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High-Pressure Calibration
A Critical Review

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A critical review of experimental technique for measuring high pressures has been made. The broad coverage includes discussions relating to (a) the establishment of a primary pressure scale using the free-piston gage, (b) the selection and precise measurement of identifiable phase changes as fixed pressure points, and (c) the use of interpolation and extrapolation techniques such as resistance gages, equations of state, and optical changes. The emphasis is on static pressure measurements above 10 kbar, but shock measurements are also considered for completeness. The pressure values to be associated with the fixed points have been analyzed in detail. Temperature measurement in the high pressure environment is also reviewed. The accuracy with which pressures can be measured has been carefully considered; the maximum accuracies now obtainable are considered to be of the order of 0.02 percent at 8 kbar, 0.25 percent at 25 kbar, 2 percent at 50 kbar, and 4 percent at 100 kbar.

Key words: Calibration of pressure scales; critically evaluated data; high pressure; high pressure phase changes; pressure measurement.

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1. Introduction

1.1. Pressure

The use of pressure as a parameter in the study of materials was pioneered principally by Professor P. W. Bridgman, who for forty years investigated most of the elements and many other materials using diverse techniques (Bridgman, 1964). By the early 1950's high-pressure phenomena began to attract widespread interest. The following list of the number of papers published in the field of high-pressure research indicates its very rapid growth in the last few years.

Year	Number of papers
1950	96
1955	243
1960	542
1964	746
1966	1025
1968	1271
1969	1367
1970	1700 (estimated)

The successful synthesis of diamond in 1954 (Hall, 1961) made possible by the development of new apparatus and techniques clearly showed the potential of high-pressure applications for industrial purposes and stimulated the growing interest in the field. For those in basic research the high pressures available using the new techniques opened up a whole new vista in investigations of properties of materials. Studies at high pressures have been successfully undertaken involving such things as chemical synthesis, melting curves, solid-solid phase boundaries, x-ray and neutron diffraction, optical phenomena, magnetic properties, NMR, EPR, Mossbauer, and ultrasonic experiments, among others. Due to the geometry and/or the complexity of the apparatus necessary to contain samples and generate the high pressures, many standard measuring techniques must be drastically modified, and associated experimental accuracies are generally reduced.

As any technological field develops, the need for precise and accurate characterization of the parameters of interest is paramount. In the high-pressure field two calibration problems are apparent: (a) the establishment of a workable and accurate high-pressure scale defined in procedural detail, and (b) the accurate determination of temperatures in a high-pressure 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, **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 **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:

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

The shear stresses are given by the deviatoric stress tensor

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

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

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

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, nonhomogeneity 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, τ, when momentarily disturbed from the equilibrium state. In many cases, especially with gases and liquids at low pressure, τ 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, τ, 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 τ) 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:

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

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[1] 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

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[1] 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 $=10^5\mathrm{N/m^2}$ (or pascal) $=10^6$ dyn/cm^2 $=0.9869$ atm $=1.0197$ kgf/cm^2. The accepted international standard (SI) unit of pressure is the pascal, or newton per meter squared.

others. Multi-anvil apparatus with multi-directional applied forces are expected to produce fewer shears than uniaxial apparatus. One would also expect a Bridgman anvil system with planar-type chambers to fit the hydrostatic approximation less well than systems containing volumes of a more three-dimensional nature.

The shear component in shockwave environments is less certain than in solid-media systems since both acceleration and strength-of-materials forces can operate. Some intercomparison studies have been made between shock and quasi-hydrostatic data, but the calibrations are basically independent. Volumetric intercomparisons through theoretical equations of state indicate a fair consistency between the two techniques. Although the shear stresses in shock waves are large, the pressures are also very high, and the ratio of shear stress to normal stress may not represent as poor an approximation to the hydrostatic condition as a first impression suggests. The actual stress state in the shock front has not yet been fully characterized, but phase transition pressures in single-crystal samples have been shown to exhibit a sizable orientational dependence attributable to shear stresses.

c. Equilibrium Pressure

As discussed in section 3, phase transformations in selected materials are the basis for a fixed-point calibration procedure at high pressure. Such points must be specifically defined in terms of the thermodynamic equilibrium condition between the two phases. We have alluded earlier to the condition of system equilibrium, wherein we mean "a stable state which a system approaches asymptotically within laboratory times." As used, this phrase applies to changes in continuously varying parameters such as pressure, temperature, electrical resistivity, etc. associated with the pressure-generating system. Equilibrium of the total system in this sense does not imply thermodynamic equilibrium of a material sample or calibration specimen within the pressure chamber. We now desire to discuss this more critical equilibrium condition.

Since fixed-point calibrations involving first-order transformations are the dominant technique used by the average high-pressure worker, a thorough characterization of the transformations in various environments should be made. The thermodynamic equilibrium transition pressure for a pure substance is defined for isobaric processes as the pressure (or temperature) at which the Gibbs free energy per atom of the two adjacent phases is equal. Such a point is readily defined in a mathematical symbolism, but for solid-solid transformations the experimental realization of this idealized condition and the determination of the equilibrium pressure and temperature to high precision requires greater insight. Furthermore, in practice many measured transformations are used to calibrate an apparatus-load scale rather than a true sample-pressure scale. An understanding of the non-reversible effects in both the apparatus and the sample is required to make precise equilibrium determinations.

Upon application of a continuously increasing load, suppose that a material undergoes a first-order transformation from phase I to a phase II (I–II) at an applied load $L_{\mathrm{I-II}}$ and an applied sample pressure $P_{\mathrm{I-II}}$. Upon continuously decreasing load the reverse transformation (II–I) will occur at an applied load $L_{\mathrm{II-I}}$ and an applied sample pressure $P_{\mathrm{II-I}}$, where $L_{\mathrm{II-I}} < L_{\mathrm{I-II}}$ and $P_{\mathrm{II-I}} < P_{\mathrm{I-II}}$. The differences $(L_{\mathrm{I-II}}-L_{\mathrm{II-I}})$ and $(P_{\mathrm{I-II}}-P_{\mathrm{II-I}})$ are commonly called hysteresis and even in the most ideal hydrostatic situations are non-zero for solid-solid transformations. The differences $(L_{\mathrm{I-II}}-L_{\mathrm{II-I}})$ reflect apparatus effects known as apparatus hysteresis as well as non-reversible effects in the sample itself, referred to as sample hysteresis.

