Compression of Mercury at High Pressure*·†

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An exact method of computing volume changes under high pressure from acoustic-wave-velocity measurements is developed. It is applicable to large as well as small compressions. To illustrate the application of the method, precision ultrasonic-velocity measurements made in mercury at pressures up to 13 kbar for three temperatures have been used to compute V as a function of T and P. The volume is determined to an accuracy of better than 0.01% at each pressure and temperature. An analytical expression for the pressure dependence of the volume in which all coefficients are expressed in terms of the bulk modulus and its derivatives is developed and shown to give a better representation of the $P–V$ data than many of the equations now in use.

INTRODUCTION

A FUNDAMENTAL problem in high-pressure research is the determination of the equation of state of condensed materials. One experimental approach to this problem is direct measurement of the volume as a function of pressure. Various methods have been devised for this. For liquids Bridgman has used a piezometer,[1,2] a piston-displacement method,[3–5] and a sylphon-bellows device[6–9] which employs a potentiometric length-measuring technique. The piezometer yielded volumes accurate to about 0.1%, the piston-displacement method to about 1%, and the sylphon bellows to a few hundredths of 1%. For solids Bridgman used a linear-compression technique[10,11] where the change in length of samples relative to that of pure iron is measured and, again, the piston-displacement method.[12–16] These methods have been refined by other investigators. Cutler *et al.*[17] and Boelhouwer[18] modified the sylphon-bellows technique by employing an external linear-differential transformer to measure the bellows motion. Doolittle *et al.*[19] determined the change in volume of a liquid by following the motion of a float

at its surface with an external linear-differential transformer. Accuracies of the order of 0.01% are attained. To measure compression in solids to very high pressures, a Debye–Scherrer x-ray powder pattern of a sample compressed in an anvil device has been used. A review of the earlier x-ray techniques is given by Jamieson and Lawson[20]; newer methods are described by Barnett and Hall[21] and Perez-Albuerne, Forsgren, and Drickamer.[22] A common problem in the x-ray methods is that pressure determination is difficult so that the volume results obtained are accurate to only about 1%. For compression measurements to ultrahigh pressure (megabars), the shock-wave method is used. Deal[23] has given a review of the techniques involved. The question of accuracy is a difficult one here, but it is certainly not better than 1% of the volume.

In all of the experimental methods enumerated above, volume is measured directly as a function of pressure. An alternative approach, inherently capable of yielding higher accuracy, is to measure the pressure dependence of the compressibility and then obtain volume as a function of pressure by integration. The compressibility and its pressure dependence may be measured to high accuracy by acoustic methods. In 1949 Lazarus[24] initiated development of the techniques necessary for making sonic-velocity measurements to high pressure. In his work on the elastic constants of cubic single crystals he assumed the samples changed length as though they had constant compressibility. In 1957 Cook[25] described a method of obtaining accurate volume results from high-pressure sonic-velocity data. He employed the less restrictive assumption that the ratio of the isothermal and adiabatic compressibilities is a constant. This approximation is reliable when the com-

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[3] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 48, 309 (1912).
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[5] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 74, 399 (1942).
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[16] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 74, 425 (1942).
[17] W. G. Cutler, R. H. McMickle, W. Webb, and R. W. Schiessler, J. Chem. Phys. 29, 727 (1958).
[18] J. W. M. Boelhouwer, Physica 26, 1021 (1960).
[19] A. K. Doolittle, I. Simon, and R. M. Cornish, A.I.Ch.E.J. 6, 150 (1960).

[20] J. C. Jamieson and A. W. Lawson, in *Modern Very High Pressure Techniques*, R. H. Wentorf, Jr., Ed. (Butterworths Scientific Publications, Ltd., London, 1962), p. 70.
[21] J. D. Barnett and H. T. Hall, Rev. Sci. Instr. 35, 175 (1964).
[22] E. A. Perez-Albuerne, K. F. Forsgren, and H. G. Drickamer, Rev. Sci. Instr. 35, 29 (1964).
[23] W. E. Deal, Jr., in Ref. 20, p. 200.
[24] D. Lazarus, Phys. Rev. 76, 545 (1949).
[25] R. K. Cook, J. Acoust. Soc. Am. 29, 445 (1957).

pression is small, perhaps less than 1%, which can of course correspond to quite high pressures for very incompressible materials. Since the velocity of sound in a material can be determined to an accuracy of 0.1% or better and this uncertainty enters the volume calculations as a relatively small additive term, volume results to better than 0.01% may be obtained. A significant advantage of this method is that it yields elastic constants and compression results simultaneously.

A disadvantage of Cook's approach is the restriction to small compressions. In this paper we develop a method which will allow the determination of accurate volume data at high pressure from elastic wave-velocity experiments regardless of the amount of compression involved. To use this method, sonic-velocity data as a function of both pressure and temperature are required; and the temperature dependence of the thermal expansion, heat capacity, and density at room pressure must be known. To illustrate the application of the method, precision sound-velocity measurements have been made in mercury over a range of temperature and pressures and used, in conjunction with available thermodynamic data, in a precision determination of volume as a function of pressure and temperature.

EXPERIMENTAL APPARATUS AND PROCEDURE

The velocity of sound in liquid Hg is determined as a function of pressure and temperature by a variant of the pulse-echo technique originally developed by Pellam and Galt.[26] The liquid Hg is placed in a stainless-steel sample holder, and the holder placed in a cylindrical pressure vessel. Pressure is generated by driving a piston into the vessel and is transmitted to the Hg by a liquid pressure-transmission medium. Electrical leads are brought into the vessel through the base-plug pressure closure. The pressure in the vessel is determined by monitoring the resistance of a coil of Au–2.1% Cr wire, which is calibrated as a function of pressure vs a free-piston gauge. Experiments on the variation of sonic velocity in Hg with pressure were performed at three temperatures; 21.9°, 40.5°, and 52.9°C.

