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An equation of state and non-linear parameter from sound velocity measurements for liquid alkali metals

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Abstract. In the present paper, an equation of state has been obtained in case of liquid alkali metals like Na, K, Rb and Cs from sound velocity measurements. The theory developed gives very good agreement for both the sound velocity and the volume as a function of pressure at different temperatures in these liquid alkali metals. Further, the variation of non-linear parameter, B/A, as a function of pressure and temperature is also studied.

Keywords. Equation of state; sound velocity; non-linear parameter; liquid alkali metals.

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1. Introduction

The temperature-dependent equation of state (EOS) of a substance is of fundamental thermodynamic importance, and the formulation of a satisfactory EOS for liquid metals would be very desirable and must address the issue of molecular bonding, association, polymerization, and the free volume in both ordered and disordered structures. However, a common procedure to obtain an EOS of liquids is through the sound velocity measurements. Since the sound velocity measurement is relatively independent of elastic distortion in high pressure devices, further, because sound velocity is proportional to a density derivative and because it can be measured very accurately, it is possible to determine the compressibility much more accurately with sound velocity than by differentiating P-V-T data. Thus, the development of an EOS on sound velocity measurement has attracted the attention of theoretical as well as experimental workers [1–4].

Recently, we have developed a method [5] to obtain an EOS in liquid metals from sound velocity measurements. In this method, the involved EOS has three adjustable parameters $B_T(0,T_A)$, $B'_A(0,T_A)$ and $B''_T(0,T_A)$, i.e., the ambient pressure and temperature isothermal bulk modulus and its pressure derivatives. If the substance under consideration does not have a phase transition, the parameters $B_T(0,T_A)$ and $B'_A(0,T_A)$ may be accurately known with sufficient accuracy whereas the second and higher derivative of the bulk modulus are not available precisely. Therefore, the aim of this paper is to obtain a two parameter EOS of liquid alkali metals which predict correct high pressure and high temperature behaviour. Further, for the first time, the variation of nonlinearity parameter, B/A [6–9] is studied both as a function of pressure and temperature which provide the certain information about the physical characteristics of the fluid, such as internal pressure, intermolecular spacing and acoustic scattering [14].

2. Theory

We start with the thermodynamic relation

$$\frac{1}{B_S(P,T)} = \frac{1}{B_T(P,T)} - \frac{[\alpha(P,T)]^2 T}{\rho(P,T)C_p(P,T)}. \tag{1}$$

Multiplying both sides of (1) with $\rho(P,T)$ gives the relation as

$$[V_S(P,T)]^{-2} = \left[\frac{V(0,T_A)}{V(P,T)}\right]\left[\frac{\rho(0,T_A)}{B_T(P,T)}\right] - [\xi/B_T(P,T)]^2 T/C_p(0,T). \tag{2}$$

In obtaining (3), we make use of the following relations

$$[V_S(P,T)]^{-2} = \rho(P,T)/B_S(P,T), \tag{3}$$

$$\frac{\rho(P,T)}{B_T(P,T)} = \frac{1}{V(P,T)B_T(P,T)} = \left[\frac{V(0,T_A)}{V(P,T)}\right]\left[\frac{\rho(0,T_A)}{B_T(P,T)}\right], \tag{4}$$

$$C_p(P,T) \cong C_p(0,T), \tag{5}$$

and

$$\alpha(P,T)B_T(P,T) = \alpha(0,T_A)B_T(0,T_A) = \xi. \tag{6}$$

Equation (6) given by Dass and coworkers [10] gives an interesting result.

$$\xi B_T'(P,T) = -\left[\frac{\partial B_T(P,T)}{\partial T}\right]_P, \tag{7}$$

which is obtained by differentiating (6) with respect to pressure at constant temperature.

In equations (1) – (7), V_S is the sound velocity, ρ is the density, B_S and B_T are the adiabatic and isothermal bulk modulus, V is the volume, C_p is the heat capacity at constant pressure, α is volume thermal expansion, B_T' is the first pressure derivative of B_T, T_A is the ambient temperature and ξ is a constant parameter independent of both the pressure and the temperature.