Four interrelated phenomena giving rise to this hysteresis have been isolated:

(1) Mechanical friction in pressure-generation apparatus such as in piston-cylinder apparatus (not the free-piston gage),
(2) pressure gradients in solid-media systems (both within the pressure-transmitting solid and within the calibration specimen itself),
(3) nucleation energy (which may differ between hydrostatic and non-hydrostatic conditions), and
(4) growth energy.

Each of the above has been discussed by various workers, often with differing terminology, but here we attempt to categorize and delineate. In non-hydrostatic media systems all four phenomena are operating during procedures generally used to "calibrate" the press load in terms of pressure using known fixed points. In some cases $L_{\mathrm{II-I}}$ may differ from $L_{\mathrm{I-II}}$ by as much as 30 percent due to (1) and (2). In such cases values of $L_{\mathrm{I-II}}$ only are used as calibration points, but serious uncertainties arise due to unknown hysteresis of types (3) and (4). Items (1) and (2) above are also the source of "smeared out" transitions in which transformations take place over a broad interval of applied load.

The first two items are obviously distinct from each other, but experimentally the two are rather difficult to separate from one another, and the separation is seldom made. Items (1) and (2) combined are spoken of as the apparatus hysteresis, and together can be separated from (3) and (4) by placing pressure sensors at the specimen itself. Jeffery, et al. (1966), using the tetrahedral-anvil press equipped for x-ray diffraction studies, used the lattice parameter of NaCl as the pressure indicator. A calibrant foil (Bi or Ba) was surrounded by NaCl and enclosed in 50–50 wt percent boron-plastic tetrahedron. Pressure was determined from the measured lattice parameter through Decker's (1966) equation of state. Load differences $L_{\mathrm{I-II}}-L_{\mathrm{II-I}}$ corresponding to differences in calculated pressures of 20 to 30 kbar were measured, whereas the differences $P_{\mathrm{I-II}}-P_{\mathrm{II-I}}$ associated with nucleation was of the order of two to five kbar.

Time-dependent variations in the pressure gradients in a solid-media hexahedral-anvil apparatus have been studied by Barnett and Bosco (1966). The pressure was indicated by a manganin gage placed inside a liquid chamber, which in turn was embedded in the pyrophyllite cube. Relaxation of the pressure in the pyrophyllite with time was measured as well as magnitudes of the gradients.

The non-reversible nature of transformations at high pressure even in a hydrostatic environment and the interpretation of this effect as a nucleation energy barrier was well understood by Bridgman (1940a) and others working in liquid chambers at the lower pressures but has not been fully appreciated by those working at much higher pressures in non-hydrostatic environments. The phenomenon has been studied rather extensively with regard to temperature-initiated solid-solid phase transformations at one bar (Smoluchowski). Temkin (1966) presents a theoretical discussion on the thermodynamics of the formation of a new phase under hydrostatic pressure.

The fact that the Gibbs free energy of two phases becomes equal as pressure is exerted on a sample of phase I does not imply that the transformation will proceed even though the equilibrium pressure has been reached. The kinetics of the transformation must be considered, and means must be available for the atoms of the specimen to rearrange into the new crystalline structure, at least in a small localized region called an embryo. High temperature is often used to provide energy for the rearrangement (Stark and Jura, 1964). The energy barrier against the rearrangement is so large at room temperature for many strong-bonding materials that the transformation never proceeds at *any* applied pressure, whereas the barrier for some metals is relatively small. Any transformation to be of value as a fixed point must exhibit a small nucleation energy. At high temperatures where the kinetics of reactions are faster, the temperature hysteresis across a phase boundary is generally small, but high pressure often increases this hysteresis by inhibiting the rearrangement. For example, in iron at one bar the temperature hysteresis of the $\alpha-\gamma$ transition is of the order of a few degrees. At higher pressure (but lower temperature) as one approaches the triple point near 100 kbar, this hysteresis has increased to about 30°.

Smoluchowski (1951) has discussed the statistical creation of embryos of phase II in a phase I matrix near the equilibrium pressure and temperature. There is an increasing probability of nucleating embryos of a given size as pressures or temperatures further into the stability field of II are reached. The fundamental reason for the appearance of such embryos in a homogeneous substance is the existence of transient local fluctuations from the normal state. These deviations may occur in any part of the substance as fluctuation of local energy or density, possibly due to localized regions of strain. The condition for growth of the new phase, and thus the occurrence of the transformation, is that the Gibbs free energy per atom of the embryo *and its surrounding* be less than the free energy per atom of the original matrix. When an embryo of II is formed in a matrix of I at conditions within the stability region of II, a free energy difference proportional to the volume (cube of the dimension) is available. This difference generally increases as one moves farther away from the equilibrium conditions. Since there exists an interface between the embryo and its surroundings with an attendant surface energy proportional to the square of the embryo dimensions, the embryo must have minimal size at a specified pressure and temperature in order to grow rather than diminish. The free energy difference is the driving force for the reaction. The embryos are generated with a statistical distribution, and the smaller embryos are unstable. The required size is smaller further from the equilibrium condition since the critical size is a function of the change ΔG in the Gibbs energy per atom due to the transformation, and this difference increases as one moves further from the equilibrium condition. At pressures and temperatures very near the equilibrium conditions one would find it necessary to wait a very long time for a sufficiently large embryo to be statistically generated, but further from the equilibrium condition the much smaller embryos required are produced profusely, and the transformation proceeds. This effect gives rise to an observed sensitivity to pressurization rate or heating rate. If a *non*-statistical energy barrier were causing the hysteresis, no time-dependence should be observed.

