

TABLE VIII. Standard deviation ( $\sigma$ ) for the equations of state (in terms of  $V/V_0$ ) and the pressure derivative of the bulk modulus ( $B_0'$ ).

Equation	21.9°C	40.5°C	52.9°C
$\sigma$ (unitless)			
Quadratic ( $V/V_0=1+aP+bP^2$ )	$235 \times 10^{-6}$	250	260
Cubic ( $V/V_0=1+aP+bP^2+cP^3$ )	18	20	21
Murnaghan's equation (20)	38	40	42
Birch's equation (21)	10	11	12
(17)	29	31	32
(15)	8	9	9
$B_0'$ (unitless)			
Murnaghan's equation (20)	8.70	8.72	8.74
Birch's equation (21)	9.10	9.14	9.17
(17)	9.72	9.78	9.81
(15)	9.38	9.44	9.47

Fig. 8. This figure specifically pertains to the volume data at 21.9°C, but the results at 40.5° and 52.9°C are almost identical. The straight lines shown at an angle to the zero deviation line represent the probable limits of error of the volume data less any systematic error in the pressure scale since this would not influence the fit of the various equations tested. It has already been indicated that, on general grounds, Eq. (18) is a poor choice as an equation of state, but in addition, as Fig. 8 shows, it gives a very poor fit to the present data. The cubic expansion of  $V$  in terms of  $P$  ( $\Delta V/V_0 = aP + bP^2 + cP^3$ ) was also fitted and found not to give a very good representation of the data, and of course the equation begins to diverge strongly toward negative infinity at pressures slightly above the experimental range. Equations (15) and (21) each represent the data with the use of only one adjustable parameter; each predicts a reasonable extrapolation of the volume to higher pressures. Murnaghan's logarithmic equation (20) and Eq. (17) do not provide an adequate representation of the volume change with pressure. In the case of Murnaghan's equation, this indicates that the bulk modulus of Hg does not vary linearly with  $P$  to 13 kbar. Figure 9 shows that the bulk modulus  $B$  does indeed deviate slightly from linearity with pressure. By obtaining a least-squares fit of a straight line ( $B_0 + B_0'P$ ) to the bulk-modulus data and noting the deviations of the data from this line, it was confirmed that the curvature of  $B$  is outside experimental error. The bulk-modulus data is also shown in Table VII.

Table VIII lists the standard deviations of the equations tested and also  $B_0'$  for Murnaghan's equation,

for Eq. (17), and for the two equations which best represent the data.

In summary, it is seen that two equations give a good fit to the volume data: Eq. (15), an expansion of  $P$  in terms of  $V_0/V$ , and the Birch equation (21). The Murnaghan and Bridgman equations are not satisfactory, and the latter is not suitable for extrapolation. No one of these equations has more theoretical justification than another. Considering its simplicity, Eq. (15) is the most satisfactory analytical representation of the  $P$ - $V$  data which satisfies all of the criteria established above. It does not appear to have been used for this purpose before. If a third term were required in this equation, it would be

$$\frac{1}{6} \frac{d^3 P}{d(V_0/V)^3} = \frac{1}{6} [2B_0 - 3B_0' B_0 + (B_0')^2 B_0 + B_0'' B_0^2].$$

The method of calculation which has been developed for the analysis of the mercury data can easily be modified to be applicable to isotropic solids. The principal difference is that, whereas the length of the liquid sample is known at all pressures, that of the solid is not. Letting the ratio of the initial length of an isotropic solid sample to the length at pressure  $P$  be  $S$ , i.e.,

$$S = l_0/l = (\rho/\rho_0)^{1/3}, \quad (22)$$

it can be shown that

$$S = 1 + \int_0^P \frac{1}{4l_0^2 \rho_0 [3(1/t_1)^2 - 4(1/t_2)^2]} dP + \frac{T}{3\rho_0 S^2} \int_0^P \frac{\alpha^2}{C_P} dP, \quad (23)$$

where  $t_1$  and  $t_2$  are the transit times for longitudinal and shear wave pulses, respectively. In this case solution of the two integrals gives  $S$  and, from Eq. (22),  $\rho$  as well as the sonic velocities. The quantity  $S$  appears outside of the integral in the second term of Eq. (23); this is correct if the integral is evaluated over a small interval  $\Delta P$  within which  $S$  may be considered constant, analogous to the procedure used with the liquid.

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