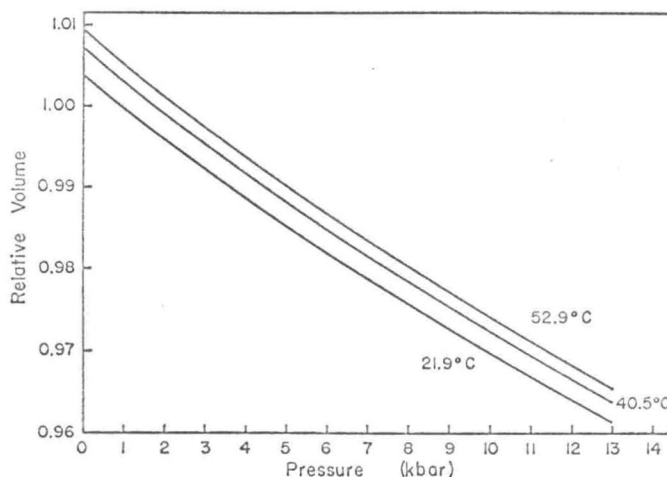


FIG. 7. The relative volume V of liquid Hg as a function of pressure at several temperatures. Volume at 1 atm and 0°C is 1.00.



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

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

and

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

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).