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Review of Some Experimental and Analytical Equations of State

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Four different polynomial equations and seven nonlinear equations, all applicable to both solids and liquids, are compared theoretically and statistically. Detailed curve-fitting results are presented for recent water and Hg isothermal data. Uncommonly used methods of statistical analysis and comparison, including generalized least squares, are described, justified compared to usual methods, and applied. In general, certain polynomial equations are found to yield significantly better fits of many different water and Hg data sets than any nonlinear equation considered. The Tait and Murnaghan equations, in particular, lead to strong systematic behavior of all residuals calculated herein with them, showing that they are inadequate models for all the data considered. Even a nonlinear equation derived from a second-order expansion of the bulk modulus K in powers of the pressure, which is shown to include several frequently used equations as special cases, is inferior to selected polynomial equations but is still the best equation examined when appreciable extrapolation is necessary. The method of volume normalization almost always used heretofore in statistical fitting of equations of state to $P-V$ data is shown to be inadequate and two alternative approaches are proposed and employed herein. Critical comparison of previous analyses of water and Hg data is made with the results of the present, more refined approach. The likelihood of important systematic errors in $P-V$ data, particularly data derived from ultrasonic measurements on liquids under pressure, is pointed out and high probability of their occurrence in some of the data analyzed is demonstrated. Even the combination of the best data apparently available and the use of better statistical-analysis methods than have been employed before does not yet allow one to obtain highly accurate values of the K_0' parameter of water or Hg, and only an order-of-magnitude estimate of the K_0'' parameter seems currently possible. Nevertheless, it appears that near room temperature K_0'' is positive for water and probably negative for Hg and that its appreciable magnitude for both materials renders a second-order expansion of K inadequate.

CONTENTS

It is the mark of an educated man to look for precision in each class of things just so far as the nature of the subject admits.

Aristotle

I. INTRODUCTION

Hayward (1967) has recently stated, "The subject of compressibility equations for liquids is really a very simple one. Unfortunately, it has been so badly treated in the literature that it has been made to appear unnecessarily complex . . ." In the present work I hope to demonstrate by example the truth of Hayward's first statement and to show, using the work of Hayward and others, the applicability of his second statement.

Isothermal compressibility equations are differential, or difference, forms of equations of state which are more commonly written in directly useful pressure–volume form. Thus, statements about compressibility equations apply, *mutatis mutandis*, to their corresponding equations of state. Although I shall here illustrate the usefulness of the equations considered using data for liquids, several of these equations have wide applicability as well to homogeneous, isotropic solids under hydrostatic compression.

The liquids water and Hg have been selected for examination herein for two related reasons: First, their general importance, and second, the high apparent precision and relative accuracy of some of the available *P-V* data for these materials. At the present state of the art, selected data for these two liquids seems "better" than any available for other liquids or solids. Such high quality probably arises from the relative ease of working with liquids as compared to solids and to the importance of these two materials, which has earned them extra attention. Mercury is important both because it is the most common dense material which is liquid at room temperature and because it is widely used both as a pressure transmitting medium and as a part of pressure gauges in *P-V* experiments on other materials. To obtain the highest accuracy in such experiments, the density of mercury must be known as a function of pressure. The importance of water both to life and to inanimate processes on earth needs no emphasis. Both in deep fresh-water lakes and in the oceans the water pressure in the depths is high, and the *P-V-T* properties of water are of great importance in oceanography and in underwater explosions. To name but a single property, since sound velocity depends on density, it is of practical importance to find how water density depends on temperature and pressure.

Although some of the equations considered here have at least a partial theoretical basis, they cannot be used to calculate total cohesive or elastic energies for the materials to which they are applied (Macdonald, 1966). Nevertheless, such semiempirical equations may be of very substantial value for smoothing, interpolation, and extrapolation of pressure–volume data and in determining values of such material parameters as isothermal compressibility and its first derivative with pressure, both evaluated at atmospheric pressure for example. Several of the equations considered may be applicable up to the very high pressures (including shock-wave range) of interest in geophysics for very slightly compressible solids and their molten state. The usefulness of equations of state in geophysics is well stated by Birch (1952). For example, the study of phase changes, elastic wave velocities, and *P-V* relations in natural minerals under high pressure is central to gaining understanding of the composition and structure of the earth's mantle and core.

The present work does not attempt to examine all reasonable empirical equations but rather attempts to consider the relations between and utility of several frequently used equations and a generalization of some of them. In particular, the Birch (1952), Keane (1954), and Mie–Lennard-Jones equations (see, e.g., Bernardes and Swenson, 1963) are not among those compared here. Their utility, particularly for solids, will be discussed elsewhere based on the methods of analysis and comparison described herein. The reader may wonder why the present effort is devoted to

examination of some semiempirical equations, eschewing detailed and/or first-principles discussion of the physical processes in a liquid or solid which lead to specific *P-V* relations. The reason is that I deal here with quite precise data from actual substances, not idealized materials. The derivation of a *P-V* relation for a real liquid or solid involves the solution of a very difficult many-body problem, where even restriction to pairwise interactions is usually improper (see, e.g., Bernardes and Swenson, 1963). No generally adequate solution is yet available. Therefore, it only seems practical at present to examine heuristic equations, albeit ones written in terms of conventional parameters having clear experimental interpretation. By this means, one may hope to discover the best "model" (expressed as a *P-V* equation) for each material investigated and thus to obtain trustworthy estimates of the material parameters involved in the equation. An obvious extension of the approach leads to *P-V-T* relations through the temperature dependence of the parameters. Clearly, the "best" model is only best in a relative sense, i.e., the best of those available for comparison with specific data. It is extremely unlikely that there exists a "universal" equation of state, of useful degree of simplicity, best for all condensed materials.

Finally, one may wonder why shock-wave data extending to very high pressures are not employed herein. The main reason is the very much larger uncertainties in shock-wave data as compared to those of some of the data considered here, where the volume under pressure is probably accurately known to within 5 or 10 parts per million. The shock-wave process does not always lead to conditions well approximated as hydrostatic, and it may involve the melting of materials originally solid. Shock-wave data are neither isothermal nor adiabatic but lead to *P-V* values associated with a Rankine–Hugoniot curve (Duvall and Fowles, 1963). The *P-V* values obtained are at least 1% uncertain and must usually be further transformed. The conversion to adiabatic or isothermal conditions involves theories whose applicability is uncertain and parameters of frequently unknown accuracy (Alder, 1963; Ahrens, 1966). The resulting isothermal *P-V* values probably contain appreciable systematic errors and may be 5% or 10% or more uncertain. The accuracy and precision of such data still seem too low to warrant their use in the present kind of detailed comparison of equations of state.

II. GLOSSARY

A. Symbols

A_k A general symbol for the kth disposable parameter in a least-squares fit; also polynomial-equation-of-state parameter expressed in terms of β_0, η, and θ. $k=0, 1, \cdots, n-1$; Eq. (13); Table III

TABLE I. Nonlinear equations.

Equation name	Acronym	First Appears in:	Form
Usual Tait equation	UTE	Eqs. (1), (1′)	$V/V_0 = 1 - (\eta+1)^{-1} \ln [1 + (\eta+1)\beta_0 p]$
Murnaghan equation	ME (SOE$_1$ with $\gamma \equiv \eta$)	Eq. (10)	$V/V_0 = (1 + \eta\beta_0 p)^{-1/\eta}$
Linear Secant-Modulus equation	LSME (SOE$_1$ with $\gamma \equiv 1$)	Eqs. (9), (9′)	$V/V_0 = 1 - \{\beta_0 p/[1 + \frac{1}{2}(\eta+1)\beta_0 p]\}$
Quadratic Secant-Modulus equation	QSME	In text	$V/V_0 = 1 - \{\beta_0 p/[1 + \frac{1}{2}(\eta+1)\beta_0 p - (1/12)(\gamma^2-1)(\beta_0 p)^2]\}$
Second-Order equation	SOE$_1$ ($\gamma \geq 0$)	Eq. (5)	$V/V_0 = \{[1 + \frac{1}{2}(\eta-\gamma)\beta_0 p]/[1 + \frac{1}{2}(\eta+\gamma)\beta_0 p]\}^{1/\gamma}$
Second-Order equation	SOE$_0$ γ or $q \equiv 0$	Eq. (6′)	$V/V_0 = \exp\{-\beta_0 p/[1 + \frac{1}{2}\eta\beta_0 p]\}$
Second-Order equation	SOE$_2$ ($q \geq 0$)	Eq. (6)	$V/V_0 = \exp\{-(2/q) \tan^{-1} \times[(\frac{1}{2}q)(\beta_0 p)/(1+\frac{1}{2}\eta\beta_0 p)]\}$

b Parameter in the QSME; $(\gamma^2-1)/12$

B Parameter in the UTE; Eq. (1)

C Parameter in the UTE; Eq. (1)

d_i Composite residual. $i=1, 2, \cdots, N$; Eq. (14) and text

$\langle d \rangle$ Mean value of d_i's; $N^{-1}\sum\limits_{i=1}^{N} d_i$

d_{rms} Root-mean-square value of d_i's; $[N^{-1}\sum\limits_{i=1}^{N} d_i^2]^{1/2}$

E_Z A parameter in σ_Z; $Z=x$ or y, V or p; Eq. (17)

f Number of degrees of freedom; $N-n$

f_m Median of M distribution

F_Z A parameter in σ_Z; $Z=x$ or y, V or p; Eq. (17)

g Number of zero crossings of $d_i(x_i)$; $u-1$

g_0 A particular value of g; u_0-1

$\langle g \rangle$ Expected mean value of g (binomial distribution)

H_Z Parameter in σ_Z; $Z=x$ or y, V or p; Eq. (17)

J Parameter in the UTE; Eq. (2)

K Isothermal bulk modulus; sometimes denoted elsewhere by B; $-V(\partial P/\partial V)_T$; β^{-1}

K' $(\partial K/\partial P)_T$

K'' $(\partial^2 K/\partial P^2)_T$

K_0 $(K)_{p=0}$; β_0^{-1}

K_0' $(K')_{p=0}$; also denoted here by η; elsewhere denoted by B_0', n, etc.

K_1 $-V_0(\partial P/\partial V)_T$

K_2 $pV_0/(V_0-V)$; Eq. (9)

K_∞' $(\partial K/\partial P)_{T,p\to\infty}$

L Parameter in the DGE; $(\eta-1)^{-1}$; Eq. (11′)

M Basic generalized least-squares parameter; Eq. (15)

M_0 A particular value of M

n Number of disposable parameters in an equation of state; $k=0, 1, 2, \cdots, n-1$

N Number of data points; $i=1, 2, \cdots, N$

N_1 Maximum possible number of zero crossings of $d_i(x_i)$; $N-1$

p Reduced pressure; $P-P_0$

P Pressure variable

P_0 Value of P at $V=V_0$

P_s A probability related to the distribution of M; see text

q $[2K_0K_0'' - (K_0')^2]^{1/2} \equiv [2\psi - \eta^2]^{1/2}$; $q^2 \equiv \theta \equiv -\gamma^2$

r Parameter in the UTE; formally equal to $\eta+1$

r_Z Relative standard deviation (s.d.) of parameter Z; here Z may be A_k, β_0, η, etc.; thus, $r_\eta \equiv |(\text{s.d. of } \eta)/\eta|$

R_{x_i} Generalized least-squares residual; X_i-x_i

R_{y_i} Generalized least-squares residual; Y_i-y_i

s_d Standard deviation of least-squares residuals; $[M/f]^{1/2}$ or $[M/(f-1)]^{1/2}$; see text

s_d' Standard deviation with nonzero $\langle d \rangle$; $[S/f)^{1/2}$ or $[S/(f-1)]^{1/2}$; see text

s_f For a least-squares fit of an equation of the form $y=f(x)$, s_f is the s.d. of y at a given value of x or y; thus, we define $s_f(X_i)$ as s_0 for $X_i=X_1$, s_1 at $p\approx100$ bar, s_m at $\approx X_{max}/2$, s_N at $X_N \equiv X_{max}$, and s_e at $100X_{max}$

S Least-squares sum of squared residuals; Eq. (14)

S_p Contribution to S arising from the pressure residuals

t $(V_0-V)/V_0$

t_a $(V_a-V)/V_a$

T Temperature

u Number of runs in a set of least-squares residuals

u_0 A particular value of u

V Volume or specific volume

V_a An estimated or initial value of V_0

V_c Value of V at $z=z_c-$

V_m Value of V as $z\to\infty$

V_0 Value of V appropriate at $P=P_0$, $p=0$

V_{0m} Measured value of V_0

w $(V_0-V)/V$

w_a $(V_a-V)/V$

x Symbol for an independent variable; at the ith data point the *calculated* value of x is x_i

X Symbol for an *observed* value of x; at the ith data point, $X=X_i$

y Symbol for a dependent variable; at the ith data point, the *calculated* value of y is y_i

Y Symbol for an *observed* value of y; at the ith data point, $Y=Y_i$

z $\beta_0 p$

z_c Value of z at which a phase change occurs

z_c- $(z_c-\epsilon)$ with $\epsilon \to 0$

z_n Value of z at which K' first passes through zero

β Isothermal compressibility; K^{-1}

β_0 $(\beta)_{p=0}$; K_0^{-1}

β_1 $-V_0^{-1}(\partial V/\partial P)_T$; K_1^{-1}

γ $[(K_0')^2-2K_0K_0'']^{1/2} \equiv [\eta^2-2\psi]^{1/2}$

η A simpler symbol for K_0' (dimensionless)

θ q^2; a dimensionless material parameter involving K_0, K_0', and K_0''

θ_1 A probability in the binomial distribution of u

λ $\langle d \rangle/d_{rms}$

ρ_{x_i} Ordinary least-squares residual; X_i-x_i

ρ_{y_i} Ordinary least-squares residual; Y_i-y_i

Π The two-tailed probability that u_0 occurred by chance

σ_Z Expected standard error of the Zth variable; generalized least-squares weighting involves the variances $\sigma_{x_i}^2$ and $\sigma_{y_i}^2$

σ_{A_k} Calculated standard error of the parameter A_k

ψ A simpler symbol for K_0K_0'' (dimensionless)

B. Equations

1. Nonlinear Equations

There are many different ways the equations of Table I may be written. For consistency, they are all given here with V/V_0 on the left and involving the parameters β_0, η, γ, and q. Alternatively, they may all be solved for p as a function of V/V_0. The present form of the equations assumes that V_0 is known exactly. Procedures applicable in the usual situation, where this is not the case, are discussed in the text.

2. Polynomial Equations

The four polynomial equations considered are of the form

$$y= \sum_{k=0}^{n-1} A_k x^k.$$

When V_0 is known exactly, $A_0 \equiv 0$ and the equations may be summarized as in Table II, where $t \equiv (V_0-V)/V_0$ and $w \equiv (V_0-V)/V$. Expressions for some

TABLE II. General polynomial equations.

Name	Acronym	y	x
Bridgman equation	BE	t	p
Inverse Volume equation	IVE	w	p
Slater equation	SE	p	t
Davis–Gordon equation	DGE	p	w

of the A_k's in terms of pressure derivatives appear later in Table III. The highest degree of x which appears in a polynomial equation will frequently be indicated with a prefix; thus, 3BE denotes the Bridgman equation of third degree.

III. SPECIFIC EQUATIONS

Before discussing in some detail prior work in this field and some new specific curve-fitting results, I shall define and compare the main isothermal equations of state which will be considered herein. The isothermal bulk modulus K is defined as $-V(\partial P/\partial V)_T$. Its inverse β is the corresponding compressibility, which should be distinguished from the *ersatz* compressibility, $\beta_1 \equiv -V_0^{-1}(\partial V/\partial P)_T \equiv K_1^{-1}$, occasionally used by some authors without discriminating it from β. Here V_0 is the value of V, the specific volume, at some reference pressure (frequently 1 atm) P_0. Let $p \equiv P-P_0$, the pressure variable most appropriate in an equation of state, especially one for liquids where P_0 cannot be zero.

A. Usual Tait Equation

In the past, the Usual Tait equation (abbreviated UTE) has been usually written in the form (Gibson and Loeffler, 1941)

$$V_0-V=C \log_{10} [(B+P)/(B+P_0)]. \qquad (1)$$

This leads immediately to

$$K \equiv \beta^{-1}= (V/J)[B+P], \qquad (2)$$

where $J \equiv C \log_{10} e$. It has been shown elsewhere (Macdonald, 1966) that the constants J (or C) and B of the above are not as easy to interpret or relate to theory as are the following simple modifications of them. Introduce p instead of P, define $r \equiv V_0/J \equiv \eta+1$, and let $\beta_0 \equiv (\beta)_{p=0} \equiv [r(B+P_0)]^{-1}$. Here, because of its frequent appearance the simple symbol η is used for $K_0' \equiv (\partial K/\partial P)_T$ evaluated at $p=0$. Then (1) and (2) become

$$V/V_0=1-r^{-1}\ln(1+r\beta_0 p) \qquad (1')$$

and

$$K=(V/V_0)[K_0+rp]. \qquad (2')$$

Here $K_0 \equiv \beta_0^{-1}$, and the (V/V_0) in Eq. $(2')$ is that given by $(1')$. The Tait equation is a nonlinear equation in the sense that its parameters enter non-linearly.

Note that β_0 is the usual initial compressibility, a frequently employed thermodynamic quantity whose interpretation and temperature dependence, unlike those of the Tait B, are well known for many materials. Further discussion of r [which usually falls in the range $(3 < r < 13)$] is given later on in this work and elsewhere (Macdonald, 1966). Although it is not yet clear if any occasions exist for which it is more appropriate to use the Usual Tait equation rather than one of the equations discussed in the next sections, it is quite clear (Macdonald, 1966) that if such an occasion does exist the outmoded parameters B and C should no longer be used.

Hayward (1967) has pointed out that the Usual Tait equation is not that originally proposed by Tait (1888). Since it has nevertheless been designated "the" Tait equation by a long succession of authors (including the present author), we shall retain this time-hallowed but faulty usage here, merely adding the adjective "usual." The actual Tait equation, strongly supported by Hayward as superior to the Usual Tait equation and any others, will be discussed below. Finally, Hayward has noted that the *ersatz* bulk modulus, $K_1 \equiv \beta_1^{-1}$, is, for the UTE, given by

$$K_1 \equiv (V_0/V)K = K_0 + rp, \qquad (3)$$

written with the present, more transparent, parameters. It is thus a linear function of p.

B. The Second-Order Equation

In this section, I shall discuss a general nonlinear equation of state which includes within it two other equations which have been shown to be of value under special conditions. In later sections, the applicability of the general equation to P-V data will be discussed and exhibited by means of statistical curve-fitting results on water and mercury.

It has been found that at least over a considerable pressure range, K (*not* K_1) is or is very nearly linear in pressure p for many liquids and solids. (For details see Moelwyn-Hughes, 1951, 1964; Harris and Moelwyn-Hughes, 1957; Macdonald, 1966; Anderson, 1965, 1966; and references therein.) This suggests that a Taylor series expansion of K in terms of p around the point $p = 0$ would be appropriate. To second-order one has

$$K \cong K_0 + K_0'p + \tfrac{1}{2}K_0''p^2, \qquad (4)$$

where K_0'' is $(\partial^2 K/\partial P^2)_T$ evaluated at $p = 0$. Until the compression is considerable $(\beta_0 p \gtrsim 1)$, the second-order term may be nearly negligible for most solids since the dimensionless quantity $|K_0 K_0''|$ is expected to be small compared to unity or even $|K_0'|$ (Anderson, 1966; Ruoff, 1967a). Unpublished work of P. B. Ghate (private communication) suggests, however,

that such smallness is unlikely for several solids. Further, Ruoff (1967b) has recently calculated approximate values of $K_0 K_0''$ and K_0'' (adiabatic rather than isothermal) for several solids and found non-negligible values. Unfortunately, there seem to be no accurate experimentally derived values for K_0'' yet available. Since the symbols m and n appear in the frequently used Mie–Lennard-Jones power-law expression for the interaction energy of a pair of molecules or atoms, we shall eschew them here and use two neutral symbols chosen to achieve the maximum simplicity of subsequent equations. One such symbol is the $\eta \equiv K_0'$ already introduced; the other is $\gamma \equiv [(K_0')^2 - 2K_0 K_0'']^{1/2}$. Then (4) becomes

$$K \cong K_0 + \eta p + (1/2K_0)\,[(\eta^2 - \gamma^2)/2]\,p^2$$
$$= K_0\{1 + \eta z + [(\eta^2 - \gamma^2)/4]z^2\}, \qquad (4')$$

a compressibility equation in the sense of Hayward. Here $z \equiv \beta_0 p$. Note that the physical interpretation of η is quite clear from its definition as K_0'.

