REVIEWS OF MODERN PHYSICS VOLUME 38, NUMBER 4 OCTOBER 1966

Some Simple Isothermal Equations of State

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Previous work on the Tait equation of state, usually applied to liquids, is discussed together with a review of work on a closely related simple equation arising both from the theory of finite strain and from microscopic considerations. The latter equation has been primarily used for fitting hydrostatic compression pressure–volume data for solids. A detailed discussion of methods for assessing goodness-of-fit of data to equations of state is presented along with an analysis of ways to help decide which of two similar equations is the more applicable for given data. Nonlinear least squares fitting of the above two-parameter equations of state is carried out for the first time using published P–V–T data for water, a very compressible hydrocarbon liquid, zinc, lithium, sodium, potassium, and rubidium and the results compared with those of previous analyses of these data. Careful fitting of the present type can lead to new conclusions and insights not so apparent from less careful fitting of the present equations or from fitting with other equations. For most of the materials and data considered here the finite-strain equation was found to be superior to the Tait equation. Reasons are advanced, however, why both equations should be primarily considered only as empirical, with theoretical justifications for them applicable only over limited pressure–volume ranges.

INTRODUCTION

In recent years there seems to be renewed interest in the semi-empirical Tait equation (abbreviated TE) relating volume of a material under hydrostatic compression to the applied pressure. Although the TE was originally proposed for water and has been applied to a wide variety of other liquids, it is now being put forward as an appropriate equation for fitting pressure–volume results for such compressible solids as the alkali metals. This paper discusses some useful but infrequently applied methods of comparing the applicability of different equations of state and employs them in comparing, for several materials, the TE with a closely related but frequently superior equation (the modified equation, abbreviated ME).

It is important to point out that the conclusion that the TE is *the* equation of state of a given material, frequently drawn in an uncritical manner on the basis of a "reasonable" fit to the data, should only be made after a careful comparison with other equations and examination of several goodness-of-fit criteria. Although the ME has been used for a number of years, its existence, close relation to the TE, and wide applicability to both solids and liquids seems unknown to those who have employed the TE. The present paper draws together the work of the several investigators who have used the TE with those who have employed the ME (all without consideration of the TE), discusses their work in some detail, and presents and discusses improved analyses of some published pressure–volume data.

The TE (see Appendix) suffers from the defect that it leads to negative volumes at sufficiently high pressures. In the Appendix, it is shown how simple modifications of the TE lead to the modified equation

$$V/V_0=(1+n\beta_0 p)^{-1/n}. \qquad (1)$$

Here β_0 and V_0 are the isothermal compressibility and volume, respectively, at $P=P_0$, a reference pressure conveniently taken as one atmosphere. The reduced pressure $p\equiv P-P_0$, and n is a pressure-independent parameter usually greater than unity which is also nearly temperature-independent. Of course, n and β_0 are pressure-independent only in the absence of polymorphic transformations, a condition assumed throughout this paper. As shown in the Appendix, the ME may be made to agree identically with the TE to second order in $\beta_0 p$ and very nearly to third order. The ME only leads to zero volume in the limit $p\rightarrow\infty$, however, and hence may be expected to be superior to the TE at least at such high pressures that $V/V_0<0.2$ or so. It should be applicable to both solids and liquids.

DISCUSSION OF PREVIOUS WORK

Although Eq. (1) was derived independently by Macdonald and Barlow[1] as in the Appendix in order to obtain an improvement to the TE, and although the ME was stated by the author[2] to fit almost all of Bridgman's data on compression of solids and liquids very well, it was later discovered to be by no means a new equation. As Gilvarry[3] has mentioned, it is identical to Murnaghan's[4] equation derived from his "integrated linear theory of finite strain." The derivation of (1) from this macroscopic theory gives it a theoretical justification which Gilvarry feels is superior to that of equations obtained thus far from quantum mechanics or a lattice model.

Equation (1) is also a simplified version of a very general equation of state given by Gilvarry.[5] He has shown[6] that for solids n in (1) may be identified as $2\gamma_{\mathrm{Av}}+\frac{1}{3}$, where γ_{Av} is the average value of the Grüneisen parameter over the pressure range of interest. The ME has been used independently by Ryabinin[7] who, ap-

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[1] J. R. Macdonald and C. A. Barlow, Jr., J. Chem. Phys. **36**, 3062 (1962).

[2] J. R. Macdonald, J. Chem. Phys. **40**, 1792 (1964).

[3] J. J. Gilvarry, J. Appl. Phys. **28**, 1253 (1957).

[4] F. D. Murnaghan, *Finite Deformation of an Elastic Solid* (John Wiley & Sons, Inc., New York, 1951), Chap. 4; Proc. Natl. Acad. Sci. **30**, 244 (1944).

[5] J. J. Gilvarry, Phys. Rev. **102**, 331 (1956).

[6] J. J. Gilvarry, Phys. Rev. **102**, 325 (1956).

[7] Yu. N. Ryabinin, Z. Tekh. Fiz. **30**, 739 (1960) [English transl.: Soviet Phys.—Tech. Phys. **5**, 693 (1960)].

parently unaware of Gilvarry's work, derived (1) from theoretical results of Debye and Grüneisen and obtained $n=2\gamma+\frac{1}{3}$. In addition, Cook and Rogers[8] have independently derived the ME (wrongly identified as the TE yet shown to be the same in form as Murnaghan's equation) from the virial theorem and the Thomas–Fermi atomic model. They obtained $n=\gamma+1$, in disagreement with the above results. The value $n=2\gamma+\frac{1}{3}$ follows immediately from (1), the Debye–Slater[9] expression for γ, and the present assumption of a pressure-independent n. The Debye–Slater relation was derived for an isotropic material with volume-independent Poisson ratio. Finally, Gombas,[10] in a treatment of alkali metals, has given an expression for $\beta\equiv-V^{-1}(\partial V/\partial P)_T$ consistent with (1) provided $n=10/3$. This value of n is discussed later for several alkali metals.

In unpublished work, the author has found that nonlinear least-squares fitting of Bridgman's data (in regions of no polymorphic transition) on the compression of many solids and liquids yields excellent values of the initial compressibility, β_0, and plausible results for n. This work was not published because it was found that Murnaghan,[4] Riabinin,[11] and Cook and Rogers[8] had, to some extent, done it earlier. However, more precise and meaningful comparisons between theory and experiment may be made than any carried out by these authors.[11a]

Recently, in a paper marked I, Ginell and Quigley[12] have applied the TE to Bridgman's data for alkali metals. These authors seem unaware of the ME and although they consider that their results show the TE to be applicable, several of their derived constants have implausible values. A better comparison of both the ME and TE with these data is presented below.

Gilvarry[3] has shown how Eq. (1) (or his generalization of it) may be modified to take temperature dependence into account. He assumes n to be temperature-independent, however. The only temperature dependence then remaining on the right-hand side is that of β_0. Its dependence is frequently known or can be readily measured independently. However, sometimes n does apparently vary somewhat with temperature as well.