A pulsed oscillator, balancing network, preamplifier, and amplifier obtained from the Arenberg Ultrasonic Laboratory, Inc. are arranged as shown in Fig. 1. A 5-Mc/sec pulse of 10-μsec duration at a 60-cps repetition frequency is used, and the pulse and sample echoes are displayed on a Tektronix 547 cathode-ray oscilloscope (CRO). It is somewhat difficult to make highly accurate, absolute wave-velocity measurements by the simple pulse-echo technique since it is difficult to account for the relative phase shift between echoes. Therefore, in this work the change in transit time relative to the transit time at 1 atm is measured using

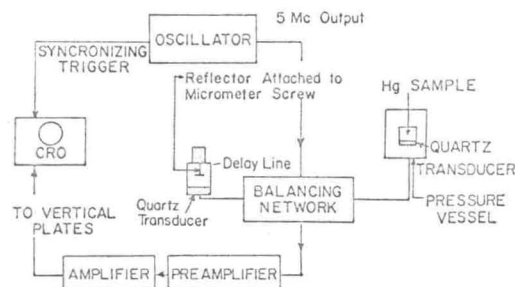[26] J. R. Pellam and J. K. Galt, J. Chem. Phys. 14, 608 (1946).

FIG. 1. The high-frequency-pulse equipment.

the first echo only. The initial transit time is computed from the 1-atm sonic-velocity data for liquid Hg of Hubbard and Loomis[27] (accurate to 0.02%) and the known length of the sample. Correction for the change in sample length due to T and P was made using the measured linear-expansion coefficient for the Type 303 stainless steel used for the sample holder[28] [$16.2 \times 10^{-6}(°C)^{-1}$] and Bridgman's linear-compression data for Fe[11] [$-\Delta l/l_o = 1.904 \times 10^{-7}P - 0.22 \times 10^{-12} P^2$ (for P in bars)]. Since the magnitude of the length change is small, high accuracy is not needed in making these corrections.

The change in transit time was determined using a variable-Hg delay line consisting of a pot of Hg with a quartz transducer at its bottom and a steel reflector inserted into it from the top. The reflector is connected to a micrometer screw so that changes in its position can be accurately determined. At the outset of each particular high-pressure experiment, a convenient cycle of the unrectified first echo from the specimen and from the delay line is placed in phase on the CRO by adjusting the level of the reflector in the delay line. With the unrectified signals the cycles can be matched to within ±1.4 nsec. With application of pressure to the sample a change in transit time results causing a shift in position of the sample echo on the CRO. By adjusting the reflector height in the delay line the same cycles were again brought into coincidence. The change in transit time is then given by $\Delta t = 2\Delta d/c$, where Δd is the change in micrometer reading and c is the sonic velocity in Hg at room temperature and 1 atm. After application and release of pressure, the transit time is found to return to its original value to within 1.4 nsec. In each pressure run half the data points were taken with increasing pressure, and half, with decreasing pressure. Since the delay-line micrometer permits the transit-time change to be determined on the average to about 0.06% and since the sample length can be measured to about 0.03%, the change in velocity is determined to about 0.09%. The absolute velocity itself, however, is determined to 0.04%, including the

[27] J. C. Hubbard and A. L. Loomis, Phil. Mag. 5, 1177 (1928).
[28] Metals Handbook, T. Lyman, Ed., (American Society for Metals, Cleveland, Ohio, 1948), p. 555.
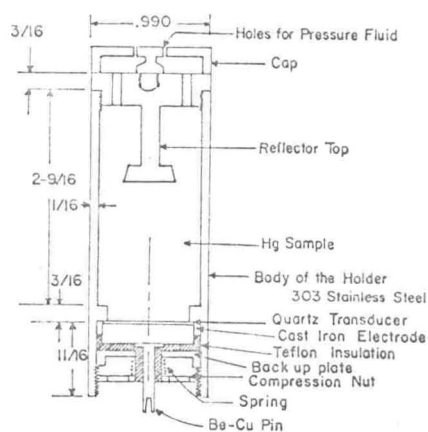
FIG. 2. The sample holder for liquid Hg (dimensions in inches).

uncertainty of the 1-atm data of Hubbard and Loomis, since the velocity change is only a fraction of the calculated velocity.

The sample holder for the liquid Hg, shown in Fig. 2, was constructed from Type 303 stainless steel. It is closed at the bottom by the quartz transducer and fitted at the top with a 1.2-cm-diam reflector set accurately parallel to the transducer. Holes in the reflector top allow the pressure-transmission fluid (pentane or hexane) to bear on the Hg. A final cap, which contains small holes out of line with those in the reflector top, is threaded into the reflector top. This cap acts as a baffle for preventing Hg from escaping from the top of the holder. Loss of mercury into the steel pressure vessel often results in an embrittlement of the latter and an explosive failure.

The diameter of the transducer surface in contact with the liquid Hg (1.9 cm) constitutes the sample diameter. Since the wavelength of 5-Mc/sec ultrasonic waves in liquid Hg is about 0.03 cm, the sample-diameter-to-wavelength ratio is about 60, well above the figure of 20 which Mason[29] cites as the minimum allowable value if the sound pulses are to be propagated as if the sample were infinite. The sample length over which the sound pulse radiates as a plane wave (the Fresnel region) is determined by the diameter of the radiating surface and the wavelength of the sound.[30] In the present case, where the reflector diameter is the limiting diameter, it can be shown that the Fresnel region extends for 22 cm. Therefore, the echo of importance here (the first echo), which travels a distance of about 7.8 cm, is well within the plane-wave region.