Equation $(4')$ can be readily integrated to obtain a second-order equation of state (SOE_1). The result may be written

$$\frac{V}{V_0} = \left[\frac{1 + \tfrac{1}{2}(\eta - \gamma)\beta_0 p}{1 + \tfrac{1}{2}(\eta + \gamma)\beta_0 p}\right]^{1/\gamma}, \quad \gamma^2 \geq 0, \qquad (5)$$

where K_0^{-1} has been replaced by β_0. Murnaghan (1949) has given a somewhat similar expression which is also supposed to be derived from a K quadratic in p. It is not, however, unless his general parameters a and b are related by $a \equiv -b$.

In a talk abstract, Ho and Ruoff (1967) have mentioned using an integration of Eq. (4) to fit P-V data on Na, but the form of the equation of state is not given. In a later paper, Ruoff (1967b) has given an adiabatic form of Eq. (5), written in an equivalent but less transparent manner and with $P_0 = 0$. His equation involves adiabatic parameters in place of the present isothermal ones. It is worth pointing out that the adiabatic and isothermal equations are not really equivalent transforms of each other, for the stated conditions, even though they have the same form. There are two ways a P-V equation of state for adiabatic conditions may be obtained from Eq. (4). In the first, the parameters on the right are simply transformed from isothermal to adiabatic conditions (Anderson, 1966). Integration of the resulting isentropic expression for K leads to Ruoff's result. Alternatively, the left side of Eq. (4) may be directly transformed to isentropic conditions by relating all quantities involved to the energy and volume derivatives of the entropy. The final expression for the isentropic K will generally involve higher powers of P than the original isothermal expression of Eq. (4). Thus, the final isentropic equation of state obtained by subsequent integration will differ from that obtained by the first method.

Equation (5) includes the case $\gamma^2 = \eta^2$ appropriate when the K_0'' term in (4) is zero or of negligible

importance over the experimental pressure range. As we shall see later, cases may arise where $\gamma^2 < 0$ and the K_0'' term is then far from negligible. On defining $q^2 \equiv -\gamma^2 \equiv \theta$, integration of (4') with $q^2 \geq 0$ leads to the SOE_2

$$\frac{V}{V_0} = \exp\left\{-\left(\frac{2}{q}\right)\tan^{-1}\left[\frac{1}{2}(q)\left(\frac{\beta_0 p}{1+(\eta/2)\beta_0 p}\right)\right]\right\},$$

$$\gamma^2 \leq 0. \quad (6)$$

When $q = \gamma = 0$, (5) and (6) coalesce to the SOE_0

$$\frac{V}{V_0} = \exp\left[-\frac{\beta_0 p}{1+(\eta/2)\beta_0 p}\right]. \quad (6')$$

A less convenient form of Eq. (6) has been given by Rose (1967) who assumed, on the basis of theoretical calculations of the parameters, that $q^2 > 0$ for Cu, Ag, Al, and Ni. In making his calculations, Rose apparently misinterpreted certain results of Ghate (1966) for the strain dependence of single-crystal elastic constants and used them incorrectly in obtaining K_0''. In addition, the quantity K_0'' involves fourth-order elastic constants, and Rose could not compare his calculated values of such constants with experimental values since none of the latter has yet been measured. It seems significant, however, that Rose's (1966) own theoretical values of the third-order constant c_{123} are in very poor agreement with experiment and are not in close agreement with an
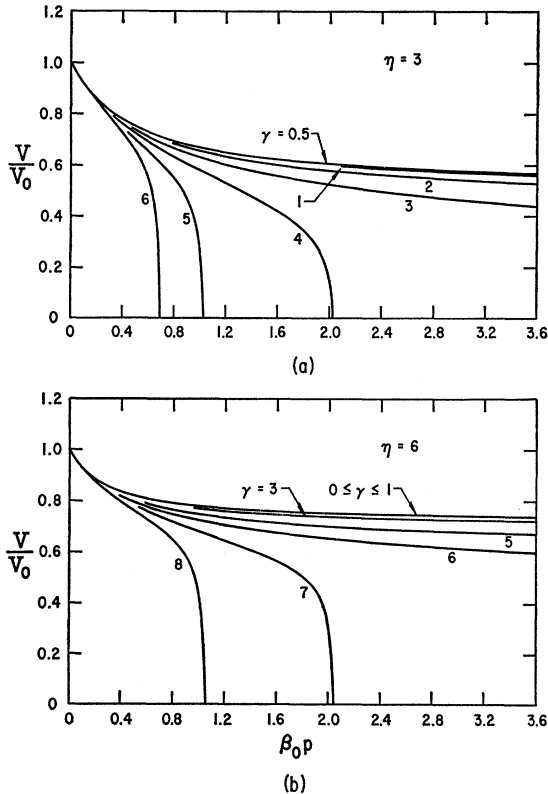

(a)

(b)

FIG. 1. Second-Order equation $(\gamma \geq 0)$ curve shapes for $\eta = 3$ and 6 and various values of γ.
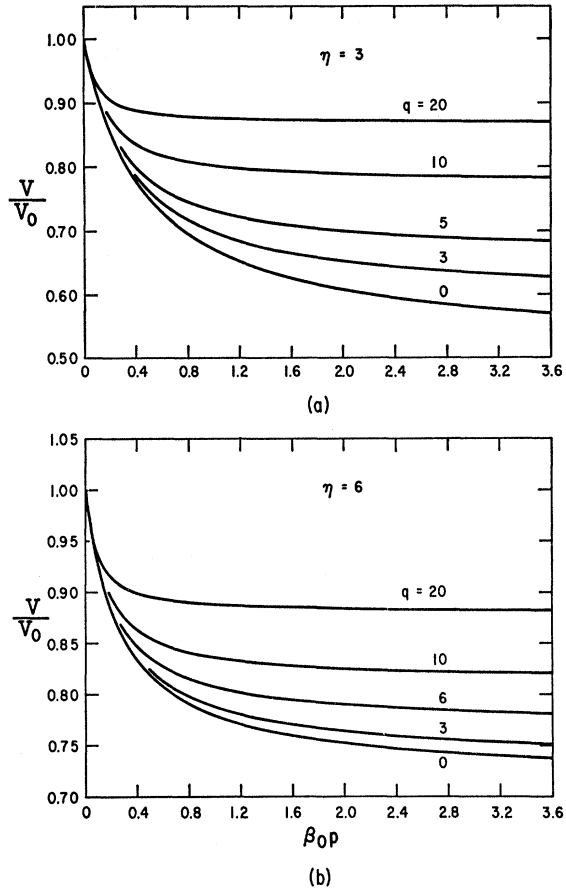

(a)

(b)

FIG. 2. Second-Order equation $(q \geq 0)$ curve shapes for $\eta = 3$ and 6 and various values of q.

independent and somewhat different theoretical calculation of c_{123} for Cu and Ag (Lincoln, Koliwad, and Ghate, 1967). Thus, no credence can be given to Rose's fourth-order constant values and to his corresponding results for K_0''.

Although η is a simple material parameter with a clear experimental interpretation, the significance of γ^2 arises primarily from its connection with K_0, K_0', and K_0''. In practice, γ or q may be either regarded as a free parameter used in curve fitting or as a disposable parameter whose specific choice yields a specific equation of state. Note that since the Second-Order equation is an even function of γ or q, only positive values of these quantities need be considered. To third order the power series expansions of the Second-Order equation (both SOE_1 and SOE_2) and the Usual Tait equation are, respectively,

$$V/V_0 = 1 - z + \left[\frac{1}{2}(\eta+1)\right]z^2$$
$$- \left[\frac{1}{12}(3\eta^2+6\eta+\gamma^2+2)\right]z^3 + \cdots \quad (7)$$

and

$$V/V_0 = 1 - z + (\frac{1}{2}r)z^2 - (\frac{1}{3}r^2)z^3 + \cdots. \quad (8)$$

It is clear the two expansions are identical to third order if one selects $r = \eta + 1$ and $\gamma^2 = r^2 + 1 = (\eta+1)^2 + 1$. Figures 1 and 2 illustrate the dependence of the

Second-Order equation on z for $\eta=3$ and 6 and a variety of γ and q values. In Fig. 1 all curves with $0\leq\gamma\leq1$ lie too close together to be resolved.

As the figures show, Eqs. (5) and (6) exhibit difficulties at high compressions. Consider the variation with γ^2 of V/V_0 at high values of z. We see that for $\gamma^2>\eta^2$, V/V_0 reaches zero and goes negative for a finite z! If we define V_m as the limiting value (when such exists) of V as $z\rightarrow\infty$, then $V_m=0$ for $\gamma^2=\eta^2$. This is not an unreasonable result. When $0\leq\gamma^2\leq\eta^2$, however, Eq. (5) leads to $V_m/V_0=[(\eta-\gamma)/(\eta+\gamma)]^{1/\gamma}$, which may be quite close to unity! Further, for $-\infty<\gamma^2\leq0$, (6) leads to $V_m/V_0=\exp[-(2/q)\times\tan^{-1}(q/\eta)]$, a quantity that may again be relatively close to unity. Note that the values predicted by (5) and (6) for V_m/V_0 when q and γ are zero may be shown to be the same, namely $\exp(-2/\eta)$.

Although it may seem illogical to continue to consider an equation of state for which V_m/V_0 may be as large as 0.7 to 0.8, it should be remembered that an equation of state is only required to be applicable up to a value of z where a phase change occurs, not necessarily for the full range of z to infinity. Beyond a phase change, another equation of state, or the same one with different parameters, will be applicable. Thus, one must only require, for $\gamma^2<\eta^2$, that $V_m<V_c$, where V_c is the specific volume at z_c-, and z_c is the value of z at which the phase change occurs. As we shall show later, this inequality is appropriate and holds for water. Similarly, if it should turn out that for a certain material $\gamma^2>\eta^2$ and V/V_0 could thus go negative, the SOE_1 might still be applicable provided a phase change occurred before V/V_0 began to fall off rapidly toward zero.

The above possible difficulties with V/V_0 are associated with similar anomalies in the behavior of K and K' with p or z. These all arise from the truncation of the infinite power series for K after its quadratic term. As discussed above, these difficulties may be of no practical importance if the resulting equation of state is only required to hold in a pressure region where higher terms make a negligible contribution.

When $z\rightarrow\infty$, on the other hand, Eq. (4') leads to $|K|\rightarrow\infty$. It is clear that the results $K\rightarrow-\infty$ and $K'\rightarrow-\infty$ following when $\gamma^2>\eta^2$ and $z\rightarrow\infty$ are nonphysical. In fact, it is unreasonable to expect that K' could even go negative. The value of z at which K' becomes zero, $z_n\equiv2\eta/(\gamma^2-\eta^2)\equiv-K_0'/K_0K_0''$, must therefore appreciably exceed z_c if the SOE_1 is to be useful up to or near z_c. How applicable can we expect the Second-Order equation to be at high values of z when alternatively, $\gamma^2\leq\eta^2$ and $K\rightarrow\infty$ in the limit, as it thermodynamically should? Note that K' will, in this case, be a monotonically increasing function of z, a thermodynamically allowed possibility. Keane (1954) and Anderson (1968) have shown, however, that it is at least plausible to consider

$$K_\infty'\equiv(\partial K/\partial P)_{T,p\rightarrow\infty}$$

to be finite, positive, and somewhat smaller than $K_0'\equiv\eta$. Keane has derived an equation of state on this basis whose K' decreases monotonically from K_0' to K_∞'. Although Anderson (1968) has used a variety of shock-wave measurements on several solids to show that the Keane equation is slightly superior to the $\gamma^2=\eta^2$ Second-Order equation (see Part D of this section where this equation is termed the "Murnaghan" equation), the difference is small and the likely inaccuracy of the data and lack of isothermal conditions suggest that the case for the superiority of the Keane equation up to high compressions has not been fully proved. Only a small difference between the K_0' values used in data fitting with the Keane equation and with the Murnaghan equation would render the resulting curves the same within the likely experimental error of the data used by Anderson. At the same time, it is by no means proved that K' must either always decrease or increase monotonically with pressure in a wide pressure range where no phase change occurs. It may even increase with z for some materials over K_0' and then decrease and approach a K_∞' less than K_0' as z continues to increase. Some light on the restrictions on the behavior of K' for the liquids H_2O and Hg will be shed by the later curve-fitting results of the present work.

C. The Linear Secant-Modulus Equation

When $\gamma\equiv1$, (5) reduces to the original Tait equation, termed the Linear Secant-Modulus equation (LSME) by Hayward. This equation may also be written (Hayward, 1967) in the form

$$K_2\equiv[V_0p/(V_0-V)]=K_0+\tfrac{1}{2}(\eta+1)p, \qquad (9)$$

thus linear in p for the difference-type *ersatz* bulk modulus K_2. The Linear Secant-Modulus equation may also be rearranged to

$$p=wK_0[1-\tfrac{1}{2}(\eta-1)w]^{-1}, \qquad (9')$$

where $w\equiv(V_0-V)/V$. Partly because of the simplicity of (9) and its linear dependence on p (P_0 was implicitly taken zero by Hayward who thus used P rather than p), Hayward has bravely stated that Eq. (9) is "unquestionably superior" and "is for several reasons the best" of several equations he discussed. He gives no statistical comparison of these several equations, however, and his reasons are weak and unconvincing. Also, whenever γ is taken fixed at a specific constant value, as here for the Linear Secant-Modulus equation, the present results show that a special relation is established between K_0' and K_0K_0'', one that certainly cannot be expected to be applicable in general. It is by deriving the Linear Secant-Modulus equation as a special case of the Second-Order equation that this relation becomes obvious, although it can be inferred from direct calculation of K. Note that for Eq. (9), $V_m/V_0=(\eta-1)/(\eta+1)$, a result apparently unnoticed by Hayward.

Hayward has shown that the Linear Secant-Modulus equation is not only of the form of Tait's original equation, but it also is equivalent to the Tumlirz and Tammann equations. Concerning these equations Hayward states, "It is typical of the present confused thinking in this field that these are still regarded as two distinct equations..., although they are nothing of the kind." Unfortunately, Hayward made this same type of error himself, as we shall see in Sec. III.D.

Hayward has suggested that quadratic (and even cubic) terms in p be added to Eq. (9) to allow it to cover high-pressure regions for compressible fluids. While there is theoretical justification to expect that it would be useful to express the basic thermodynamic quantity K in a Taylor series around $p=0$ and experimental evidence to show that such a series may be usefully truncated for some materials at the linear or quadratic level (except probably at high compressions), the only justification for adding higher-order terms to the artificial construct K_2 can be empirical, i.e., that doing so leads to equations which fit P-V data better than any others with the same number of adjustable parameters. It thus does not seem sensible to add quadratic and perhaps higher terms to K_2 to improve its applicability and utility if equivalent or superior results can be obtained with a quadratic K. The quantitative results to follow show, for example, that Hayward's forthright statement that a quadratic K_2 "is the best equation for water over very large pressure ranges" is not well based. Finally, from a practical viewpoint, Anderson (1965, 1966) has shown how K_0, K_0', and perhaps even K_0'' may be derived from ultrasonic measurements at modest pressure, which then allows Eqs. (5) or (6) to be used to estimate compression to high pressures, provided higher-order terms are negligible.*

D. The Murnaghan Equation

When $\gamma \equiv \eta$, Eq. (5) reduces to

$$V/V_0 = (1+\eta\beta_0 p)^{-1/\eta}, \qquad (10)$$

a widely used equation which has been recently examined in some detail (Macdonald, 1966) and may be abbreviated as the ME. Here the "M" may stand for Murnaghan (1944), who apparently was the first to publish it although an adiabatic form of the equation was presented in 1942 OSRD reports by Kirkwood and co-authors, or modified (Macdonald and Barlow, 1962; Macdonald, 1966). Note that setting $\gamma = \eta$ in (4') reduces the K expansion to a linear relation. Such a linear expansion and the resulting Murnaghan equation have been used and found satisfactory at least in the medium pressure range by, among others, Moelwyn-Hughes (1951, 1964) (whose compressibility equation

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* *Note added in proof:* Barsch and Chang (1969) have recently used values of K_0, K_0', and K_0'' derived from ultrasonic measurements on several cesium halides to reach interesting conclusions on the relative applicability of several equations of state for these materials.

of state was termed the Linear Tangent-Modulus equation by Hayward); Macdonald (1966), particularly for water (see also Macdonald and Barlow, 1962); Anderson (1965, 1966); Swenson (1966); and Monfort and Swenson (1965). A theoretical relation between η and the Grüneisen parameter for solids has been discussed earlier (Macdonald, 1966, where η is designed by n) and shows, along with the relation $\eta \equiv K_0'$, that η is not the "arbitrary constant" it was termed by Hayward. Further, Moelwyn-Hughes (1951, 1964) has expressed η as $\frac{1}{3}(n+m+6)$, where n and m are the Mie–Lennard-Jones equation parameters. For mercury he used $m=6$, the value appropriate for attraction by London dispersion forces alone. Then, $\eta \cong \frac{1}{3}n+4$. With his value of $m+n$ of 15.5 ± 1.0, one finds $\eta \cong 7.2\pm0.3$ for mercury. Our later determinations of η agree poorly with this result and with a value of 8 derived by Fürth (1945), principally from thermal data. In a recent discussion (Macdonald, 1966) of the Murnaghan equation, the corresponding compressibility equation is explicitly given in Eq. (A12) of the 1966 work and shows that K is linear in pressure. In spite of this result and the stated connection with the work of Anderson, who used the linear K relation, Hayward has treated the Murnaghan equation and the Moelwyn-Hughes–Anderson equation as two distinct equations, although they are nothing of the kind.

The similarity at the K level of the Usual Tait equation in Eq. (1') and the Murnaghan equation of (10) should be noted. The UTE suffers from the defect that at very high pressures it leads to negative V; it was by making simple modifications in the UTE to avoid this catastrophe that the author (Macdonald and Barlow, 1962) was first led to the Murnaghan equation. If the Usual Tait equation and the Murnaghan equation are expanded in powers of p, it is found (Macdonald, 1966) that the results agree exactly to second order and almost exactly to third when r is taken as $\eta+1$, as already stated. Nevertheless, actual least-squares curve fitting of P-V data for even a relatively incompressible fluid like water shows that higher-order terms are important because the value of η obtained from the UTE curve fitting disagrees with that obtained from ME fitting of the same data. In spite of their important differences, the Usual Tait equation and the Murnaghan equation have often been mistaken for one another at the compressibility equation level, usually because of failure to distinguish between β and β_1.

E. The Davis–Gordon and Bridgman Equations

Davis and Gordon (1967) have recently given a discussion and comparison of some equations of state in connection with their work on Hg. They find the following equation (the DGE) particularly appropriate for this material:

$$p = wK_0[1+\tfrac{1}{2}(\eta-1)w], \qquad (11)$$

TABLE III. Variables and parameters of four polynomial equations of state.