There have been several independent derivations of the TE. Some of these might also be applicable for deriving the ME. In 1956, Simha and Hadden[13] showed from cell theory that r (a parameter in the TE corresponding to n in the ME) should be approximately independent of pressure and temperature and that B (see Appendix), the second parameter in the TE, is related to the cohesive energy density of the liquid. It is more meaningful to relate B to the initial compressibility, as in the present work. Recently, Nanda and Simha[14] found (using cell theory and the principle of corresponding states) that for oligomer and polymer liquids r varied theoretically with reduced volume or temperature only from 9.4 to 11.1 over a wider than experimental temperature range. Application of the TE to experimental results for many hydrocarbons with the constant value $r\cong 11.2$ yielded[15] good agreement between experimental values of V/V_0 and those predicted by the TE. Although the same value of r could be used for different materials and different temperatures, somewhat greater fitting accuracy could have been obtained had r been allowed to vary (see later discussion). The ordinary least-squares method used to obtain values of the Tait constant B is also subject to some criticism as discussed in the following section. Thus, the utility of the constant value of r found in the study is not a conclusive proof of its actual constancy. This same value of r has been used,[16] in apparently the same way, in a TE fitting to results for polymer liquids and glasses up to pressures of about 2000 atm.

Ginell[17] has also derived the TE equation without reference to the work of Simha and Hadden.[13] For this derivation, the virial equation of state in closed form was used. The derivation had a geometric basis and used association or cluster theory. The meaning of the TE parameters (see Appendix) $J\equiv V_0/r$ and B (designated L by Ginell) was also examined by Ginell on the basis of association theory.[18] Further, Ginell and Quigley[12] have given a qualitative discussion of why the TE might be applicable to polycrystalline solids.

In concluding this section on previous work, which must certainly still be incomplete, it is pertinent to mention that a compilation of 56 equations of state appears in Ref. 19. In addition, a lengthy, yet still quite incomplete annotated bibliography of high-pres-

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[8] M. A. Cook and L. A. Rogers, J. Appl. Phys. **34**, 2330 (1963).

[9] J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939), p. 239, Eqs. (4.3), (4.5).

[10] P. Gombas, Ann. Phys. (Leipzig) **9**, 70 (1951).

[11] Yu. N. Ryabinin, Fiz. Metal. i Metalloved. **9**, 312 (1960).

[11a] *Note added in proof.* Since this work was completed, a valuable approach to the ME quite different from that herein has come to my attention [O. L. Anderson, J. Phys. Chem. Solids **27**, 547 (1966)]. Anderson assumes that the bulk modulus (β^{-1}) is linear with pressure [see Eq. (A12) of the Appendix] and determines adiabatic values of β_0^{-1} and n by precision sound velocity measurements at low pressures. These results are then converted to corresponding isothermal values. Anderson finds good agreement between the ME, with such parameters derived from low-pressure measurements, and compression results for many solids up to very high pressures. In some instances, this "extrapolation from the origin" method of determining ME parameters will be preferable to the statistical approach examined herein. The latter has the advantage of obtaining the parameters directly from many data points, averaging out random errors to some degree. Careful error analysis and comparison of the ME parameters obtained for the same material by the two approaches should help in deciding which method is most appropriate in any given instance.

[12] R. Ginell and T. J. Quigley, J. Phys. Chem. Solids **26**, 1157 (1965).

[13] R. Simha and S. T. Hadden, J. Chem. Phys. **25**, 702 (1956).

[14] V. S. Nanda and R. Simha, J. Chem. Phys. **41**, 1884 (1964).

[15] W. G. Cutler, R. H. McMickle, W. Webb, and R. W. Schiessler, J. Chem. Phys. **29**, 727 (1958).

[16] V. S. Nanda and R. Simha, J. Chem. Phys. **41**, 3870 (1964).

[17] R. Ginell, J. Chem. Phys. **34**, 1249, 2174 (1961).

[18] R. Ginell, J. Chem. Phys. **35**, 1776 (1961).

[19] *Handbuch der Experimentalphysik*, W. Wien and F. Harms, Eds. (Academische Verlagsgesellschaft M. B. H., Leipzig, 1926–1937), Vol. 8, part 2, pp. 224–228.

sure technology is available.[20] Finally, the ME, transformed to the dielectric realm, has been found useful in relating dielectric constant, rather than volume, to applied hydrostatic pressure.[1]

DISCRIMINATION BETWEEN EQUATIONS

In the past, a decision on the adequacy of an equation of state has frequently been made on the basis of a "sufficiently" low standard error, s_e, determined from a simple least-squares fitting. While this may indeed be an important criterion, it is by no means always unambiguous or sufficient; thus, I shall here discuss and illustrate others which can help one decide on the applicability of an equation and make a sensible choice between two or more such equations.

Sometimes people have transformed equations in ways which allow simple linear least-squares analysis. Thus, the ME can be written

$$p=(n\beta_0)^{-1}[(V/V_0)^{n}-1], \tag{2}$$

the form in which it is given by Gilvarry.[3] If $(V_0/V)^n$ is taken as a new variable with a value of n assumed, $(n\beta_0)^{-1}$ may be found by ordinary linear least squares. (A similar transformation may be used with the TE.) Then, that n which minimizes s_e may be determined by successive least-square runs. This last step has not usually been applied. With the availability of nonlinear least-squares (NLS) computer programs which determine all parameter values simultaneously,[21] one might be tempted to fit p–V data directly to an equation such as (2). Usually, however, relative experimental errors in p are considerably smaller than those in V, and to good approximation one need only consider those in V. But forming such a quantity as $(V_0/V)^n$ $(n\neq-1)$ may seriously bias the error distribution. If that of V is originally approximately normal, it will certainly not be for $V^{-n}(n\neq-1)$. Therefore, it is usually much preferable to fit experimental data not to an equation such as the ME written as in Eq. (2) but instead written as in Eq. (1), involving V/V_0 directly. Nonlinear least squares can then be applied to obtain β_0 and n without biassing. In the following work, all fitting is done with the appropriate equation involving V/V_0 on the left directly. This requirement rules out the Hudleston equation,[22] which cannot be solved explicitly for V/V_0.

Table I. Fitting of synthetic data. The quantity k is n for the ME and r for the TE results.

		ME	TE
ME data	s_e	1.74×10^{-6}	3.23×10^{-3}
	k	8.99982	12.371
	β_0	0.0999981	0.11342
	R	1.0	0.640
	Designation	M/M	M/T
TE data	s_e	4.27×10^{-3}	2.78×10^{-6}
	k	6.7852	9.99975
	β_0	0.086932	0.0999965
	R	1.65	1.0
	Designation	T/M	T/T

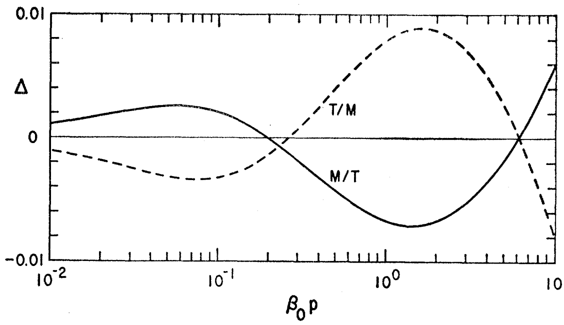

Fig. 1. The deviations, $\Delta\equiv(V/V_0)_{\text{obs}}-(V/V_0)_{\text{pred}}$, versus $\beta_0 p$ for fitting of TE derived data by means of the ME, T/M, and for fitting ME data by means of the TE, M/T.

