), (5) and (6). Experimental values from Birch [17] $P = 0$ at $V/V_0 = 1$.

V/V_0	Eq. (26)	Eq. (27)	Eq. (28)	Experimental
0.9627	1.01	1.00	1.00	1
0.9324	2.02	2.01	2.01	2
0.9067	3.04	3.03	3.03	3
0.8845	4.08	4.04	4.05	4
0.8649	5.13	5.06	5.08	5
0.7910	10.6	10.3	10.3	10
0.7397	16.66	15.6	15.7	15
0.7004	22.9	21.0	21.2	20
0.6685	29.6	26.7	26.9	25
0.6416	36.6	32.1	32.7	30

Table – 2
Values of isothermal bulk modulus K (GPa) for NaCl crystal calculated from Eqs. (22), (23) and (24). Extrapolated values of K based on experimental data [17] are given in the last column. Values of $K = K_0 = 23.84$ GPa at $P = 0$ and $V/V_0 = 1$.

V/V_0	Eq. (22)	Eq. (23)	Eq. (24)	Ref. [17]
0.9627	29.1	29.0	29.1	28.9
0.9324	34.3	34.0	34.1	33.6
0.9067	39.4	38.8	38.9	38.1
0.8845	44.5	43.4	43.7	42.5
0.8649	49.6	47.9	48.3	46.7
0.7910	85.5	69.4	70.8	66.1
0.7397	102	89.6	92.6	83.6
0.7004	130	109	114	99.8
0.6685	160	128	135	115
0.6416	491	146	156	129

Table – 3

Values of pressure derivative of isothermal bulk modulus dK/dP for NaCl crystal calculated from Eqs. (25), (26), (27) and the Stacey equation (30). dK/dP = K₀ = 5.35 at P = 0 and V/V₀ = 1.

V/V ₀	Eq. (25)	Eq. (26)	Eq. (27)	Eq. (30)
0.9627	5.16	5.03	5.07	5.02
0.9324	5.03	4.80	4.87	4.79
0.9067	4.94	4.62	4.71	4.62
0.8845	4.86	4.48	4.58	4.48
0.8649	4.80	4.86	4.48	4.38
0.7910	4.69	3.94	4.12	4.01
0.7397	4.48	3.68	3.90	3.80
0.7004	4.41	3.50	3.85	3.64
0.6685	4.36	3.35	3.64	3.52
0.6416	4.32	3.24	3.54	3.42

Values of $K^I = \frac{dK}{dP}$ calculated from equation (25-27) are found to decrease continuously as pressure is increased (Table 3). At higher pressures approaching 30 GPa, the rate of variation of K^I becomes small. It has been reported by earlier workers [18, 19,] that K^I tends to a limiting value K^I_∞ as P → ∞. An empirical equation of state was developed by Keane [20] using the relationship.

$$K_0^I - K_\infty^I = -\frac{K_0 K_0^I}{K_1^I} \dots\dots\dots (28)$$

where K₀^{II} is the value of $\frac{d^2K}{dP^2}$ at P = 0. The analysis presented by Anderson [18] using the Born-Mie potential, yields

$$K_0^I - K_\infty^I = \frac{4}{3} \dots\dots\dots (29)$$

Recently, Stacey [20] has developed a more useful equation for K^I which can be expressed as follows-

$$K^I = K_0^I - K_0 K_0^{II} \left(\frac{P}{K}\right) + S \left(\frac{P}{K}\right)^2 \dots\dots\dots (30)$$

where

$$S = (K_\infty^I)^3 - K_0^I (K_\infty^I)^2 - K_0 K_0^{II} K_\infty^I \dots\dots\dots (31)$$

Equation (30) is an empirical relationship and is applicable for both $K = K_T$ and $K = K_S$. It is found that P and K asymptotically approach a maximum value of their ratio, $P/K \rightarrow (P/K)_\infty$ as P → ∞. There is a corresponding asymptotic limit to dK/dP i.e.