Davidson and Lee (1964) working under hydrostatic conditions determined an average hysteresis interval of 0.79 kbar for the Bi(I–II) transformation and showed that it was dependent on the pressurization rate. Zeto, et al. (1968) concluded that the generally observed hysteresis in the Bi I–II transition is nucleation limited. Their work was carried out under hydrostatic conditions, and the observed hysteresis interval was shown to be highly time-dependent. This result suggests the statistical generation of nucleation sites. In the work of Jeffrey, et al. (1966) the measured hysteresis on the Bi I–II transformation under non-hydrostatic conditions was several times larger than the hysteresis measured by Zeto, et al. (1968) and by Davidson and Lee (1964). The work by Jeffrey, et al. suggests a greatly increased nucleation energy in the solid environment. This fact implies the existence of strain energy set up around the embryo due to its formation and indicates that hysteresis measurements in hydrostatic environments *cannot* be used to interpret results in non-hydrostatic environments.

Nucleation mechanisms have been suggested for various types of solid-state transformations but are not well-understood, especially as they apply to the ultra-high pressures. Reconstructive-type transformations are expected to have higher nucleation energies than displacive-type transformations. The interrelationship of reconstructive-type transitions with diffusion processes and the decrease of diffusion rates at high pressure suggest an increase in nucleation-associated hysteresis in such materials at the higher pressures. The use of second-order transformations, in which nucleation is unimportant, as possible fixed points might be profitable.

With an understanding of nucleation hysteresis one realizes that to obtain a reproducible fixed point associated with a first-order phase transformation, an equilibrium pressure must be determined in a hydrostatic environment under conditions where large amounts of both phases exist. The equilibrium point is now specified as the point at which the transformation *rate* between the two phases is zero. This condition can generally be obtained by reversing pressure after nucleation initiates the transformation and adjusting pressure in the appropriate direction to reduce the reaction rate. In practice the reaction rate is zero within detectable limits over a non-zero pressure interval for solid-solid transformations but zero only at a unique pressure for solid-liquid transformations. Thus the equilibrium pressure is not uniquely defined experimentally in solid-solid transformations. Bridgman referred to this pressure interval over which no reaction rate could be detected as the "region of indifference". The width of this region has been studied at pressure for the Bi I–II, Tl II–III, and Ba I–II transformations by Zeto, et al. (1968). The variation of the reaction rate with pressure is very strong on either side of the "region of indifference" and implies that the "region of indifference" is a consequence of the existence of a small but finite energy barrier associated with the growth of phase II in contact with phase I. This non-reversible effect represents the final obstacle to the experimental attainment of a thermodynamic equilibrium in solid-solid phase transformations. Solid-solid phase boundaries exhibit "regions of indifference" varying from tens of bars in the case of Bi I–II and Tl II–III to over one kbar for Ba I–II and to many kbar in the case of strong-bonding materials at room temperature.

1.2 Analogy with the Temperature Scale

The problems encountered in trying to define a pressure scale are analogous to those encountered in the establishment of the temperature scale. A short discussion regarding the development of the temperature scale will be given as it appears to give insight for the establishment of a pressure scale.

In 1854, J. P. Joule and W. Thomson proposed the Thermodynamic Temperature Scale which is now recognized as the fundamental scale to which all temperature measurements should ultimately be referable. The basic definition of the Thermodynamic Temperature Scale is closely tied to the second law of thermodynamics. This temperature scale can be established from experimental measurements of the quantities that appear in the second law equation. The temperature so defined is identical to that of the ideal (perfect) gas equation of state. The behavior of real gases differs from that of the ideal gas law and consequently this non-ideal behavior must be corrected for. This process involves the use of numerous correction terms.

In order to establish a practical scale for international use on which temperatures could be conveniently and accurately measured, the directors of the national laboratories of Germany, Great Britain, and the United States agreed in 1911 to undertake the unification of the temperature scales in use in their respective countries. A practical scale was finally agreed upon; it was recommended to the Seventh General Conference on Weights and Measures in 1927 (Septieme, 1928) and adopted under the name International Temperature Scale (ITS).

The ITS was designed to represent the thermodynamic scale as closely as possible. It was based on assigned values for six reproducible equilibrium temperatures (fixed points). The fixed points were the ice point, the normal boiling points of oxygen, water and sulfur and the freezing points of silver and gold. The concept of 100° for the fundamental interval was used to define the ITS by calling the ice and steam points *fundamental fixed points*. The other four were called *primary fixed points*.

In 1948, the Advisory Committee on Thermometry of the International Committee on Weights and Measures (Neuvieme, 1949) suggested the adoption of the triple point of water to replace the ice point as it was generally felt that it was a more precise thermometric reference than the ice point. This proposal was accepted and in 1954 it was assigned the value 273.16 K exactly. The zero of the Celsius scale had already been adopted in 1948 as being 0.01° below the triple point of water which gives the relation:

$$T\ \text{K} = t\ {}^\circ\text{C (therm 1954)} + 273.15^\circ. \qquad (5)$$

The redefinition of the Kelvin scale discarded the concept of a fundamental interval of 100°. It was decided therefore to designate all six fixed points of the scale as *defining fixed points* which are to be considered exact by definition. In 1960, the International Temperature Scale was renamed the International Practical Temperature Scale (Onzieme, 1971).

The International Practical Temperature Scale of 1968 (IPTS–68) was adopted by the International Committee on Weights and Measures (International, 1969) and replaces the IPTS–48 as amended in 1960. The IPTS–68 is a practical scale chosen in such a way that the temperature measured on it closely approximates the thermodynamic temperature. The difference is within the limits of the present accuracy of measurement. It is based upon the assigned values of the temperatures of a number of reproducible equilibrium states (defining fixed points) and on standard instruments calibrated at those temperatures.

The defining fixed points and numerical values assigned them are given in table 1. These values in each case define the equilibrium temperature corresponding to a pressure of 1 atm (standard) defined as 1,013,250 dyn/cm^2.

TABLE 1. Estimated uncertainties of the assigned values of the defining fixed points[a] in terms of thermodynamic temperatures

Defining fixed point	Assigned value	Estimated uncertainty
Triple point of equilibrium hydrogen	13.81 K	0.01 K
17.042 K point H_2	17.042 K	0.01 K
Boiling point of equilibrium hydrogen	20.28 K	0.01 K
Boiling point of neon	27.102 K	0.01 K
Triple point of oxygen	54.361 K	0.01 K
Boiling point of oxygen	90.188 K	0.01 K
Triple point of water	273.16 K	Exact by Definition
Boiling point of water	100 °C	0.005 K
Freezing point of tin	231.9681 °C	0.015 K
Freezing point of zinc	419.58 °C	0.03 K
Freezing point of silver	961.93 °C	0.2 K
Freezing point of gold	1064.43 °C	0.2 K

[a] Based on IPTS–68 scale.