A useful criterion to help decide whether the TE or ME is the more applicable to given data can be developed as follows. If the ME is fitted by NLS to exact data derived from the TE, or *vice versa*, one would expect a smooth and individual curve of $\Delta\equiv(V/V_0)_{\text{obs}}-(V/V_0)_{\text{pred}}$. The results of such fitting with $N=45$ data pairs are shown in Table I and the distinctive deviation or error curves obtained are shown in Fig. 1. In these calculations, the "exact" data was rounded off to six decimal places, and the fitting calculations carried out with eight places. The exact values of the parameters used in calculating synthetic data from the ME and TE were $n=9$, $r=10$, $\beta_0=0.1$ and resulted in a minimum V/V_0 of about 0.54 for the TE. The quantity R in Table I is defined later. The accuracy of the NLS fitting was set to yield parameter values precise to only four to five decimal places, and it is evident from the results of fitting of each equation and its own "exact" data shown in Table I that the NLS procedure used worked correctly.

The deviation curve obtained from fitting "exact" TE data using the ME is denoted by T/M. Then, correspondingly, M/T denotes the deviation curve obtained using ME data fitted by the TE. Figure 1 shows that the T/M and M/T curves are nearly each other's negatives. Qualitatively, in terms of the general pattern of signs of the deviations alone, the two results are completely opposite in sign. This large difference in behavior is a most useful result. An extremely important property of NLS fitting as above to equations such as the ME and TE is that the deviation pattern obtained seems invariant (within wide limits) to the span of $\beta_0 p$ covered. Thus, deviation curves of the same shape and pattern are obtained, when N is sufficiently large and random errors sufficiently small,

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[20] A. Zeitlin, *Annotated Bibliography on High-Pressure Technology* (Butterworths, Washington, 1964).

[21] D. W. Marquardt, J. Soc. Ind. Appl. Math. **2**, 431 (1963).

[22] L. J. Hudleston, Trans. Faraday Soc. **33**, 97 (1937); D. M. Newitt and K. E. Weale, J. Chem. Soc. **1951**, 3092.

whether the span of $\beta_0 p$ is 0 to 0.2, 0.2 to 10, 0.1 to 5, etc. Therefore, error patterns such as those shown in Fig. 1 may be compared qualitatively with those obtained from fitting experimental data by either the ME or TE no matter what the experimental pressure range.

If random errors are sufficiently small, the NLS error curves obtained by fitting experimental data using the ME and TE may frequently be used to yield a high degree of discrimination between the two equations, leading to a useful criterion for a choice as to which one best represents the data. If TE fitting yields an error curve having the M/T pattern of Fig. 1 while at the same time ME fitting yields an unidentifiable or random pattern, then clearly the ME is the better choice on this criterion. Alternatively, if ME fitting yields a T/M pattern while TE fitting yields a random pattern, then the TE is the more applicable. This pattern comparison is a crude way of carrying out a cross-correlation between experimental error curves and those of Fig. 1 or equivalent. Its utility is illustrated in the next section. There are, of course, a number of distinguishable gradations in the error patterns obtained by fitting experimental data with the ME and TE which only allow less certain conclusions concerning their relative applicability. In particular, if both error curves have the same pattern, say T/M or random, then the present type of test is almost useless unless an actual, numerical cross-correlation analysis is carried out. Such similar patterns might occur when the experimental errors (systematic or random) in the data were large enough to obscure the differences between ME and TE results or when neither the ME nor TE were really applicable.

Another test which is almost certainly correlated with that above but which may be useful in its own right is described below. If the ME, for example, applies well to a given set of data, it should apply as well to any partition of that set and should yield (in the absence of experimental errors) the same parameter values. Suppose we divide a set of experimental data (preferably with $N>15$) into two parts. Let the first part (A) include all pressure values from $P=P_0$ up to some pressure, P_1, preferably sufficiently high that higher than third-order terms are necessary in the Tait or modified equation of state. This subset should then allow a reasonable determination of $n(\equiv n_A)$ and a good determination of $\beta_0(\equiv\beta_{0A})$. The second part (B) should use the same V_0 and P_0 and should include all data points with $P\geq P_1$; the resulting $n(\equiv n_B)$ should be particularly sensitive to the nonlinearity of the p–V curve.

In order to find a good criterion, the "exact" ME and TE data sets were divided into two parts, one (A) containing 23 points between $\beta_0 p=0$ and $\beta_0 p=0.2$ and the other (B) with 22 points distributed from $\beta_0 p=0.25$ to 10. The four resulting subsets were then fitted by both the ME and the TE. It was found that for the T/M situation n_A and β_{0A} both exceeded n_B and β_{0B} by approximately the same ratio, respectively. On the other hand, the M/T results yielded $r_B>r_A$ and $\beta_{0B}>\beta_{0A}$. The ratio $R\equiv k_A\beta_{0A}/k_B\beta_{0B}$, where $k\equiv n$ for fitting with the ME and $k\equiv r$ for the TE fitting, will then be a goodness-of-fit parameter and should also allow some discrimination between the ME and the TE.

In the absence of experimental error, Table I shows that R should be unity for M/M- and T/T-type fittings, should exceed unity for T/M, and should be less than unity for M/T fits. In the presence of not too large random errors, if TE and ME R's are obtained using the same experimental data, the ME would be preferred if R_M were closer to unity than R_T, and the TE preferred in the opposite case. If R_M and R_T were nearly the same, no valid discrimination could be made. Finally, the deviation of the one of these quantities closest to unity from unity should roughly indicate the importance of random or systematic errors and/or the degree to which the equation in question is a useful representation of the data. The fairly large deviations of R from unity for the M/T and T/M situations shown in Table I arise from the wide span of $n\beta_0 p$ or $r\beta_0 p$ encountered in these calculations. For the available pressure ranges of most materials, the minimum V/V_0 will be considerably greater than 0.54 and the M/T and T/M values of R (without appreciable random errors) will be closer to unity than those shown. Note that for this wide a range Table I indicates that $r\simeq n+3.3$ when both equations are used with the same data. As shown in the Appendix, $r=n+1$ in the much narrower pressure range where only second-order terms need be considered.

To summarize, four discrimination and goodness-of-fit tests are usually readily applicable. (1) If one of the s_e's obtained by ME and TE NLS fitting (with both parameters free) is substantially smaller than the other, and the smaller s_e is small enough that large random or systematic errors in the data seem unlikely, the equation yielding the smaller s_e would be preferred. (2) That equation which yields a β_0 in closer agreement with the β_0 value obtained from independent p–V measurements near $p\sim 0$ would be preferable. (3) If ME fitting yielded an unidentifiable or random error pattern and TE fitting an M/T pattern, the ME would be the more applicable. (4) Finally, if R is substantially closer to unity for one equation than the other, the one yielding the value closest to unity should be preferred.

