Proposed Thermodynamic Pressure Scale for an Absolute High-Pressure Calibration

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The field of high pressure has developed rapidly over the past few years to a point where relatively sophisticated experiments are being attempted. In many experiments it is no longer sufficient to qualitatively estimate the pressure or to base conclusions on experimental results tied to an empirical pressure parameter. One desires to accurately know the pressure dependence of physical quantities related to a true thermodynamic scale. A fundamental pressure measurement must be directly or indirectly tied to a measurement of f/α, where f is the force exerted on an area α, or to a measurement of $-(\partial F/\partial V)_T$ where F is the Helmholtz free energy at volume V and temperature T. In practice, accurate high-pressure measurements based on

$$P = f/\alpha, \qquad (1)$$

and using the piston–cylinder technique, are hampered by internal friction in the pressure-transmitting medium surrounding the sample, friction between the piston and cylinder, and distortion of the piston under stress, whose area must be determined. These corrections, which must be applied to the measurement, are usually difficult to determine accurately and cannot, in general, be unambiguously determined experimentally, but normally involve theoretical approximations. The other approach,

$$P = -(\partial F/\partial V)_T, \qquad (2)$$

is also difficult experimentally because one does not usually known how to measure the free energy. Theoretical attempts to evaluate F for particular materials have proven useful to obtain a practical pressure scale.[1,2]

We propose to obtain a thermodynamic pressure scale following a well-known technique often applied in the case of the thermodynamic temperature scale.[3] If a set of physical quantities, which are related by a thermodynamic relationship involving the thermodynamic pressure, can all be separately measured as functions of an empirical pressure parameter, then the thermodynamic relation can be used to express the thermodynamic pressure as a function of this same empirical pressure parameter. By empirical pressure parameter we mean any physical measurable quantity which is reproducible and varies monotonically with pressure. (For our purposes we also desire this parameter to have the value zero at $P = 0$.) An example of such a parameter is the change in the electrical resistance of a properly prepared manganin wire in a hydrostatic pressure medium.

Consider the thermodynamic relations[4]

$$B_T = -V(\partial P/\partial V)_T = B_s + \alpha^2 V^2 B_s T(\partial P/\partial V)_T/C_p, \qquad (3)$$

where B_T and B_s are the isothermal and abiabatic bulk moduli, respectively, $\alpha = 1/V(\partial V/\partial T)_p$ is the volume thermal expansion coefficient, and C_p is the specific heat at constant pressure. These

equations can be solved for $(\partial P/\partial V)_T$ yielding

$$(\partial P/\partial V)_T = -B_T/V = -B_s/[V(1+\alpha^2 VB_s T/C_p)]. \qquad (4)$$

Let Π represent the value of some empirical pressure parameter and suppose that B_T and V or B_s, V, α, and C_p can be measured as functions of Π. We then integrate Eqs. (4) along an isotherm to get

$$P(\Pi) = -\int_0^\Pi \frac{B_T}{V}\left(\frac{\partial V}{\partial \Pi}\right)_T d\Pi = -\int_0^\Pi \frac{B_s(\partial V/\partial \Pi)_T d\Pi}{V(1+\alpha^2 VB_s T/C_p)}. \qquad (5)$$

These are expressions for the thermodynamic pressure P as a function of Π, and once the terms in the integrand have been measured over a range of the parameter Π then $P(\Pi)$ is experimentally known and the empirical pressure parameter has been calibrated in terms of the true thermodynamic pressure.

Before Eq. (5) can be proposed as a usable pressure calibration technique, we must consider the accuracy attainable by this method of measuring $P(\Pi)$. B_s can be measured using ultrasonic techniques to an absolute accuracy of 2 parts in 10^3 or even better with some materials. Volume measurements are presently accurate to 1 part in 10^3 and could likely be improved by an order-of-magnitude in a hydrostatic medium (which is now possible to 60 kbar).[5] Measurements of α are only accurate to a few percent and an accurate measurement of C_p at high pressure would be rather difficult. Fortunately, $\alpha^2 VB_s T/C_p = \alpha\gamma T \ll 1$, and is 0.05 for NaCl, for example, near room temperature. (γ is the Gruneisen parameter.) The quantity $\alpha\gamma T$ can be measured at atmospheric pressure with an accuracy approaching 3% and it decreases slowly with pressure such that one can estimate the value of $1+\alpha\gamma T$ at elevated pressures with nearly the same accuracy as at atmospheric pressure. Thus we can use the first integral in Eq. (5) determining $B_T = B_s/(1+\alpha\gamma T)$ with an absolute accuracy of about 3 parts in 10^3 and a statistical scatter possibly as small as 5 parts in 10^5.