It is clear from (2) that to obtain the value of $V_S(P,T)$ as a function of pressure and temperature, we need the values of $V(P,T)/V(0,T_A)$ and $B_T(P,T)$ where $V(P,T)/V(0,T_A)$ represents the volume compression of the concerned liquid as a function of pressure and temperature and is obtained from the temperature-dependent EOS.

In references [5,11], we have used three parameter temperature-dependent EOS as

$$V(P,T)/V(0,T_A) = [(1+\beta)\exp\{Z(P-P_{\text{th}})\} - \beta]^{-1/\eta} \tag{8}$$

$$B_T(P,T) = B_T(0,T_A)[1+\beta\exp\{Z(P-P_{\text{th}})\}] \tag{9}$$

and

$$B_T'(P,T) = B_T'(0,T_A)\exp\{-Z(P-P_{\text{th}})\} \tag{10}$$

where $\beta = B_T'(0,T_A)/[B_T(0,T_A)Z]$, $\eta = B_T'(0,T_A) + B_T(0,T_A)Z$, and Z is a pressure and temperature independent parameter.

Equations (8)–(10) can be easily reduced to two-parameter EOS by taking $Z = [3B_T(0,T_A)]^{-1}$. Further, $P_{\text{th}} = \alpha(0,T_A)B_T(0,T_A)(T-T_A)$ is the thermal pressure which is used to convert an isothermal EOS into a temperature dependent EOS [5,11,12].

2.1 Non-linear parameter, B/A

The ratio, B/A, known as Beyer's non-linear parameter, is given in terms of measurable quantities [6–9,13] as

$$\begin{aligned} B/A = {} & 2\rho(P,T)V_S(P,T)[\partial V_S(P,T)/\partial P]_T \\ & +[2V_S(P,T)T\alpha(P,T)/C_p(P,T)][\partial V_S(P,T)/\partial T]_P. \end{aligned} \tag{11}$$

Equation (11) can also be written as

$$\frac{B}{A} = \left(\frac{B}{A}\right)' + \left(\frac{B}{A}\right)'', \tag{12}$$

where

$$\left(\frac{B}{A}\right)' = 2\rho V_S\left(\frac{\partial V_S}{\partial P}\right)_T, \tag{13}$$

and

$$\left(\frac{B}{A}\right)'' = [2V_S T\alpha/C_p]\left(\frac{\partial V_S}{\partial T}\right)_P. \tag{14}$$

In (13) and (14), all the parameters except T and C_p are functions of both the pressure and temperature which have been dropped henceforth for the sake of simplicity.

Before proceeding further, we derive some relations which are to be used in obtaining the values of $(B/A)'$ and $(B/A)''$.

Multiplying (1) with B_T and making use of (3) and (6), we get

$$\left(\frac{\gamma-1}{\gamma}\right) = \xi^2 T/[\rho C_p B_T], \tag{15}$$

and

$$\gamma = \frac{B_S}{B_T} = \frac{C_p}{C_v} = \rho V_S^2/B_T. \tag{16}$$

Differential of (2) with respect to pressure at constant temperature gives

$$\left[\frac{\partial V_S}{\partial P}\right]_T = [V_S^3/2B_T]\left[\frac{\partial \rho}{\partial P}\right]_T + [\rho V_S^3 B_T'/2B_T^2] - [\xi^2 T V_S^3 B_T'/(C_p B_T^3)]. \tag{17}$$

Multiplying both sides of (17) with $2\rho V_S$ gives the value of $(B/A)'$ as

$$\left(\frac{B}{A}\right)' = L + M + N, \tag{18}$$

where

$$L = -[\rho V_S^4/B_T]\left(\frac{\partial \rho}{\partial P}\right)_T$$

$$= -[\rho^2 V_S^4/B_T]\left[\frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T\right] = -[\rho^2 V_S^4/B_T^2] = -\gamma^2, \tag{19}$$

$$M = [\rho^2 V_S^4/B_T^2]B_T' = \gamma^2 B_T', \tag{20}$$

and

$$N = -2\left[\xi^2 T \rho V_S^4/(C_p B_l^3)\right] B_T'$$
$$= -2\left[\rho^2 V_S^4/B_T^2\right][\xi^2 T/\rho C_p B_T]B_T' = -2\gamma^2\left(\frac{\gamma-1}{\gamma}\right)B_T'$$
$$= -2\gamma(\gamma-1)B_T'. \tag{21}$$