Equation	y	x	A_1	A_2	A_3
3BE	t	p	β_0	$-\frac{1}{2}(\eta+1)\beta_0^2$	$(1/12)\,(3\eta^2+6\eta+2-\theta)\beta_0^3$
3IVE	w	p	β_0	$-\frac{1}{2}(\eta-1)\beta_0^2$	$(1/12)\,(3\eta^2-6\eta+2-\theta)\beta_0^3$
3SE	p	t	β_0^{-1}	$\frac{1}{2}(\eta+1)\beta_0^{-1}$	$(1/12)\,(3\eta^2+6\eta+4+\theta)\beta_0^{-1}$
3DGE	p	w	β_0^{-1}	$\frac{1}{2}(\eta-1)\beta_0^{-1}$	$(1/12)\,(3\eta^2-6\eta+4+\theta)\beta_0^{-1}$

where again $w\equiv(V_0-V)/V$. Note the similarity to Eq. (9′), the LSME. To indicate the degree of a polynomial equation such as the DGE, I shall prefix the degree to the equation designation. Thus, Eq. (11) may be denoted as the 2DGE. The Davis–Gordon equation of second degree stems from a truncated Taylor series expansion around $V_0/V=1$ and was used by Bridgman (1936) many years ago. A similar equation (the 2SE) involving $(V_0-V)/V_0$ instead of w has been discussed by Slater (1939). Written in inverse form, the second-order Davis–Gordon equation becomes

$$V/V_0=[1-L+(L^2+2L\beta_0 p)^{1/2}]^{-1}, \qquad (11')$$

where $L\equiv(\eta-1)^{-1}$. Its series expansion is

$$V/V_0=1-z+[\tfrac{1}{2}(\eta+1]z^2-[\tfrac{1}{2}(\eta^2+1)]z^3+\cdots. \qquad (12)$$

Davis and Gordon have also considered Bridgman's second-degree Taylor expansion of V in powers of p around $p=0$. When one expands to third degree, one finds necessarily that the result (the 3BE) is just Eq. (7), the third-degree series expansion of the SOE. Similarly, the 2BE is given by Eq. (7) when this SOE series is truncated after the second-degree term. The third-degree Bridgman equation has recently been used, without identification of the coefficients with pressure derivatives of K, by Kell and Whalley (1965) for fitting water P-V-T results.

F. Polynomial Equations

For later reference and use, four nonequivalent but closely related polynomial equations of state of third degree are summarized in this section. Two are the already discussed 3BE and 3DGE; the other two are the cubic Slater equation (3SE) and the cubic Inverse Volume equation (3IVE), the latter involving V^{-1} as the dependent variable (which is proportional to density). These equations may all be written in the form

$$y=\sum_{k=1}^{3} A_k x^k, \qquad (13)$$

where specific choices of the x and y variables and the pertinent coefficients (expressed in terms of pressure-volume derivatives) are summarized in Table III. In this table, $w\equiv(V_0-V)/V$ as before and $t\equiv(V_0-V)/V_0\equiv(V/V_0)w$. We have expressed all the parameters in terms of β_0, η, and $\theta\equiv q^2\equiv-\gamma^2$.

Should any of these equations be extended to fourth or higher degree, the coefficients (A_4, etc.) could be expressed in terms of K_0, K_0', K_0'' and higher-pressure derivatives of K evaluated at $p=0$. This is currently unnecessary, since even K_0'' can scarcely be very accurately determined from experiment thus far, much less K_0''' and even higher derivatives. Thus, in any comparison made herein of, e.g., the 4BE with the 3BE, the new coefficient necessary will be introduced linearly, as, e.g., the free parameter A_4, rather than as a complicated function of the various pressure derivatives. Note that since all four of the polynomial equations are derived from Maclaurin expansions, the derivatives K_0, K_0', and K_0'' refer to the point V_0, P_0, at which p, w, and t are all zero. This point may be that at $P=P_0=1$ atm or, for solids, it may appropriately be taken at $P=P_0=0$. Note that surface-tension effects are not explicitly considered here.

Finally, the 3SE is the reversion or inverse of the 3BE and the 3DGE the reversion of the 3IVE, both to third degree. The true reversions of these equations involve an infinite number of series terms (or the roots of cubic equations); since the series obtained by reversion are truncated after the third power, none of the equations is entirely equivalent to any other. Further, it should be clear from their form that none of the four equations is likely to be of value for extrapolation very far outside the fitting range.

IV. ANALYSIS OF DATA

A. Analysis Method

In previous work (Macdonald, 1966), some methods of statistical curve fitting and of assessment of the degree of fit obtained were described in detail. With the availability of more accurate P-V data and considerable information concerning their measurement errors, it becomes worthwhile and sometimes essential to apply more sophisticated and powerful methods than those discussed earlier.

Most of the equations already discussed may be written in either the form $y=f(x)$, where $y\equiv V$ or V/V_0 and $x\equiv p$, or the related inverse form $x=g(y)$, but it is impractical to write some, such as the 3BE of Eq. (7), in both forms. When both forms may be used, ordinary unweighted (or weighted) linear or nonlinear least squares operating on a given set of

data leads to somewhat different values of the least-squares parameters, depending upon which form is used. The question thus arises of which to use. In one case, observed x values X_i are supposed to be known exactly and hence to be error free; the least-square residuals are then of the form $\rho_{y_i} \equiv Y_i - y_i$, where Y_i is an observed value of y and y_i is the corresponding calculated value. In the other case, the Y_i's are (often implicitly) assumed known exactly and the calculated residuals are $\rho_{x_i} \equiv X_i - x_i$.

In most experiments, there is likely to be some error in both variables (we restrict attention here to the situation for which there is only a single "independent" variable of the x type). Only when a variable is intrinsically discrete (because, e.g., of quantum-mechanical or whole-number reasons) is there a possibility of obtaining all exact values. Even when both variables contain random or systematic errors, one may still frequently make a distinction between them. Especially in the physical sciences, one variable, termed "independent," is frequently brought, insofar as possible, by the experimenter to a set of chosen values; it is thus controlled. In this common situation, errors will still generally occur and the actual or true values of x will be different from the controlled, chosen values making up the set $\{X_i\}$. The variable is then nonrandom, but the error between an X and the corresponding true x value will be a random variable. Thus, the correlation between the error vector and the true set is nonzero in this case. This situation is significantly different from that where the variable in question is uncontrolled. There, the error vector and the true set are uncorrelated and X is a random variable.

For the simple case of linear regression, the statisticians (Berkson, 1950; Geary, 1953; Scheffé, 1959) have considered the question of the choice of regression equation $[y=f(x)$ or $x=g(y)]$ in great detail. For both variables containing uncontrolled error, neither regression yields an unbiased estimate of the parameter relating x and y. When the independent variable x is controlled, however, it has been shown that the usual regression, $y=f(x)$, yields an unbiased estimate of this parameter provided some usual statistical restrictions are satisfied.

In P–V experiments, P may sometimes, but not always, be controlled in the above sense. Unfortunately, we almost always need to deal with $f(x)$'s and $g(y)$'s nonlinear in their parameters. The best regression choice has apparently not been studied in the general nonlinear situation. It turns out that we can avoid the need to make a choice at all and gain additional important advantages if we adopt a generalized least-squares procedure first given by Deming (1943) and recently discussed in considerable detail by Wolberg (1967). See also Williamson (1968).

It is assumed, as is nearly always the case, that errors occur simultaneously in both the y and the x variables; the residuals then may be written $R_{y_i} \equiv Y_i - y_i$, $R_{x_i} \equiv X_i - x_i$. We have used different symbols for these residuals since they will, in general, be calculated by a different procedure from that leading to ρ_{y_i} or ρ_{x_i}. Only when all $R_{x_i} \equiv 0$ will $\{R_{y_i}\} = \{\rho_{y_i}\}$; similarly for all $R_{y_i} \equiv 0$. Next, introduce the weights $w_{y_i} \equiv \sigma_{y_i}^{-2}$ and $w_{x_i} \equiv \sigma_{x_i}^{-2}$. Here $\sigma_{y_i}^2$ and $\sigma_{x_i}^2$ are the expected variances of the measured values of the variables, quantities assumed known from the experimental conditions or from direct measurement. It will be assumed that the observations are stochastically independent. Deming's idea then was to minimize the magnitude of the function S with respect to simultaneous variation of all the parameters of the fitting equation, where

$$S \equiv \sum_{i=1}^{N} \{w_{y_i} R_{y_i}^2 + w_{x_i} R_{x_i}^2\} \equiv \sum_{i=1}^{N} \{N_{y_i}^2 + N_{x_i}^2\}$$

$$\equiv \sum_{i=1}^{N} d_i^2 \equiv S_y + S_x. \tag{14}$$

Here N is the number of data points; N_{y_i} and N_{x_i} are standardized residuals of the form (R_{z_i}/σ_{z_i});

$$S_y \equiv \sum_{i=1}^{N} N_{y_i}^2;$$

and

$$d_i^2 \equiv N_{y_i}^2 + N_{x_i}^2.$$

Minimization of S leads to calculated values of R_{y_i} and R_{x_i} (and hence to calculated values of y and x) and to values for the parameters appearing in either $y=f(x)$ or $x=g(y)$. But note that S is symmetric in x and y. Thus, the least-squares value of S will be independent of which form, $y=f(x)$ or $x=g(y)$, is employed. The importance of the weighted residuals in x to S may be conveniently estimated by the ratio S_x/S. This ratio will be zero when the observed and true values of x are assumed to coincide; then $\{\sigma_{x_i}\} \rightarrow \{0\}$, $\{w_{x_i}\} \rightarrow \{\infty\}$, $\{R_{x_i}\} \rightarrow \{0\}$, and $\{N_{x_i}\} \rightarrow \{0\}$.

When residuals are distributed normally and independently, as they frequently will be to good approximation, least-squares and maximum likelihood parameter estimates are identical (Draper and Smith, 1966, Section 10.2). Even when the errors are not normally distributed, Guest (1961) has pointed out that least-square estimates will almost always be adequate. In the linear situation, that where the functional relationship between x and y is linear in the parameters, least-squares parameter estimates will be unbiased—averages of the parameters obtained from continued replication of the experiment will approach their true values. Further, the Markoff theorem states that in this case, whatever the form of the error distribution function, the least-squares parameter estimates will be the best linear unbiased estimates (BLUE), those having the smallest possible variances.

Unfortunately, we will usually be dealing with functional relationships nonlinear in their parameters. Even when $y=f(x)$ is linear in the parameters involved, our minimization of Eq. (14), which involves the R_{x_i}, will in general introduce some over-all nonlinear parameter dependence. For this case, the usual statistical estimates will generally be at least somewhat biased (Draper and Smith, 1966). They may still be used in many situations as convenient approximations, nevertheless. Further, Wolberg (1967) has implied that unless the errors are very large, the usual expressions for the estimates are reasonable for most experiments, and he takes all such estimates as unbiased, provided the true errors are uncorrelated, a reasonable assumption. We shall use his expressions for the n parameters A_k, their standard deviations σ_{A_k}, and their correlations ρ_{lk}, with the expectation that these quantities and S itself will usually at least be good approximations to unbiased estimates of the quantities in question in cases where systematic errors are negligible and random errors relatively small.

It should be noted that although the true x and y errors may usually be assumed to be uncorrelated, the least-squares calculated residuals, say $\{N_{y_i}\}$ and $\{N_{x_i}\}$, will usually be highly cross correlated. This correlation is a necessary consequence of the form of the equation to be fitted. We have no way (without indefinitely replicating the experiment and also eliminating all systematic errors) to obtain true values of the errors; all we can do is minimize S and obtain a calculated (not-true) curve and estimated values of the parameters. Because of the correlation between the x and y residuals, little or no additional information is obtained by considering the individual residual sets $\{N_{y_i}\}$ and $\{N_{x_i}\}$ separately. In testing residuals for normality and autocorrelation, we shall therefore only consider the composite residuals

$$d_i \equiv (N_{x_i}{}^2 + N_{y_i}{}^2)^{1/2}\,\mathrm{sgn}\,(N_{y_i}).$$

Note that even when the measurements are stochastically independent and there are no systematic errors, the d_i's themselves will be correlated to some degree (Draper and Smith, 1966, Section 3.7) because of the n relations involving them arising from the least-squares determination of n parameters. There are N residuals but only $f \equiv N-n$ degrees of freedom.

Wolberg gives an expression for the ("unbiased") standard-error estimate of y, $s_f(x)$, which can be calculated for any x value. For simplicity, we shall, in the later curve-fitting work, routinely calculate s_f for only a few points within the experimental range: $X=0$ or X_1 if $X_1 \neq 0$, where $s_f \equiv s_0$; $X \cong X_{\max}/2$, where $s_f \equiv s_m$; and $X = X_{\max}$, where $s_f \equiv s_N$. It is important to note that the general expression for s_f may be readily evaluated for a given set of data and a given "model" (functional equation choice) at x values outside the experimental range. Thus, when it is desired to extrapolate beyond this range, the expected

error in the calculated y_i at any large x_i may be obtained and serves as a measure of the worth of the extrapolation *provided* the model is appropriate. Some equations of state will be far better for extrapolation than others; thus it is worthwhile to calculate s_f at $X = 100 X_{\max}$, where we define $s_f \equiv s_e$.

A valuable feature of S, according to Wolberg and Deming, is that its distribution function is a chi-squared distribution whose mean value is just the number of degrees of freedom, $f \equiv N-n$. Thus, we should find upon continued replication of the experiment that $\langle S \rangle$ (where $\langle\,\rangle$ denotes the mean value) should approach $(N-n)$. Although this result is apparently not quite correct in general, it is nevertheless frequently useful.

Equation (14) shows that S is made up of a sum of squares of the standarized variable d_i, as it should be to satisfy a chi-squared distribution. Further, there are $(N-n)$ degrees of freedom associated with this sum. It is necessary, however, for a sum of squares which satisfies a chi-squared distribution to be associated with a standardized variable whose mean is zero (Hald, 1952; Peng, 1967). But

$$\langle d \rangle \equiv N^{-1} \sum_{i=1}^{N} d_i \neq 0,$$

in general (see Deming, 1943, p. 182), although the sum will usually be very much smaller than $\langle d_i{}^2 \rangle^{1/2} \equiv d_{\mathrm{rms}}$. To evaluate the needed correction, define

$$M \equiv \sum_{i=1}^{N} (d_i - \langle d \rangle)^2,$$

a quantity which does indeed have a chi-squared distribution provided it can be transformed from a sum of N correlated squares to a sum of the squares of $(N-n)$ stochastically independent variables. Hald (1952, Section 10.6) shows how this may be done. It will not, of course, be possible in general if the measurements are not stochastically independent and/or systematic errors are present. Expansion of the sum for M leads to

$$M = S - \langle d \rangle^2 N \qquad (15)$$

on using Eq. (14). It is clear that when $S \gg \langle d \rangle^2 N$, as will usually be the case, S and M may be used interchangeably. Whenever this inequality is not well satisfied, however, one should use M instead of S in considering results associated with dependence on a chi-squared distribution. Although $M \cong S$ quite closely in much of the present work, we shall nevertheless use M rather than S since a slight gain of accuracy results. Because the variance of M is known to be $2f$, we expect the mean of M to be f and its standard deviation to be $(2f)^{1/2}$.

When the least-squares sum M is calculated for a given model and data set, yielding the value M_0, we will usually not find $M_0 = f \equiv N-n$. If we can be

satisfied that the measurements were stochastically independent and that no systematic errors were present (see below), M should nevertheless obey a chi-squared distribution. Although a value of M such as M_0 much different from f could arise from chance, when the probability of finding such a value is very low the result may indicate instead that, e.g., all the σ_{y_i}'s and σ_{x_i}'s were under or overestimated. Multiplying all these quantities by a constant c changes M proportional to c^{-2} but does not affect the estimated values of the parameters and their standard deviations.

The quantity M obeys a chi-squared distribution whose mean is f and whose median we shall term f_m. For $15 \leq f \leq 30$, $f_m \approx f - 0.66$, for example. Suppose we have a calculated value of M, M_0, available. Now let P_s be the two-tailed probability defined as follows. If $M_0 \leq f_m$, P_s is twice the single-tail probability (obtained from a table of the cumulative chi-squared distribution) of finding by chance an $M \leq M_0$, while if $M_0 > f_m$, P_s is twice the probability of finding $M \geq M_0$ by chance. As an example, for $f = 23$ and $M_0 = 9.26$ or 44.2, P_s would be 1%. It increases to 5% when $M_0 = 11.7$ or 38.1. Such low values of P_s would indicate a high chance that the scales of $\{\sigma_{y_i}\}$ and $\{\sigma_{x_i}\}$ were chosen incorrectly (possibly that of only $\{\sigma_{y_i}\}$ or $\{\sigma_{x_i}\}$ might be wrong, not both), and the most natural procedure would be to correct them using $\sigma_{\text{new}} = c\sigma_{\text{old}}$ and $c^2 = M_0/f$. This leads to a new M_0 equal to f. The resulting estimated σ_{x_i} and σ_{y_i} would then be likely to be more nearly correct than the original ones. Of course if, for example, $S_x/S \ll 1$, then only σ_{y_i} would be important in affecting S or M. The c correction would then only be pertinent for σ_{y_i}, and the values of σ_{x_i} whether right or (not too far) wrong would be unimportant.

Systematic errors (or bias) in the data have the effect that the average values of the measured variables do not approach the true values as the experiment is indefinitely replicated. This is because systematic errors, by definition, recur without change on replication, while stationary random errors average out. Systematic errors may lead to strong correlation between successive measured values and residuals and may then be discovered by an examination of the residuals. Even when they are absent (measurements stochastically independent), systematic errors arise if the model is poorly chosen. If the functional equation does not fit the data well after removal of any outlying residuals from stochastically independent data, the successive residuals will again show considerable correlation and the means of the estimated parameters will not approach their true values as the experiment is replicated and reanalyzed.

In this work, I shall be considerably concerned with both random- and systematic-error contributions to total uncertainty. Recent discussion of such contributions has been given by Eisenhart (1968). Since the numerical values quoted herein are always esti-

mates of the true values of the quantities considered, I shall generally omit the word "estimated" for brevity.

To assess the trustworthiness of the results of curve fitting, we shall examine the standardized residuals, d_i. First, they may be tested for approximate normality by plotting their cumulative distribution function on probability graph paper (Hald, 1952, Section 6.6); a straight line should result for normal data. Second, we may examine the residuals plotted versus x and assess randomness and possible correlation qualitatively. If $N - n \approx N$, the correlation among the residuals arising from the n relations involving them is negligible (Draper and Smith, 1966, Section 3.7), and we may be primarily concerned with correlation arising from systematic sources.

We may obtain an approximate quantitative measure of the correlation as follows. Let n_1 be the number of positive d_i residuals, n_2 the number of negative ones, and u the number of runs—successive residuals of the same sign. Draper and Smith (1966, Section 3.9) give a test based on given (measured) values of n_1, n_2, and u. But n_1 and n_2 as well as u have distributions of their own, and it seems preferable to consider the test based on a binomial distribution of u alone. Excluding zero values of the residuals, one sees that they may have only positive or negative signs; thus, the basic probability of the occurrence of either sign is $\theta_1 = 0.5$. For N residuals, there is actually a maximum of $N_1 \equiv N - 1$ zero crossings, g, or changes of sign of the residuals possible. When $N - n \approx N$, it will be an adequate approximation to ignore the correlations between residuals arising from the n relations mentioned earlier. Then, at least approximately, we may consider $g \equiv u - 1$ as following a binomial distribution with $\theta_1 = 0.5$ and with N_1 events. The mean of g is then $\langle g \rangle \equiv N_1/2$ and its standard deviation s_g is $(N_1/4)^{1/2}$. Suppose a particular value of u, u_0, is found experimentally. Let Π be the two-tailed probability that this u_0 occurred by chance. The value of $1 - \Pi$ for a value u_0 found in a least-squares fitting will then indicate the probability that important correlations are present and that u_0 did not occur by chance from an essentially uncorrelated set of residuals.

We may readily obtain Π from a table of the cumulative binomial distribution (National Bureau of Standards, 1950). Let Π_1 be the value obtained from this table on entering it with $g_0 \equiv u_0 - 1$, N_1, and $\theta_1 = 0.5$. Then because of the symmetry of the binomial distribution about its mean when $\theta_1 = 0.5$, $\Pi = 2\Pi_1$. As an example, if $u_0 = 18$ and $N_1 = 27$, one finds $\Pi \cong 24.78\%$, not an outstandingly high value. When $u_0 = 16$ and $N_1 = 27$, however, $\Pi = 70.11\%$, suggesting that correlation is probably unimportant in this case. For $N_1 = 27$ and $u_0 = 5$, on the other hand, one finds $\Pi \cong 4.9 \times 10^{-3}\%$, entirely negligible. In this case, where $u_0 \ll \langle u \rangle$, $\Pi = 2(1 - \Pi_1)$, rather than $2\Pi_1$.

Although the parameters will be biased and statistical measures such as S, standard deviations, and various probabilities will not be very trustworthy when systematic errors are present, or possibly even when the model is nonlinear in its parameters, we shall nevertheless list all such quantities derived from the curve fitting for comparison purposes. They will help us decide on the best model for a given purpose (interpolation, extrapolation, parameter determination, etc.) provided we are sufficiently careful in the interpretation and use of the calculated values.