Although these four tests are by no means entirely independent, they are each sufficiently different to be useful. Agreement of all four tests may be considered conclusive.

EXPERIMENTAL DATA FITTING RESULTS

Results of fitting experimental p–V data on water, a high molecular weight hydrocarbon liquid, and some alkali metals by the ME and TE are presented in this section. The analysis of results for these materials does not show the full range of applicability of equations like

Table II. Fitting results for some of Bridgman's water data (1–12 000 kg/cm²). ME fitting results above and TE below in each pair.

T °C	$10^4 s_e$	Error distribution	R	n r	$10^{11}\beta_0$ (cm²/dyn)	Low-pressure values $10^{11}\beta_0$ (cm²/dyn)
0	0.829	U	1.03	6.896	5.161	5.10[a]
	0.992	M/T	0.955	8.527	5.249	
20	4.53	(M/T)	0.785	6.336	4.579	4.58[b]
	5.46	(M/T)	0.755	7.893	4.644	4.64[a]
40	2.79	(M/T)	0.926	6.311	4.398	4.42[a]
	4.36	M/T	0.839	8.121	4.527	
60	2.91	U	1.06	6.290	4.420	4.43[a,b]
	2.45	(M/T)	0.935	8.102	4.551	
80	3.42	U	1.102	6.312	4.549	4.57[b]
	2.15	(M/T)	0.975	8.141	4.689	
100	6.99	T/M	1.27	6.532	4.948	4.80[b]
	4.21	(T/M)	1.11	8.416	5.116	

[a] M. D. Pena and M. L. McGlashan, Trans. Faraday Soc. **55**, 2018 (1959). Some values determined from graphical interpolation or extrapolation.

[b] D. Tyrer, J. Chem. Soc. **105**, 2534 (1914).

the ME and TE to solids and liquids and is only intended to be illustrative of possibilities.

A. Water

Table II shows results obtained for water using data of Bridgman.[23] The maximum deviations, Δ, in these fittings and those presented later generally did not exceed about $2s_e$, showing the smoothness of the data used. All s_e's calculated involved $(N-2)^{-\frac{1}{2}}$ since there are two degrees of freedom involved in fitting either the TE or ME. The maximum value of $n\beta_0 p$ for the water data was of the order of 4. The symbol U in Table II indicates that the Δ deviation distribution was unidentified and not of either the M/T or T/M type. Those designations in parentheses such as (M/T) had one or at most two points opposite in sign to the indicated error distribution type.

The very small s_e values shown in Table II indicate that either the TE or ME can represent the data well. These values do not discriminate very well between the two equations. Test 2, however, definitely suggests that the ME is superior on the whole. The experimental β_0 values of Tyrer given were obtained from directly measured adiabatic values and are likely to be less accurate at the higher temperatures. Except for the 100°C results, which are ambiguous, Test 3 also indicates that the ME is more applicable than the TE. The R test is not very meaningful for these data since N was rather small. Like Test 1 it shows, however, a slight ME superiority for the three lower temperatures and TE superiority for the three higher ones.

Table II shows some dependence of both r and n on temperature. This dependence is significant. If the 0°C fitting, for example, is carried out with the following fixed values: $n=6.311$, $r=7.893$, then it is found that the corresponding s_e's obtained are very nearly an order of magnitude larger than those shown. Further, the ME and TE β_0 values obtained are about 4% smaller, both below the most likely value. Thus, much worse fits would be obtained if n or r were held temperature-independent. In their extensive work of applying the TE to liquids, Gibson and Loeffler[24] used a value of the TE parameter $C(\equiv J\ln 10)$ leading to the constant value $r\cong 7.31$ for water at all temperatures. This value was apparently not obtained by least squares. Since it falls outside the range of the r's given in Table II, its use with Bridgman's data would lead to much larger s_e's than those shown.

B. A Hydrocarbon Liquid

Table III shows results obtained on fitting p–V data[15] for the very compressible hydrocarbon 1-cyclopentyl-4 (3-cyclopentylpropyl) dodecane. Here, the maximum value of $n\beta_0 p$ was of the order of 9. Again, the results of applying both equations seem to be within the experimental accuracy of the data. Here, however, Tests 1, 3, and 4 all indicate that the TE is preferable to the ME. The TE β_0 values shown are therefore probably slightly closer to the (unknown) true values for this material than those following from the ME. Incidentally, the separate n, r, and β_0 values obtained from the A–B partition of each data set necessary to calculate R values generally, but not always, spanned the corresponding values shown in Table III.

Cutler, McMickle, Webb, and Schiessler[15] analyzed their dodecane data using the TE with a temperature-independent constant equivalent to the choice $r=11.2$. When this constant value is used, the resulting β_0's are 3 to 5% larger than those shown in the table. The values of s_e are only increased by 50% or less. Thus,

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[23] P. W. Bridgman, J. Chem. Phys. **3**, 597 (1935).

[24] R. E. Gibson and O. H. Loeffler, J. Am. Chem. Soc. **63**, 898 (1941).

Table III. Fitting results for 1-cyclopentyl-4 (3-cyclopentylpropyl) dodecane (1–10336.5 bars). ME fitting results above and TE below in each pair.

T °C	$10^4 s_e$	Error distribution	R	n r	$10^{11}\beta_0$ (cm²/dyn)
37.8	6.80	U	1.13	8.834	6.329
	6.07	U	1.05	10.61	6.465
60.0	8.63	T/M	1.22	8.948	7.257
	6.86	U	1.09	10.93	7.504
79.4	10.3	T/M	1.35	8.724	7.645
	7.62	T/M	1.19	10.75	7.933
98.9	12.1	T/M	1.60	8.484	8.368
	7.59	(T/M)	1.38	10.71	8.839
115.0	16.0	T/M	1.30	8.556	9.409
	10.5	T/M	1.09	10.86	10.00
135.0	9.73	T/M	1.28	8.575	10.26
	4.22	(T/M)	1.08	10.93	10.95

the appropriateness of a temperature-independent r cannot be as thoroughly ruled out here as it could be in the water case. A constant value near $r=10.8$ appears to be somewhat superior to 11.2 for this material, however.

To investigate the fitting accuracy possible with these data somewhat more, a ηp^2 term was added to both the ME and TE and the parameter η determined by NLS along with β_0, n, and r. The s_e's of both the augmented ME and TE fittings of the 98.9°C data, for example, fell to about 4.7×10^{-4} upon addition of the ηp^2 term. In spite of the reduced s_e's, the resulting error patterns were still by no means random but showed considerable regularity. The values of n, r, and β_0 obtained were all somewhat increased over those shown. The quantity η was negative for both augmented ME and TE fitting. Its magnitude was appreciably larger for the ME than the TE fitting, however, again indicating the greater applicability of the TE as compared to the ME for this material.

C. Four Alkali Metals

Tables IV and V show TE and ME fitting results using Bridgman's[25] room-temperature data for four alkali metals taken over two different overlapping pressure ranges. No very accurate independent determinations of β_0 seem available; those of Richards[26] yield for $10^{11}\beta_0$ the values 0.90, 1.56, 3.17, and 4.00 cm²/dyn for Li, Na, K, and Rb, respectively. Except for Rb, the ME β_0 values are generally closer to Richards' results than the TE β_0's. It seems likely that Richards' β_0 for Rb is too high.