The high-pressure system used in this work is the piston-and-cylinder apparatus shown in Fig. 3. The vessel is of three-piece construction. The inner cylinder is forced into the middle cylinder under a load of about 400 tons, placing the inner cylinder in compression. The outer cylinder is a soft-iron-pipe safety ring. This

vessel is capable of containing about 30 kbar pressure. The top of the vessel is sealed by a standard Bridgman seal. Load is applied to the piston from a 400-ton hydraulic ram. The bottom of the vessel is sealed by a tapered plug through which the necessary electrical leads are brought. Sheathed leads are sealed into a steel plug with epoxy cement.[31] The ability of this type of plug to retain the electrical leads at high pressure depends in part on the radial force developed as the plug is forced into the taper at the bottom of the pressure vessel. Consequently, the clearance allowed at the bottom of the plug is critical; excessive support of the plug will result in blowout of the leads. A disadvantage of this type of plug design is that it is sometimes difficult to control the quality of the plugs, with the result that a sheath may be ejected.

Sonic-velocity experiments were carried out at 21.9°, 40.5°, and 52.9°C. For the higher-temperature experiments the entire pressure vessel was heated. Temperature inside the vessel was determined by a Chromel–Alumel thermocouple brought through the tapered bottom plug; its calibration was traceable to a platinum resistance thermometer. At pressures up to 13 kbar the calibration of a Chromel–Alumel thermocouple changes by negligible amount.[32] A temperature gradient of less than 0.3°C existed across the sample at the higher temperatures; this gradient was found to be insensitive to pressure. The probable error in the stated temperature is about ±0.25°C.

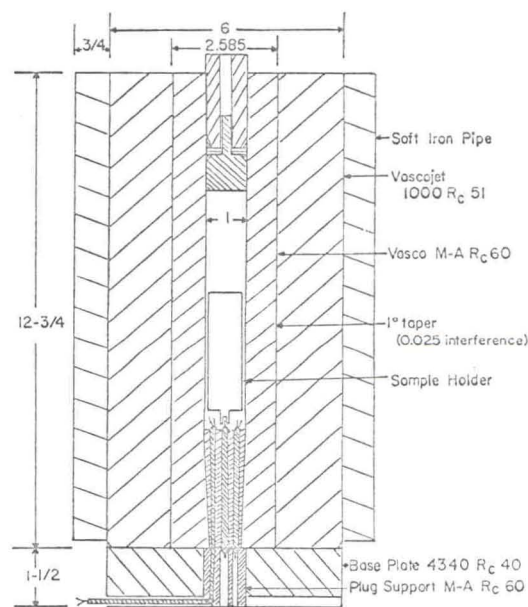FIG. 3. The pressure vessel (dimensions in inches).

[29] W. P. Mason, *Physical Acoustics and the Properties of Solids* (D. Van Nostrand Co., Inc., Princeton, N.J., 1958), p. 40.
[30] W. P. Mason, Ref. 29, p. 96.

[31] L. A. Davis, R. B. Gordon, J. K. Tien, and R. J. Vaisnys, Rev. Sci. Instr. 35, 368 (1964).
[32] R. E. Hanneman and H. M. Strong, Symp. High Pressure Technology, ASME Winter Annual Meeting, New York, 1964 (1964), Paper No. 64 WA/PT-21.

Pressure was measured with a wire resistance gauge. Such a gauge must be calibrated against a primary pressure standard or against pressure-fixed points, such as phase-transition pressures, which have been themselves accurately established relative to a primary standard. In this work the gauge was a loosely wound coil of 0.005-in.-diam Au–2.1% Cr alloy of about 13-Ω resistance. The details of the gauge preparation and calibration against a precision free-piston gauge have been given elsewhere.[33] The gauge resistance is determined with the aid of a six-dial potentiometer to an accuracy of 5 ppm, which means that it was possible to detect a pressure change on the order of 6 bar. The calibration of the gauge is given in Table I. The coefficients given there were obtained by a quadratic least-squares fit of the gauge-resistance-vs-pressure data. The standard deviation of the data from the least-squares curve was 0.00008 Ω in approximately 12 Ω, which is equivalent to 6 bar.

There is some difficulty with drift in the calibration of Au–Cr pressure gauges. A check on the gauge calibration at 21.9°C at the time of the velocity experiments showed that it had drifted by an approximately

TABLE I. Coefficients of the pressure gauge calibration curve, $\Delta R/R_0 = AP + BP^2$.

Temperature (°C)	A (bar^{-1}×10^{-6})	B (bar^{-2}×10^{-13})
21.9	1.070	−4.7
40.5	1.057	−7.4
52.9	1.044	−6.2

linear factor of 0.4%±0.2% over the eight-month period between the free-piston-gauge calibration and the velocity experiments in such a way as to make the relative change of resistance smaller for a given change of pressure. Since it would have been prohibitively difficult and expensive to check the calibration at the other two temperatures, it is assumed that the calibration drifted in the same way for those temperatures. The calibration in Table I represents the corrected calibration and is therefore reliable to about 0.4%.

RESULTS

For the purpose of calculation, the measured pressure dependence of the sound velocity given in Table II is fitted to the equations

$$P = A + Bc_T + Dc_T^2, \qquad (1)$$

$$c_T = A' + B'P + D'P^2, \qquad (2)$$

where P is pressure and c_T is sonic velocity at temperature T. Equation (1) is found to give a better fit at each T since the standard deviation in each case is

[33] L. A. Davis and R. B. Gordon, Rev. Sci. Instr. **38**, 371 (1967).

TABLE II. Sonic velocity in Hg.[a]

$T=21.9$°C		$T=40.5$°C		$T=42.9$°C	
Pressure	Velocity	Pressure	Velocity	Pressure	Velocity
1	1450.1	1	1441.5	1	1435.8
299	1457	516	1453	464	1447
584	1463	932	1463	925	1457
989	1472	1 458	1474	1 485	1469
1 276	1478	1 930	1484	1 942	1478
1 532	1483	2 144	1488	2 511	1490
2 106	1495	2 769	1500	2 537	1491
3 254	1517	3 080	1507	3 019	1500
3 264	1518	3 893	1522	4 232	1524
3 490	1522	4 298	1530	4 548	1530
4 565	1542	4 483	1533	4 942	1537
5 772	1564	5 539	1552	5 470	1546
5 907	1566	5 642	1555	6 885	1572
6 138	1570	6 518	1569	6 915	1573
7 542	1594	7 168	1581	7 746	1587
8 310	1606	7 175	1581	8 255	1595
8 858	1615	8 309	1599	9 533	1616
8 950	1616	8 538	1604	9 954	1623
9 894	1632	9 399	1618	10 939	1639
10 695	1644	10 318	1632	11 203	1642
10 926	1648	10 384	1634	11 503	1647
11 485	1656	11 830	1656	11 792	1651
11 532	1657	11 922	1657	12 968	1669
11 985	1664	12 315	1663	13 023	1670
12 035	1665	13 270	1677	13 332	1675
		13 709	1684		
		14 213	1691		
		14 695	1698		
		14 921	1701		