B. Consistency of the Data

All of the equations of state considered in Sec. III involve P_0 through $p \equiv P - P_0$ and V_0 through such combinations as V/V_0 or V_0/V. At $p=0$, V/V_0 is unity by definition, and t and w are thus zero. The proper choice of P_0 and V_0 is a matter of considerable importance when different equations of state are to be considered. Herein, we shall always take $P_0=1$ atm $\cong 1.01325$ bar; thus, V_0 will be the most appropriate value of V at $P_0=1.01325$ bar, where $p=0$. How should V_0 be determined assuming it is not known exactly *ab initio*?

Consider a somewhat more general polynomial equation than (13), namely

$$y= \sum_{k=0}^{n-1} A_k x^k, \qquad (16)$$

where n is the number of free disposable coefficients and the pair (y, x) might be, e.g., (V, p), (V^{-1}, p), (p, V), or (p, V^{-1}). The four resulting equations are equivalent to those in Sec. III.F if $n=4$, except that there is here the loss of a degree of freedom because of the presence of the disposable parameter A_0. Further, note that least-squares fitting of Eq. (16) may be carried out either with the linear A_k's directly as they appear or with substitutions for them such as those of Table III where the β_0, η, θ parameters appear nonlinearly. The S value obtained should be the same for either approach. To determine the best V_0 let us consider fitting P-V data with Eq. (16), using one of the (y, x) combinations above. The data may or may not include a measured value of V_0 at $p=0$. If no value of V_0 was determined as part of the experiment yielding other V values, then clearly the V_0 most consistent with the rest of the data will be A_0 for the (y, x) choice of (V, p) and A_0^{-1} for the choice (V^{-1}, p). For the choices (p, V) and (p, V^{-1}), the most appropriate V_0 will be the pertinent root of the polynomial equation obtained by taking $p=0$ and $V=V_0$. If a measured value of V_0 of high expected accuracy is available from a different experiment, it can, of course, be used along with the P-V data in question provided the $P=P_0$ and $V=V_0$ values added to the data are weighted separately using appropriate weights generally different from those for the other points.

Unfortunately, when (p, V) or (p, V^{-1}) are used in (16), a good least-squares fit is difficult to obtain because of the high correlation between the A_k parameters introduced by these forms of (16) where the range of variation of V is much more limited than that of P. This difficulty may be avoided by instead using the choices (p, t_a) and (p, w_a), where $t_a \equiv (V_a-V)/V_a$, $w_a \equiv (V_a-V)/V$, and V_a is an estimated fixed value of V_0. The final consistent value of V_0 is then again determined as the zero of a polynomial. For example, for the choice (p, t_a) the equation for finding the root would be of the form

$$0=A_0+A_1[(V_a-V_0)/V_a]$$
$$+ \cdots +A_{n-1}[(V_a-V_0)/V_a]^{n-1}.$$

The real root nearest V_a would be the one to choose for V_0 unless the original choice of V_a had been very poor. A first-order approximation for the root is sufficient when V_a is well chosen. Note that when a change of variable is made, consistent weighting must be used, as discussed in detail later, in all determinations of V_0 and subsequent curve fitting to allow consistent comparisons. For example, if $\sigma_V(p)$ is the appropriate weighting (through $w_V \equiv \sigma_V^{-2}$) for the V variable, then that for V^{-1}, $\sigma_{V^{-1}}$, would be $V^{-2}\sigma_V$, that for the w variable would be $(V_0/V^2)\sigma_V$, and that for t would be $V_0^{-1}\sigma_V$. The expressions for $\sigma_{V^{-1}}$ and σ_w only apply accurately when $\sigma_V/V \ll 1$. This inequality is well met for all the data considered herein, and the above relations will thus be employed as appropriate.

In order to obtain best estimates of the Davis–Gordon equation or Slater equation A_i $(i>0)$ parameters, one may first find V_0 accurately as above, then carry out a second fitting of the data with the equation in question, making use of the V_0 value obtained from the first fitting in forming the t or w employed in the second fitting. This three-step procedure may sometimes be avoided at the cost of considerably increased parameter nonlinearity of the fitting equation and consequent possible difficulty in obtaining convergence to the least-squares solution. Again use w_a or t_a for the Davis–Gordon equation or Slater equation, respectively, but take the V_a involved in w_a or t_a as a free parameter itself whose final least-squares value will be the best estimate for V_0. In addition, do not introduce A_0 at all. Then V_a takes the place of A_0; the number of degrees of freedom will be the same; and the best value of V_0 will be obtained directly if convergence is achieved. Note that with this procedure only σ_V need be introduced, not σ_w or σ_t, and the calculated R_{x_i} will be residuals of V_i. This approach will be simplest when good initial approximations of the parameters are known, making convergence quicker and more likely. When this is not the case, the above free-A_0 procedure is a better choice; it will be frequently used herein.

We have discussed two procedures above. In one, in order to aid convergence we introduce a change of variable, a free A_0 parameter, and a fixed V_a, and finally obtain a best estimate of V_0 indirectly. In the other, no A_0 is introduced (it may be taken fixed at zero) and V_a is a free parameter whose least-squares value gives V_0 directly. The latter method is preferable when convergence will not be greatly slowed thereby. For example, it may be readily used for the Bridgman equation or Inverse Volume equation by taking the V_a in t_a or w_a free. Finally, there will be equations where the two situations coalesce and no change of variable is necessary. We can then introduce a free A_0 parameter whose initial value is V_a and whose final least-squares value is the best estimate for V_0. Thus, the Murnaghan equation may be written $V = A_0(1 + \eta\beta_0 p)^{-1/\eta}$. Of course if it is desired to obtain results in terms of the conventional variable V/V_0 rather than V, then the best estimate of V_0 may be found from a preliminary fitting and used to obtain results pertinent to V/V_0. For example, a further fitting of the equation may be carried out using the new variable V/V_0, with proper normalization achieved through the use of the best estimate of V_0 in forming V/V_0.

The V_0's obtained from fittings with various equations of state will not in general be exactly equal. The V_0 obtained from the best-fit equation is, by definition, the value most consistent with the rest of the data. Thus, in comparing the appropriateness of various equations of state for the same data it is important that V_0 values be found from fitting the data with each equation separately. Biased comparisons will be obtained, for example, if in the usual way one uses a single, inconsistent, fixed V_0 for the V/V_0 variable employed in all fitting. For any equation fitted using an inconsistent V_0, the resulting least-squares parameters will be systematically biased and will be likely to be less accurate than those obtained using the above procedure. This difficulty seems to have shown up in Kell and Whalley's (1965) fitting of their water data (all temperatures) using the 3BE. It possibly explains the strongly nonzero residual averages apparent in most of their individual runs at constant temperature. The appearance of a nonzero residual average $\langle d \rangle$ is a general consequence of least-squares fitting of any equation which lacks a disposable A_0 type of parameter, unless the normalization is made consistent as above.

When the data does include a measured value of V at $p = 0$, say V_{0m}, the same fitting of a given equation with a free A_0 or V_a parameter may be carried out as before. It is unlikely, in general, that the V_0 obtained from such fitting will equal V_{0m}. Nevertheless, V_{0m} should be retained as part of the data in any subsequent fitting involving the variables V/V_0, w, or t, and V_0, not V_{0m}, should be used for normalization. Note that when a free A_0 is introduced

its standard deviation is equal to the s_f value at the point $(V_0, 0)$.

When A_0 or V_a is a disposable parameter, it is of course counted in determining f, the number of degrees of freedom. When the most appropriate V_0 has been obtained for a given equation and is then used for normalization in an equation involving the variable V/V_0, no free parameter of the A_0 type explicitly appears in the conventional approach, and A_0 is replaced by either unity or zero depending on the variables used and the form of the equation. Clearly, were the equation fitted with the addition of a *free* parameter of the A_0 type in place of the fixed constant, one would obtain just unity or zero for this parameter as the case might be. Thus, the unity or zero actually used in the equation when V_0 is chosen consistently and A_0 is not free is really effectively free, not fixed. The number of degrees of freedom will then be the same as that in the situation where a free A_0 or V_a explicitly appears. As we shall see later, however, even using the proper value of f and the most consistent V_0 by no means eliminates further difficulties inherent in the usual approach which takes V/V_0 as a dependent or independent variable and involves no free parameter of the A_0 type. For simplicity, subsequent reference to the A_0-free situation should be understood to include the related alternate situation where V_a rather than A_0 is free.

Since the standard deviation (s.d.) of the residuals is probably the most significant single quantity for comparing various models and equations of state, its definition and calculation is worth especial examination. The usual definition of the s.d. for a residual set $\{d_i\}$ is $s_d' \equiv (S/f)^{1/2}$. But remember that $\langle d \rangle \neq 0$ in general, especially when A_0 is not free. Now the s.d. is a measure of the absolute magnitude of the residuals, and M may be quite different from S when $\langle d \rangle \neq 0$. Rather than have the usually unknown effect of $\langle d \rangle \neq 0$ melded into the s.d. as it is in s_d', it seems far preferable to define $s_d \equiv (M/f)^{1/2}$, which is based on squares of $(d_i - \langle d \rangle)$ and quote $\langle d \rangle$ separately when it is significantly different from zero. Of course, when $\langle d \rangle = 0$, s_d' and s_d are identical.

Three situations need to be considered. First, if A_0 is free, s_d and s_d' are given as above. Note that $s_d \neq [M/(f-1)]^{1/2}$ here since the loss of a degree of freedom associated with $\langle d \rangle$, which is itself involved in M, is the same loss as that associated with A_0 and should not be counted twice. Second, consider the case where A_0 is *fixed* at some value not known to be the "best" value, that which would be found in the first case above. Then, although f is numerically increased by unity over that of the first case, s_d' is formally still given by $(S/f)^{1/2}$. On the other hand, the loss of the degree of freedom in M arising from the presence of $\langle d \rangle$ is not now counted in f, and we here must use $s_d = [M/(f-1)]^{1/2}$. Note that the $(f-1)$ in this case is numerically equal to the f of the first case. Finally,

when A_0 is fixed at its "best" value as above, f is again increased by unity over the free case but A_0 is really (known to be) effectively free. Thus, here we should use $s_d' = [S/(f-1)]^{1/2}$ and $s_d = [M/(f-1)]^{1/2}$, numerically equal to the results obtained in the free-A_0 case.

If σ_y and σ_x are chosen correctly and there is no bias, one should obtain $M = f$ on the average, and $s_d = 1$ in the usual situation of A_0 free. We may express the rms value of the d_i's as

$$d_{\mathrm{rms}} \equiv (N^{-1} \sum_{i=1}^{N} d_i^2)^{1/2} = \left(\frac{S}{N}\right)^{1/2},$$

nearly equal to s_d' when $f \approx N$ and also to s_d in the usual situation considered herein where $\langle d \rangle \cong 0$ and $M \cong S$. Finally, rather than use $\langle d \rangle$ when it is appreciably different from zero, the normalized quantity $\lambda \equiv \langle d \rangle / d_{\mathrm{rms}}$ is more significant.

If $\{d_i\}$ involves only random errors and is normally distributed, there is only a 0.27% chance that a given $|d_i|$ will exceed $3s_d$. Anscombe and Tukey (1963) have given a rejection rule for outliers which, for $N = 27$ and $f = 23$ for example, leads to rejection of the residual of largest magnitude provided it exceeds about $2.6s_d$. When a residual has thus been rejected, the analysis is repeated without the associated data point and the same rejection rule applied again, etc. This rule is based on a premium of 2.5%. That is, if a residual is rejected which really belonged to the distribution followed by the other residuals (and hence should not have been rejected), then the average error variances of the parameters would be increased by 2.5%. In the following work, we shall apply this rule where applicable and determine final V_0's only from data adjusted by this procedure.

Finally, in order to compare with ordinary least-squares results, we shall sometimes wish to take either σ_{x_i} or σ_{y_i} zero and choose the nonzero one equal to unity. Such a unity value does not, however, imply that the real σ_{x_i} or σ_{y_i}, the best estimate for the standard deviation of a single measurement of X_i or Y_i (or of the standard deviation of the average value of X_i or Y_i when the data are averages of individual measurements), is unity. This choice is merely a convenience to reduce the present procedure to ordinary unweighted (strictly, unity-weighted) least squares. It only does so, however, when the σ taken as unity applies to the dependent variable. Further, in the ordinary least-squares situation with unity weighting, the expected value of M will not be f. Generalized least squares, unlike simple least squares, allows unity weighting (or any other weighting) to be applied to either the dependent or independent variable. When the unity choice is made, the resulting s_d or s_d' is the ordinary least-squares standard deviation of the fit for the pertinent variable.

What is the pertinent variable, however, in the

present situation where we have taken pains to use appropriate transformed weighting, σ_w when w is one of the variables, σ_t when t is used, etc.? Consider first the situation where $\sigma_p = 1$ and $\sigma_V = 0$. Then $R_{V_i} = 0$ and $R_{p_i} = N_{p_i} = (p_i)_e - (p_i)_c$, where the "e" and "c" subscripts stand for "experimental" and "calculated." Thus, s_d obtained with this weighting from a Bridgman equation, Inverse Volume equation, Slater equation, or Davis–Gordon equation fitting, for example, will measure the random error (if the model is appropriate and systematic errors in the data are negligible) of p and P.

The situation is slightly more complex when $\sigma_p = 0$ and $\sigma_V = 1$. Consider, for completeness, a relatively general transformation of y or x. Take, for example, $\xi \equiv f(x)$, where $f(x)$ is a transformation having a finite, nonzero first derivative df/dx for all x of interest. For simplicity, denote experimental x and ξ values as x_{ei} and ξ_{ei} and calculated values as x_{ci} and ξ_{ci}. Now let $\delta_i \equiv x_{ei} - x_{ci}$; then $N_{x_i} = \delta_i / \sigma_{x_i}$. Further, provided* $|\sigma_{x_i}/x_i| \ll 1$ for all i's, $\sigma_{\xi_i} \cong |d\xi/dx|_{x_{ei}\sigma_{x_i}}$. We now wish to calculate $N_{\xi_i} \equiv (\xi_{ei} - \xi_{ci})/\sigma_{\xi_i}$ in terms of x_i. To do so we use the expansion around x_{ei}, $\xi_{ci} \equiv f(x_{ci}) = \xi_{ei} - \delta_i(d\xi/dx)|_{x_{ei}} + o(\delta)$, and find, to first order in δ

$$N_{\xi_i} \cong \frac{\delta_i(d\xi/dx)|_{x_{ei}}}{\sigma_{x_i} |d\xi/dx|_{x_{ei}}} = N_{x_i} \operatorname{sgn}\left[\left(\frac{d\xi}{dx}\right)\Big|_{x_{ei}}\right],$$

provided $|\sigma_{x_i}/x_i| \ll 1$. Except for possible changes in sign, we see that $N_{\xi_i} \cong N_{x_i}$. For all at least reasonably good fits, the neglect of $o(\delta)$ and the condition on $|\sigma_{x_i}/x_i|$ will be well met. Further, for the present sort of data, when $x_i = V_i$, $d\xi/dx$ will be bounded and nonzero for all transformations of interest.

Now when $(y, x) = (V, p)$ or (p, V) and $\sigma_p = 0$, $\sigma_V = 1$, $R_{V_i} = N_{V_i} = V_{ei} - V_{ci} \equiv \delta_i$, as expected. The above general results show that, in addition, when $(y, x) = (t, p)$, (p, t), (w, p), or (p, w), we find $N_{t_i} \cong N_{w_i} \cong -N_{V_i} = -\delta_i$. Thus, in all cases of interest when t or w is used as a variable with the above weighting choice, s_d and s_d', which are formed from the N_{ξ_i} alone for this weighting, refer to the V_i variable just as in the $(y, x) = (V, p)$ or (p, V) case. These results are convenient since they allow us to compare directly s_d values obtained from all the polynomial equations considered with those obtained when $(y, x) = (V, p)$, as for the Murnaghan equation and other nonlinear equations. Note that although the s_d's all refer to the V_i variable, they will be obtained from fittings with different equations and may thus be expected to differ in general for this reason alone.

Although direct replication of a data set is the

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* This is an approximate condition, adequate for the transformations considered herein. C. A. Barlow (private communication) has shown that if $G(x) \equiv |\ln[|(df/dx)/(df/dx)_0|]|$, a more general approximate condition is $\sigma_{x_i}(dG/dx)_{x_i} \ll 1$. More exactly, he shows that it is sufficient to require that the variance of $G(x_i)$ for any fixed value of i be much less than unity.

best way to allow the consistency of the data to be determined and appropriate values for σ_{x_i} and σ_{y_i} selected, another less ideal method is available when no replicated data are available. This is the method of partitioned data (Monfort and Swenson, 1965; Macdonald, 1966). A given data set is divided into two or more subsets and each used separately in curve fitting. For example, one might separate the data into the first half and the last half or the even data points and the odd ones. If systematic errors are absent from the data, if the model is appropriate, and if random errors are not extreme, one would expect quite stable parameter values to result from the fittings; thus a given parameter value obtained from a subset should be close to the corresponding value obtained by fitting the complete set. Unfortunately, this method confounds the effects of systematic errors in the data and in the choice of the model. It can show that something is wrong but not always what is wrong.

The above procedure is particularly important when one desires to combine two quite different data sets. Suppose, for example, one has available static $P-V$ results for a given temperature and covering a relatively limited pressure range and, as well, shock-wave results reduced to the same temperature, thus isothermal. Although the transformed shock-wave data will cover a much higher pressure range, they will almost certainly be far less accurate and precise than ultrasonic or static data. It would be quite improper, therefore, to throw the static and dynamic data sets together and do ordinary unweighted (unity-weighted) least-squares fitting. Rather, generalized least squares should be used with appropriate weightings for each X_i and Y_i value of each data set. Such weighting, if properly selected, will compensate for the great difference in accuracy of the two sets and will make it reasonable to combine them. In addition, one should carry out fitting of a given equation of state separately with each such weighted set. The results obtained from the two separate sets and the combined set should all give the same parameter results quite closely, provided there are no systematic errors in the data or any arising because the equation examined is inappropriate. It is strongly recommended that this procedure be followed when combining shock wave and other data sets for subsequent analysis. One can then determine quantitatively how well a single equation fits both sets.

V. APPLICATION TO WATER

A. Previous Work

A detailed nonlinear-least-squares statistical curve-fitting comparison of the Usual Tait equation and the Murnaghan equation for Bridgman (1935) water data (0–12 000 kg/cm²) was carried out by Macdonald

(1966). It showed the Murnaghan equation to be generally superior to the Usual Tait equation for water except possibly at temperatures near 100°C. At the time this work was done, the extensive statistical study of Ginell and Ginell (1965) of water using the Usual Tait equation was unknown to the author. Unfortunately, the Ginell study uses the old Tait parameters and a cumbersome statistical method. The standard errors of the results for the Tait parameter B (termed C by the Ginells) are very large and for some data implausible negative values of B are obtained. Thus the weight assigned to this study cannot be large.

Eckart (1958) and Hayward (1967) have both applied the Tumlirz, or LSME, to the analysis of water data. Eckart found reasonably good fitting of several sets of quite ancient data but did not carry out a true statistical least-squares analysis of the data. Hayward, using the modern, apparently very precise and accurate data of Kell and Whalley (1965) covering the range from 0–1 kbar, contented himself in showing that $K_2(p)$ was closely a linear function of p and in making somewhat unsupported statements based on this result. However, he apparently used Kell and Whalley's interpolated data based on (at each temperature) a Bridgman equation fitting rather than the original $P-V$ data which were used by Kell and Whalley to obtain their equation-of-state parameters. Thus, his conclusions possibly apply to this series equation of state more than to the water data.

Finally, Li (1967) has recently carried out a painstaking analysis of a variety of water compression data using the Usual Tait equation in the form of Eq. (1). Unfortunately, this is also not a least-squares statistical analysis. What is more, Li fixed one of the UTE parameters, C, at the value 0.3150 found long ago by Gibson and Loeffler (1941). He uses this value for all data sets at all temperatures even though there is no longer justification for a constant value of C (see Cutler, McMickle, Webb, and Schiessler, 1958; Macdonald, 1966; and Hogenboom, Webb, and Dixon, 1967), and a statistical study (Macdonald, 1966) had already demonstrated, at the time Li wrote his paper, that much higher fitting accuracy could be obtained using the Usual Tait equation for water with C (actually r) temperature dependent.