Putting the values of L, M and N into (18), we get

$$\left(\frac{B}{A}\right)' = \gamma[B_T'(2-\gamma) - \gamma]. \tag{22}$$

Differentiation of (2) with respect to temperature at constant pressure under the assumption that C_p is independent of temperature gives

$$\left(\frac{\partial V_S}{\partial T}\right)_P = -[V_S^3/2B_T]\left(\frac{\partial \rho}{\partial T}\right)_P + [\rho V_S^3/2B_T^2]\left(\frac{\partial B_T}{\partial T}\right)_P$$
$$+ \left[\xi^2 V_S^3/(2C_p B_T^2)\right] - [\xi^2 T V_S^3/(C_p B_T^3)]\left(\frac{\partial B_T}{\partial T}\right)_P \tag{23}$$

Multiplying both sides of (23) by $2V_S T\alpha/C_p$, we get

$$\left(\frac{B}{A}\right)'' = O + P + Q + R, \tag{24}$$

where

$$O = -[T\alpha V_S^4/C_pB_T]\left(\frac{\partial\rho}{\partial T}\right)_P$$

$$= -[T\rho\alpha V_S^4/C_pB_T]\left[\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_P\right] = T\alpha^2\rho V_S^4/C_pB_T$$

$$= T\xi^2\rho V_S^4/C_pB_T^3 = [\rho^2V_S^4/B_T^2][\xi^2T/\rho C_pB_T]$$

$$= \gamma^2\left(\frac{\gamma-1}{\gamma}\right) = \gamma(\gamma-1). \tag{25}$$

$$P = [\rho V_S^4T\alpha/C_pB_T^2]\left(\frac{\partial B_T}{\partial T}\right)_P$$

$$= [V_S^4T\alpha\rho/C_pB_T^2][-\xi B_T']$$

$$= -[\rho V_S^4T\xi/C_pB_T^3][\xi B_T']$$

$$= -[\rho^2V_S^4/B_T^2]\left[\frac{\xi^2T}{\rho C_pB_T}\right]B_T'$$

$$= -\gamma^2\left(\frac{\gamma-1}{\gamma}\right)B_T' = -\gamma(\gamma-1)B_T'. \tag{26}$$

$$Q = [T\alpha\xi^2V_S^4/C_p^2B_T^2]$$

$$= [T^2\alpha^2\xi^2V_S^4/C_p^2B_T^2]\left(\frac{1}{T\alpha}\right)$$

$$= [T^2\xi^4V_S^4/C_p^2B_T^4]\left(\frac{1}{\alpha T}\right)$$

$$= [\rho^2V_S^4/B_T^2]\left[\frac{\xi^4T^2}{\rho^2C_p^2B_T^2}\right]\left(\frac{1}{\alpha T}\right)$$

$$= \gamma^2\left(\frac{\gamma-1}{\gamma}\right)^2\left(\frac{1}{\alpha T}\right) = (\gamma-1)^2/\alpha T. \tag{27}$$

$$R = -[2T^2\alpha V_S^4\xi^2/C_p^2B_T^3]\left[\left(\frac{\partial B_T}{\partial T}\right)_P\right]$$

$$= -2[T^2\xi^3V_S^4/C_p^2B_T^4][-\xi B_T']$$

$$= 2[\rho^2V_S^4/B_T^2]\left[\frac{\xi^4T^2}{\rho^2C_p^2B_T^2}\right]B_T'$$

$$= 2\gamma^2\left(\frac{\gamma-1}{\gamma}\right)^2B_T' = 2(\gamma-1)^2B_T'. \tag{28}$$

Putting the values of O, P, Q and R into (24) and simplifying the result, we get

$$\left[\frac{B}{A}\right]'' = (\gamma-1)\left[B_T'(\gamma-2)+\gamma+\frac{\gamma-1}{\alpha T}\right]. \tag{29}$$

Putting the values of $[B/A]'$ and $[B/A]''$ into (12) gives

$$\frac{B}{A} = [B_T'(2-\gamma) - \gamma + (\gamma-1)^2/\alpha T]. \tag{30}$$

Thus, (22), (29) and (30) will give the values of $(B/A)'$, $(B/A)''$ and (B/A) as a function of pressure and temperature.

