

environment. The objective of this report is to evaluate existing experimental techniques, apparatus, data, and empirical or theoretical analyses as they apply to high-pressure calibration at room temperature. The characterization of temperature in the high-pressure environment will also be considered to a much lesser degree in this report.

#### a. Definitions of Pressure

In an idealized system where pressures are homogeneous in space, hydrostatic, and time-independent, one can simply define pressure as the applied force per unit area. Such idealized conditions are seldom precisely obtained and often only crudely met, but can be very well-approximated with proper media using a proper time scale. For example, pressures in a column of fluid (liquid or gas) are generally considered hydrostatic; however, if a bullet passes through the fluid, a shock front containing time-dependent shears is set up. Furthermore, the system is not homogeneous since pressure increases with depth in the fluid due to gravitational body forces. If applied pressures are several kilobars and times of the order of minutes are considered, the hydrostatic approximation is very good. The approximation is less satisfactory in solid environments.

In order to specify precisely the terminology and describe the non-ideal features of an arbitrarily stressed system in a particular non-ideal laboratory situation, we introduce the symmetric stress tensor,  $\mathbf{T}$ , which is defined at each point in space. Measurable stress over finite areas can then be calculated by averaging. We note that each component of the stress tensor, in general, depends upon position and time,  $T_{ij}(\mathbf{r}, t)$ , where  $\mathbf{r}$  is the position vector. The pressure, which is also a function of position and time, is defined as the negative of the average of the three normal stress components:

$$P(\mathbf{r}, t) = -\frac{1}{3}(T_{11} + T_{22} + T_{33}). \quad (1)$$

The shear stresses are given by the deviatoric stress tensor

$$T'_{ij}(\mathbf{r}, t) = T_{ij}(\mathbf{r}, t) - \delta_{ij}P(\mathbf{r}, t). \quad (2)$$

We are now in a position to define unambiguously the meaning of hydrostatic pressure, which is characterized by zero deviatoric shear stress and isotropic normal stresses. Mathematically we write:  $T'_{ij}(\mathbf{r}, t) = 0$ , and

$$-P(\mathbf{r}, t) = T_{11}(\mathbf{r}, t) = T_{22}(\mathbf{r}, t) = T_{33}(\mathbf{r}, t). \quad (3)$$

We note that this definition does not require static (i.e., time-independent) conditions although time-dependent changes generally involve shear. Equations (3) define hydrostaticity at a point. If a region of space is to be

hydrostatic, each point in the volume must satisfy the hydrostatic condition, which does not necessarily imply homogeneous (i.e., constant in space) conditions. According to the above definition of pressure, non-homogeneity in a hydrostatic medium at equilibrium can arise only from volume (body) type forces such as gravitational, magnetic, or electric forces, which in practice are often very small compared to applied forces. It is important to note that neither homogeneous pressure nor homogeneous stress implies hydrostaticity, but simply constancy in space.

In laboratory pressure systems the time dependence in  $T_{ij}$  generally arises from a change of the system from one equilibrium state to another. In a practical manner we define equilibrium as the state which a system approaches asymptotically within a laboratory time scale. All systems under pressure will support time-dependent shear stress components with some characteristic relaxation time,  $\tau$ , when momentarily disturbed from the equilibrium state. In many cases, especially with gases and liquids at low pressure,  $\tau$  may be a small fraction of a second and is usually (but not always) negligible compared with measuring times, while in highly viscous liquids and solids the relaxation times may be of the order of many hours or even years. In the formalism discussed one can clearly distinguish between plastic solid and viscous liquid behavior during this stress relaxation. For the liquid case the deviatoric stress  $T'_{ij}$  will in time approach a zero value, but for solids  $T'_{ij}$  will approach some non-zero final deviatoric stress state.

The approach to equilibrium will be highly dependent upon the details of the system. In solid-medium systems stress relaxation will be very complicated. For systems containing only fluids in which the viscosity of the fluid can be assumed constant throughout the system, the approach to equilibrium is characterized by the stress components decreasing with time approximately exponentially. Spatial pressure differences within the system will obey the expression  $\Delta P \propto e^{-t/\tau}$  where the characteristic time,  $\tau$ , is directly proportional to the viscosity of the liquid but highly dependent upon the geometry of the chamber. One of the important consequences associated with this discussion is the fact that time-dependent shear stresses are generally associated with pressure changes, and adequate time (several times  $\tau$ ) must be allowed for the system to approach equilibrium before reliable measurements can be made.

To experimentally measure pressure one must measure the normal stress over a finite area. If  $P$  is homogeneous over that area, as it very nearly is in a fluid chamber, the simple force per unit area relationship is valid, and pressures can be determined to high accuracy. (See the section on the primary pressure scale.) Pressures determined by force per unit area in solid-media systems measure some average stress over the specified area which may differ from the true average

normal stresses on the surface as well as from pressures at points inside the bulk of the chamber. In general, such errors will be of the order of the shear strength of the solid materials. The errors associated with measurements of material properties under these non-hydrostatic stress conditions may be more serious than the associated error in pressure since the property measurement errors are dependent upon the stress sensitivity of the parameter being considered.