Using $C=0.3150$, Li goes on to calculate the old Tait parameter B for virtually every $P-V$ point available in every data set he examined. On averaging those B's which remain relatively constant within the range 0.4 to 1.0 kbar, he finally obtains analytical expressions for B as a function of temperature. The temperature dependence of β_0 instead of B would have been much more significant; further, the apparently arbitrary omission of many data points, the lack of least-squares determination of the C and B coefficients, and the very considerable differences between the results obtained from different

data sets, renders the results of dubious value. There are, apparently, mistakes in some of the B-vs-temperature results: Except for the first term the $B(T)$ expressions following from the data of Amagat ($T \geq$ 45°C) and Newton and Kennedy ($T \geq 25$°C) are exactly the same (to the four figures given of each constant).

Although Li makes no comparison between his B values and those obtained earlier by any other authors such as Gibson and Loeffler (1941) and Ginell and Ginell (1965), he does attempt to show that the Murnaghan equation is not as applicable for water as the Usual Tait equation. To do this he uses two sets of Bridgman's data [neither set was the full one used by the author (1966), and the origin of one set was not stated]. Again using $C=0.3150$, he finds B values generally somewhat higher than those following from the other sets of data analyzed. Because of the restrictive choice $C=0.3150$ and the lack of even a one-parameter least-squares fitting, these results scarcely allow one to dismiss these Bridgman data and certainly do not bear on the relative applicability of the Murnaghan equation and the Usual Tait equation. The present author's previous comparison, using Bridgman data which covered a much higher pressure range, remains reasonably valid, although a much improved treatment of better data is given herein.

In addition, Li endeavors to show the inapplicability of the Murnaghan equation relative to the Usual Tail equation by using the ancient P-V water data of Ekman (1908) which has been criticized by Eckart (1958). Using β_0 values which were derived from direct, low-pressure sound-velocity measurements, Li calculates η for several pressures in the range $0.2 >$ $p > 0.6$ kbar and finds a systematic variation of η of 4% to 8% over this range. Little or no such pressure dependence should occur if the Murnaghan equation were indeed applicable and random and systematic errors in the data sufficiently small. As we shall see below, the Murnaghan equation is indeed not the best-fitting equation of state (although it is superior to the Usual Tait equation); the errors in the Ekman data are probably by no means negligible in such a calculation of η; and finally it is inappropriate to neglect the probable errors in β_0 as Li's procedure does. Better measures of the precision of η obtained from analysis of more precise and accurate water data are presented later.

B. Weighting of Data

We shall first illustrate the analysis methods described above and investigate equation-of-state applicability using the 0°C P-V data of Kell and Whalley (1965). These authors have been extremely careful and painstaking in attempting to identify and eliminate or reduce all sources of systematic error in their experiment. The largest likely contributor is un-certainty in the density of Hg under pressure, a quantity calculated using an equation of state, and thus not a contributor itself to random error. When better density data becomes available, the Kell–Whalley water data can be readily improved. For the 0°C data, $N=27$ and V_{0m} did not exist as a part of the measurements. The maximum pressure applied was about 1000 bar and the minimum V was about 0.95. Values of V were given to six decimal places. In order to eliminate round-off errors which would otherwise appear (Macdonald, 1964), all calculations described below were carried out on a digital computer using double-precision arithmetic involving the equivalent of approximately 13 decimal digits.

In this section, we shall be primarily discussing the determination of the most appropriate V and p weighting, the search for and elimination of any outliers, and the determination of the most appropriate V_0 for each equation of interest. Although V_{0m} was not measured directly by Kell and Whalley along with their $p > 0$ measurements, the derivation of their V values from the basic measurements did involve the choice $V_0 = 1.0001604$ (Kell, 1967; Bigg, 1967). Nevertheless, to make the final equation-of-state comparision as unbiassed as possible, I shall use not this V_0 but the V_0's arising from initially fitting the equations with disposable A_0 parameters, as discussed in Sec. IV.B.

Weighting of X_i and Y_i data values should properly be based upon the most likely random error expected for each individual X_i and Y_i measurement. These standard-error values should ideally be determined by repeated replication of the experiment. Further, replication should not only be used to obtain estimated values of the standard deviations of the individual measurements for weighting; the data obtained should then be melded together and used in the generalized least-squares analysis. Since Kell and Whalley give no replicated 0°C data, we shall base the weighting on their statements of accuracy of the measurements and on the random sources of error listed in their extensive error analysis table. Let Z stand for either p or V. Then at the σ_Z level, the random errors considered are of two types: (a) those which are independent of pressure, H_Z in magnitude, and (b) those depending linearly on pressure, ($E_Z +$ $F_Z p$). The sources of these types of errors, as listed by Kell and Whalley, suggest that they are stochastically independent of one another. Thus, we may write

$$\sigma_Z{}^2 = H_Z{}^2 + (E_Z + F_Z p)^2 \qquad (17)$$

as the general form for $\sigma_p{}^2$ and $\sigma_V{}^2$.

In a conventional least-squares analysis, such as that used by Kell and Whalley, $\sigma_p = 0$ and $\sigma_V = H_V$, a constant usually taken as unity. It turns out that the H_V value which causes the 3BE M_0 to be essentially f is 2.48×10^{-6}. We shall designate this choice

Table IV. Least-squares results for water at 0°C with A_0 disposable and different weightings.[a]

Equation-weighting	M	S_p/S	u	A_0	s_0	s_m	s_N	s_e
	s_d	$P_s(\%)$	$\Pi(\%)$	r_{A_0}	r_{A_1}	r_{A_2}	r_{A_3}	r_{A_4}
4BE-A	22.18	0	18	1.00015973	1.27×10^{-6}	9.61×10^{-7}	2.15×10^{-6}	8.80×10^8
	1.004	90	17	1.35×10^{-6}	4.77×10^{-4}	1.30×10^{-2}	2.08×10^{-1}	1.15
3BE-A	22.95	0	16	1.00016037	1.08×10^{-6}	9.43×10^{-7}	1.88×10^{-6}	2.33×10^1
	0.9988	93	56	1.12×10^{-6}	2.60×10^{-4}	3.99×10^{-3}	2.36×10^{-2}	...
3BE-B	9.389	16	14	1.00016012	8.99×10^{-7}	8.90×10^{-7}	2.75×10^{-6}	2.58×10^1
	0.6389	1.1	85	9.41×10^{-7}	2.49×10^{-4}	4.16×10^{-3}	2.65×10^{-2}	...
3DGE-B	8.994	16	13	-1.20×10^{-2}	1.82×10^{-2}	1.83×10^{-2}	6.81×10^{-2}	5.69×10^5
	0.6253	0.8	56	1.60	2.97×10^{-4}	8.43×10^{-3}	3.15×10^{-2}	...
3BE-C	23.76	35	13	1.00015987	7.91×10^{-7}	8.80×10^{-7}	3.55×10^{-6}	2.83×10^1
	1.016	84	56	8.32×10^{-7}	2.44×10^{-4}	4.35×10^{-3}	2.93×10^{-2}	...
3DGE-C	22.46	35	15	-1.69×10^{-2}	1.58×10^{-2}	1.78×10^{-2}	8.68×10^{-2}	6.15×10^5
	0.9881	99	85	9.90×10^{-1}	2.84×10^{-4}	8.70×10^{-3}	3.35×10^{-2}	...

[a] A weighting: $\sigma_p = 0$; $\sigma_V = 2.48 \times 10^{-6}$; B weighting: $\sigma_p{}^2 = (10^{-2} \text{ bar})^2 + (10^{-4}p)^2$, $\sigma_V{}^2 = 5 \times 10^{-12} + (2 \times 10^{-6} + 2 \times 10^{-9}p)^2$; C weighting: $\sigma_p{}^2 = (1.5 \times 10^{-2} \text{ bar})^2 + (10^{-4}p)^2$, $\sigma_V{}^2 = 10^{-12} + (10^{-6} + 2 \times 10^{-9}p)^2$.

as weighting A. On the other hand, the Kell–Whalley error table, supplemented by correspondence with Kell, suggests the following values (weighting B): $H_V \sim 5^{1/2} \times 10^{-6}$, $E_V \sim 2 \times 10^{-6}$, $F_V \sim 2 \times 10^{-9}$ bar^{-1}; $H_p \sim 10^{-2}$ bar, $E_p \sim 0$, and $F_p \sim 10^{-4}$.

Table IV shows the results of a further search for the most appropriate weighting for the 0°C data. The search has been carried out on the basis that the 0°C data set is a representative sample of the universe of all possible 0°C sets, since this is the most reasonable hypothesis to make when only a single set is available, as is frequently the case. Although evidence obtained by fitting some of Kell and Whalley's $T>0$°C data sets (see Sec. V.D) suggests that the 0°C set has lower inherent residuals than the others, we shall nevertheless adjust the weighting to yield $M_0 \sim f$; an exact equality is unnecessary here since the standard deviation of the chi-squared distribution is $(2f)^{1/2}$, relatively large for $f \sim 25$. The above adjustment will still serve an illustrative purpose and, further may be expected to lead to weighting and results more appropriate than those of weighting A.

The Kell–Whalley $T>0$°C data contain a few P-V sets which are essentially replications at the same, or virtually the same, temperature. Residuals derived from fitting two such sets are found to be highly correlated; thus, one must conclude that the Kell–Whalley data contain some systematic as well as random errors. In subsequent work, I hope to apply a statistically valid approach to eliminate or greatly reduce this type of systematic error in all the $T \geq 0$°C

data. For the present, the available data are still apparently appreciably more precise and accurate than any other data available and thus allow better discrimination between various equations of state. Further, it turns out that the systematic error in the 0°C set does not keep the residuals from being normally distributed and essentially random. Thus, for a given run the residuals for that run may still be considered random even though they contain "random" errors which would reappear unchanged upon replication and which are thus actually systematic. This type of error will be termed "random systematic."

In Table IV the A_0 parameter was free and adjustable throughout. To determine the most appropriate weight I decided to employ the Bridgman equation and the Davis–Gordon equation, since these two equations allow comparison of, respectively, σ_V and the s_f's for the V-fit, and σ_p and the p-fit s_f's. In order to exhibit V_0 directly, the BE fits in the table were carried out with the (y, x) pair taken as (V, p); then, $A_0 = V_0$ and, contrary to the case when (t, p) is used, no V_a needed to be introduced. Row 1 shows some of the results obtained for the 4BE with A weighting. All headings have already been defined except the r_{A_k}'s which are the relative standard deviations of the A_k parameters. No results for normality are shown in the table because all fittings included in it led to good normality of the residuals. Further, there were no d_i outliers present in the fittings of Table IV which needed to be eliminated; for example, $\max |d_i/s_d|$ was 2.0 for Row 1 and 2.2 for Row 2.

Table V. Sum of squares M and number of runs u for various equations obtained with A_0 free and with C weighting: $\sigma_p{}^2 = (1.5 \times 10^{-2} \text{ bar})^2 + (10^{-4}p)^2$; $\sigma_V{}^2 = 10^{-12} + (10^{-6} + 2 \times 10^{-9}p)^2$.

Equation	M/u	Equation	M/u
2SE	2479/4	4BE	21.04/20
2BE	1232/4	4IVE	20.94/20
2DGE	894.5/4	4DGE	19.62/20
2IVE	217.4/6	4SE	19.50/20
3IVE	27.89/13	UTE	517.1/4
3BE	23.76/13	ME	357.9/6
3DGE	22.46/15	LSME	95.25/6
3SE	19.64/20	SOE$_0$	90.67/6
4*SE	76.08/9	SOE$_2$	27.14/13
4*DGE	55.07/9		
4*BE	32.46/14		
4*IVE	21.31/18		

The results of Row 1 are far from ideal, both because the probability Π of 18 runs occurring by chance is low and because the relative standard deviations of A_3 and A_4 are too high for comfort. Similar results were obtained with the 4DGE. Therefore, further analysis was carried out using as appropriate models the 3BE and 3DGE; the 2BE and 2DGE gave completely inadequate fits showing great systematic error. Note the improvement in the results of Row 2 over those of Row 1. Since neither the Bridgman equation nor the Davis–Gordon equation is adequate for extrapolation, we find very large values of s_e as expected.

Rows 3 and 4 show the results of fits using B weighting. It is immediately apparent from the low values of M that the constants in this weighting are too large if this data set is representative. If so, P_s shows that there is only about a 1% chance of obtaining these values of M, which are about two standard deviations of f smaller than f. Since there is a multiple infinity of ways of changing the constants in the expressions for σ_V and σ_p which will lead to $M \approx f$, I chose to guide and limit the choices by applying a simple, arbitrary criterion as an illustration of possibilities. The criterion for the 3BE is that a change in $\sigma_V(p)$ which leads to $s_f(p)$ values closer to the changed $\sigma_V(p)$ is desirable. Similarly for the 3DGE, any change in $\sigma_p(w)$ which results in $s_f(w)$ values closer to the changed $\sigma_p(w)$ is desirable.

The nonzero value of A_0 found in Row 4 for the 3DGE indicates that the estimated V_0, $V_a = 1.0001604$, used in forming the w_a variable of the DGE is not completely consistent with the data for the equation. The consistent V_0, obtained as a polynomial zero, will be listed later.

The s_0, s_m, and s_N values in the table are associated, respectively, with $p \cong 4.29$, 268, and 1025 bar. For B weighting, the corresponding σ_V values are 3.01×10^{-6},

3.38×10^{-6}, and 4.63×10^{-6}, while the σ_p values are 1.00×10^{-2}, 2.86×10^{-2}, and 0.103 bar. Comparison of corresponding σ and s_f values for Rows 3 and 4 indicates that the σ_V values are too large and that H_p is probably too small.

In order to bring closer agreement between the assumed weightings and the resulting s_f's, several different weightings were investigated which would lead to $M_0 \sim f$. It was found that the σ_V weightings were fairly dominant in determining both the $V s_f$'s and the $p s_f$'s—that is, changes in σ_p produced less change in the $p s_f$'s than did changes in σ_V. Thus, major changes in weighting were confined to σ_V. Further, no effort was made to achieve exact equalities or to change the form of the weightings. The C weighting used for the runs of Rows 5 and 6 was found to yield appreciably improved results, however, and will therefore be used in the subsequent analysis. It is defined by $H_V = 10^{-6}$, $E_V = 10^{-6}$, $F_V = 2 \times 10^{-9}$ bar^{-1}, $H_p = 1.5 \times 10^{-2}$ bar, $E_p = 0$, and $F_p = 10^{-4}$.

For C weighting, the σ_V values are, in the same order as above, 1.42×10^{-6}, 1.83×10^{-6}, and 3.21×10^{-6}, while the σ_p values are 1.5×10^{-2}, 3.07×10^{-2}, and 0.104 bar. Comparison with the corresponding s_f's of Rows 5 and 6 will show the improvement achieved. Although there are some significant changes in the r_{A_k}'s as the weighting is changed, probably the most significant changes occur in S_p/S and in the s_f values. For the present data (but not in general), it turns out that the actual differences in the A_k's themselves found on going from A to C weighting are well within the A_k standard deviations. Nevertheless, the 35% S_p/S value found with C weighting, or even the 16% following from B weighting, indicates that random errors in the P measurements should not be neglected here, and that generalized least-squares analysis is more appropriate than ordinary least squares.

It should be especially emphasized that if the σ_V and σ_p B weighting had been changed by multiplying both weightings by a constant c, it would have been possible to achieve $M_0 \sim f$, but the B-weighting s_f's would have remained unchanged. Although the change would have brought σ_V values closer to the $V s_f$'s, they would not be as close as they are with C weighting. Further, the concomitant reduction in σ_p would have caused the s_0 associated with p to be even further from the corresponding σ_p than it is with B weighting. Thus, to achieve a maximum degree of agreement between σ_V and σ_p and the corresponding s_f's, a much greater relative change in σ_V than in σ_p was required. It is, of course, this essentially forced change which leads to the high S_p/S value found with C weighting.

C. Comparison of Equations

Table V shows generalized least-squares results for M and u for most of the equations of state discussed

herein. The Kell–Whalley 0°C data with $N=27$ and C weighting were used with A_0 a disposable parameter. Incidentally, the use of A or B weighting, rather than C, would not have changed the ordering in M shown in Table V. The dependent variable of all the nonlinear equations was V/V_0, as in Table I.

The first set of four equations, with $n=3$ and very low u values, clearly involves too simple models. In the third set, the asterisk indicates that the third-order term x^3 in each equation has been omitted; the number of degrees of freedom, 23, for each equation of this set is thus the same as that for each of the equations of the second set. Note that of the lass five equations on the right, the nonlinear equationt of state, only the SOE$_2$ is comparable to the best of the polynomials. Of the eight simpler equations with $f=24$, only the nonlinear LSME and SOE$_0$ have M values below that of the best polynomial of this class, the 2IVE. Finally, the very considerable improvement achieved using the Second-Order equation as q goes from zero (the SOE$_0$) to its best free value (the SOE$_2$) is evident. Nevertheless, it appears that even the nonlinear SOE$_2$ is not quite as good a model within the range of the data as some of the simple polynomial equations.

Table VI presents more detailed results for some of the equations of most interest. Here we have employed an improved conventional approach in order to illustrate its inherent deficiencies while at the same time allowing comparison of the fitting capabilities of the various equations. In the usual approach, V/V_0 is used as a variable, no free parameter of the A_0 type appears, and V_0 is a constant taken the same for all equations compared using a single data set. The improved approach illustrated by the results of Table VI and applicable when V_0 is not known exactly uses for normalization the most consistent V_0 found separately for each equation, takes A_0 zero but removes an otherwise present degree of freedom because of the introduction of the most consistent V_0, and uses weighting appropriate for the volume variable (V/V_0, t, or w) employed so that all M's and s_d's are directly comparable. Incidentally, the r_{V_0} values shown in the table are, of course, obtained not from an $A_0=0$ run but from one in which A_0 or V_a is free.

For comparison with the 3BE-C results shown in the middle of Table VI, the last row presents 3BE-A results. Except for the last line all results in this table involve Weighting C. The residuals of all the equations listed in the table were substantially normally distributed. Excellent normality was found for all equations below the SOE$_0$ in the table, while normality was poorer for the SOE$_0$ and the equations above it, which all show relatively high M values. As might be expected, the normality of the 2SE residual set was poorest of all. Note that even though M is slightly smaller for the 4SE than the 3SE, the 3SE s_d is smaller than that of the 4SE because of the

change in f in passing from one to the other of these equations. Incidentally, s_d and s_d' are equal to six or more significant figures for the 3SE and 4SE, and $\lambda \cong -7.1 \times 10^{-4}$ and -1.2×10^{-5}, respectively, for these fits.

The use of a fixed V_0 in the present fittings leads to serious perturbations of the s_f values unless the V_0 values used are presumed to be exact. This is, of course, not usually the case. Nevertheless, when V_0 is fixed its likely uncertainty does not enter into the calculation of the s_f's. Thus, for example, the s_f pertinent at $p=0$, where $V=V_0$, is forced to be zero, clearly incorrect. Lesser perturbations occur for s_f's associated with $p>0$ values. When V_0 is not known exactly, it is desirable to calculate s_f's with A_0 (or V_a) free so that its error affects the s_f's. The effect can be seen by comparing the (correct) s_f's of Row 5 of Table IV with the corresponding perturbed ones of the 3BE of Table VI. Note that since the s_0's of the runs of Table VI (for which $p \cong 4.29$ bar) would have been so perturbed as to be useless, we have given instead $s_f = s_1$, associated with $p \cong 100$ bar.

In addition to errors in all s_f's arising from the assumption implicit in the conventional approach that V_0 is known exactly, errors arise from the same cause in the σ_{A_k}'s and r_{A_k}'s as well ($k \geq 1$). Even though a proper value of f may be readily used, there is one less free parameter with A_0 and V_a fixed than with one or the other free. Thus, the r_{A_k}'s found with A_0 and V_a fixed are smaller than those obtained with A_0 or V_a free. For example, the $r_{A_1} \cong r_{\beta_0}$ of the 3BE-C run of Table IV, obtained with A_0 free, is appreciably larger than the corresponding 3BE r_{β_0} shown on the ninth row of Table VI, where $A_0 \equiv 0$ and V_a is fixed at the value of V_0 given.