[a] Pressure in bars, velocity in meters per second.

about a factor of 3 smaller than for Eq. (2). Equation (1) presents a more reasonable picture physically since it predicts a steady increase of velocity with pressure while Eq. (2) predicts a maximum in c_T with pressure and a subsequent decrease. The standard deviations from the least-squares curve of Eq. (1) for the three experimental temperatures are shown in Table III along with the coefficients of the curves. The solid curves in Fig. 4 represent the least-squares equations.

It is possible to use the sound-velocity data described above, in conjunction with certain other data, to calculate the specific volume of Hg as a function of T and P. The calculation starts with the relation between the sound velocity and adiabatic compressibility

$$\beta_{\text{ad}} = 1/\rho c_T^2 \qquad (3)$$

and the relation

$$\beta_T = \beta_{\text{ad}} + (T\alpha^2/\rho C_P), \qquad (4)$$

where β_T is isothermal compressibility at temperature T,

TABLE III. Least-squares coefficients of the curve $P = A + Bc_T + Dc_T^2$ and the standard deviation (σ) of the velocity data.

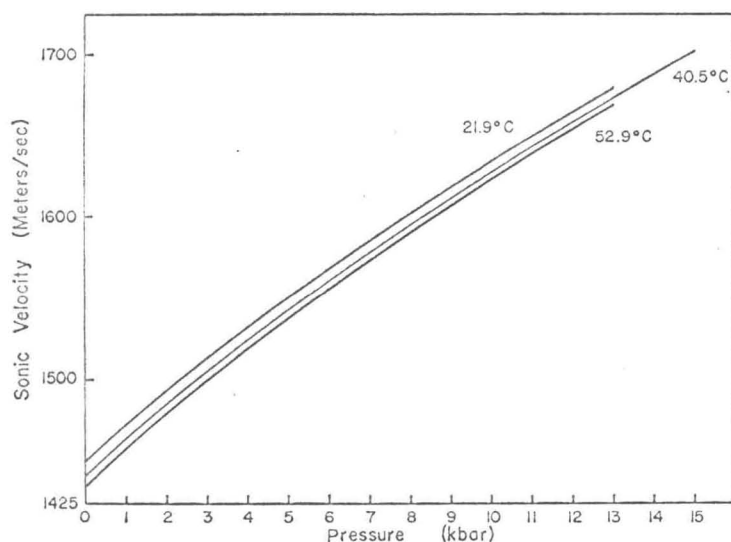| Temperature (°C)	21.9°	40.5°	52.9°
A (bar×10^5)	4.1489	3.9067	4.0715
B (bar per m/sec×10^2)	−1.025	−0.9885	−1.006
C (bar per m^2/sec^2×10^{-2})	5.096	4.976	5.034
σ (m/sec)	0.2	0.3	0.3

FIG. 4. The sonic velocity c_T in liquid Hg as a function of pressure at several temperatures.

T is absolute temperature, α is volume thermal-expansion coefficient, ρ is density, and C_P is specific heat at constant pressure. Since

$$\beta_T = -(1/V)(\partial V/\partial P)_T = (1/\rho)(\partial \rho/\partial P)_T, \quad (5)$$

where V is volume, it follows from Eq. (3) that

$$(\partial \rho/\partial P)_T = (1/c_T{}^2) + (T\alpha^2/C_P). \quad (6)$$

Therefore, on integration with respect to P,

$$\rho_{P,T} = \rho_{o,T} + \int_1^P \frac{1}{c_T{}^2} dP + T\int_1^P \frac{\alpha^2}{C_P} dP, \quad (7)$$

where $\rho_{o,T}$ is density at 1 atm and T, and $\rho_{P,T}$ is density at P and T. Evaluation of the two integrals over a range of T yields ρ as a function of P and T. The integral of $1/c_T{}^2$ at a given temperature can be evaluated directly from the least-squares velocity curves, using numerical integration, under the assumption that $1/c_T{}^2$ varies linearly for small $\Delta P = P_2 - P_1$. To evaluate the second integral, two additional relations can be used, viz.,

$$(\partial \alpha/\partial P)_T = -(\partial \beta_T/\partial T)_P \quad (8)$$

and

$$(\partial C_P/\partial P)_T = -(T/\rho)[(\partial \alpha/\partial T)_P + \alpha^2]. \quad (9)$$

If β_T is known as a function of T at $P = P_1$, the initial slope of the α-vs-P curve may be determined for any temperature. Then, over the interval $\Delta P = P_2 - P_1$, the change of α can be approximated by

$$\alpha_P = (\partial \alpha/\partial P)_{T,P_1}(P - P_1) + \alpha_{P_1}, \quad P_1 \leq P \leq P_2. \quad (10)$$

If α vs T is known at P_1, α vs T at P_2 may be found from (10). Therefore, in (9), $(\partial \alpha/\partial T)_P$ can be expressed as

$$\left(\frac{\partial \alpha}{\partial T}\right)_P = \left[\frac{(\partial \alpha/\partial T)_{P_2} - (\partial \alpha/\partial T)_{P_1}}{\Delta P}\right](P - P_1) + \left(\frac{\partial \alpha}{\partial T}\right)_{P_1},$$
$$P_1 \leq P \leq P_2. \quad (11)$$

Using (11) and the square of (10), Eq. (9) may be integrated analytically to find ΔC_P if ρ is assumed constant over ΔP. This produces a negligible error if ΔP is small. On performing the integration, ΔC_P is found to be very small so that C_P may be assumed constant for the integration in (7). Only the integral of α^2 at each temperature needs then to be evaluated. This can be found by using the square of (10) and integrating analytically. The density at P_2, $\rho_{P_2,T}$ is therefore determined.