2.2 *Some applications*

Some of the interesting results now can be obtained here

The ratio of $(B/A)''$ to $(B/A)'$ can be written as

$$\begin{aligned}[B/A]''/[B/A]' &= \frac{(\gamma-1)[B_T'(\gamma-2)+\gamma+(\gamma-1)/\alpha T]}{-\gamma[B_T'(\gamma-2)+\gamma]} \\ &= \left[\frac{1-\gamma}{\gamma}\right] - \frac{(\gamma-1)^2}{\alpha T\gamma[B_T'(\gamma-2)+\gamma]} \\ &\cong \left[\frac{1-\gamma}{\gamma}\right].\end{aligned} \tag{31}$$

Equation (31) represents the same result as given by Nomoto [15].

Further, we can also obtain the relations for isobaric acoustic parameter, K', given by Rao [16], isothermal acoustic parameter, K, given by Carnvel and Litovitz [17] and isochoric acoustic parameter, K'' [14].

The sound velocity is a function of pressure and temperature and therefore its change can be written as

$$\left(\frac{\partial V_S}{\partial T}\right)_V = \left(\frac{\partial V_S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial V_S}{\partial T}\right)_P. \tag{32}$$

Dividing both sides by the term αV_S and using the relation $(\partial P/\partial T)V = \alpha B_T$, we get

$$\frac{B_T}{V_S}\left(\frac{\partial V_S}{\partial P}\right)_T = -\frac{1}{\alpha V_S}\left(\frac{\partial V_S}{\partial T}\right)_P + \frac{1}{\alpha V_S}\left(\frac{\partial V_S}{\partial T}\right)_V$$

or

$$K' = K + K''. \tag{33}$$

It will be interesting to have a relation between K' and (B/A) on one hand and between K and (B/A) on the other hand.

From (33), $(\partial V_S/\partial P)_T$ can also be expressed in K' as

$$\left(\frac{\partial V_S}{\partial P}\right)_T = \frac{V_S}{B_T}K'. \tag{34}$$

Multiplying (34) with $2\rho V_S$ we get

$$2\rho V_S \left(\frac{\partial V_S}{\partial P}\right)_T = 2[\rho V_S^2/B_T]K'$$

or

$$\left(\frac{B}{A}\right)' = 2\gamma K' \qquad (35)$$

Expressing $(B/A)'$ in terms of (B/A), we get

$$2\gamma K' = \gamma[(B/A) - (\gamma - 1)^2/\alpha T]$$

or

$$2K' = \left(\frac{B}{A}\right) - (\gamma - 1)^2/\alpha T. \qquad (36)$$

Thus, it is clear from (36) that $(B/A) > 2K'$. Similar result can also be obtained for K, i.e., $(B/A) > 2K$. These results confirm the findings of Madigosky *et al* [18]. But it is worthwhile to mention here that these results are general in nature and does not confine to a particular class of liquids.

3. Calculations and discussion

Experimental data of sound velocity are taken from Shaw and Caldwell [1] in case of Na, K, Rb and Cs.

Equations (2), (8) and (9) are combined to compute the sound velocity as a function of pressure at different temperatures. The calculated and the experimental data of sound velocity are compared in figure 1 for Na, K, Cs and Rb, respectively, at selected temperatures at which the error (i.e., discrepancy between the exponential data and theory) is maximum. The computed results are in good agreement with the experimental data in the whole range of pressure and temperature in each liquid as the maximum error is not more than 1%.

By making use of (8) and taking the values of relevant parameters from table 1 of [5], the volume is computed for Na, K, Cs and Rb as a function of pressure at different temperatures. For comparison, the experimental data are taken from Makarkov *et al* [3] for Na, K and Cs. The computed and experimental volume are compared in figure 2 at selected temperatures at which the error is maximum. The calculated data are found to be on higher side than the reported results in each liquid.

Using the input data from table 1 of [5] values of $(B/A)', (B/A)''$ and B/A are calculated for Na, K, Cs and Rb as a function of pressure and temperature. The calculated $(B/A)'$ is found to increase with increasing pressure in each liquid. However, $(B/A)''$ is found to have a small negative value, whose magnitude increases as the pressure increases. Thus, the calculated values of B/A then tend to increase with increasing pressure and also exhibit a maximum as shown in figure 3. However, (B/A) decreases with rise in temperature in each liquid as shown in figure 4.