In order to have a continuous temperature scale, it is necessary to specify the means to be used for interpolation between the fixed points. Temperatures intermediate to the fixed points are determined by standard interpolation thermometers. Specifications are given for the construction of the thermometers and formulas are given for the calculation of international temperatures from their indications.

Below 0 °C, the resistance temperature relation of the thermometer is found from a reference function and specified deviation equations. From 0 °C to 630.74 °C, two polynomial equations are used. The interpolation instrument used from 630.74 °C to 1064.43 °C is the platinum – 10 percent rhodium/platinum thermocouple. The interpolation function is represented by a quadratic equation. Above 1064.43 °C the IPTS–68 is defined by the Planck law of radiation with 1004.33 °C as the reference temperature and a specified value of c_2.

The pressure scale must be established in a manner similiar to the temperature scale. It must involve; (1) a primary scale with specific measuring devices (for example the free piston gage), (2) fixed points, and (3) interpolation gages with specified functional relationships over specified ranges. These three topics are discussed in turn throughout the review.

2. The Primary Pressure Scale

In any branch of metrology, the establishment and universal acceptance of a primary scale upon which all interpolation and extrapolation functions and devices can be based and to which they can be referred is of fundamental importance. In general, the establishment of such a scale will involve specific procedures, apparatus, and precautions associated with the measurement in question and will be as closely related to the fundamental definition of the measured quantity as apparatus will permit.

The techniques and apparatus associated with the primary scale should be as simple as possible and should be a direct measurement of the quantity itself. It is preferable not to involve averaging, differentiation, integration, or other mathematic manipulations implied by a theoretical treatment. It is not expected that specific procedures and details will be permanent but, rather, that they will be temporarily accepted by the scientific community until a more direct and reliable or more accurate technique can be demonstrated. The fundamental nature, the reliability, and the accuracy will be of prime importance in contrast to sensitivity, convenience, and availability. It would be desirable to have but one technique or apparatus extend over all ranges of the measured quantity, but such a condition is generally not possible.

Based on criteria of this type, two basic measuring systems with variety of modifications and adaptions have been proposed and used rather widely as a basis of a primary pressure[2] scale: (a) the mercury manometer (including multiple and differential manometers), and (b) the free-piston or dead-weight pressure gage (also called a piston manometer, pressure balance, or unpacked-piston gage). In a practical sense the use of the mercury manometer has been limited to pressures of a few hundred bars. One very elaborate system built by Bett, Hayes, and Newitt (1954) was designed for use to 2300 bars although no measurements above 700 bars have been reported by these researchers. The free-piston gage is in common use to over ten kbar and has been successfully used to 26 kbar by Johnson and Heydemann (1967) and to 25 kbar by Konyaev (1961) but with serious difficulty.

Since pressure comparisons require uniformity of pressure throughout the system or combination of systems, a primary pressure scale must be based on a truly hydrostatic system. Both of the systems proposed above are so based. At higher pressure (above 50 kbar), this requirement of hydrostaticity represents a rather severe ultimate limitation on a primary pressure scale as discussed herein. Other scales applicable to higher pressures have been proposed as discussed in other sections of this report, but they cannot be considered to fit the above criteria of a primary scale and cannot be currently considered as such.

At pressures above 25 kbar, several apparatus of the piston-cylinder type have been built and pressure values have been reported. In these systems, various techniques have been used to approximate the conditions of the free-piston gage, but to date such approximations have diverged rather drastically from the criteria outlined above. It appears obvious that the best

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[2] In this report we interpret pressure to mean pressures above ambient or atmospheric pressure.

current approximation to a primary scale above 25 kbar is the piston-cylinder system. However, significant improvement must be made in this technique before its reliability will be greater than indirect extrapolation techniques directly tied to the primary scale at lower pressures.

2.1. The Free-Piston Gage

The use of a piston-cylinder pressure system for which both the force and the area are directly measurable as a primary pressure scale is the obvious approach. However, a consideration of the lack of reproducibility and the unknown nature of the frictional forces between the piston and the cylinder as well as the packing inserted to prevent leakage around the piston in a hydrostatic system leads one immediately to the consideration of techniques where friction can be reduced drastically or, if possible, eliminated.

Work before 1920[3] demonstrated that by oscillating a close fitting packing-free piston through a finite angle or by continuously rotating such a piston one could obtain pressures reproducible to better than one part in 10^3 provided care was taken to obtain an adequate initial fit between piston and cylinder. This result represents a dramatic improvement over a piston with packing. Force is applied in such a system by directly loading the free piston with weights placed on an appropriate hanger which rotates with the piston and simultaneously balances the pressure applied to the bottom of the piston as it protrudes into the pressure chamber. Michels (1923, 1924) strongly recommended the use of a continuously rotating cylinder, and most investigators in recent years have used this technique.

The removal of the piston packing, of course, allows leakage of the pressure transmitting fluid past the piston, and the piston slowly falls. Therefore, fluid must be supplied to the pressure chamber if the piston is to remain "floating". The leak must be slow enough to allow adequate time for balancing and adjustments. It is significant to realize that the free-piston gage acts completely like a barometer for a fixed-volume system since an increase in weight on the piston simply compresses the enclosed liquid and increases the chamber pressure while simultaneously measuring this pressure.

Historically, the continuous stimulus to obtain higher precision and higher accuracy led to further analysis, theoretical and experimental, of the leakage flow and the elastic distortion of the system. An analysis of the viscous flow through the crevice around the piston shows that the viscous forces (which in this system represent the only vertical frictional force) can be completely accounted for by the introduction of an effective piston area A_e in place of the measured area A_0 of the piston. This effective area is to a first approximation equal to the mean area of the piston and the cylinder providing the two are concentric.