It is apparent that in the course of calculating $\rho_{P_2,T}$ both C_P and α have been determined as a function of T at P_2. Clearly, then, β_T may be calculated as a function of T at P_2 from Eq. (4). It follows that the calculation may be now repeated starting with the integration of $1/c_T{}^2$ over the interval $\Delta P = P_3 - P_2$ and the determination of $(\partial \alpha/\partial T)_P$ at P_2 from Eq. (8). By continual repetition of these calculations all the quantities β_T, α, C_P, ρ, and β_{ad} may be determined as a function of temperature and pressure. In the experiments described above the change of velocity with

TABLE IV. One-atmosphere input data to the compression calculation.

Temperature, t (°C)	21.9°	40.5°	52.9°
Density, ρ (g/cm³) [a]	13.54122	13.49573	13.46551
Thermal-expansion coefficient, α (°C⁻¹×10⁴) [b]	1.81069	1.80825	1.80699
Specific heat, C_P (ergs/g·deg×10⁻⁶) [c]	1.390	1.385	1.382
Sonic velocity c_T (m/sec) [d]	1450.1	1441.5	1435.8

[a] Reference 36.
[b] Reference 35.
[c] Reference 34.
[d] Reference 27.

TABLE V. Calculated variables.

Pressure P (kbar)	Isothermal compressibility β_T (bar^{-1})	Thermal-expansion coefficient α (°C^{-1})	Density ρ (g/cm^3)	Volume V ($V = 1.0$ at 0°C)	Adiabatic compressibility β_{ad} (bar^{-1})
		$T = 21.9$°C			
1	3.881×10^{-6}	1.766×10^{-4}	13.5948	1.00000	3.395×10^{-6}
2	3.751	1.724	13.6468	0.99621	3.289
3	3.632	1.685	13.6973	0.99254	3.192
4	3.522	1.648	13.7463	0.98900	3.102
5	3.419	1.614	13.7941	0.98557	3.018
6	3.324	1.581	13.8407	0.98225	2.941
7	3.235	1.551	13.8862	0.97904	2.868
8	3.15	1.52	13.931	0.9759	2.799
9	3.07	1.50	13.974	0.9729	2.735
10	3.00	1.47	14.017	0.9699	2.674
11	2.93	1.45	14.058	0.9671	2.616
12	2.87	1.42	14.099	0.9643	2.562
13	2.80	1.40	14.139	0.9615	2.510
		$T = 40.5$°C			
1	3.963×10^{-6}	1.762×10^{-4}	13.5503	1.00330	3.444×10^{-6}
2	3.827	1.719	13.6032	0.99941	3.334
3	3.702	1.680	13.6545	0.99565	3.234
4	3.587	1.643	13.7043	0.99203	3.141
5	3.481	1.608	13.7528	0.98853	3.055
6	3.383	1.576	13.8001	0.98514	2.975
7	3.290	1.545	13.8462	0.98186	2.900
8	3.20	1.52	13.891	0.9787	2.829
9	3.12	1.49	13.935	0.9756	2.763
10	3.05	1.46	13.978	0.9726	2.701
11	2.98	1.44	14.020	0.9697	2.641
12	2.91	1.41	14.062	0.9668	2.585
13	2.84	1.39	14.102	0.9640	2.532
		$T = 52.9$°C			
1	4.018×10^{-6}	1.760×10^{-4}	13.5207	1.00550	3.477×10^{-6}
2	3.878	1.717	13.5742	1.00154	3.365
3	3.749	1.677	13.6261	0.99773	3.262
4	3.632	1.640	13.6764	0.99405	3.167
5	3.523	1.605	13.7254	0.99050	3.080
6	3.422	1.572	13.7732	0.98707	2.998
7	3.327	1.542	13.8197	0.98375	2.921
8	3.24	1.51	13.865	0.9805	2.850
9	3.16	1.48	13.910	0.9774	2.782
10	3.08	1.46	13.953	0.9743	2.719
11	3.01	1.43	13.995	0.9714	2.659
12	2.94	1.41	14.037	0.9685	2.602
13	2.87	1.39	14.078	0.9657	2.548

pressure, for three temperatures, has been established while the change of velocity with temperature at 1 atm is given by Hubbard and Loomis.[27] The values for C_P at 1 atm and various temperatures are given by Douglas et al.[34] to an accuracy of 0.3%. Values for α at atmospheric pressure and T have been taken from the work of Beattie et al.,[35] which establishes α within about 1 part in 10^5. The density ρ is given by Bigg,[36] who used the most recent determination of the density of Hg at 20°C, in conjunction with Beattie's expansion formula, to determine ρ as a function of temperature to within about 4 ppm. Using the data for ρ and the sonic-velocity data of Hubbard and Loomis, the adiabatic compressibility of liquid Hg may be calculated according to Eq. (3). Using β_{ad}, and α and C_P from the above sources, β_T may be calculated according to Eq. (4). All the data are thus established for the initiation of the calculation at $P_1 = 1$ atm. The numerical values of the input data are shown in Table IV.