All but one of the ME s_e values are appreciably smaller than those obtained from the TE fitting. Most of the s_e values are quite high, however. Many of the error patterns are the same for TE and ME fits, but they seem nevertheless to favor the ME over the TE slightly. We have not calculated R values for these data since data from two separate runs and their combination are here analyzed. Since the runs cover somewhat different pressure ranges, parameter differences for the separate runs on a given material should be significant for deciding on the applicability of the TE or ME. Tables IV and V show that the triads of s_e, n, and β_0 values obtained with the ME are appreciably more stable (less internal variation) than the corresponding triads obtained with the TE. All the tests thus seem to indicate that the ME is considerably superior to the TE for these materials and data.

As mentioned, Gombas[10] used the value $n=10/3$ in a theoretical equation of state he derived for the alkali metals which reduces to a differential form of the ME for sufficiently low pressures. Although the present pressure limits appreciably exceed his range, it is very interesting to find most of the n values in Table V quite close to 10/3.

Ginell and Quigley[12] have analyzed the Bridgman data used in obtaining the numbers in Tables IV and

Table IV. TE fitting results for alkali metals. Top row of each triad: 1–40 000 kg/cm², middle row: 1–100 000 kg/cm², bottom row: combined data (1–100 000 kg/cm²).

Material	$10^4 s_e$	Error distribution	r	$10^{11}\beta_0$ (cm²/dyn)
Li	2.82	M/T	4.685	0.8732
	9.90	T/M	5.441	0.9211
	16.5	U	5.469	0.9288
Na	9.89	M/T	5.116	1.540
	21.6	T/M	6.311	1.745
	41.2	(M/T)	6.273	1.751
K	12.0	M/T	5.611	3.366
	18.6	M/T	6.630	4.169
	44.3	M/T	6.302	3.802
Rb	17.3	M/T	5.429	3.607
	9.80	T/M	6.306	4.313
	44.6	M/T	6.082	4.056

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[25] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 55–70, 71–87 (1948).

[26] T. W. Richards, J. Am. Chem. Soc. **37**, 1643 (1915).

V by means of the TE. Their results may be shown to be fairly close to those in Table IV in some cases but very far off in others. They analyzed the data by first interpolating to yield equally spaced pressure values, then numerically differentiating, and finally fitting the resulting $\partial P/\partial V$ points by linear least squares. No s_e values obtained were quoted. This fitting procedure may be expected to bias the original errors in the data and perhaps to introduce new errors. Three of their values for $L \equiv B(\cong 1/r\beta_0)$ were negative, for example. Since their corresponding V_0 and J values were positive, the associated r values must also be positive and the β_0's negative. But negative β_0's (or B's) in the TE do not then lead to the proper type of dependence of V/V_0 on p.

Two of Ginell and Quigley's negative L values were obtained from data which led to the last two K rows in Table IV. The values of r and β_0 given there lead to $1/r\beta_0 \cong 3.62\times 10^9$ and 4.17×10^9 dyn/cm^2 for the middle and bottom K rows, respectively. The small amount of variation suggests that the data used in the two runs is reasonably consistent and that no negative values of L should appear.

In integrating the differential form of the TE, Ginell and Quigley use V_0 (specific volume) as an additional parameter and find wide variation in it between the various alkali metals. For example, their quoted fitting results for the 0–40 000 kg/cm^2 Rb data lead to $V_0 \cong 0.68$, $r \simeq 6.43$, and $\beta_0 \simeq 5.44\times 10^{-11}$ cm^2/dyn. If $r = 6.43$ is taken fixed, and β_0 obtained by NLS using the TE with the same data, I find $s_e = 7.93\times 10^{-3}$ and $\beta_0 \cong 4.40\times 10^{-11}$ cm^2/dyn. Alternatively, if β_0 is held fixed at 5.44×10^{-11} cm^2/dyn, the TE yields $s_e = 1.49\times 10^{-2}$ and $r = 7.334$. It is clear that all these results are far inferior to the Table IV NLS determination of parameters with both parameters free to vary.

D. Sodium

Beecroft and Swenson[27] (abbreviated B–S) have carried out a thorough P–V–T study for Na. It is of interest to use their results in a further test of TE and ME applicability, to investigate the temperature dependence of n and β_0 obtained from ME fitting, and to compare with the Na results in Table V.

Table V. ME fitting results for alkali metals. Top row of each triad: 1–40 000 kg/cm^2, middle row: 1–100 000 kg/cm^2, bottom row: combined data (1–100 000 kg/cm^2).

Material	$10^4 s_e$	Error distribution	n	$10^{11}\beta_0$ (cm^2/dyn)
Li	1.70	*U*	3.218	0.8589
	16.9	T/M	3.470	0.8593
	16.4	(M/T)	3.578	0.8800
Na	3.89	(M/T)	3.417	1.488
	32.8	T/M	3.875	1.519
	35.7	(M/T)	4.002	1.583
K	10.6	T/M	3.518	3.106
	13.5	(M/T)	3.522	3.048
	15.3	U	3.583	3.130
Rb	5.52	T/M	3.318	3.311
	29.3	T/M	3.212	3.115
	26.9	U	3.346	3.301

Table VI. ME fitting results for Na (0–20 000 atm). Original data of Beecroft and Swenson (Ref. 27).

T °K	$10^4 s_e$	Error distribution	n	$10^5\beta_0$ (atm^{-1})	$-10^5 a_1$ (atm^{-1})
20	5.03	M/T	4.144	1.417	1.351
51	5.76	M/T	3.999	1.411	1.340
77	5.09	(M/T)	4.051	1.450	1.387
77	4.19	M/T	4.428	1.477	1.417
115	5.96	M/T	4.049	1.481	1.405
138.6	4.20	(M/T)	4.093	1.512	1.443
171	3.96	(M/T)	3.947	1.527	1.462
201	5.41	(M/T)	4.123	1.614	1.537
204	7.18	U	3.835	1.559	1.477
246	5.10	M/T	3.972	1.645	1.567
297	4.64	M/T	3.747	1.653	1.580
297	6.70	M/T	3.759	1.651	1.562
297	4.33	M/T	4.193	1.708	1.642
349	4.70	(M/T)	3.726	1.720	1.642

Table VI shows the results obtained with ME fitting. The largest value of $n\beta_0 p$ is here only about 1.4. TE fitting generally yielded somewhat larger s_e's and β_0 values one to two percent larger than those in Table VI. B–S fitted their $(V-V_0)/V_0$ results to the cubic $a_1p+a_2p^2+a_3p^3$, essentially by least squares. Slightly different values of the cubic coefficients than those given by B–S are obtained when the quoted $(V-V_0)/V_0$ data are fitted directly to the above cubic by least squares. The results obtained for $-a_1$ are shown in the last column of Table VI. They should, of course, equal corresponding β_0 values since both quantities give the initial compressibility. Although β_0 and $-a_1$ are highly correlated, the a_1 dependence on temperature is considerably more irregular than the β_0, and a_1 is generally about 5% smaller than β_0. On the other hand, the cubic fitting uses three adjustable parameters and the ME only two. It is not surprising, therefore, that the cubic s_e's found are often only about half as large as the s_e's in Table VI.