The introduction of an effective area, the determination of which is discussed later, allows one to make allowance for noncircular pistons or cylinders, inaccurate measurement of the piston or cylinder dimensions at zero pressure, and changes of dimensions with time, as well as the most dominant effect, the distortion of the piston and cylinder caused by the chamber pressure itself. The refinement of measurements by the use of the free-piston gage and the reliability of pressure determination made with the gage depend on the proper evaluation made of this effective area and how it changes with pressure and under various operating conditions.

For low pressures, where the mercury manometer discussed below has its greatest utility and accuracy, a direct comparison between the two gages will yield an experimental measurement of the effective area based on the mercury manometer as the primary scale. Extensive intercomparison of this type has led to a better understanding of the free-piston gage. Michels (1923, 1924) and Keyes and Dewey (1927) showed theoretically that the effective area is not dependent on the viscosity of the fluid in the crevice. Beattie and O. C. Bridgeman (1927) reported on experimental verification of this result to within an accuracy of 0.002 percent for good lubricating oil at low pressure, but Dadson (1958) reports a small variation of the effective area depending upon the fluid used. Beattie and Bridgeman further showed that measurable variation of effective area of approximately 0.05 percent can occur due to aging of the metal parts over a period of five years. Further change is surely caused by wear if the piston is used excessively. When the piston was balanced in a different position along its axial length, variation of the effective area amounting to a few parts in 10^4 was measured by Roebuck and Ibser (1954) and others. These measurements illustrate nonuniform dimensions of the piston and cylinder along their axial length. This effect is not commonly understood and is spoken of as a taper error. The so-called cork-screw effect becomes evident when the balancing force for a fixed pressure depends on the direction of rotation of the piston. This effect, of course, is caused by helical microgrooves produced within the piston-cylinder system as the two are lapped to their final fit. Michels (1923, 1924) and also Bett and Newitt (1963) demonstrated the existence of a minimum angular rotation speed of the piston below which the piston will not be concentric with the cylinder. This condition causes a change in the viscous-flow pattern and a resulting change in effective area. All of the above-mentioned limitations can be and have been overcome by more modern machine processes, but an understanding of these effects is essential for checking the operation of a free-piston gage and the construction of a gage for use as a primary scale.

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[3] See extensive bibliography by Meyers and Jessup (1931).

Numerous articles have also been written describing ways of applying torque to keep the piston rotating without applying a vertical force and also novel ways of placing weights on and off the balance. It is the concensus of many authors that the simplest system of applying weights is the best and that measurements should be made while the piston is "coasting".

In addition to being cognizant of the above pitfalls, one must make a variety of rather standard and obvious corrections when high precision work is done. These corrections have been well outlined by Cross (1964), Johnson, et al. (1957), and Johnson and Newhall (1953). They include: (a) temperature expansion of the pistons and cylinder, (b) local variation of the gravitational constants, (c) air buoyancy of weights, (d) fluid head to the pressure measuring chamber, and (e) fluid buoyancy on the piston.

If an accuracy better than a few parts in 10^4 is desired, great care must be taken to determine the effective area A_e at low pressures and then to determine the variation of this area with pressure. Dadson (1955, 1958) used special measuring techniques developed by Taylerson (1953) on two separate piston-cylinder systems and calculated an area ratio. He then balanced the two systems against each other to directly measure the area ratio. The calculated and observed ratios agreed to approximately one part in 10^5 when proper care was taken.

Using the above-mentioned modern machining and measuring techniques Dadson (1955, 1958) has shown that at a few atmospheres pressure agreement of approximately one part in 10^5 can be obtained between properly operated piston-cylinder gages and a mercury manometer. If the mercury manometer itself is considered as the primary scale, the effective area can, however, be measured to a high precision since the balancing process is sensitive to a few parts in 10^6. At higher pressures, the elastic deformation of the piston and cylinder caused by the internal pressure changes the effective area a comparatively large amount and in a somewhat unknown manner. The effort to refine a primary pressure scale based on the free-piston gage has been dominated during the last decade by theoretical and experimental attempts to evaluate this particular change in effective area. This effort has resulted in an effective increase in accuracy of approximately an order of magnitude at pressures above one kbar.

This elastic distortion is so severe for a standard free-piston gage that different piston-cylinder systems are often needed to cover different pressure ranges in order to prevent excessive fluid flow through the enlarged crevice. This high rate of leakage reduces the sensitivity of measurements involving the instrument and at the higher pressures represents a very serious limitation of this simple free-piston gage. Nevertheless, Konyaev (1961) has shown that if rapid piston movement is allowed, a single piston cylinder can be used from 0 to 25 kbar. Bridgman (1909a, 1911a) designed a re-entrant cylinder system illustrated diagrammatically in figure 1, in which the pressure exerted, as indicated by the arrows, closed the crevice at higher pressures and eliminated the problem of leakage. This geometry, however, is not favorable for the evaluation of elastic distortion errors. Early attempts to experimentally evaluate the elastic distortion by reference to a mercury manometer, Michels (1923, 1924), Beattie and Edel (1931), and H. Ebert (1935), were inconsistent and misleading and were such as to be inconclusive as to the order of magnitude of the effect. Theoretically, the problem is very complex even if an idealized, perfectly cylindrical geometry is assumed at zero pressure. Factors involved are the highly pressure-dependent viscosity of the liquid, the shape of the crevice as a function of axial length, and the elastic deformation of a finite length piston and cylinder. A further complication at the higher pressures is a change of elastic parameters of the metal with pressure.

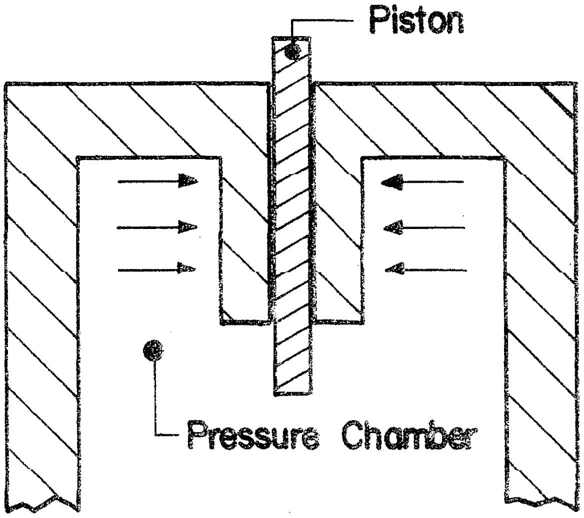

FIGURE 1. Bridgman's re-entrant type cylinder showing use of counter pressure to decrease gap at high pressures.