The results of the calculation for α, β_T, β_{ad}, ρ, and V as a function of P at 21.9°, 40.5°, and 52.9°C are shown in Table V. Figures 5–7 show the variation of α, β_T, and V with pressure. No variation of C_P with P

[34] T. B. Douglas, A. F. Ball, and D. C. Ginnings, J. Res. Natl. Bur. Std. 46, 334 (1951).
[35] J. A. Beattie, B. E. Blaisdell, J. Kaye, H. T. Gerry, and C. A. Johnson, Proc. Am. Acad. Arts Sci. 74, 371 (1941).
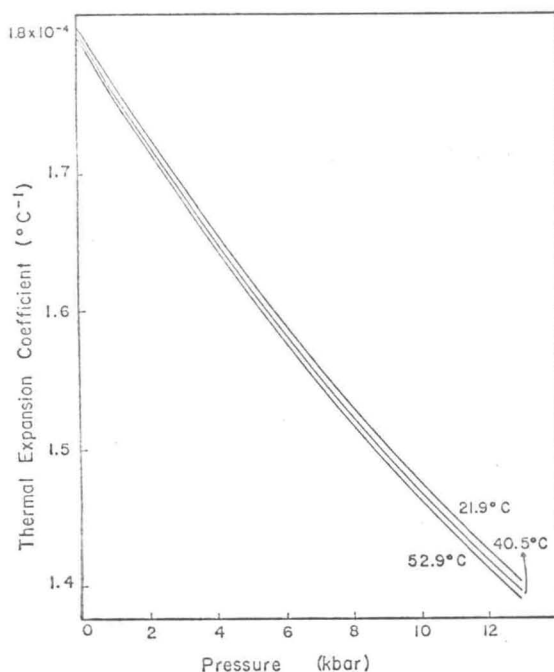[36] P. H. Bigg, Brit. J. Appl. Phys. 15, 1111 (1964).

FIG. 5. The volume thermal-expansion coefficient α of liquid Hg vs pressure at several temperatures. Considering experimental error, the three curves are actually just barely distinguishable from one another.

greater than experimental error is detected, hence its calculated variation with pressure has not been shown in a table or graph.

The procedure adopted here for estimating the probable error associated with each of the calculated results is to place various perturbations on the input data for the calculation and to observe its effect on the results. Since the three major sources of uncertainty in the present work are the results of the experimental determination of sonic velocity as a function of pressure, the 1-atm velocity data of Hubbard and Loomis, and the C_P data of Douglas et al., three perturbations, each involving only one of these variables, are investigated. The uncertainties in α and ρ at atmospheric pressure and in the temperature are negligible in comparison. The errors in β_T and β_{ad} at atmospheric pressure are taken into account automatically by considering the three major uncertainties.

To account for the errors in the velocity experiments, all the uncertainty may be assumed, for convenience, to be in the pressure scale. The possible systematic error in the scale itself is of the order of 0.4%. To this must be added a measure of the random uncertainty as indicated by the standard deviation σ of the velocity data from the least-squares curves. The equivalent of this σ on the pressure scale is about 17 bars. This uncertainty varies in percentage over the pressure scale, but a reasonable average is 0.3%. The total uncertainty on the pressure scale is therefore about 0.7%. In accordance with this, the least-squares velocity curve at 21.9°C

was adjusted so that a given velocity would correspond to a pressure higher than the experimentally determined value by 0.7%, and the 52.9° data was adjusted to predict a pressure lower by 0.7%. This adjustment may be made by multiplying the coefficients of the least-squares curves by an appropriate constant. The curve at 40.5°C was unadjusted. This perturbation can also be viewed as an adjustment of the slope of c_T vs T at each pressure. Since the perturbation involves a change of slope rather than a uniform increase or decrease of the data, it will affect the results for the three temperatures differently at a given pressure. Choosing the maximum effect should give a reliable estimate of the largest likely error.

The effects on α, β_T, V, and C_P of performing the calculation with the perturbation on the pressure scale are shown in Table VI. They are shown only for 13 kbar for the sake of brevity. To a first approximation the effect of the perturbation on each quantity decreases linearly, with decreasing pressure, to its value at 1 atm. Since the calculated change in C_P for each temperature was about 0.25% at 13 kbar, it follows, according to the effect of the perturbation on C_P (about $\pm 0.75\%$), that no information can be gained from the present work regarding the sign of change or rate of change of C_P with pressure.

The second perturbation on the data was constructed by reducing the value of C_P at 1 atm and 21.9°C by 0.3% and by raising it 0.3% at 52.9°. The third perturbation was obtained by decreasing the sonic velocity at 21.9° and 1 atm by 0.02% and by raising it at 52.9°C by the same percentage. The effects on α, C_P, β_T, and V of carrying out the calculations with these perturbations are also shown in Table VI. An estimate of the uncertainty of each quantity is then obtained by taking the sum of the perturbation effects, and it amounts to $\pm 0.4\%$ for β_T, $\pm 1.0\%$ for α, $\pm 1.3\%$ for C_P, and $\pm 0.0094\%$ for V. Once again, to a first approximation,
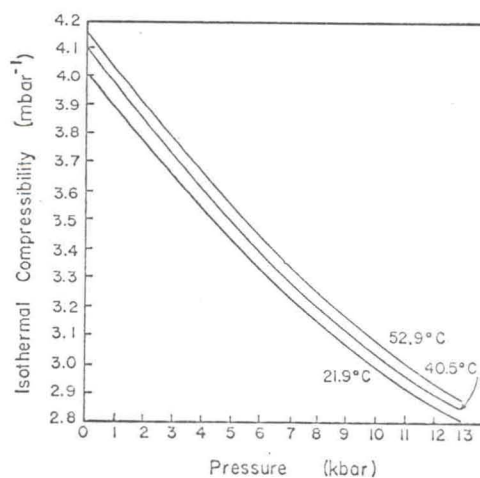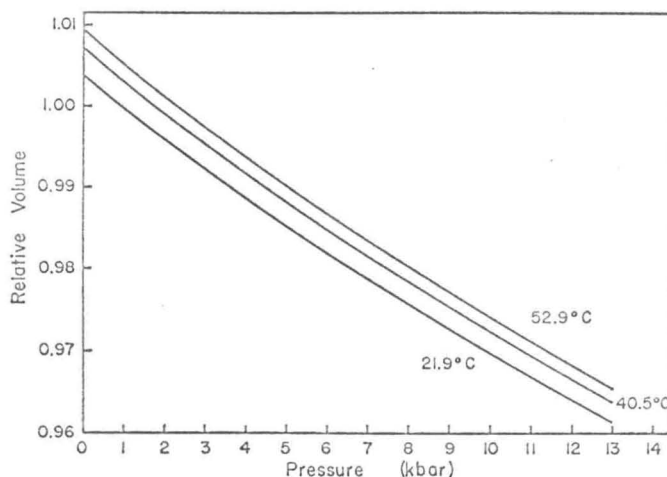

FIG. 6. The isothermal compressibility β_T of liquid Hg as a function of pressure at several temperatures.

