

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):

$$V = V_0 + (dV/dP)_{P=0}P + \frac{1}{2}(d^2V/dP^2)_{P=0}P^2, \quad (18)$$

where

$$(dV/dP)_{P=0} = -V_0/B_0$$

and

$$(d^2V/dP^2)_{P=0} = V_0(1+B_0')/B_0^2.$$

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<sup>40</sup> have determined the values of  $B_0$ ,  $B_0'$ , and  $B_0''$ , where  $B_0''$  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<sup>41</sup> has suggested expanding the bulk modulus as a function

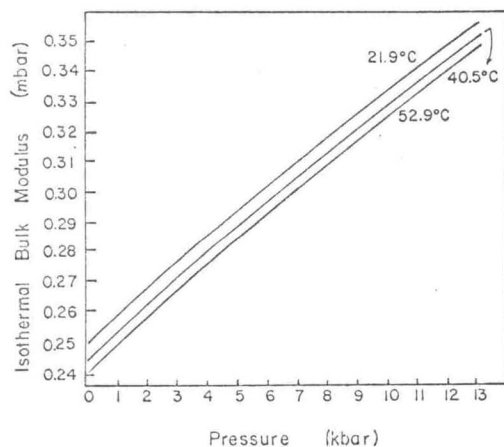


FIG. 9. The isothermal bulk modulus  $B$  of liquid Hg vs pressure at several temperatures.

<sup>40</sup> O. L. Anderson and E. Schreiber, *J. Geophys. Res.* **70**, 5241 (1965).

<sup>41</sup> F. D. Murnaghan, *Proc. Symp. Appl. Math.*, Brown University, Providence, R.I., 1947 **1**, 167 (1949).

TABLE VII. Bulk modulus of Hg.<sup>a</sup>

| $P$ (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   |

<sup>a</sup> Units of kilobars.

of  $P$ , according to the relation

$$B = -V(dP/dV) = B_0 + B_0'P. \quad (19)$$

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

$$\ln(V_0/V) = (1/B_0') \{ \ln[(B_0 + B_0'P)/B_0] \}, \quad (20)$$

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  $B_0''$  and this coefficient is negative, the bulk modulus will eventually pass through a maximum with pressure and then become negative. Birch<sup>42,43</sup> has used Murnaghan's<sup>44</sup> theory of finite strain and a series expansion of  $F$  in terms of  $V$  to derive the equation

$$P = \frac{3}{2}B_0 \left[ (V_0/V)^{7/3} - (V_0/V)^{5/3} \right] \{ 1 - \xi [(V_0/V)^{2/3} - 1] \}, \quad (21)$$

where

$$\xi = \frac{3}{4}(4 - B_0').$$

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  $B_0'$  is greater than 4.

Each of the equations enumerated above has been tried against the Hg volume data.  $B_0$  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  $B_0'$ ; this is chosen to give a minimum standard deviation. The deviations of these equations from the volume data are shown in

<sup>42</sup> F. Birch, *J. Appl. Phys.* **9**, 279 (1938).

<sup>43</sup> F. Birch, *Phys. Rev.* **71**, 809 (1947).

<sup>44</sup> F. D. Murnaghan, *Am. J. Math.* **59**, 235 (1937).