In order to estimate the accuracy in the measurement of $P(\Pi)$ by this method we replace the integral in Eq. (5) by a sum.

$$P = -\sum_{k=1}^n B_k\left(1 - \frac{V_{k-1}}{V_k}\right), \qquad (6)$$

where B_k and V_k specify the n individual measurements of B_T and V at various values of Π. Now

$$(\delta P)^2 = \sum_{k=1}^n \frac{B_k^2(V_k-V_{k-1})^2}{V_k^2}\left(\frac{\delta B_k}{B_k}\right)^2 + \left(\frac{B_1 V_0}{V_1}\right)^2\left(\frac{\delta V_0}{V_0}\right)^2$$
$$+ \left(\frac{B_n V_{n-1}}{V_n}\right)^2\left(\frac{\delta V_n}{V_n}\right)^2 + \sum_{k=1}^{n-1}\left(\frac{B_{k+1} V_k}{V_{k+1}} - \frac{B_k V_{k-1}}{V_k}\right)^2\left(\frac{\delta V_k}{V_k}\right)^2, \qquad (7)$$

TABLE I. Possible accuracy of pressure measurements at selected values of pressure using NaCl.

Pressure	8 kbar	25 kbar	55 kbar	77 kbar
(σ_p/P)	1.4×10^{-2}	5.8×10^{-3}	4.1×10^{-3}	3.7×10^{-3}
δ	0.11 kbar	0.14 kbar	0.22 kbar	0.29 kbar
Present accuracy[a]	0.002 kbar	0.06 kbar	1 kbar	2 kbar

[a] These values were determined at the Symposium on the Characterization of the High Pressure Environment, National Bureau of Standards, Oct. 1968.

where we have assumed all B_k and V_k are statistically independent, which would not include any systematic errors in their measurement. In order to simplify Eq. (7), we assume $\delta B_k/B_k = \sigma_B/B$ and $\delta V_k/V_k = \sigma_v/V$ for all k, B_k increases nearly linearly with pressure, and that the measurements are sufficiently closely spaced so that $V_{k-1}/V_k = 1$. Then

$$\frac{\sigma_p}{P} \cong \left[\left(\frac{s_B}{B}\right)^2 + \frac{1}{n}\left(\frac{\sigma_B}{B}\right)^2 + \frac{B_n{}^2 + B_0{}^2}{P^2}\left(\frac{\sigma_v}{V}\right)^2 \right]^{1/2}, \qquad (8)$$

where we have introduced s_B/B to account for systematic errors in the measurement of B_T. We note that any systematic errors in the measurement of V will cancel.

Let $s_B/B = 3 \times 10^{-3}$, $\sigma_B/B = 5 \times 10^{-5}$, and $\sigma_v/V = 3 \times 10^{-4}$, and assume that measurements of B_T and V are made at intervals of 1 kbar using a sample of NaCl. The uncertainty in the measured pressure is then given in Table I at selected pressures. These pressures were chosen in that they correspond to the equilibrium value of the transitions in Hg, Bi, and Ba which are commonly used as high pressure calibration points. The final row of the table gives the accuracy of the best measurement of these points to date. The data in the table demonstrate that the proposed technique does not compete with the free piston gauge below 10 kbar but is comparable near 25 kbar. Above 25 kbar this technique is considerably more accurate than the piston–cylinder apparatus, providing a hydrostatic environment is available and ultrasonic measurements can be extended into this range. It is interesting that the % error using this technique decreases as we get to higher pressures approaching a limiting value which is set by the absolute accuracy of the determination of the isothermal bulk modulus.

[1] D. L. Decker, J. Appl. Phys. 36, 157 (1965); R. N. Jeffery, J. D. Barnett, H. B. Vanfleet, and H. T. Hall, J. Appl. Phys. 37, 3172 (1966).

[2] D. J. Pastine, Phys. Rev. 166, 703 (1968).

[3] A. B. Pippard, The Elements of Classical Thermodynamics (Cambridge University Press, New York, 1957), p. 89.

[4] Derived using standard thermodynamic expressions. For example, J. C. Slater, Introduction to Chemical Physics (McGraw-Hill Book Co., New York, 1939).

[5] J. D. Barnett and C. D. Bosco, J. Appl. Phys. 40, 3144 (1969).