Three somewhat unrelated approaches have been extensively pursued in an attempt to evaluate the elastic distortion errors. First, a detailed analysis of the deformation has been made using elastic theory with unproven assumptions followed by an evaluation of the assumptions based on experimental intercomparisons of gages so analyzed. Since a well constructed free-piston gage can be balanced with a sensitivity of 0.01 bar at pressures of 10 kbar, predicted discrepancies of gages of different construction can be readily checked against each other and yield an indirect check on the assumptions of the theory. Second, a controlled-clearance piston gage was developed by Johnson and Newhall (1953) in which the distortion of the cylinder is eliminated by use of a counterpressure applied in an annular ring surrounding the cylinder as shown in figure 2. In this geometry, the piston extends well outside the

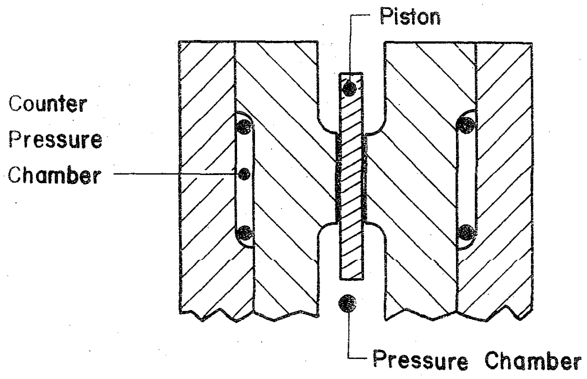

FIGURE 2. Geometry of controlled-clearance gage showing counter pressure chamber.

cylinder in order to assure the proper analysis of the piston distortion. This distortion generally is much smaller than the distortion of the cylinder, and thus the analysis is more reliable. Third, in the evaluation of elastic distortion in the simple free-piston system, Dadson (1955, 1958) proposed the use of the "similarity" principle in which two gages are so constructed that intercomparison between them will yield distortion information of both based on rather broad assumptions that the elastic deformation is similar in the two systems rather than using detailed elastic theory on either alone. In a second approach of this type called the "flow" method, Dadson has also shown consistency with the similarity method using the general theory of viscous flow without recourse to detailed viscosity values or analysis but by requiring consistency between related gages of specific dimensions.

All three of the above approaches have improved our understanding of the inherent deformation problem in a piston-cylinder gage and have independently demonstrated improved reliability and precision. Furthermore, the intercomparison of the three approaches afforded by the measurement of the freezing point pressure of mercury at 0 °C and approximately 7.570 kbar as discussed elsewhere in this report allows critical evaluation of the relative validity of the approaches. Since our current evaluation of the primary pressure scale is based to a large measure on these three approaches, each will be discussed in order.

a. Theoretical, Followed by Gage Intercomparison

The rigorous solution of infinitely long cylinders and pistons is straightforward, and the solutions are known as the Lamè equations. As a first approximation, Johnson and Newhall (1953) made some simple calculations based on an elementary theoretical treatment in which they assumed that the drop in pressure in the crevice along the length of the piston takes place over a small interval and is uniform below and above this point. The Lamè equations were assumed to apply to the long cylindrical sections above and below. Using some simple cases, they showed that the change in effective area varied linearly with the measured pressure in this approximation and that the pressure coefficient λ in the relationship $A_e=A_0\ (1+\lambda P)$ was of the order of 3×10^{-7} per bar for a simple free-piston gage made of steel. They illustrated uncertainties in λ of the order of 100 percent depending upon where the sharp pressure drop occurred along the piston length, where the piston was located in its travel, and also upon detailed construction of the piston-cylinder assembly. At ten kbar, this represents an uncertainty of the order of 0.3 percent. Johnson, et al. (1957) later reported a brief experimental comparison of a simple piston gage with a control gage assumed as the standard. The distortion of the simple gage even at pressures below 300 bars was shown to be linear, and the measured distortion coefficient λ indicated a pressure gradient near the upper portion of the piston. Zhokhovskii (1959a, 1959b, 1960, 1964) has carried out a rather straightforward but thorough analysis based on the assumption that the change in radius a of the piston and radius b of the cylinder at a general position x, along the length of the piston could be evaluated using the Lamè equations in terms of the pressure in the crevice at the point x. Since the Lamè equations apply rigorously only to long rods and hollow cylinders where the pressures are uniform along the length, one would expect serious discrepancies if the pressure variation along the piston length were abrupt, but the assumption would be more satisfactory if the pressure gradients were small and appeared over a large portion of the crevice length. Zhokhovskii's analysis makes no other assumption as to the functional variation along the length of the crevice but does assume perfectly cylindrical geometry and that no other deformation takes place except that described above by the Lamè equation.

Zhokhovskii's analysis was carried out for both simple piston gages and gages using cylinders with counter pressure. The latter is an extension of Bridgman's re-entrant cylinder system in which the chamber pressure extends completely along the working length of the piston. This system should not be confused with the controlled-clearance gage designed by Johnson and Newhall for which the geometry is significantly different and the counter pressure is independently adjustable from the measured pressure. In all cases studied by Zhokhovskii, the effective area was shown to change proportionally to the pressure being measured. The proportional relationship can be written alternatively in terms of the change in area ΔA or in terms of the pressure difference ΔP between the true pressure and the calculated pressure assuming no change in area. Thus

$$A_e=A_0\ (1-\lambda P),\ \frac{\Delta A}{A_0}=-\lambda P,\ \text{or}\ \Delta P=-\lambda P^2. \quad (1)$$

Since λ is small $\Delta P \ll P$ and the three equations are equivalent within the linearity approximation.