FIG. 7. The relative volume V of liquid Hg as a function of pressure at several temperatures. Volume at 1 atm and 0°C is 1.00.

the uncertainty in each quantity decreases linearly with decreasing pressure to its value at 1 atm. These have been listed previously, except for β_T, for which it is 0.8%.

Selection of the appropriate value of the interval ΔP to be used in the calculation of the thermodynamic variables is a matter of trial and error. It was found that there was no need to use an interval smaller than 125 bar. The residual error for each variable which results from using this interval is between one and two orders of magnitude smaller than the uncertainty of the variable.

The thermodynamic calculations which have been described were programmed for an IBM 1620 computer. In order to compute the derivatives $(\partial\beta/\partial T)_P$ and $(\partial\alpha/\partial T)_P$ of Eqs. (8) and (9), respectively, it was necessary to fit curves by the least-squares method to the β_T-vs-T and α-vs-T data at each step of pressure. Curves of the type

$$\beta_T = A + BT + GT^2 \qquad (12)$$

and

$$\alpha = D + ET + FT^2 \qquad (13)$$

are chosen since they accurately describe the variation at 1 atm of β_T and α with T over the range of 0°–100°C. The suitability of these equations for fitting the temperature data at higher pressures can be easily checked as the calculation proceeds, and, if necessary, different equations could be used over different intervals of pressure. In the present work the use of a quadratic in T leads to a perfect fit since there are only three data points with temperature variation; since the data display a definite curvature, use of a straight line would not be suitable.

Each of the three perturbations described above left the data at 40.5°C unperturbed, while the data at 21.9° and 52.9° were adjusted in opposite directions. The perturbations were purposely chosen this way to maximize the variation in the derivatives $(\partial\beta/\partial T)_P$ and $(\partial\alpha/\partial T)_P$ and thus establish the maximum likely un-

certainty in the calculated results. The largest uncertainties occur in α and C_P because of their strong dependence on these derivatives through Eqs. (8) and (9), respectively. The uncertainty in β_T is smaller because the uncertainties of α and C_P affect it only through the additive term in Eq. (4), $T\alpha^2/\rho C_P$, which is about 10% of β_T. The volume is obtained with high accuracy because it involves the uncertainties in the velocity data and α and C_P through the small additive integrals in Eq. (7). The accuracy of β_{ad} is affected mainly by the uncertainty in the sonic velocity since the volume is quite accurate, and thus it is accurate to about 0.14%.

DISCUSSION

High accuracy in pressure measurement can only be attained below about 13 kbar where calibration against free-piston gauges is possible. The possibility that more precise volume data at very high pressure may be obtained by appropriate extrapolation of relatively precise data taken below 13 kbar than by direct measurement has been pointed out by Anderson.[37] For this reason it is of interest to consider the question of the best analytical representation of experimental $P-V$ data. The precision volume results for Hg provide an

TABLE VI. Magnitude of the perturbation effects on the calculated variables at 13 kbar.[a]

Variable	β_T	α	C_P	V
C_P perturbation	0.07	0.2	0.30	0.0019
Pressure scale perturbation	0.26	0.6	0.75	0.0057
One-atmosphere velocity perturbation	0.07	0.2	0.25	0.0018
Total	0.40	1.0	1.3	0.0094

[a] In percent.

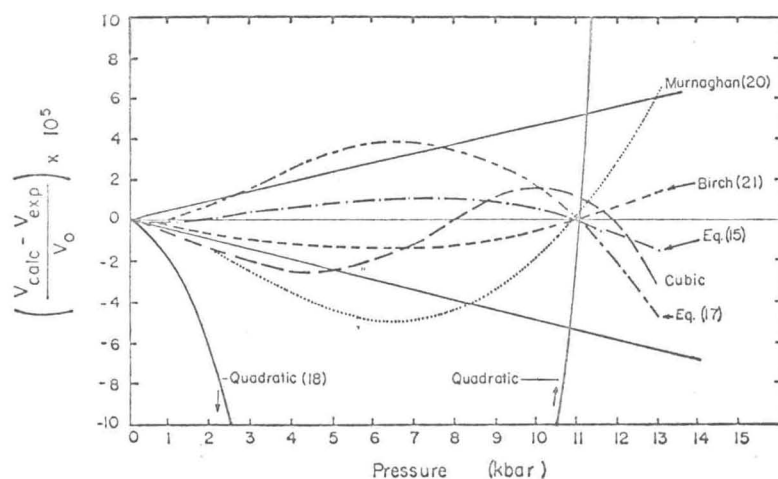[37] O. L. Anderson, J. Phys. Chem. Solids 27, 547 (1966).

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

$$P = \frac{dP}{d(V_o/V)_{V=V_o}}\left(\frac{V_o}{V}-1\right)$$

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

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

$$\frac{dP}{d(V_o/V)_{V=V_o}}=B_o$$

and

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

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

$$P = B_o(\Delta V/V)+\tfrac{1}{2}B_o(B_o{}'-1)(\Delta V/V)^2+\cdots,\quad (15)$$

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 $B_o{}'$ is greater than 1.