When curve fitting was carried out for the second 297°K set of data using the ME augmented with a ηp^2 term (added in with $n\beta_0 p$), the resulting s_e was appreciably smaller than that obtained with the cubic although both fittings involve three parameters. The error distribution obtained appeared random, n was reduced to about 1.5, the β_0 value found fell between the ordinary ME β_0 and $-a_1$, and η was small and positive. As a further comparison test, some of the data were analyzed by NLS using the ordinary ME but written in the form of Eq. (2). For example, the second 297°K data set led to a s_e of about 101 atm, $n \cong 3.902$, and $\beta_0 \cong 1.683\times 10^{-5}$ atm^{-1}. The n and β_0 values are significantly, but not greatly, different from those shown in Table VI obtained with V/V_0 as the dependent variable.

Since it is not known that the ordinary ME is a very good approximation to the true equation of state for sodium, it is not possible to conclude unequivocally

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[27] R. I. Beecroft and C. A. Swenson, J. Phys. Chem. Solids **18**, 329 (1961).

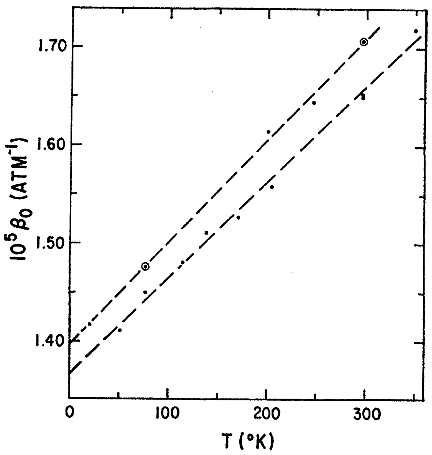

FIG. 2. Initial compressibility β_0 derived from uncorrected Na p–V–T data, versus absolute temperature.

that the β_0 values are better estimates of the true initial compressibility than the $-a_1$'s. In a paper discovered after the calculations of Table VI were carried out, Monfort and Swenson[28] state that the B–S pressure scale was in error and that all pressures given in B–S should be increased by 3%. This change results in a reduction of Table VI β_0 and a_1 values by the factor 0.971. The results in Table VI and Fig. 2 have been left unchanged, for easier comparison with the original B–S results. From now on the factor 0.971 will be applied to all quoted β_0 and a_1 values derived from the B–S data.

Richards'[26] value for β_0 at room temperature is 1.56×10^{-11} cm^2/dyn while B–S have deduced a value of about 1.618×10^{-11} cm^2/dyn from ultrasonic data. The first two room-temperature values of $-a_1$ in Table VI correspond to about 1.514×10^{-11} and 1.499×10^{-11} cm^2/dyn, respectively. The corresponding values of β_0 are about 1.584×10^{-4} and 1.582×10^{-11} cm^2/dyn, appreciably closer to the B–S ultrasonic value, and, for that matter, to Richards' result as well. In a re-analysis of his Na data, Swenson[28] quotes a value of the room-temperature bulk modulus which leads to $\beta_0 \cong 1.587\times10^{-11}$ cm^2/dyn, in close agreement with the present β_0 results.

The above agreement plus the greater regularity of the β_0's suggest that they are indeed better estimates than the $-a_1$'s. On the other hand, the almost ubiquitous appearance of the M/T error pattern in Table VI (although it appears less strongly in Table V) suggests that unless there are systematic errors in the p–V data, there are some small, yet real, systematic deviations between the ME and the actual p–V behavior of Na. Such discrepancies might still allow β_0 to be a better estimator than $-a_1$, however. The lack of close agreement between the Na n's and β_0's of Table V and the room-temperature results in Table VI certainly still leaves the question open, however, as to whether the systematic deviations arise from experimental errors or from some failure of applicability of the ME.

Figure 2 shows the dependence of β_0 (uncorrected) on temperature. It is not immediately obvious from Table VI that the β_0 results fall so regularly into two groups. The dashed lines shown are the linear least-square fits for these groups separately. For the lower line, the result (corrected for pressure scale error) is $\beta_0 = 1.327\times10^{-5}(1+7.155\times10^{-4}T)$ atm^{-1}. The s_e's for the upper and lower lines were 6.77×10^{-3} and 8.44×10^{-3}, respectively. A quadratic fit only changed the s_e's to 8.09×10^{-3} and 8.40×10^{-3}. The two points indicated with circles are derived from data extending to only 12 000 atm for which a different sample holder was used. It is not known why the β_0 values should separate so clearly into two groups; random experimental error alone may be the culprit or perhaps there was some difference in the experimental procedure for the two subsets. In any event, it appears that β_0 can be well represented by a linear temperature dependence in the range here shown.

In considering the temperature dependence of n, it seems reasonable to examine the two subsets separately. The n values for temperatures of 20°, 77° (second in Table VI), 201°, 246°, and 297° (third in table) correspond to β_0 values associated with the upper line. These n's show no significant temperature dependence. On the other hand, the remaining n's show a quite regular but slight dependence. If all the low temperature values are taken as approximations to some number near 4, then n decreases down to 3.73 at 349°K. This slight dependence leads, through the use of $\gamma = \frac{1}{2}(n-\frac{1}{3})$, to smaller dependence of γ on T than may be inferred from results given by B–S. The result that the ME can represent the p–V data very well with a pressure-independent n also suggests that γ for Na varies with volume less than concluded by B–S. Nevertheless, B–S point out that the Poisson ratio is a function of volume for Na. In spite of the apparent usefulness of the ME, this result suggests that the theoretical relation $n = 2\gamma + \frac{1}{3}$ should only be used with caution, if at all, and that therefore n should perhaps best be considered only a heuristic, slightly temperature-dependent fitting parameter.

Cook and Rogers[8] have suggested that for materials such as Na and H_2O, which may be expected to have significant concentrations of thermodynamic defects at room temperature and atmospheric pressure, the ME should be applied only for the high-pressure region, above about 12 kbars for Na and H_2O. Their own high-pressure analyses for these materials, when extrapolated to zero pressure, do not yield good values of β_0. On the other hand, in the present work the ME has been used over the full pressure range available (which includes many data points below 12 kbars) and has led to excellent values of β_0. It therefore appears that it can

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[28] C. E. Monfort and C. A. Swenson, J. Phys. Chem. Solids **26**, 291 (1965).

account adequately for the effects of Schottky defects and holes in liquids, when important, on the p–V relation provided NLS fitting with both parameters free is employed.

Because the present treatment is intended to illustrate possibilities rather than to be comprehensive, no detailed analysis is included here of Monfort and Swenson's K data[28] or of Swenson's recent Li results.[29] These authors have suggested that the ME (not identified or related to earlier equations of state) with $n=3.8$ will fit the Na, K, and Li p–V data extrapolated to zero degrees. Apparently, no NLS fitting with free parameters was carried out, and the value 3.8 was arrived at as a compromise between experimental values of $d(\beta^{-1})/dP$ of 3.95 for Na, 3.85 for K, and 3.6 for Li. The present results for Na suggest a value of n at $T=0°\mathrm{K}$ of 4 to 4.2.