Zhokhovskii's theoretical results can be summarized in one equation which gives the value of the constant λ in terms of Young's moduli E and E' for the cylinder and piston respectively, the Poisson ratios σ and σ' for the cylinder and piston, the radius b of the piston, and the internal and external radii a and R of the cylinder:

$$\lambda=\frac{(3\sigma'-1)}{E'}+\frac{1}{b}\,(k-k_1) \tag{2}$$

where

$$k=\frac{a}{2E}\left[\frac{R^2+a^2}{R^2-a^2}+\sigma\right]+\frac{b}{2E'}\,(1-\sigma') \tag{3}$$

and k_1 has a different value for a piston with a regular cylinder and a piston with a cylinder with counter pressure. For a regular cylinder

$$k_1=\frac{b\sigma'}{E'} \tag{4}$$

and for a cylinder with counter pressure

$$k_1=\frac{a}{E}\left[\frac{2R^2}{R^2-a^2}-\sigma\right]+\frac{b}{E'}\,\sigma'. \tag{5}$$

In the case of the cylinder with counter pressure, the use of the Lamè equations for the cylinder appears rather questionable since near the upper end of the cylinder the internal pressure approaches atmospheric pressure but the counter pressure is still the pressure being measured. Since in Zhokhovskii's approach, the pressure used in the Lamè equations is the pressure in the crevice, an obvious contradiction to physical reality occurs.

Zhokhovskii and coworkers have published several experimental papers—Zhokhovskii and Bakhvalova (1961), Bakhvalova (1964), Zhokhovskii (1958)—showing the result of intercomparisons of gages with a variety of dimensions and material of construction, some with cylinders using counter pressure and some with regular cylinders. Comparisons were made using a differential-resistance high-pressure gage (Zhokhovskii and Bakhvalova, 1960), consisting of two manganin coils used as pressure transducers. Each resistance coil was placed in a separate pressure chamber with a valve connecting the two chambers, and the coils were electrically connected into parallel arms of an equal-arm Wheatstone bridge. The bridge was balanced at high pressures when the two pressure chambers were communicating with each other. The valve between the two was then closed, a free-piston gage was attached to each chamber separately, and the gages were caused to float simultaneously. Since the chambers were not in communication, the unbalanced Wheatstone bridge yields the pressure difference existing between the two free-piston gages. Repeated measurements to check the reliability of the differential-resistance gage indicated uncertainties introduced by the gage were less than 0.5 bar at an operating pressure of 2000 bars when the pressure difference was less than 40 bars. Uncertainties less than two bars at operating pressures to 9000 bars were introduced when pressure differences were less than 200 bars. Improvement in this precision was later made, but no data were given to evaluate magnitudes involved.

Theoretical calculations of expected changes in effective area were made on each of several individual gages, and predicted discrepancies between various sets of two gages were calculated. The experimental intercomparisons of the regular piston-cylinder assemblies were made using the technique described above. At ten kbar agreement of the experimental discrepancies with the predicted discrepancies was 0–5 bar. Correspondingly better agreement was obtained at lower pressures. In general, agreement for systems with counter pressure was approximately the same. Nevertheless, disagreement between theory and experiment as high as 15 bar was observed for one system using a cylinder with counter pressure. Further experimental work on the systems with counter pressure, including bell mouthing the cylinder at the upper end, indicated that for cylinders with counter pressure the crevice near the top of the piston becomes too restricted. Zhokhovskii also designed and constructed a gage which, based on the same theoretical approximation, would have an effective area that would not change with pressure. Experimental intercomparisons, however, indicated uncertainties of the same order as given above.

From a consideration of these results, one concludes that a primary pressure scale based on the equation proposed by Zhokhovskii accompanied by appropriate testing to assure the absence of taper, noncylindrical geometry, or unsuitable clearance could not possibly yield a scale more accurate and reliable than five bars at ten kbar and in general would be less reliable.

b. Controlled-Clearance Gage

The controlled-clearance gage developed in 1953 by Johnson and Newhall and illustrated in figure 2 eliminates immediately the problem of excessive leakage at the higher pressures. The increased complexity is offset by the additional versatility available in varying the jacket pressure, thus permitting measurements to be made at an optimum piston fall rate at all times. An inherent improvement in sensitivity and convenience thus results. Nevertheless, different sized piston-cylinder assemblies are desirable to give higher sensitivity at lower pressures, although a single system can be used from zero to the maximum pressure. In such a gage, the initial clearance is less critical for routine work, but uniformity and an initial, precise fit of the piston-cylinder system are still of prime importance for the establishment of a primary scale. The fundamental advantage of a controlled-clearance gage is the elimination, in principle at least, of the distortion of the cylinder. In any of the theoretical approaches to the distortion of the piston-cylinder system, the change in effective area due to the distortion of the cylinder is several times the change due to the distortion of the piston, and the two effects add. The size of the area correction term for the controlled clearance gage is thus reduced appreciably and changes its sign. Furthermore, the analysis of the cylinder using elasticity theory is more complicated and less reliable than that for the piston.

In the operation of the controlled-clearance gage, the cylinder is forced by means of the jacket pressure to fit the piston. How well this fit can be made is a limiting factor in the accuracy of the technique. For routine operation of moderate accuracy and precision, a measurement of the torque required to rotate the piston will tell when the two are well matched but not closed. Extreme care must be taken to avoid mechanical contact and friction. Operation of the gage is significantly more elaborate, as discussed below, when the highest precision is desired and if excessive wear and scoring of the assembly are to be prevented. Since the deformation due to the jacket pressure P_j is assumed linear, the jacket pressure P_j' necessary to completely close the crevice is given in terms of the measured pressure P_m by

$$P_j' = P_{j0}' + LP_m \tag{6}$$

where P_{j0}' is the pressure required to close the crevice at atmospheric pressure. Values of L, according to Johnson and Newhall, vary between 0.35 and 0.7 for usable gages. The value of P_{j0}', of course, is highly dependent on the initial clearance. The values of P_{j0}' and L must be experimentally obtained as discussed below.