A related but alternate approach has been suggested by Onat[38] and by Vaisnys[39] whereby the pressure is expanded in powers of $\ln V$ about $V = V_o$:

$$P = (dP/d\ln V)_{V=V_o}(\ln V - \ln V_o)$$

$$+\tfrac{1}{2}(d^2P/d\ln V^2)_{V=V_o}(\ln V - \ln V_o)^2+\cdots.\quad (16)$$

Again, the coefficients may be expressed in terms of B_o and $B_o{}'$, viz.,

$$(dP/d\ln V)_{V=V_o}=-B_o$$

and

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

so that Eq. (16) may be written as

$$P = -B_o\ln(V/V_o)+\tfrac{1}{2}B_oB_o{}'[\ln(V/V_o)]^2+\cdots.\quad (17)$$

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).

of his compression data with a Taylor-series expansion of V in powers of P about $P=0$ (the rest he put in tabular form):

$$V = V_o + (dV/dP)_{P=0}P + \tfrac{1}{2}(d^2V/dP^2)_{P=0}P^2, \quad (18)$$

where

$$(dV/dP)_{P=0} = -V_o/B_o$$

and

$$(d^2V/dP^2)_{P=0} = V_0(1+B_o')/B_o^2.$$

He found that, within the accuracy of his data, this equation gave a good representation of the compression of many substances. Recently Anderson and Schreiber[40] have determined the values of B_0, B_o', and B_o'', where B_o'' is the second derivative of the bulk modulus evaluated at 1 atm, for polycrystalline magnesium oxide. They used this data in conjunction with Eq. (18), expanded to include the additional terms in P^3 and P^4, to express the equation of state of MgO. Examination of this type of expansion, however, shows that it does not meet all the stipulations required for a satisfactory P–V relation. Since the coefficients of all the odd powers of P will be negative and the coefficients of all the even powers will be positive, the expansion predicts that the volume will approach negative infinity, with increasing pressure, if it is cut off at an odd power of P and that it will approach positive infinity when the last term involves an even power of P. In the latter case the volume will also be a double-valued function of the pressure.

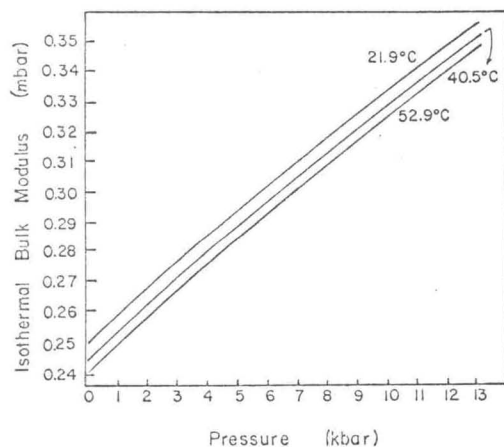In another approach to a P–V equation, Murnaghan[41] has suggested expanding the bulk modulus as a function

FIG. 9. The isothermal bulk modulus B of liquid Hg vs pressure at several temperatures.

[40] O. L. Anderson and E. Schreiber, J. Geophys. Res. 70, 5241 (1965).
[41] F. D. Murnaghan, Proc. Symp. Appl. Math., Brown University, Providence, R.I., 1947 1, 167 (1949).

TABLE VII. Bulk modulus of Hg.[a]

P (kbar)	T (°C)		
	21.9°	40.5°	52.9°
0	248.4	243.1	239.6
1	257.6	252.4	248.9
2	266.6	261.3	257.9
3	275.3	270.1	266.7
4	284.0	278.7	275.4
5	292.5	287.3	283.9
6	300.8	295.6	292.3
7	309.1	303.9	300.5
8	317	312	309
9	325	320	317
10	333	328	325
11	341	336	333
12	349	344	341
13	357	352	348

[a] Units of kilobars.

of P, according to the relation

$$B = -V(dP/dV) = B_o + B_o'P. \quad (19)$$

On integration this gives the so-called "Murnaghan logarithmic equation,"

$$\ln(V_o/V) = (1/B_o')\{\ln[(B_o+B_o'P)/B_o]\}, \quad (20)$$

which satisfies the listed requirements. Equation (19) can be expanded to include terms of higher power in the pressure, but this may lead to peculiarities in the resulting pressure–volume expression: If the bulk modulus expression is expanded, for example, to include B_o'' and this coefficient is negative, the bulk modulus will eventually pass through a maximum with pressure and then become negative. Birch[42,43] has used Murnaghan's[44] theory of finite strain and a series expansion of F in terms of V to derive the equation

$$P = \tfrac{3}{2}B_0[(V_o/V)^{7/3} - (V_o/V)^{5/3}]\{1-\xi[(V_o/V)^{2/3}-1]\},$$
$$(21)$$

where

$$\xi = \tfrac{3}{4}(4-B_o').$$

Since the definition of strain (for strains larger than infinitesimal) is arbitrary, this equation has no particularly unique relation to elasticity theory. It does meet the requirements for an equation of state listed at the beginning of this section, provided B_o' is greater than 4.

Each of the equations enumerated above has been tried against the Hg volume data. B_o is fixed at its independently determined value at $P=0$. Each of the equations then has only one adjustable parameter, which may be expressed in terms of B_o'; this is chosen to give a minimum standard deviation. The deviations of these equations from the volume data are shown in

[42] F. Birch, J. Appl. Phys. 9, 279 (1938).
[43] F. Birch, Phys. Rev. 71, 809 (1947).
[44] F. D. Murnaghan, Am. J. Math. 59, 235 (1937).

TABLE VIII. Standard deviation (σ) 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
σ (unitless)			
Quadratic ($V/V_0 = 1 + aP + bP^2$)	235×10^{-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 ($\Delta V/V_o = aP + bP^2 + CP^3$) 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 ($B_o + B_o'P$) 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_o' 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_o/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

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

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.,

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

it can be shown that

$$S = 1 + \int_0^P \frac{1}{4l_o^2 \rho_o [3(1/t_1)^2 - 4(1/t_2)^2]} \, dP$$

$$+ \frac{T}{3\rho_o S^2} \int_0^P \frac{\alpha^2}{C_P} \, dP, \qquad (23)$$

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), ρ 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 ΔP within which S may be considered constant, analogous to the procedure used with the liquid.

ACKNOWLEDGMENT