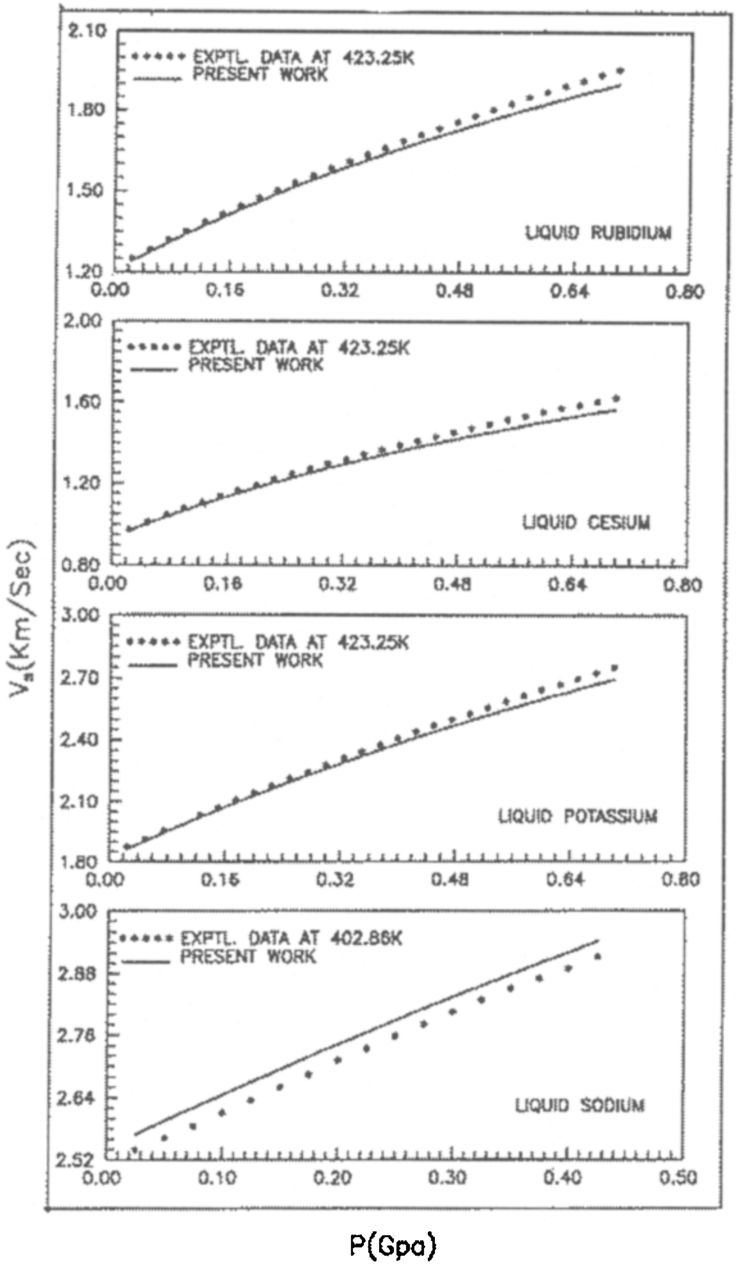

Figure 1. Variation of sound velocity, V_s, as a function of pressure at indicated temperature in case of liquid Na, K, Cs and Rb.

