



FIG. 8. The deviations of the volume data from the least-squares fitted equations of state. Limits of experimental error indicated by sloping straight lines.

opportunity for testing the usefulness of various isothermal P - V equations.

To be useful in the representation of P - V data for a given phase, an equation must be single valued and continuous for all pressures, V must be greater than zero but decrease for all P , and dV/dP must decrease continuously. These conditions suppose no phase changes under pressure; if phase changes occur, the extrapolation method is no longer useful. Of equations satisfying the above conditions, the most satisfactory will be that which can best fit existing data with the smallest number of fitting coefficients. A further desirable property is that the coefficients be directly related to some physical property of the material considered.

A direct approach to developing a P - V equation would be to express the Helmholtz free energy as a power series in V and use the relation $P = -(\partial F/\partial V)_T$. An equivalent, and easier, method is to use a Taylor series expansion of the pressure in terms of the volume. The expression for F then follows from integration of P with respect to V .

Considering the conditions listed above for a pressure-volume equation, a likely choice is to expand the pressure in powers of V_0/V , about $V_0/V=1$ or $V=V_0$. This expression, up to the quadratic term, is

$$P = \frac{dP}{d(V_0/V)_{V=V_0}} \left(\frac{V_0}{V} - 1 \right) + \frac{1}{2} \frac{d^2P}{d(V_0/V)^2_{V=V_0}} \left(\frac{V_0}{V} - 1 \right)^2 + \dots, \quad (14)$$

where V_0 is initial volume. The coefficients of the expansion can be written as

$$\frac{dP}{d(V_0/V)_{V=V_0}} = B_0$$

and

$$\frac{d^2P}{d(V_0/V)_{V=V_0}} = B_0(B_0' - 1),$$

where B_0 is the bulk modulus at 1 atm and B_0' is the derivative of the bulk modulus with respect to pressure, evaluated at 1 atm. Equation (14) can be expressed, therefore, as

$$P = B_0(\Delta V/V) + \frac{1}{2} B_0(B_0' - 1)(\Delta V/V)^2 + \dots, \quad (15)$$

where $\Delta V = (V_0 - V)$. This equation meets the requirements listed above since it is single valued and continuous, and it predicts a volume which steadily decreases at a decreasing rate with increasing pressure but always remains real and positive, provided that B_0' is greater than 1.

A related but alternate approach has been suggested by Onat³⁸ and by Vaisnys³⁹ whereby the pressure is expanded in powers of $\ln V$ about $V=V_0$:

$$P = (dP/d \ln V)_{V=V_0} (\ln V - \ln V_0) + \frac{1}{2} (d^2P/d \ln V^2)_{V=V_0} (\ln V - \ln V_0)^2 + \dots, \quad (16)$$

Again, the coefficients may be expressed in terms of B_0 and B_0' , viz.,

$$(dP/d \ln V)_{V=V_0} = -B_0$$

and

$$(d^2P/d \ln V^2)_{V=V_0} = B_0 B_0',$$

so that Eq. (16) may be written as

$$P = -B_0 \ln(V/V_0) + \frac{1}{2} B_0 B_0' [\ln(V/V_0)]^2 + \dots, \quad (17)$$

This equation also meets the requirements listed above.

A number of other equations to describe the pressure-volume relations of materials have been proposed by various investigators. Bridgman expressed a great deal

³⁸ E. T. Onat (private communication).

³⁹ R. J. Vaisnys (private communication).