A thermodynamic definition of pressure is also possible. The definition in eq (3) above presupposes stress measurements involving forces and areas. On the other hand, if energies within volumes are considered (either measured or calculated), one can define pressure in an idealized system where the deviatoric stress is zero and the deformation is pure dilation as:

$$P = - \left( \frac{\partial A}{\partial V} \right)_T \quad (4)$$

where  $A$  is the thermodynamic Helmholtz free energy function ( $A = U - TS$ ,  $dA = -P dV - S dT$ ). Since energy is directly related to force through the definition of work, the two definitions of pressure are equivalent. In any measurement, care must be taken to meet the appropriate conditions of the idealizations including homogeneity and time variations. Definition (4) has been used extensively in theoretical calculations but has been used very little in attempts to measure pressures by measuring energy content. (See section 2.4.) After various approximations theoretical calculations have yielded equations of state for specific substances, and their use in calibrations will be discussed in section 4.1.

#### b. Hydrostaticity

Experimental pressure measurements and the associated calibration techniques may be classified into three areas: (1) measurements in fluid (liquid or gas) systems where hydrostatic conditions exist in an equilibrium state, (2) measurements in static solid-media systems where nominal equilibrium exists but shear stresses are not zero, and (3) measurements in dynamic shock-wave fronts where time-dependent shear stresses are present.

As will be discussed later, only in case (1) can a meaningful primary pressure scale be operationally defined and precise calibration work carried out. Calibration of type (2) and (3) measurements involve indirect methods with inherent inaccuracies. The fluid systems may be used at a variety of pressures and temperatures, but a practical limit to attainable hydrostatic pressures is imposed by the solidification of the pressure-transmitting fluid as the pressure is increased. At low temperatures this restriction is very serious. For example, near 0 K all known substances except helium are solid, and it solidifies at approximately 25 bar<sup>1</sup> at these temperatures. Since melting pressures

generally increase with temperature, higher hydrostatic pressures are realizable at higher temperatures, and if high enough temperatures were used hydrostatic conditions could be achieved at any static pressure produced. Near room temperature hydrostatic pressure studies have historically been limited to approximately 30 kbar since most liquids and gases have freezing pressures below 30 kbar. The freezing pressures at room temperature for some fluids—notably helium, nitrogen, and some organic liquid mixtures—have never been reached but are known approximately by extrapolation (Babb, 1964; Reeve, 1964). In these cases the containment problem represents a more serious limitation to the attainable hydrostatic pressures.

Many organic fluids such as pentane, iso-pentane, and methanol supercool (or, more accurately, superpress) remaining fluid well above their equilibrium freezing pressure. The hydrostaticity of such liquids is eventually limited by the approximate logarithmic increase of viscosity with pressure. Since viscosity is also very sensitive to temperature, higher temperatures allow higher hydrostatic pressures. For example, ordinary glasses have been used at temperatures well above their softening point as pressure-transmitting media. If high viscosity conditions are used, pressure changes must be made slowly and the system be allowed to come to equilibrium before measurements are made. As an example, Barnett and Bosco (1967) have shown that hydrostatic pressures to 60 kbar are possible at room temperature using a one-to-one (by volume) mixture of pentane and iso-pentane. Their data indicate that shear stresses in this mixture relax in times of the order of minutes at 60 kbar.

In a fluid system high accuracies are obtainable in calibration studies. At 8000 bars accuracies of one part in 5000 are possible (Dadson and Greig, 1965; Yasunami, 1967a) while at 25,000 bars current accuracy is approximately one part in 400. If the hydrostatic condition at room temperature can be maintained to the limits permitted by solidification of known materials, a significant improvement in calibration could take place at the higher pressures.

Calibration under quasi-hydrostatic type (2) conditions is much less accurate. By using relatively low-shear-strength materials such as indium, AgCl, or polyethylene, shear stresses and related pressure gradients can be reduced sufficiently to make quasi-calibration type measurements with reproducibility of two to three percent below 50 kbar and three to five percent to 100 kbar. Various intercomparisons and extrapolation procedures have been used, as will be discussed later, to calibrate average pressures under such conditions. Present state of the art measurements suggest that the accuracies can be of the same order as the reproducibility, but that workers in the field seldom expend the necessary effort to attain this accuracy. There exist a variety of solid-media apparatus with differing geometries, some of which represent a better approximation to hydrostatic conditions than

<sup>1</sup> The use of bar and kbar throughout this review follows the current common practice of workers in the field. We note for the uninitiated that 1 bar = 10<sup>5</sup> N/m<sup>2</sup> (or pascal) = 10<sup>6</sup> dyn/cm<sup>2</sup> = 0.9869 atm = 1.0197 kgf/cm<sup>2</sup>. The accepted international standard (SI) unit of pressure is the pascal, or newton per meter squared.