Although I have followed common practice in Table VI by comparing equations with $V_a = V_0$ and A_0 fixed, it should now be clear that better practice would require A_0 or V_a to be free unless V_0 is known exactly. Incidentally, when the free-A_0 approach is used, it is still desirable, in order to get best estimates for the parameters, that the fixed V_a used be equal to the consistent V_0 found separately. When the free-V_a approach can be employed, this complication is, of course, unnecessary. I strongly recommend that future work in this area eschew the practice of implicitly assuming that V_0 is known exactly unless it actually is!

The s_f's (s_1, s_m, s_N, and s_e) given in the table do not all apply to the same quantities. For the nonlinear equations, the s_f's are the standard deviations of the y variable V/V_0. Those for the BE's apply to the variable $t \equiv (V_0-V)/V_0$ and are thus directly comparable; but the IVE s_f's are associated with the different variable $w \equiv (V_0-V)/V$, which is, however, sufficiently close to t for the present data that s_f's can be cross compared. Finally, the s_f's of the DGE's and SE's are the standard deviations of $y=p$ values.

TABLE VI. Detailed fittings for various equations; V_0 fixed at value shown for each equation and C weighting used except for the last row, which uses A weighting.

Equation	V_0 $10^6 r_{V_0}$	M s_d	S_p/S $P_s(\%)$	u $\Pi(\%)$	$10^5\beta_0(\text{bar}^{-1})$ $10^4 r_{\beta_0}$	η $10^3 r_\eta$	q $10^2 r_q$	s_1 s_m	s_N s_e
2SE	1.00018345	2479	43	4	5.1611	7.231	...	8.66×10^{-2}	6.23×10^{-1}
	7.38	10.16	≪0.01	0.001	10.3	10.5	...	1.65×10^{-1}	1.34×10^4
2IVE	1.00015386	217.4	46	6	5.0849	5.073	...	1.12×10^{-6}	8.35×10^{-6}
	2.04	3.01	≪0.01	0.05	2.49	2.34	...	2.30×10^{-6}	1.89×10^{-1}
UTE	1.00017070	517.1	41	4	5.1263	6.151	...	1.87×10^{-6}	1.11×10^{-5}
	3.28	4.64	≪0.01	0.001	4.32	4.37	...	3.51×10^{-6}	1.38×10^{-3}
ME	1.00016881	357.8	40	6	5.1214	6.012	$\gamma=\eta$	1.55×10^{-6}	9.26×10^{-6}
	2.72	3.861	≪0.01	0.05	3.57	3.65	...	2.92×10^{-6}	8.44×10^{-4}
LSME	1.00016420	95.23	36	6	5.1096	5.684	$\gamma=1$	7.80×10^{-7}	4.85×10^{-6}
	1.40	1.992	≪0.01	0.05	1.78	1.79	...	1.50×10^{-6}	4.14×10^{-4}
SOE₀	1.00016401	90.65	36	6	5.1092	5.674	$\gamma=0$	7.61×10^{-7}	4.73×10^{-6}
	1.36	1.943	≪0.01	0.05	1.74	1.75	...	1.46×10^{-6}	3.95×10^{-4}
SOE₂	1.00016014	27.14	36	13	5.09946	5.409	5.305	6.09×10^{-7}	3.53×10^{-6}
	0.926	1.086	50	56	1.77	5.06	5.47	8.32×10^{-7}	3.21×10^{-3}
3IVE	1.00016030	27.88	35	13	5.09999	5.430	4.880	6.00×10^{-7}	4.09×10^{-6}
	0.908	1.101	44	56	1.64	3.99	3.41	8.76×10^{-7}	2.64×10^1
3BE	1.00015987	23.76	35	13	5.09845	5.358	6.187	5.43×10^{-7}	3.48×10^{-6}
	0.832	1.016	84	56	1.48	3.49	1.58	7.91×10^{-7}	2.32×10^1
3DGE	1.00015954	22.46	35	15	5.09728	5.298	7.453	1.14×10^{-2}	8.52×10^{-2}
	0.855	0.9882	99	85	1.69	5.34	3.36	1.61×10^{-2}	5.09×10^5
3SE	1.00015885	19.64	36	20	5.09453	5.144	9.919	1.08×10^{-2}	7.84×10^{-2}
	0.808	0.9241	67	3	1.64	5.61	2.15	1.50×10^{-2}	4.70×10^5
4BE	1.00015909	21.04	36	20	5.09579	5.240	7.772	6.11×10^{-7}	3.98×10^{-6}
	0.924	0.9779	97	3	2.23	10.5	8.99	8.57×10^{-7}	8.97×10^3
4SE	1.00015866	19.50	36	20	5.09377	5.100	10.536	1.22×10^{-2}	9.73×10^{-2}
	0.946	0.9414	78	3	2.66	16.8	11.6	1.94×10^{-2}	1.96×10^3
3BE	1.00016037	22.94	0	16	5.09951	5.379	6.097	6.01×10^{-7}	1.85×10^{-6}
	1.12	0.9986	93	56	1.56	3.08	1.22	8.80×10^{-7}	1.88×10^1

All the equations of Table VI have been written in forms that involve the physically significant parameters β_0, η, and $\theta \equiv q^2$ or q. Equation (1') for the Usual Tait equation thus involves $\eta+1$ in place of the parameter r. The use of β_0, η, and θ or q as explicit parameters allows their standard errors to be obtained directly, a considerable virtue since the parameters themselves are generally found to be somewhat correlated. Values of θ and its standard error obtained from the higher-order polynomial fittings have been used to calculate the q and r_q values shown in the table, allowing direct comparison with the q which is obtained directly from SOE₂ fitting. To save space, values of A_4 and r_{A_4} for the 4BE and 4SE have been omitted from the table. They are, respectively, 1.61×10^{-16} $(1\pm5.02\times10^{-1})$ bar⁻⁴ and 2.31×10^5 (1 ± 2.14). It is thus clear that these higher-order parameters are very poorly determined.

Although we have not shown results in the table for the 4*IVE, a good-fitting equation for the present

data, it is worth mentioning that its β_0 and η parameters fall between those of the 3DGE and the 3SE, r_{β_0} is only 1.22×10^{-4}, and r_η is 2.14×10^{-3}, both somewhat better than those of the 3BE or 3SE.

Hayward (1967) has stated that the Linear Secant-Modulus equation is the best empirical equation for water up to about 3 kbar and that the Linear Secant-Modulus equation with an additional free parameter, say b, (the Quadratic Secant-Modulus equation or QSME) is the best equation for water over very large pressure ranges. The results of Table VI show how far from the truth the first part of this statement is. To check the second assertion, the Quadratic Secant-Modulus equation was run with C weighting and A_0 free, yielding $M = 28.83$, a value slightly greater than that for the SOE$_2$, an equation with the same f value. This result together with the Quadratic Secant-Modulus equation value of u of 13 suggests that the Quadratic Secant-Modulus equation is comparable or slightly inferior to the SOE$_2$ for the present data and is not necessarily the best equation for water over a very large pressure range. As mentioned earlier, the Second-Order equation should be chosen over the Quadratic Secant-Modulus equation unless the latter shows appreciable superiority for the data in question.

One may conclude from the results of Table VI that only the SOE$_2$ is useful for appreciable extrapolation (the other nonlinear equations give too poor a fit and the polynomials blow up on extrapolation), but that polynomial equations such as the 3BE, the 3DGE, the 3SE, and possibly the 4*IVE are likely to be superior for fitting and interpolation within the range of given data. The quartic equations such as the 4BE and 4SE, while leading to slight reductions in M, show significantly increased values of s_f's and parameter relative errors over the corresponding cubics.

Figure 3 shows a comparison of the normalized residuals d_i versus p for the poorly fitting Murnaghan equation and the good fitting 3SE of Table VI. Note how the small "random" deviations of the 3SE also appear in the ME curve superimposed on large systematic deviations arising from inadequacy of the Murnaghan equation model.

It turns out that all of the three equations with $u = 20$, a high value relatively unlikely to occur by chance from random variation, have almost identical $\{d_i\}$'s. Corresponding individual d_i's are quite closely the same. This fact suggests that our original assumption, that the 0°C water data were representative, seems somewhat unlikely. The present results suggest instead that the data have, by chance, smaller errors than might be expected and that thus the change from B to C weighting was not the most reasonable procedure. If this is the case, the present results still suffice to allow close comparison to be made between the various equations of state and show that the 3SE seems the best of all for the present data. Analysis
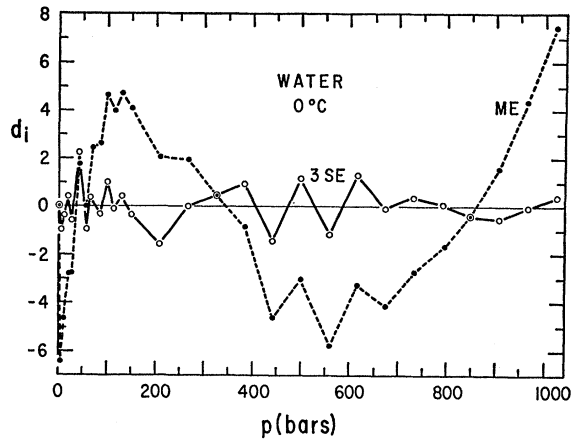

FIG. 3. Plot of the normalized d_i residuals versus p for 0°C water obtained from data fitting with the 3SE and Murnaghan equations.

with B weighting also indicates that the 3SE is superior to the other equations for the present data; B weighting leads to d_i values for such equations as the 3BE, the 4*IVE, and the 3SE reduced by a nearly constant factor of 1.58 over those found with C weighting.

Examination of the results of the table shows that for such reasonably good fitting equations as the 3BE, the 3DGE, and the 3SE there is no agreement of β_0, η, and q parameters within one or two of their standard deviations. On the other hand, there is agreement within one standard deviation or less between the results for the 3SE and 4SE. This is added evidence that the 3SE is the best model for the present data. If so, the appreciably different parameter results obtained for the SOE$_2$, for example, must be taken to be biased and in error because of systematic deviations arising from an inferior model choice. That systematic errors of this kind can definitely lead to biased parameter values and standard deviations is shown by the results in the table. For example, the 2IVE is a very poor model and fit, yet it leads to apparent r_{β_0} and r_η values comparable to or better than those of the 3SE! Unless the model is applicable, as the 3SE seems to be, the various parameter values and standard deviations obtained must be discounted as biased.

Elsewhere (Macdonald, 1964), I have considered to some extent the question of when it is appropriate to stop adding higher degree terms in a polynomial fitting of data (see also Margulies, 1968). As Hald (1952, Section 20.3) shows, the t distribution may be used to help decide whether adding a further A_k term to a polynomial is statistically justified or not. If the hypothesis is made that $A_k = 0$, then $t = (r_{A_k})^{-1}$ with $f = N - n$ degrees of freedom. Using the quoted values of r_{A_4} obtained for the 4BE and 4SE, we find that it is statistically significant to go from the 3BE to

TABLE VII. Detailed fitting results for water data of Kell and Whalley (K–W) at 50.007°C and Vedam and Holton (V–H) at 50°C. Weightings as indicated; here and subsequently, weighting A is given by $\sigma_p=0$, $\sigma_V=1$.

Equation-weighting; data source	$10^6 s_d$ u	V_0 $10^6 r_{V_0}$	$10^5\beta_0$ (bar^{-1}) $10^4 r_{\beta_0}$	η $10^2 r_\eta$	θ $10 r_\theta$	ψ $10 r_\psi$
3SE-A	5.14	1.0121094	4.40867	5.424	59.5	44.4
K–W	11	2.5	7.8	2.0	2.5	1.5
3SE-C	2.42×10^6	1.0121095	4.40883	5.430	58.5	44.0
K–W	11	2.0	7.8	2.3	3.2	1.9
SOE$_1$-A	34.4	1.012105	4.4308	6.153	−40.1	−1.10
V–H	11	30	12	0.33	0.12	1.1
3DGE-A	33.4	1.012086	4.4152	5.966	−26.3	4.66
V–H	12	30	16	0.69	0.68	1.3

the 4BE but not at all from the 3SE to the 4SE. These conclusions are consistent with the variation of u arising from these changes and again point to the 3SE as the best minimum-parameter equation for the present data.

The parameter standard deviations given in Table VI do not include contributions from systematic errors in the data. Using estimates of these systematic errors presented in Table 5 of Kell and Whalley (1965), we find that the systematic standard error of V_0 is about $\pm3\times10^{-6}$, considerably larger than the (random) standard error of Table VI. The number 3×10^{-6} does not include uncertainty in the conversion factor from milliliters to cubic centimeters. To first order, the systematic standard error of β_0 is about $\pm7\times10^{-9}$ or $\pm4\times10^{-8}$ bar^{-1}, where the second figure includes uncertainty in the density of mercury not included in the first figure, and even the first figure is comparable to the random standard error of β_0 for the 3SE fit.

Kell and Whalley give no estimates of systematic error depending on p^2 and p^3; thus, no explicit estimates of systematic errors of η and q can be derived from their work. We may be confident, however, that the actual uncertainty of these quantities is appreciably larger than three times the standard deviations given in the table. Thus, even using the present extremely good data, η and especially q values, cannot be taken as very closely defined. In particular, we might crudely estimate $q\simeq10$ with an over-all uncertainty of perhaps $\pm25\%$ for water at 0°C if C weighting is appropriate. The phase change for water at 0°C occurs between 6 and 7 kbar, and the corresponding V_c is greater than 0.83 and less than 0.85. Using the SOE$_2$ and 3SE parameters of Table VI to calculate V_m, the minimum value of V allowed by the SOE$_2$ with $q\geq0$, one finds $V_m\simeq0.75$ and 0.80, respectively, both adequately below V_c. For η of 5 to 6, q must be about 16 before $V_c<V_m$. As Table VI

and the above error considerations show, such a large value of q is quite unlikely and would lead to a much poorer fit of the data using the SOE$_2$ than that of Table VI.

The 3SE parameter values of Table VI lead to $K/K_0\simeq1+5.1z+31z^2$. At the maximum value of z for the Kell–Whalley data, this expression becomes $K/K_0\simeq1+0.27+0.084$, showing that the last term, which involves $\psi\equiv K_0 K_0''$, is by no means negligible. Further, it is not sufficiently smaller than the second term that truncation of the K/K_0 series after the second-order term is likely to be justified over the entire, quite limited pressure range considered. In the present case then, the Second-Order equation of state may only be regarded as a heuristic fitting equation and the K_0' and K_0'' parameter values derived from its use are not likely to be the true values implicit in the data but are biased. This is also clear from Table VI since the SOE$_2$ is by no means the best fitting equation therein. Anderson (1965, 1966) has suggested that truncation after the ηz term of the K/K_0 expansion may be sufficient for many materials. The differences between the Murnaghan equation η and that found with the SOE$_2$, neither of them very close to the better 3SE η value, show that this hypothesis is invalid for water.

D. New Data

When this paper was essentially completed, the recent water P–V data of Vedam and Holton (1968), derived from ultrasonic propagation measurements, came to my attention. Although these data are apparently about two orders of magnitude less precise (four decimal digits in V) than those of Kell and Whalley, they are important because they cover the pressure range up to 10 kbar, a range about 10 times wider than that of Kell and Whalley. Thus, higher-order parameters such as η and θ should be derivable with

smaller standard deviations than the precision of the volume values initially suggests.

Since Vedam and Holton present no high-pressure 0°C data, we examine their 50°C data set, for which $N = 21$. The results of many curve-fitting trials with A_0 free and with $\sigma_p = 0$ and $\sigma_V = 1$ (see Sec. VI for discussion of the appropriateness of this choice in a similar situation) show that the 3DGE leads to apparently random residuals and is the best fitting equation. Fairly close behind it is the SOE$_1$, a nonlinear equation with the same n value as the 3DGE. The 4DGE gives a good fit but with two parameters lacking in statistical significance. Although the 4SE fit yields an s_d slightly lower than that of the 3DGE, its parameter relative errors are considerably larger. Further, the 3SE yields a very poor fit, as do the 4IVE, 4BE, 3IVE, 3BE, etc. Of the nonlinear equations with only A_0, β_0, and η free, the Murnaghan equation seems the best, but it still yields an s_d nearly three times as large as that of the 3DGE and a u_0 of only 4. The Quadratic Secant-Modulus equation, as usual, is inferior to the Second-Order equation (and Murnaghan equation as well here) and leads to $s_d \simeq 9.1 \times 10^{-5}$ and $u_0 = 5$.

Surprisingly, Vedam and Holton make no comparison of their results with corresponding ones of Kell and Whalley. Comparison shows that the four-figure, 0–1-kbar, specific-volume results at 0° and 50°C of Vedam and Holton (termed reliable four-figure values by these authors), with $N = 6$ for each temperature, actually usually differ from the corresponding six-figure results of Kell and Whalley by no more than one or two digits in the fourth place, although the 100°C results show one difference of about eight digits in the fourth place. Rather than compare the high-pressure 50°C Vedam–Holton results with only the 0°C Kell–Whalley results, I have carried out curve fitting of the 50°C Kell–Whalley data using the 3SE, the best fitting equation (by a small margin) for the 50°C data as it was for the 0°C data. Significant fitting results are presented in Table VII. As an aid in comparison, more decimal figures are given here for some of the parameters than is strictly justified by their standard deviations. No data points had to be eliminated for overly large residuals, and all residuals were normally distributed to good approximation. Weighting C is that already defined and used for the 0°C water data. Weighting A is here the choice $\sigma_p = 0$, $\sigma_V = 1$ rather than that with $\sigma_V \neq 1$ defined earlier as A.

Finally, although the significant dimensionless parameter $\psi \equiv K_0 K_0'' \equiv \frac{1}{2}(\eta^2 + \theta)$ may be calculated directly from η and θ results, r_ψ can only be calculated from the results of an η, θ run if the correlation of η^2 and θ is known. But only the correlation of η and θ, not η^2 and θ, is obtained from a fit directly involving these parameters (it is nearly -1 for the present data). Therefore, the values of ψ and r_ψ shown in Table VII have been obtained directly by carrying out additional fitting with each pertinent equation written to involve ψ instead of θ as one of the free parameters.

The results shown in Rows 1 and 2 of the table indicate that changing from A to C weighting does not alter the parameter values significantly. Note that the degree of fit is appreciably poorer for the 50°C Kell–Whalley data than for the 0°C data. There the 3SE-C yielded $s_d \simeq 0.92$ with $u_0 = 20$; here the corresponding s_d is 2.4 with $u_0 = 11$. The r_Z's are correspondingly larger for the 50°C data as well. In particular, the directly determined value of ψ for the 3SE-C 0°C data fitting is 62.4, and $r_\psi \simeq 0.038$. Note that although the corresponding 19% relative error of the 50°C ψ result is considerably larger than desirable, it is still insufficiently large that one should accept the null hypothesis that ψ is not statistically different from zero. In the present instance, we may conclude that there is less than a 0.1% probability that the true ψ is indeed zero. Since the value of K_0 at 50°C is larger than that at 0°C for water, the indicated reduction in ψ in going from 0° to 50°C suggests the likelihood of an even greater decrease in K_0'' with increasing temperature for water in this range.

Although the s_d's for the Vedam–Holton SOE$_1$ and 3DGE are nearly the same, the higher-order parameters determined from these two fittings are considerably different. In spite of these differences and the extended range of the Vedam–Holton data ($V_{min} \simeq 0.82$), we evidently have no strong basis for choosing the SOE$_1$ or the 3DGE as the better model for these particular data.