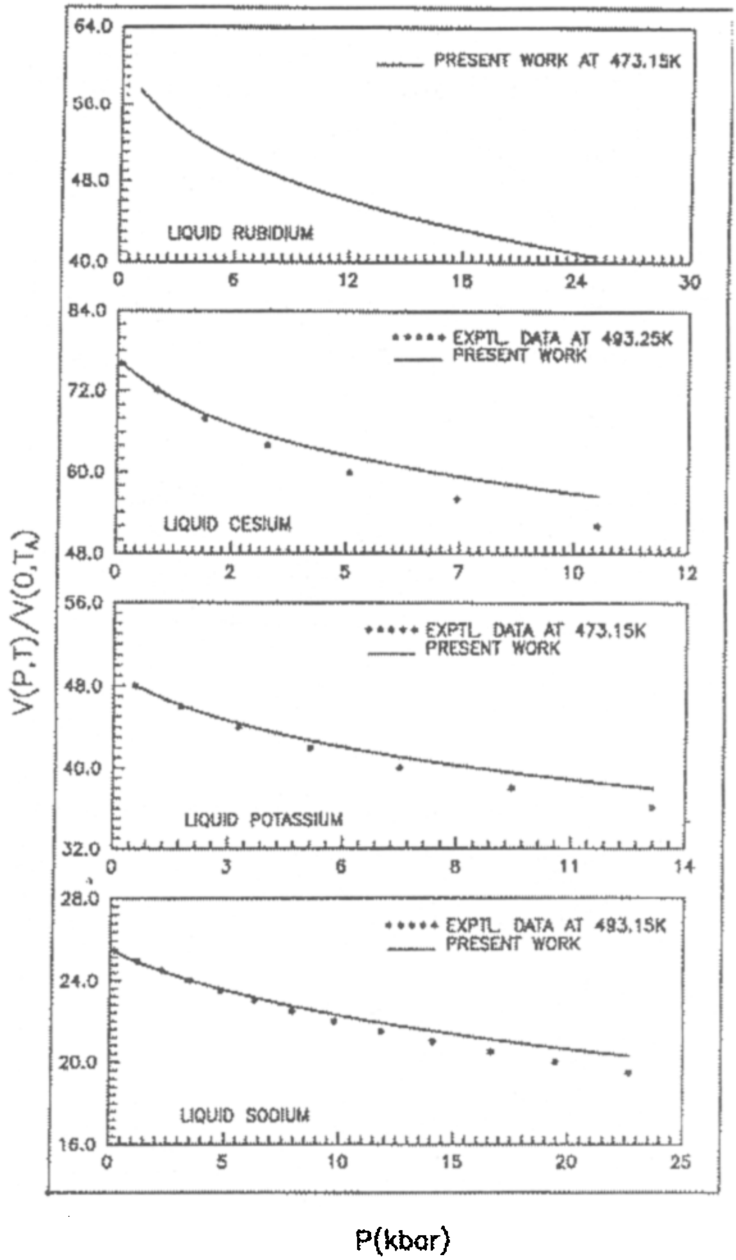

Figure 2. Variations $V(P,T)/V(0,T_A)$ as a function of pressure at indicated temperature in case of liquid Na, K, Cs and Rb.