$$K^I = \frac{1}{(P/K)_\infty} \dots\dots\dots (32)$$

On differentiating equation (30) with respect to P, we get,

$$\frac{d^2K}{dP^2} = \frac{1}{K} [K_0 K_0^{II} + 2S \frac{P}{K}] \left[1 - \frac{P}{K} \frac{dK}{dP}\right] \dots\dots\dots (33)$$

In the limit P → ∞, equation (32) and (33) leads to the prediction that $d_2K/dP_2 \rightarrow 0$. Using (32) in equation (25)-(27) for dK/dP, we get the following relationships, respectively (in the limit V/V₀ → 0 as P → ∞

$$9(K_\infty^I)^2 - 9K_0^I K_\infty^I + 12K_0^I - 16 = 0 \dots\dots\dots (34)$$

$$9(K_\infty^I)^2 - 15K_\infty^I + 4 = 0 \dots\dots\dots (35)$$

And

$$9(K_\infty^I)^2 - 24K_\infty^I + 16 = 0 \dots\dots\dots (36)$$

Equation (34) is based on the Born-Mie equation derived from the inverse power function, equation (35) is based on Brennan-Stacey equation corresponding to the exponential function, and equation (36) is based on the function (17). Equation (34) yields two roots K^I_∞ = K^I₀, -4/3 and 4/3. The first value is the same as that reported by Anderson in the form of equation (29). Equation (35) yields two values K^I_∞ = 4/3 and 1/3, where as for equation (36) the two

roots are equal (K^I_∞ = 4/3). These values of K^I_∞ when substituted in the corresponding equations.

$$\frac{d^2K}{dP^2} = -\frac{1}{K} \frac{dK}{dP} - \frac{1}{K} \left(\frac{dK}{dP}\right)^2 + \left(\frac{1}{K} - \frac{4}{3} \frac{P}{K^2}\right) (m^2 + 3m + 4) + \frac{112}{27} \frac{P}{K^2} \dots\dots\dots (37)$$

$$\frac{d^2K}{dP^2} = -\frac{1}{K} \frac{dK}{dP} - \frac{1}{K} \left(\frac{dK}{dP}\right)^2 + \left(\frac{1}{K} - \frac{4}{3} \frac{P}{K^2}\right) \left[K^2 \left(\frac{V}{V_0}\right)^2 + 2K \left(\frac{V}{V_0}\right) + 4\right] + \frac{112}{27} \frac{P}{K^2} \dots\dots\dots (38)$$

And

$$\frac{d^2K}{dP^2} = -\frac{1}{K} \left(\frac{dP}{dK}\right) - \frac{1}{K} \left(\frac{dK}{dP}\right)^2 + \left(\frac{1}{K} - \frac{4}{3} \frac{P}{K^2}\right) \left[\left\{2 + \left(K_0^I - \frac{8}{3}\right) \frac{V}{V_0}\right\} + 4\right] + \frac{112}{27} \frac{P}{K^2} \dots\dots\dots (39)$$

For d^2K/dP^2 in the limit P → ∞ (i.e. dK/dP → K^I_∞ and (P/K)_∞ → 1/K^I_∞) yield the result that $d^2K/dP^2 = 0$ which is consistent with the model recently development by Stacey [20]. Equations (32) and (33) also yield that $d^2K/dP^2 = 0$

Conclusion

Values of K and dK/dP for NaCl upto a pressure of 30 GPa have been obtained by Birch [17] from an analysis of experimental data [21]. The results reported by Birch have been found to be reliable and were used by Anderson and Isaak [22] to study the dependence of the Anderson-Gruneisen parameter upon compression at extreme conditions. We have plotted dK/dP versus K/P in Figure 1 using the data for NaCl. We note that the condition (32) is satisfied at K/P = 2.2 in the extrapolated range of data. This concept of fixed endpoint introduced by Stacey [20] yields K_∞^I = 2.2. Now, we calculate dK/dP with the help of Stacey equation [19] using P/K as reported by Birch [10]. Value of K₀^{II} = -0.14 GPa⁻¹ has been taken from the ultrasonic measurements for NaCl reported by Hart and Greenwood [23]. Values of dK/dP obtained from equation (30) are included in Table 3 for the sake of comparison. They compare well with the values estimated from other equations.

Endnotes

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