The results of Table VII show appreciable differences between the Row 1 and Row 4 parameters, especially the higher-order ones. Vedam and Holton give values (termed "isothermal compressibility"!) for the quantity $(\partial V/\partial P)_T$, not β. If the quoted 50°C value for $(\partial V/\partial P)_T$ at $p = 0$ is converted to β_0, one obtains about 4.416×10^{-5} bar^{-1}, very close to the 3DGE value in the table, which seems to be the most appropriate value following from their data. Note that although only four significant figures are given in the V data, $s_d \simeq 3 \times 10^{-5}$. Random roundoff alone might be expected to lead to a somewhat higher figure on the average; further, 3×10^{-5} is about an order of magnitude smaller than the maximum errors Vedam and Holton expect. Thus, the result suggests the presence of very considerable smoothing, itself a possible source of systematic error. Unfortunately, Vedam and Holton do not distinguish between random and systematic error in their data and thus do not discuss possible sources of the latter explicitly, especially those considered by Wilson (1959) for similar ultrasonic measurements. It is, of course, always desirable to judge the reliability of data by direct consideration of all details of the experimental method and procedures leading to the data in question. By this means one should be able to set a reasonably accurate upper bound on the magnitudes of the vari-

ous kinds of systematic error possibly present. Although we can never be objectively certain of the absence of systematic errors, we can frequently bound those that may remain. This approach is preferable to that I have had to follow in much of the present work of inferring the presence of considerable systematic errors in the data from statistical analysis and comparisons.

Although the Row 1 and Row 4 η values differ by many times their standard deviations, it is the θ and ψ differences which are most startling. The Row 1 θ value is consistent in sign and magnitude with the apparently more precise 0°C θ result. But the Row 4 θ is negative, suggesting that γ, not q, is the appropriate variable in the SOE for water. As we see, these differences lead to an order-of-magnitude difference between the two ψ values! It is relatively cold comfort that both ψ values are positive so at least the sign of the last term of Eq. (4) remains unchanged. Note that even the small value of $\psi = 4.66$ leads to a value of $(\psi/2)z^2_{max}$, the last term in the second-order expansion of K/K_0, of about 0.44 for the Vedam–Holton data at maximum z. The probability that the great difference in ψ values occurred because of chance variations in the random error components of one or both of the two data sets compared is exceedingly small. The difference most probably arises from systematic errors in the data. It is probably significant that a high likelihood of appreciable systematic errors in the data appears from the analysis of Sec. VI which also deals with ultrasonically derived P–V results, there for liquid Hg. Some possible sources of systematic errors likely to be of importance in such measurements and derivations are discussed there.

The very fact that the best-fitting equation is different for the two sets of 50°C data is suggestive of the presence of systematic error. Although the 3SE and 3DGE equations are similar models and should allow some significant cross comparison of parameters (albeit ones which almost certainly reflect appreciable systematic error effects), it is of interest to compare the predictions of the two data sets when the same model, not necessarily the best-fitting one, is used for fitting both sets. Luckily, the 3DGE-A yields, for the Kell–Whalley data, $s_d{\simeq}5.19{\times}10^{-6}$, not significantly worse than that of the 3SE-A. In addition, one finds: $V_0{\simeq}1.0121101$, $\beta_0{\simeq}4.41075{\times}10^{-5}$ bar^{-1}, $\eta{\simeq}5.484$, $\theta{\simeq}24.73$, and $\psi{\simeq}27.8$. The relative standard errors of V_0, β_0, and η are comparable to those found with the 3SE-A; on the other hand, $r_\theta{\simeq}0.50$ and $r_\psi{\simeq}0.20$. Thus, the value of θ found is not highly significant; that of ψ, however, has a very high probability of being significantly different from zero provided r_ψ is not itself strongly biased by the presence of systematic errors. Comparison with the results of Row 4 of Table VII still indicates very considerable differences between the η and ψ estimated values, differences of many standard deviations of the largest

such deviations involved. Since the Kell–Whalley 3DGE-A V_0 and β_0 values are apparently considerably better determined than those following from the high-pressure Vedam–Holton data, it is of interest to use these values as fixed parameters in a 3DGE-A fit of the Vedam–Holton data. Unfortunately, such a fitting does little to reduce the η, θ, and ψ discrepancies discussed above for the two sets of data. For example, it leads to $\eta{\simeq}5.922$, $\theta{\simeq}-24.2$, and $\psi{\simeq}5.41$ instead of the corresponding values in the last row of Table VII.

The estimated systematic errors in the 50.007°C Kell–Whalley data should not be much larger than those already discussed for the 0°C data. On the other hand, Vedam and Holton state that their specific volumes should be good to a few parts in 10^4 up to 7 kbar and to one part in 10^3 at higher pressures. In order to obtain a feel for the effect of systematic errors consistent in magnitude with these estimates, I have arbitrarily modified the Vedam-Holton V data values by adding $\Delta V_i = \pm 10^{-15} p_i^3$ to each V_i. These changes lead to about a $\mp 0.8\%$ change in β_0, about a $\mp 6\%$ change in η, and to the addition to θ of about ± 19.4 when the modified data is fitted with the 3DGE as before. The quantity r_θ remains essentially unchanged for the negative increments but is increased to 0.38 for the positive increments, rendering the θ value obtained, about -7.0, somewhat difficult to distinguish from zero in this case. Since the addition of the above ΔV_i to the Kell–Whalley V data leads to a negligible change in the 3SE parameters shown in Row 1 of the table but to a great change in the Vedam–Holton 3DGE θ result, it seems plausible to assign the main cause of the difference between the results of Rows 1 and 4 to systematic errors in the Vedam–Holton data. Clearly, relatively small systematic errors can have a very appreciable effect on θ; to determine it accurately one needs both excellent data and as wide a compression range as possible.

E. Water Conclusions

The present results indicate that the Usual Tait equation is a very poor choice for water and that it is not worthwhile for people to continue to derive a plethora of C and B Tait-equation parameters as they have in the past for water and organic liquids. If the Usual Tait equation is ever used, it should be written to involve the parameters r (or $\eta+1$) and β_0 directly. The results also indicate that uncritical use of the Murnaghan equation for water and perhaps even some solids should be eschewed.

Unless the residual set $\{d_i\}$ can be reduced until d_i depends essentially randomly on X_i or Y_i, systematic errors remain. Even when this has been accomplished, if it requires a many-parameter equation of state, one suspects that systematic errors are present in the data (and are compensated by the excess parameters), rather than systematic errors arising

from mismatch between data having only random errors and the selected model. The author knows of no published results with the Usual Tait equation or Murnaghan equation where it has been made clear that systematic errors of either kind are negligible. They are, in fact, clearly present in the previous ordinary least-squares fitting of Bridgman's (1935) water data (Macdonald, 1966). Most authors who have used the Murnaghan equation (and other equations of state) do not give standard deviations of the fits and parameters obtained, do not estimate systematic errors, and do not plot residuals. In the rare cases when residuals are shown, they almost invariably exhibit major systematic errors. In addition to the authors already listed in Sec. III.D, others (Drickamer *et al.*, 1966; Drickamer, 1968; Urvas *et al.*, 1967; and Stephens and Lilley, 1968) have recently used the Murnaghan equation for a variety of data. It particularly appears from the work of Grover *et al.* (1967) that at least some of the x-ray diffraction data of Drickamer are incorrect. Here it is therefore very likely that there are systematic errors in the data itself. Even were they absent, one wonders if the Murnaghan equation is a sufficiently good model to eliminate systematic errors of the remaining type when it is used in analyzing P-V data for many solids and liquids.

The present results show that it would be quite inadequate to derive β_0 and η for a material like water from the results of ultrasonic measurements at modest pressure and use these isothermal parameter values in the Murnaghan equation to estimate compression at high pressure, as Anderson (1965, 1966) has suggested. Since the Murnaghan equation is evidently an inappropriate model for water in the 0–1-kbar range, it can hardly be expected to be better for higher pressures. The above estimation procedure should not be employed for other materials, except perhaps to obtain crude estimates, unless it has first been shown with as accurate data as possible that the Murnaghan equation is an adequate model for the material in question. Analysis of the type discussed herein, as well as accurate data over at least an appreciable compression range, will generally be required to show the presence or absence of systematic errors and the consequent applicability of the Murnaghan equation or other equation, such as the Second-Order equation, for such estimation.

Finally, the present results show that for water at 0°C a polynomial equation of state is likely to be a better model, at least over a limited pressure range, than any of the nonlinear equations of state considered herein with the same number or fewer free parameters. In the Kell–Whalley relatively low pressure range, the third-degree Slater equation is markedly superior to the SOE_2. Only the SOE_2 is appropriate for extrapolation to higher pressures, however. Such extrapolation, for example for water at $T \geq 0°C$, must

be somewhat suspect, nevertheless, since the SOE_2 definitely leads to systematic errors of the model-data mismatch type. Clearly, a better nonlinear equation of state is still needed; an examination of some further possibilities will be the subject of future work.

Comparison of curve-fitting results of direct P-V data for water at 50°C with those obtained from fitting P-V values of Vedam and Holton (1968) derived at the same temperature for a wider pressure range indirectly from ultrasonic-propagation measurements shows wide discrepancies, especially in higher-order parameters such as $\eta \equiv K_0'$ and $\psi \equiv K_0 K_0''$. These discrepancies almost certainly arise from systematic errors, probably principally in the ultrasonic P-V results (provided the models used are valid for the data employed), not from random statistical variation. Although the matter is not absolutely clearcut, it appears that ψ is large and positive for water in the 0°–50°C range and is smaller at 50°C than at 0°C.

VI. APPLICATION TO MERCURY

A. Introduction

In this section we shall be primarily concerned with the recent P-V results for Hg of Davis and Gordon (1967). Data sets with $N = 13$ were obtained for $T = 21.9°$, 40.5°, and 52.9°C. Although V_0 values were not directly measured, the following values of V_0 (actually V_a by our present definitions) were used in the calculations: 1.0039775, 1.0073616, and 1.0096224, respectively.

Pressure was measured with a calibrated wire-resistance gauge and extended to about 13 kbar, where V was about 0.96 at 21.9°C. Pressure changes of about 6 bar could be detected. Calibration was carried out against a precision free-piston gauge and an ordinary least-squares fitting of the form $\Delta R/R_0 = AP + BP^2$ was obtained; here R is resistance and A and B are free parameters. The standard deviation obtained was equivalent to 6 bar. The use of the above formula tends to smooth P, and no statement was made concerning randomness of the residuals. It is therefore uncertain whether this equation is a good model or whether its use introduces systematic errors which might have been largely eliminated had higher terms in P been included.

In the Davis–Gordon work, volume was not mesured directly but was calculated from acoustic-wave velocity measurements. The initial compressibility β_0 was independently determined and was thus not taken as a disposable parameter in comparing equations of state. Values used were 4.025662×10^{-6}, 4.114246×10^{-6}, and 4.174143×10^{-6} bar^{-1} at 21.9°, 40.5°, and 52.9°C, respectively. Since β_0 is therefore not disposable, it is frequently convenient to use the variable $z \equiv \beta_0 p$ rather than p here.

In order to obtain V values, a relation between P and c_T, the measured sonic velocity, was needed. The authors used $P=A+Bc_T+Dc_T^2$ and determined the new A, B, and D coefficients by ordinary least-squares fitting. Note that here the effect of errors in c_T is forced into P, since c_T values are taken as exactly known in such a least-squares procedure. But errors in P should properly include errors arising in the resistance measurements as well. Further, again no statement was made concerning whether higher-order terms in c_T would have been needed to eliminate systematic errors of the model-data-fit type and thus reduce the residuals of this second fitting to randomicity. In both the resistance fitting and the pressure–velocity fitting, weighting of both dependent and independent variables would have been preferable, and the smoothing arising from the (possibly unduly ·truncated) equations actually used is likely to have introduced appreciable systematic errors into the final P-V results.

The above relation between P and c_T was used to obtain V values by integration from $P=1$ bar to given rounded values of P. Such integration also is likely to introduce uncertain systematic errors. Further, the P associated with each resulting V was taken as exact; thus, all the error was here forced into V even though error could have arisen from the measurement of P in the original calibration of the pressure gauge, from the measurement of resistance, from the measurement of sonic velocity, and even from the conversion from adiabatic to isothermal conditions.

The above uncertainties make comparison of equations of state and derivation of Hg parameters by the present methods (or those of Davis and Gordon) somewhat dubious. Nevertheless, we shall carry out such comparison since a number of important points will be illustrated thereby.

B. Previous and Preliminary Results

Using ordinary least squares, Davis and Gordon investigated the applicability of various equations of state to their P-V data, including the 2BE, 3BE, 2DGE, and Murnaghan equation. In all their fitting they took $A_0=0$ in the conventional, but unfortunate, way. Note that since V/V_0 is the dependent variable in some of these equations while P is in others, and unity weighting of the dependent variable was used throughout with the independent variable taken as exact, sometimes all the error or uncertainty was forced into V/V_0 and sometimes into P, even though in the calculation of the P-V data P values were forced to be exact.

Before applying the present methods to the Davis–Gordon results, the important check of trying to duplicate their s_d' and η values was made using their data and ordinary least squares. Here we define weighting A by $\sigma_p=0$ and $\sigma_V=1$ and B by $\sigma_V=0$

and $\sigma_p=1$. Then Davis and Gordon used A for the BE's and B for the 2DGE. They expressed s_d' in terms of V/V_0 in all cases and obtained $s_d'=18\times10^{-6}$ and 8×10^{-6} at 21.9°C for the 3BE and 2DGE, respectively. My calculation with the above weightings (which reduce generalized least squares to ordinary least squares) led not to these values but to about 24×10^{-6} for both equations. Thanks to helpful correspondence with Dr. Davis, the discrepancies were traced to roundoff from the original six-figure values of V to the four- and five-figure data actually published. Using the unrounded data kindly supplied by Dr. Davis, I was able to duplicate the published s_d' results; the unrounded data for all three temperatures were used thereafter. These data are given in the Appendix.

Davis and Gordon found the 2DGE to be the best of the equations they examined. Before leaving results obtained with $A_0=0$ as above, further 2DGE results are thus of interest. Using the unrounded 21.9°C data and the 2DGE with $A_0=0$ and B weighting, I found $s_d'=2.79$ bar and $s_d=2.67$ bar. Here A_0 is fixed at not the most consistent value so s_d is calculated with 11 degrees of freedom and s_d' with 12. Since λ was found to be 0.4, clearly $\langle d\rangle$ was far from zero. Using the parameters of this fit, I determined standard deviations of the V/V_0 variable directly from newly calculated residuals in V and found $s_d'\simeq8.4\times10^{-6}$ and $s_d\simeq7.8\times10^{-6}$. Further, when the same data were run with A weighting, a λ of about 0.45 was found and s_d' and s_d for the V variable were 9.9×10^{-6} and 9.3×10^{-6}, appreciably different from the comparable B-weighting results. The differences primarily arise from the difference between A and B weighting for the 2DGE with these data, not from the first set of standard deviations being associated with V/V_0 and the A-weighting ones applying to V. These results are for the best fitting equation Davis and Gordon considered. For the worst, the 2BE, these authors and I found an s_d' of 235×10^{-6} for V/V_0, and I find a corresponding s_d of 216×10^{-6}. Here $\lambda\simeq0.47$, and it is clear that in a case like this values of s_d and λ are much more meaningful than that of s_d' alone. The values of S and M were 6.62×10^{-7} and 5.13×10^{-7}, quite different indeed.

C. Comparison of Equations

One of the virtues of the generalized least-squares approach is that even when it is essentially reduced to ordinary least squares it still allows one to do more than is possible with ordinary least squares. Thus, when a given equation $y=f(x)$ cannot be explicitly written in its inverse form, one can still directly compare its parameters and other quantities obtained with the residuals all in y and X_i taken as exact and the corresponding quantities obtained when Y_i is taken exact and the residuals are all in x. When

$y = V$ and $x = p$, the first case merely involves weighting A above and the second weighting B. These two situations represent the extreme cases; all other weightings for which σ_{y_i} and σ_{x_i} are nonzero constants yield results between those of the extremes.

When constant weighting is used, weighting A is considerably more appropriate for the Davis–Gordon data than weighting B since P values are taken as exact for these data. Although Davis and Gordon give a discussion of possible errors in their results, they primarily deal with potential systematic errors in the data; little or no discussion of separate random errors is presented. Since the weighting used in the generalized least squares should involve only the estimated random errors (or at most the estimated random-systematic errors as well), we must look elsewhere for the weights to be used. It will be shown that constant weighting appears to be a reasonable approximation and thus that weighting A, or $\sigma_v = H_v$ with H_v a constant, should be used. Nevertheless, I shall present some weighting B results for comparison.

Table VIII shows results with free A_0, $P_0 = 1.01325$ bar, and weighting A for all the principal equations considered herein. Note the great span of s_d values. That for S is even greater: the S's for the 2DGE and 2BE are 570 and 3.3×10^5 times larger, respectively, than that of the 4SE, for example! Note that the s_d's for the 2BE and 2DGE are somewhat smaller here where A_0 is free than those quoted above when it was fixed. Also the λ values found here for the 2BE and 2DGE with A_0 free were about 3×10^{-3} and -2×10^{-2}, respectively. We shall not generally quote λ values when they are negligibly small. The residuals found for the various fittings show no large outliers which should be eliminated, and they are reasonably well normally distributed; this is only fair for such equations as the 2BE, 2DGE, and LSME and quite normal for ones with more parameters such as the 4DGE, 4SE, etc. Note, however, that the relatively small value of $N = 13$ leads to a small f (9 for the 4SE, for example), and the assumption that correlation between the residuals may be neglected is probably relatively poor for all the equations and becomes worse as n increases.

Examination of the r_{A_k}'s for the various equations and application of Student's t test shows that it is still highly significant to go from the 4BE to the 5BE and the 4IVE to the 5IVE. It is significant to go from the 3DGE or 4*DGE to the 4DGE or 5*DGE but not to go to the 5DGE. It is not significant to pass from the 5*SE or 4SE to the 5SE. Thus the significant equations of lowest s_d with $f = 9$ are the 4DGE, the 4SE, and the 5*DGE and those with $f = 8$ are the 5IVE and 5BE. Detailed comparison of r_{A_k}'s shows that the largest r_{A_k}'s (omitting r_{A_0}) of the 4SE, 5IVE, and 5BE are all about the same size, while the 4DGE and 5*DGE show considerably larger

TABLE VIII. $10^6 s_d$, where s_d is the standard deviation of the residuals, and number of runs u for various equations obtained using 21.9°C Hg data with A_0 free and A weighting: $\sigma_p = 0$; $\sigma_V = 1$.

Equation	$10^6 \, s_d/u$	Equation	$10^6 \, s_d/u$
2BE	169/3	4BE	1.50/5
2IVE	125/3	4IVE	1.18/5
2SE	41.1/3	4DGE	0.336/7
2DGE	7.03/3	4SE	0.327/7
4*BE	34.4/4	5SE	0.323/8
4*IVE	25.6/4	5DGE	0.319/8
4*SE	4.15/4	5IVE	0.267/8
4*DGE	0.556/6	5BE	0.265/8
3BE	13.4/4		
3IVE	9.94/4	SOE$_0$	53.5/3
3SE	1.14/4	LSME	53.2/3
3DGE	0.548/4	ME	26.8/3
		UTE	20.1/3
5*BE	9.06/5		
5*IVE	6.83/5	QSME	3.70/4
5*SE	0.861/5	SOE$_1$	1.76/4
5*DGE	0.304/8		

values (parameters less well determined). Although the s_d's of the 5IVE and 5BE are somewhat less than that of the 4SE, the 4SE involves one less free parameter and is hence simpler. Thus, of the more complicated equations which reduce the residuals to essentially random dependence on V or p, it seems most sensible to pick the 4SE as most appropriate. Clearly, none of the nonlinear equations is adequate here. As we shall see later, the Davis–Gordon 2DGE yields residuals showing strong dependence on V or p, indicating the presence of systematic error. Incidentally, the Π probability for $u_0 = 3$, 4, 5, 6, 7, 8, and 9 runs is here 0.6%, 4%, 15%, 39%, 77%, 77%, and 39%, respectively. Thus, the 4SE has a highly likely number of runs while the SOE$_1$, QSME, and 2DGE, for example, have unlikely numbers. These percentages are, however, only very approximate here because of the residual correlation arising from low f values.

Although no B-weighting results are shown in Table VIII, with such weighting the ordering of the equations by s_d is the same as shown; even more, any B-weighting s_d value may be obtained to within about $\pm 5\%$ from the corresponding one in the table by multiplying it by 3.1×10^5 bar. Thus, the actual 4SE s_d for B weighting (pertaining to p) is 0.106 bar, very significantly lower than the various possible errors mentioned by Davis and Gordon, as is also the corresponding A-weighting value of 0.327×10^{-6}.