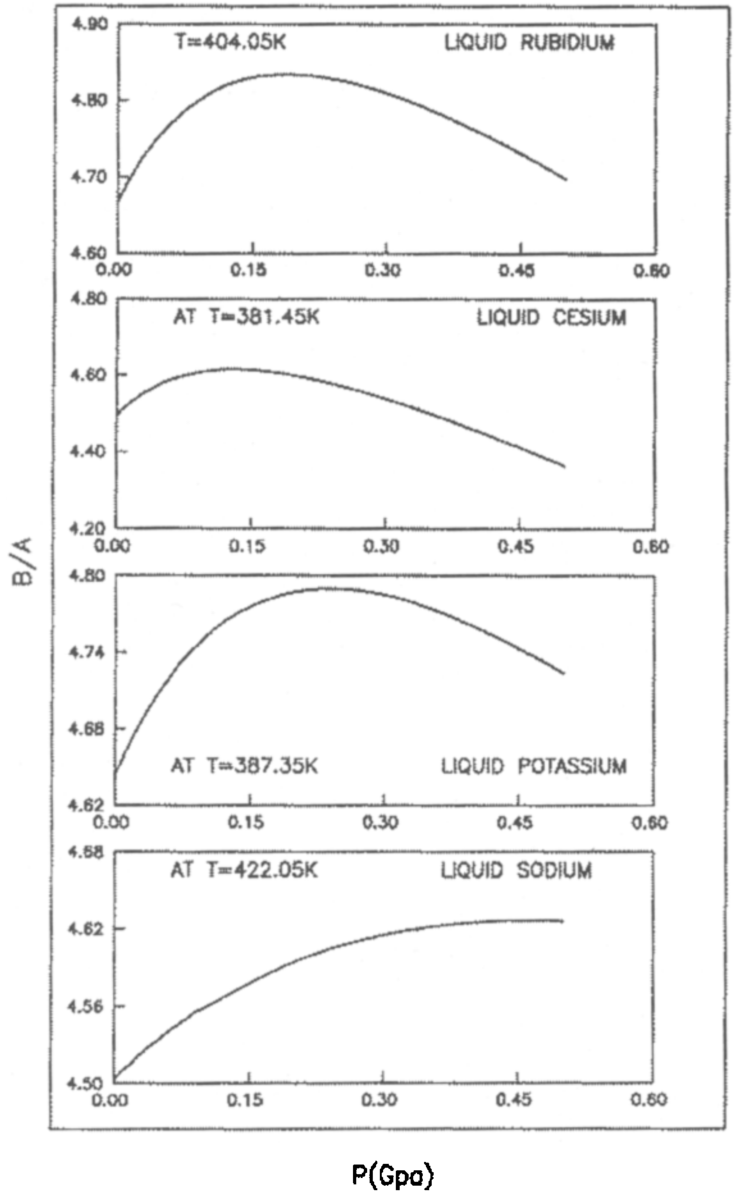

Figure 3. Variation of B/A as a function of pressure in case of liquid Na, K, Cs and Rb.

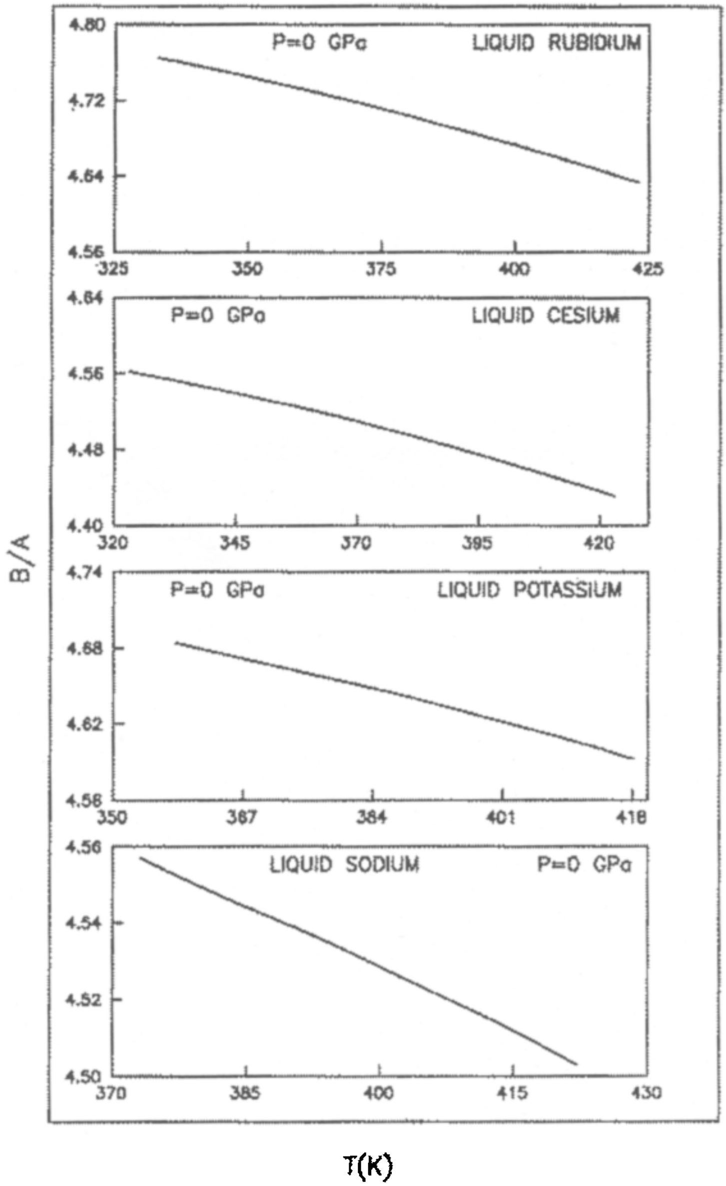

Figure 4. Variation of B/A as a function of temperature in case of liquid Na, K, Cs and Rb.

4. Conclusion

In conclusion, it can be said that the two parameter EOS is successful in describing the sound velocity and the volume as a function of pressure at different temperature in case of liquid alkali metals. For the first time the extensive calculations are done for B/A as a function of pressure and temperature. Moreover, the present calculated values of B/A are found to be in reasonable agreement with the values reported by other workers [13].

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