Since Table VI shows no trend to smaller s_e values as T is reduced, the ME is apparently as applicable at nonzero temperatures as it is in the limit $T\rightarrow 0$. Further, its application for $T>0$ can yield, as has been shown above, useful information on the temperature variation of β_0 and perhaps n. Incidentally, the value $\beta_0=1.327\times 10^{-5}$ atm applying for Na at $T=0°\mathrm{K}$ and derived from the lower least-squares line in Fig. 2 is appreciably smaller than 1.369×10^{-5} atm, the value following from Swenson's[28] re-analysis of the B–S data. The former value is probably derived from a more detailed analysis of more of the data than the latter.

DISCUSSION AND CONCLUSIONS

In order to yield stringent tests of the applicability of the TE and ME and allow utmost discrimination between them, the materials analyzed thus far were picked for their relatively high compressibilities. Except for the highly compressible dodecane, the ME was found to be superior to the TE. It appears, in fact, that the ME is the most generally applicable wide-pressure-range two-parameter equation of state for liquids and solids. It should, however, be considered primarily as an empirical equation because some of the assumptions made in deriving it theoretically are often inapplicable to real materials. As such, it should be particularly useful in deriving good values of $\beta_0(T)$ from p–V–T data, in smoothing such data, and in finding experimental errors.

Although the agreement found thus far between the ME predictions obtained with NLS fitting and the original p–V data has been quite good and usually within likely experimental error limits (even when M/T or T/M behavior could be distinguished), it is worth pointing out that the ME can frequently yield, for less compressible materials, fits about an order of magnitude better than those illustrated thus far. For example, using Bridgman's[25] 0–40 000 kg/cm² zinc data, the ME yields $s_e\cong 1.41\times 10^{-5}$, $n\cong 5.663$, and $\beta_0\cong 1.652\times 10^{-12}$ cm²/dyn. The data have four significant figures (the value of V/V_0 at the highest pressure is 0.9463) and the largest fitting error found in the predicted V/V_0 was 2.1×10^{-5}! With this good a fit, the error distribution was unidentifiable and apparently random.

In addition to the fact that the theoretical assumptions made in deriving the ME and TE are not generally applicable, there is another important reason why neither the ME nor TE should be applied beyond a certain limited pressure range. The total elastic or cohesive energy (at a given temperature but excluding the energy to transform molecules to atoms, etc.) is $W(\infty)$, where

$$W(V)=-\int_{V_0}^{V} P\,dV. \tag{3}$$

$W(V)$ for the ME, for example, may be readily calculated using (2) and (3), and even with $P_0=0$ leads to $W(\infty)=\infty$, an unacceptable value. The same result follows from the TE.

Both the ME and TE predict a finite negative pressure, p_∞, at which $V\rightarrow\infty$ (see Appendix). Any equation of state yielding such a pressure must lead to an infinite $W(\infty)$. Gilvarry's three-parameter general equation,[3] which includes the one-parameter Bardeen and Birch equations, does not suffer from this defect provided his parameters n and m both exceed unity. When $m=0$, the ME is obtained. The general equation leads to a maximum absolute value of negative pressure (at $\partial P/\partial V=0$); then the negative pressure decreases in magnitude towards zero as V/V_0 increases further towards infinity. For m and $n\geq 1$, Gilvarry's equation yields

$$W(\infty)=V_0/[\beta_0(n-1)(m-1)], \tag{4}$$

a reasonable and possibly new result which could be checked against published values of $W(\infty)$ for a variety of materials after NLS fitting provided n, m, and β_0 values. Unfortunately, this three-parameter equation of state does not allow V/V_0 to be solved for explicitly in terms of pressure for general n and m. Some discussion of the applicability of several of the equations discussed in this paragraph has been given by Gilvarry,[3] without, however, mention of the $W(\infty)=\infty$ catastrophe for the ME and TE. More recent discussion of a few equations of state for solids has been presented by Knopoff.[30]

The above results suggest that although the ME (or TE) may be very useful for positive pressures, its range of applicability should not be extended very far into the negative pressure region. Briggs[31] has measured, by centrifugal force, what seems to be the largest negative pressure or tensile strength value for water, namely, −277 atm. Equation (1) together with the room-temperature ME water parameters of Table II,

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[29] C. A. Swenson, J. Phys. Chem. Solids **27**, 33 (1966).

[30] L. Knopoff in *High Pressure Physics and Chemistry*, *I*, R. S. Bradley, Ed. (Academic Press Inc., New York, 1963).

[31] L. J. Briggs, J. Appl. Phys. **21**, 721 (1950).

lead to $p_\infty \cong -3410$ atm, in poor agreement with the above value. The value of -277 atm corresponds, through Eq. (1), to $V/V_0 \cong 1.0135$. For comparison, if V_0 for water is taken unity at NTP, then $V/V_0 \simeq 1.043$ at atmospheric pressure and the boiling point of water. This is not really a valid comparison, however, since thermal measurements yield results depending on both the attractive and repulsive parts of the internal potential while the results of low-temperature pressure measurements depend primarily on the repulsive part of the potential. The Bardeen and Birch equations lead to $V/V_0 \sim 1.5$ to 2 at the negative pressure for which $\partial P/\partial V = 0$.

Cook and Rogers[8] have taken an "internal pressure" in their derivation of the ME essentially given by $-p_\infty \equiv (n\beta_0)^{-1}$. They have set this equal to ϵ_0/v_0, where ϵ_0 is the cohesive energy at absolute zero and v_0 the specific volume. Since the ME cannot be used to calculate a cohesive energy, this approach seems inconsistent, although it led to β_0 values in generally good agreement with independently observed compressibilities for many metals. These β_0 values were obtained by using independent determinations of $v_0/\epsilon_0(=n\beta_0)$ in the ME and deriving n values graphically. The resulting n's were then used in the above relation to obtain the β_0's.

The Cook–Rogers n's are not in very close agreement with those for corresponding materials derived by NLS herein. Since the present n's and β_0's are maximally consistent with the data provided the ME is applicable, and since the present β_0's agree well with independent values, the relation $v_0/\epsilon_0 = n\beta_0$ is probably rather inexact when accurate values of n and β_0 are used. It would be surprising if it were exact since while p_∞ is the negative pressure for breakup of the material according to the ME, it has been shown above that p_∞ cannot be well related theoretically to the cohesive energy. On the other hand, since $W(\infty)$ is likely to be proportional to β_0^{-1}, at least to first order [see above Gilvarry-equation result for $W(\infty)$], the Cook–Rogers relation is of a reasonable form.