TABLE IX. Comparison of 4SE A_k's with A and B weighting for $T=21.9°C$ Hg data using $V_a=1.0039775$.

k	$A_k \pm \sigma_{Ak}$	
	A Weighting $(\sigma_p=0; \sigma_V=1)$	B Weighting $(\sigma_p=1; \sigma_V=0)$
0	$(-2.75\pm0.31)\times10^{-6}$	$(-2.70\pm0.37)\times10^{-6}$
1	1 (fixed)	1 (fixed)
2	5.1383 ± 0.0045	5.1373 ± 0.0049
3	9.94 ± 0.25	10.00 ± 0.26
4	37.4 ± 3.5	36.7 ± 3.7

In order to compare results of A and B weighting in more detail, let us consider the 4SE written in the form of Eq. (16) with $y=z$ and $x=t_a$; the A_k's are then dimensionless. Table IX shows a comparison of the resulting A_k's for the two weightings. To high accuracy here, the best V_0's may be obtained from $V_0 \cong V_a+A_0$. Note that corresponding A_k's are generally the same to within one σ_{Ak} or less. Thus, for the present data no new results of significance can be obtained by using B weighting instead of A or by any intermediate weighting with both σ_V and σ_p constant and nonzero.

Figure 4 shows the s_f's obtained from 4SE fittings at different temperatures for A and B weightings. These degree-of-fit standard deviations have been expressed in terms of the physically significant parameter p rather than z. Note that the variation between the two weighting types and the three temperatures is quite small. Even the variation with p is sufficiently small that a constant weighting, such as A, seems appropriate. Certainly, strong proportional or linear weighting does not seem very apposite. Because the first data point used in these calculations was that for $P=1$ kbar, the values of s_f at $p=0$ were obtained from the standard errors of the A_0's. Since A_0 is free here, the values of s_f are not rendered inaccurate as they are when A_0 is inappropriately taken fixed (and error free) in the usual way.

Figure 5 shows a residual plot for the 2DGE and 4SE with B weighting. Curves of much the same general shape would have been found with A weighting. Here the residuals apply to p, not z. Those of the 4SE have been increased by 10 times for plotting clarity. These results certainly indicate most graphically the systematic error remaining with the 2DGE. Similar behavior is found for the two higher-temperature data sets.

Since it was found that the 4SE reduced the residuals to essentially random dependence on p for all three temperatures, it appeared possible to apply the chi-squared distribution addition theorem to obtain a best average s_d for the three 4SE fittings at different temperatures. To do so, s_d was calculated from $[(M_A+M_B+M_C)/3f]^{1/2}$ with $f=9$, and M results

from the 4SE fitting with A weighting. Here A, B, and C refer to the 21.9°, 40.5°, and 52.9°C fittings. This operation is only allowed if the sums of squares added are stochastically independent. The intercorrelations of the d_i's were found to be $r_{AB}\cong0.04$, $r_{BC}\cong0.24$, and $r_{CA}\cong0.27$, probably sufficiently low to allow a meaningful result from the combination. The s_d value obtained was 0.349×10^{-6}, again a very low value. When this result is used as the value of H_v in $\sigma_v=H_v$ and $\sigma_p=0$ weighting, one finds the following s_d values for the 21.9°, 40.5°, and 52.9°C data, respectively: 0.933, 1.089, and 0.971, all close to unity as they should be.

What may one conclude from all the above results? First, the p and V standard deviations, generally much less in magnitude than the precision and expected accuracy of the measurements which led to the P–V data, show that a great deal of smoothing, arising from the various procedures discussed in Sec. VI.A, must have occurred. Second, the strong systematic errors apparent on using such equations as the 2DGE make it necessary to go to such relatively complicated equations as the 4SE or 5BE to obtain random residuals and a reasonable value of u. Even the 4SE is more complicated an equation than was necessary to describe the apparently more accurate water data. It thus appears extremely likely that the additional complexity in the fitting equation over that required for water arises from a melange of systematic errors in the present Hg data. One cannot, therefore, conclude that the 4SE is necessarily the best equation for Hg, and one must look on all derived parameter values with a jaundiced eye!

Although we have thus far taken β_0 values fixed at the independently determined values used by Davis and Gordon in order to achieve a measure of comparability with their results, one could argue that since we take A_0 free, and doing so makes a con-
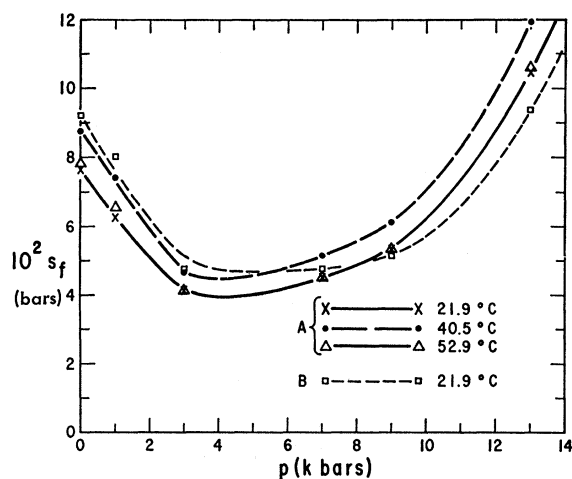

FIG. 4. Plot of the standard deviation of the variable p, s_f, versus p for 4SE fitting of the 21.9°C Hg data of Davis and Gordon.

Table X. Detailed fitting results for six different Hg data sets (see text); weighting A throughout: $\sigma_p=0$; $\sigma_V=1$.

Equation-Temperature (°C)	$10^6 s_d$ u	V_0 $10^6 r_{V_0}$	$10^6 \beta_0$ (bar^{-1}) $10^3 r_{\beta_0}$	η $10^4 r_\eta$	θ $10^2 r_\theta$	A_4 $10^2 r_{A_4}$
2DGE–21.9	7.03	1.003966	4.02566	9.4015	...	...
	3	3.4	...	8.3	...	...
4SE–21.9	0.327	1.0039748	4.02566	9.2808	−199.5	38.1
	7	0.31	...	9.7	1.8	9.3
4SE–21.9	0.340	1.0039742	4.02496	9.250	−192.1	33.3
	8	0.27	0.30	59	6.9	27
4SE–22	8.62	1.003978	4.096	10.9	−1240	2630
	9	32	9.9	1800	44	15
3DGE–20	2.85	1.003644	4.0211	8.76	−138	...
	10	6.1	1.3	171	15	...
4SE–40.5	0.383	1.0073597	4.11425	9.3479	−212.0	51.2
	9	0.36	...	11	1.9	7.6
4SE–52.9	0.346	1.0096194	4.17414	9.4166	−227.1	62.4
	7	0.33	...	9.6	1.5	5.4
3DGE–50	3.59	1.009097	4.1600	8.59	−113	...
	9	7.2	1.3	170	16	...

siderable difference in values of V_0, η, etc., we should also take β_0 free for consistency. This matter can only be settled by consideration of the precision and expected accuracy of the independently determined
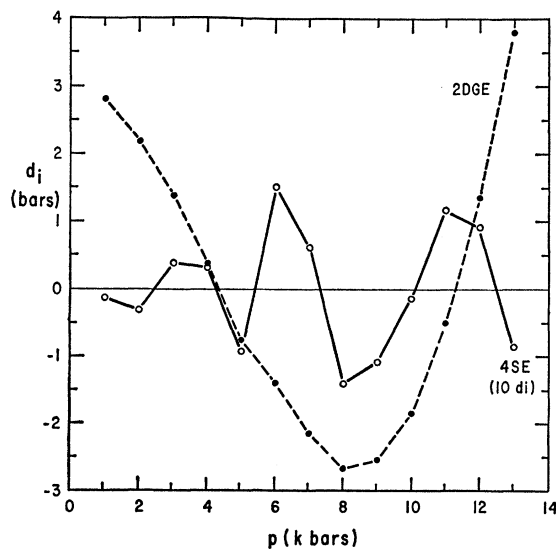

Fig. 5. Plot of the normalized d_i residuals versus p for 21.9°C Hg data obtained from fitting with the 2DGE and 4SE, using B weighting. Note that the 4SE residuals have been increased by a factor of 10.

values of β_0 used by Davis and Gordon. Since no discussion of them was given, an unequivocal decision to take β_0 free or not seems impossible.

Since Davis and Gordon did not compare their results with previous ones for Hg, we shall remedy this lack to some extent herein. Table X shows the results obtained for significant parameters using six different P-V complications. Rows 1, 2, 3, 6, and 7 follow from the Davis–Gordon results; 5 and 8 use results (with $N=11$ and 12, respectively) of Bett et al. (1954); and Row 4 (with $N=12$) uses Bridgman's (1911) early results. Weighting A was employed for all these runs, A_0 was free, and $V_a=V_0$. Except for the first row, the equation found best for each particular data set considered has been used. As before, A_4 is dimensionless.

Comparison of the results of Rows 1 and 2 shows that since the 2DGE gives a poor fit to the data, its apparently quite precise prediction for η cannot be trusted because of systematic errors of the poor model type. Davis and Gordon obtained 9.38 for η using the 2DGE with V_0 fixed. Row 3 shows what happens when β_0 is taken free rather than fixed at the Davis–Gordon value for this temperature as in Row 2. The main change is that the relative standard deviations of the η, θ, and A_4 coefficients increase considerably.

Davis and Gordon estimate the uncertainties of V and β at $P=13$ kbar as about $\pm 0.01\%$ and $\pm 0.4\%$, respectively. The total uncertainties following from their data might be as small as $\pm 4 \times 10^{-5}$ for V_0 and $\pm 10^{-8}$ bar^{-1} for β_0. Both these figures are much larger than the corresponding 21.9°C 4SE standard deviations following from the results of Table X. Nevertheless, they still probably do not include contributions from all the bias and smoothing sources described earlier, and the probable effect of these sources of error on higher-order parameters such as η and θ cannot be readily evaluated, although it is likely to be large.

Direct calculation for the data of Rows 2 and 7 yields the following values of ψ: -56.7 ± 1.6 for 21.9°C and -69.2 ± 1.6 for 52.9°C. The standard deviations given here include only the effects of random errors in the data, not the likely appreciable systematic errors in the data already discussed. Although the real values of θ and ψ may thus not be very close to those given in the table and above, the evidence nevertheless seems to indicate that ψ and θ are negative for Hg in this temperature range and that γ, not q, is the appropriate parameter here. The large magnitudes of ψ found for both water and Hg, although uncertain, still indicate that stopping the expansion of K in powers of p at second order, as in Eq. (4), is inappropriate for these materials even over the limited pressure ranges considered herein. Taking the above result for ψ at 21.9°C at face value, one finds from Eq. (4) that $z_n \simeq 0.16$. Bridgman's (1911) data indicates that z_c for Hg at this temperature is about 0.048, satisfactorily smaller than z_n. Note that z_{max} for the Davis–Gordon data was about 0.052, slightly exceeding Bridgman's z_c; nevertheless, no evidence of a phase change appears in the data.

Bridgman's (1911) 22°C data was heavily smoothed; Row 4 shows that it leads to aberrant values for θ and A_4. The θ value is, however, not of great statistical significance since its r_θ value is large. Hayward (1967) states that 20°C Bridgman data (no reference given) leads to a negative value of the higher-order parameter b in the QSME. His conclusion does not seem to be based on statistical analysis, however. Since series expansion allows one to equate b and $-(\theta+1)/12$, all the θ results of Table X indicate that b is, in fact, positive for Hg, a sign which Hayward expects for all liquids. Note, however, that the Kell–Whalley water data with θ positive lead to a definite negative sign for b. Hayward has stated that the LSME is the best empirical equation for Hg up to at least 12 kbar pressure. The results of Tables VIII and X show, ignoring the effects of possible systematic errors in the various data sets, that even the QSME, with an additional parameter, is not the best equation and that the SOE₁, among many others, is appreciably better than the QSME.

The Bett et al. (1954) data sets are derived from Hudleston's equation of state using both some of Bridgman's (1911) data and atmospheric-pressure velocity of sound measurements. Bett et al. believe that their procedure leads to better P–V results than those of Bridgman. From Rows 5 and 8 of Table X, the s_d's and r_z's are indeed better; without original good data it is impossible to state, however, how much the Huddleston equation may weight and bias the results. It certainly appears that the 3DGE can represent data calculated from the considerably more complicated Huddleston equation quite adequately. The Bett et al. data had only five decimal digits yet the 3DGE errors were in the sixth place or better! Note the exceptionally high value of u_0/N for the 20°C data set following from Huddleston-equation smoothing.

D. Mercury Conclusions

The seven different data sets examined all involve an appreciable amount of smoothing and probably contain very considerable systematic errors arising from this and other sources. The relative systematic error is likely to be particularly high for the three Davis–Gordon data sets. The probable presence of these errors renders the following conclusions somewhat uncertain.

Previous workers in the present area have generally been content to fit their data with oversimplified equations of state. The high-degree polynomial equation (4SE) found necessary in order to reduce the d_i's to approximate randomicity for the Davis–Gordon and Bridgman data probably is compensating for some of the systematic errors present in these data. The resulting parameters are thus rendered even more uncertain. A simpler polynomial equation (3SE or 3DGE) was required for the water fittings. None of the nonlinear equations was found suitable for the present Hg data; the Linear and Quadratic Secant-Modulus equations of Hayward were particularly poor.

Comparison of the results of Table X for the various data sets shows a reasonable change with increasing temperature of the Davis–Gordon η and θ values, but only fair or worse over-all agreement with the Bridgman and Bett et al. results. In view of the extensive smoothing present in all the data considered and the likely possibility of other systematic errors in the data, we must conclude that η, θ, and ψ cannot yet be determined very accurately for Hg. As a very tentative generalization based on a limited temperature range and on relatively uncertain parameters, we suggest, nevertheless, that K_0'' for both water and mercury probably decreases algebraically with increasing temperature over the limited ranges considered, 0°–50°C for water, 22°–53°C for Hg. In these ranges, K_0'' seems to be positive for water, negative for Hg, and considerably too large in magnitude to be ignored.

VII. GENERAL CONCLUSIONS

This section discusses opinions, methods, and suggestions for the future rather than the specific curve-fitting results and comparisons examined in earlier sections.

Workers in the present field, and probably others, seem willing to spend large amounts of time, effort, and money on obtaining experimental results but generally spend a disproportionately small amount of effort on planning their experiments to optimize subsequent analysis (see, e.g., Wolberg, 1967) and on the actual analysis of the expensive data obtained. Rarely is sufficient consideration given to identification and reduction of possible systematic errors in the data. Even more rarely in the physical sciences is sufficient replication carried out that the random error in each individual measurement can be properly assessed and any random-systematic error present largely eliminated. Finally, rather than following the usual procedure of carrying out no statistics at all on the experimental results or a minimum amount, authors should err the other way, by doing too much—if that is possible! Usually, weighting of all variables should be used, necessitating the introduction of generalized nonlinear least-squares procedures.

Previous workers in the P-V-T field have not usually fully appreciated the need to find an equation of state that reduces least-squares residuals to approximate randomicity; further, they never seem to examine the residuals for normality and for a likely number of runs. It has been estimated (National Bureau of Standards, 1968) that from 50% to over 90% of the data contained in literature in any specific field contains data unworthy of critical evaluation. In many cases, the lack of worth arises from "loss of information through oversimplification." An example is the frequent failure to distinguish between random and systematic estimates of uncertainty. Although systematic error can never be guaranteed entirely absent in the data, it should be bounded and minimized to the maximum possible degree in order to allow systematic error of the other type, that arising from an inappropriate choice of model, to be recognized and itself minimized by a proper fitting equation choice. As we have seen in the present work, the presence of systematic error in the data may sometimes be recognized because the final fitting equation is forced to be more complicated or have more parameters than seems likely on physical grounds or from other comparable experience.

The precision of reported data, that of both X_i and Y_i, should be such that the estimated standard deviations of a replicated X_i, Y_i pair (i fixed) is in the last place given. For example, if the random-error standard deviation, obtained by replication, of a certain P value were 0.62 bar, the associated P value should be stated as, e.g., 1071.3 bar, not 1071 or 1071.34 bar.

All experiments are limited in practice by cost, time, and equipment. Within these limitations, the experiment should be designed so that for each point the normalized residuals, N_{x_i} and N_{y_i}, are roughly equal in magnitude. Depending on the weighting, the precision required in X_i and Y_i by this condition may be very different. Note that $|N_{x_i}| \approx |N_{y_i}|$ will lead to $S_x \approx S_y$, or $S_x/S \approx 0.5$.

When u_0, a specific number of runs, differs appreciably from its most likely value, such difference can arise either from an unfortunate distribution of random errors or from systematic errors. The possible effect of random errors may be identified by either covering the same range with a larger N or, preferably, also replicating the data set several times. These measures allow one to distinguish better between random and systematic errors and to obtain the most appropriate fitting equation. They also make it more practical to partition the total amount of data in various ways, and by fitting a number of subsets separately, examine the stability of the derived parameters and the appropriateness of the fitting equation in another way. Sometimes such partitioning can bring to light appreciable systematic errors in the data as well. For example, if the s_d's obtained from separate fits of the bottom and top halves of the data differed by 5 or 10 times, one would suspect the presence of strong systematic errors in the data, a poor equation choice, or a terrible choice of weights.

At a fixed temperature, a suitable P-V data set should cover the maximum range of P practical and should have $N \gtrsim 30$ to ensure that $N-n \approx N$. Further, this set should be replicated at least 5 or 10 times, allowing σ_{p_i} and σ_{V_i} to be determined experimentally. The M_0's obtained from the replicated sets should follow a chi-squared distribution when fitting is carried out with an appropriate equation of state and weighting. If the resulting $\langle M \rangle$ is not within one or two standard deviations, $(2f)^{1/2}$, of f assuming the appropriate model is used, the weighting should be changed to bring this about. Then the replicated sets should be merged for a final fitting. It appears that with the accuracy and precision of presently available "good" data a suitable equation of state for a fixed temperature should have no more than three to four free parameters, counting V_0. In the present work, most of the parameters of all the equations were highly correlated, suggesting the possibility of an adequate equation of state with fewer parameters.

Unless V_0 is known exactly or to far greater accuracy than other V values, V_0 should not be taken fixed in the usual way but should be a free parameter. Two methods of handling V_0 when it is not exactly known have been described herein. The one in which $V_0 = V_a$ is taken as free is preferable when generalized nonlinear least-squares convergence is not too slow or as a final fitting method after the other method has been used.

Finally, the present work indicates that, at least for the water and Hg data examined, $K_0 K_0''$ is far too large that a second-order series approximation for K in terms of p (Eq. 4) is a good approximation even over the relatively small compression ranges considered. For the 0°C water data at maximum pressure ($\sim 10^3$ bar), $K/K_0 \cong 1 + 0.27 + 0.084$, showing that the successive series terms decrease only slowly even for this relatively low pressure. Since a second-order expansion is not generally sufficient for the water and Hg data, Anderson's (1965, 1966) hypothesis that the Murnaghan equation of state, arising as it does from a linear expansion of K, is sufficient for extrapolation to very high compressions is definitely inappropriate for these materials. Any such "extrapolation from the origin" is dangerous to use without independent checks.

The present work illustrates some of the kinds of analysis of P-V data which can be, but rarely are, carried out. I hope it will help demonstrate the possibility and desirability of better planning and analysis of experiments in this area, especially needed, in my opinion, as data precision and accuracy continue to improve.

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APPENDIX: UNROUNDED DAVIS–GORDON P-V RESULTS FOR Hg

P (kbar)	V (21.9°C)	V (40.5°C)	V (52.9°C)
1	1.000018	1.003304	1.005497
2	0.996209	0.999405	1.001537
3	0.992539	0.995650	0.997726
4	0.988996	0.992029	0.994051
5	0.985570	0.988529	0.990502
6	0.982254	0.985143	0.987070
7	0.979038	0.981862	0.983745
8	0.975916	0.978680	0.980521
9	0.972883	0.975589	0.977391
10	0.969933	0.972584	0.974349
11	0.967061	0.969660	0.971390
12	0.964262	0.966813	0.968509
13	0.961532	0.964037	0.965702

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