The TE yields $P_\infty \equiv p_\infty + P_0 = -(r\beta_0)^{-1} + P_0 = -B$. The results in Table II for water lead to $P_\infty \cong p_\infty \cong -2690$ atm, somewhat smaller than the ME result. For comparison, values of the "internal pressure" of water quoted by Dorsey[32] are near 11 000 atm. The quantity B has been interpreted in a number of ways. It has been suggested that it is related to the cohesive energy density of the material,[13] that it is an internal pressure,[33] that B or $B+P$ is the difference between the expansive thermal pressure and the attractive cohesive pressure of the material,[18,23,34,35] and that B is a measure of the excluded volume of large particles.[18] I have suggested above, however, that $P_\infty = -B$ is not a valid measure of the tensile strength of the material, since neither the TE nor ME can yield a cohesive energy. Therefore, it seems to me that all of the above interpretations of B are inapplicable and that B, if it must be introduced, should merely be interpreted as $\simeq (r\beta_0)^{-1}$. It seems far better to use instead the normal thermodynamic quantity β_0 in the TE or ME and to investigate its temperature dependence rather than to use B, whose interpretation is uncertain and whose temperature dependence involves those of both r and β_0.

To summarize, the present results suggest that:

1. The ME is generally superior to the TE but both equations should be considered only as heuristic equations of state useful in the positive pressure range up to very high pressures.
2. Both the ME and the TE should be written in forms involving the initial compressibility parameter β_0 directly, and no interpretation then need be given to the Tait parameter B.
3. The n and r parameters should not be taken temperature independent.
4. Fitting of experimental p–V results to an equation of state should be carried out, wherever possible, with V/V_0 as the explicit dependent variable expressed directly on the left-hand side of the equation of state.
5. All fitting of the ME or TE to experimental data should be done by means of NLS directly at the p–V level, and as many of the goodness-of-fit and discrimination tests discussed herein as possible applied. Certainly, the conclusion that a material obeys the TE should not be made without such tests and without comparison with the ME and any other reasonable equation of state such as the Birch equation.

ACKNOWLEDGMENT

The computational help of Marilyn White is much appreciated.

APPENDIX: THE TAIT AND MODIFIED EQUATIONS

1. Tait Equation

The TE has been frequently written as[24,34,35]

$$V_0 - V = C \log_{10} [(P+B)/(P_0+B)], \quad \text{(A1)}$$

where $V_0 \equiv V(P_0)$, a reference volume. The parameters B and C are taken pressure-independent. Let us now write

$$J \equiv C \log_{10} e \quad \text{(A2)}$$

$$r \equiv V_0/J = V_0 \ln 10/C, \quad \text{(A3)}$$

$$\beta_0 \equiv [r(P_0+B)]^{-1}, \quad \text{(A4)}$$

and

$$p \equiv P - P_0. \quad \text{(A5)}$$

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[32] N. E. Dorsey, *Properties of Ordinary Water-Substance* (Reinhold Publishing Corp., New York, 1940), p. 181.

[33] A. Wohl, Z. Physik. Chem. **99**, 234 (1921).

[34] R. E. Gibson and J. F. Kincaid, J. Am. Chem. Soc. **60**, 511 (1938).

[35] R. E. Gibson and O. H. Loeffler, J. Am. Chem. Soc. **61**, 2515 (1939).

The TE rewritten in terms of these new quantities becomes

$$V/V_0 = 1 - r^{-1}\ln(1+r\beta_0 P). \qquad \text{(A6)}$$

The quantity r (or C/V_0) has been taken to be essentially temperature independent for many materials[13–16,24,34,35] although some slight dependence has been reported.[18,33]

The isothermal (instantaneous) compressibility $\beta \equiv -V^{-1}(\partial V/\partial P)_T$ calculated from (A6) is

$$\beta = \beta_0 (V_0/V)[1+r\beta_0 p]^{-1}, \qquad \text{(A7)}$$

a differential form of the TE. It is clear that when $P = P_0$, $\beta = \beta_0$. If P_0 is taken as atmospheric pressure, then β_0 may be identified as the isothermal "initial" compressibility of the material considered. Since B is usually much greater than P_0, the temperature dependence of β_0, which may be appreciable, is then just the inverse of that of B, provided r is temperature-independent.

Note that (A7) is relatively complicated and that (A1) and (A6) have the disadvantage that they yield $V<0$ above the pressure

$$p_L \equiv (r\beta_0)^{-1}(e^r - 1) = (P_0+B)(e^r - 1) \qquad \text{(A8)}$$

at which $V=0$. There is a negative pressure, p_∞, at which $V \to \infty$. From (A6), it is

$$p_\infty \equiv -(r\beta_0)^{-1} = -(P_0+B), \qquad \text{(A9)}$$

or

$$p_\infty \equiv -B. \qquad \text{(A10)}$$

2. Modified Equation

The negative volume catastrophe of the TE makes it theoretically unappealing even though p_L is usually of the order of millions of atmospheres and so beyond the range of most measurements. It is therefore desirable to modify the TE slightly in a way which will avoid this difficulty and so perhaps extend the range of applicability of the equation. One may modify Eq. (A6) as follows.[1] First, to avoid $V<0$ behavior, write $x \equiv \ln(1+r\beta_0 p)^{1/r}$ and replace $V/V_0 = 1-x$ by $V_0/V = 1+x$, the same to first order in x. This result, itself a possibly useful equation of state, may be further modified by replacing $(V_0/V)-1$ by $\ln(V_0/V)$, again the same to first order in $(V_0/V)-1$. On making the transformation $r \to n$ in x, one finally obtains

$$V/V_0 = (1+n\beta_0 p)^{-1/n}. \qquad \text{(A11)}$$

From (A11) it follows that

$$\beta = \beta_0[1+n\beta_0 p]^{-1} = \beta_0(V/V_0)^n, \qquad \text{(A12)}$$

considerably simpler than (A7) yet again equal to β_0 when $p=0$.

The transformation $r \to n$ has been made in order to distinguish between these parameters and to allow (A6) and (A11) to agree to as high order in $\beta_0 p$ as practical. Expand V_0/V in a power series in $\beta_0 p$ using first (A6) then (A11). On comparing the results term by term, one finds equalities for zero and first orders whatever the values of r and n. The second-order terms may also be made equal if we take $n = r-1$. When this value is substituted into the third-order term of the ME, the coefficient of $(\beta_0 p)^3$ becomes $(r^2/3) - (7/6)r + 1$. That of the TE is $(r^2/3) - r + 1$, virtually the same except for a difference of $r/6$. Thus, the relation

$$n = r - 1 \qquad \text{(A13)}$$

makes the ME and TE identical to second order and almost identical to third.

Bridgman and others have conventionally expressed experimental p–V results for many solids by means of

$$V/V_0 = 1 - ap + bp^2 - Cp^3 + \cdots. \qquad \text{(A14)}$$

If we compare term by term with the power series expansion of (A11), we find

$$a \equiv \beta_0, \qquad \text{(A15)}$$

$$b \equiv (n+1)\beta_0^2/2, \qquad \text{(A16)}$$

$$c \equiv (2n^2+3n+7)\beta_0^3/6, \qquad \text{(A17)}$$

etc. Thus, a test of whether Bridgman's results may be well fitted in the low to medium pressure range by the modified equation is whether $b/a^2 = (n+1)/2$ and $c/a^3 = (2n^2+3n+7)/6$ using the same n in both relations. This comparison is only fruitful, of course, when $n\beta_0 p$ is so small that higher than third-order terms in the expansion of (A11) may be neglected.