In a controlled-clearance gage as designed by Johnson and Newhall, the piston is made to extend from the cylinder at both ends by more than one piston diameter. This arrangement tends to eliminate nonuniform deformation of the piston due to end effects and makes more reasonable the use of simple elastic theory. Johnson, et al. (1957) presented a rather general mathematical development of the change in effective area of a piston constrained as is the case in a controlled-clearance piston gage. They assumed a radially isotropic piston material, perfectly cylindrical geometry, and uniform end-loading of the piston. Using an analysis based on the integration of the deformation caused by a series of differential pressure steps along the piston, they showed that the effective area is equal to the average of the area at the top and the bottom of the piston provided the two ends are far removed (more than one diameter) from any pressure gradient. No assumption was necessary concerning the shape or pressure profile along the length of the piston. For isotropic piston materials this conclusion leads to an expression for λ of

$$\lambda = \frac{(3\sigma - 1)}{E} \tag{7}$$

assuming the piston fits the cylinder perfectly. This equation yields an approximate value of -8×10^{-8}/bar for a carboloy piston. For highly accurate pressure determinations, the gage is balanced for one given P_m at several different settings of P_j, and the leakage of liquid through the crevice is measured at each jacket pressure. This fluid-flow rate can be easily measured by noting the fall rate of the piston itself provided the rest of the pressure chamber is completely free of leaks. Since the deformation of the cylinder with jacket pressure should be linear, and since the viscous-flow rate between two parallel surfaces varies as the cube of the separation of the surfaces, a plot of the jacket pressure against the cube root of the flow rate should yield a straight line provided the crevice is uniform. The linearity of such a plot gives an excellent check of how well the piston and cylinder fit. A nonlinear plot immediately illustrates scoring, noncylindrical geometry, or a leaky chamber. If a gage is used to measure very high pressures (greater than ten kbar), some nonlinearity may be introduced by the break down of linear elastic theory. An extrapolation of this linear plot to zero flow-rate is now taken as the required jacket pressure for a perfect fit of the cylinder to the piston. Corrections must then be made of the measured value P_m at a very low leak to an idealized value of no leak when the cylinder would perfectly fit the piston.

The use of this technique and extrapolation procedure is referred to as "measurement with no leak" although all measurements are actually made with measurable leakage past the piston. The correction from the low-leak condition to the "no leak" condition is of the order of 0.1 percent at ten kbar. Newhall, et al. (1963), used simple elastic theory to make this correction. Bennett and Vodar (1963) have analyzed with greater care the leakage flow and have illustrated an alternative but more complex method of making this final correction to the zero-leak condition based upon more general elastic theory and additional experimental viscosity data. The analysis of Bennett and Vodar indicates that the pressure gradient is highest near the upper region of the cylinder, but their work confirms the simple analysis of the change in effective area with pressure given above. Cross (1964) assumes the area of the cylinder A_c can be written

$$A_c = A_0 \, [1 - b(P_j' - P_j)] \tag{8}$$

and determines the constant b by measuring the change in chamber pressure P_m with an auxiliary gage of very high sensitivity as the jacket pressure P_j is changed. Since P_j' is obtained from the extrapolation mentioned above, A_c is experimentally determined. It is interesting to note that in the limit of zero fluid flow in the "no-leak" condition, the fluid velocity itself is zero, and frictional forces in the crevice need not be considered. The effective area can then be determined from geometrical conditions only.

The action of the viscous fluid in the crevice as it narrows to a few microns average thickness is still an unknown feature of the gage. When the crevice approaches such a small average thickness, there exists obvious variation in this thickness both around the perimeter and along the length. For example, from data taken at a low-leak condition, Bennett and Vodar (1963) predicted jacket pressure necessary to "seize" the piston. They then proceeded to decrease the crevice dimension by applying jacket pressure until mechanical and/or electrical contact was made. In all cases, the measured contact was experienced at a lower jacket pressure than predicted. This obviously indicates the existence of high spots and argues strongly in favor of the extrapolation procedure over a direct measure of contact. Yet, one still wonders whether the extrapolated fit is consistent with the techniques used in measuring the piston area at atmospheric conditions or whether the atmospheric measurement was also of high points. It is rather evident that the use of a larger-diameter piston cylinder assembly will reduce the percentage uncertainty associated with the crevice flow near zero leak. This fact is one reason for the increased reliability of large-diameter piston systems used at the lower pressure. At the higher pressures, however, the handling of the excessively large weights required to load the larger pistons creates other rather severe problems.

Yasunami (1967a, 1967b) has reported the construction of a controlled-clearance gage with a diameter of 1.1 centimeters usable to 10 kbar in which he has used a lever to multiply the gravitational force associated with the weights rather than applying the weights directly to the piston. Adequate details have not been reported in the open literature to allow an evaluation of systematic errors involved in this work. Since errors in lever arm as well as undetermined frictional forces in the pivot point cause first-order errors in the effective area of the gage, precise evaluation of possible errors is of fundamental importance. The problem is intensified by the large force (approximately ten tons in Yasunami's work) which the pivot must support. Zhokhovskii, et al. (1959) and Konyaev (1961) have used an auxiliary free-piston "hydraulic-multiplier" system in a similar manner to apply higher loads to a regular free-piston gage. Some approach such as this appears necessary if one is to increase the accuracy and reliability of the controlled-clearance piston gage at very high pressures.

The temperature of the piston under operating conditions may be considerably higher than the rest of the apparatus due to the viscous friction within the crevice. Newhall, et al. (1963) crudely estimated at 20 °C increase above ambient temperature and treated it as if the total piston were at this temperature. The 20 °C estimate is much larger than is generally expected for the effect. Since uncertainties of the order of 0.01 percent result from errors of 10 °C, attention must be paid to this item if greater accuracy is desired.

The major development and use of controlled-clearance gages have been for pressures below 10 kbar although a commercial unit rated at 14 kbar maximum pressure is available. Johnson and Heydemann (1967) and Heydemann (1967) have recently developed a controlled-clearance gage usable to 26 kbar. They incorporated Bridgman's tapered support-ring principle to decrease the distortion of the cylinder and also included a jacket-pressure chamber to obtain fine adjustment of the crevice. In their particular design it was not possible to supply additional fluid to the chamber without disturbing the crevice clearance and thus they were unable to evaluate the constant b in equation (8). Due to the complex cylinder support they were unable to use elastic theory to extrapolate to the "no-leak" condition, and, as a result, they obtained much lower accuracy (60 bar in 25 kbar) than that for which one would hope. Nevertheless, they did demonstrate the feasibility of making measurements at 26 kbar, and it is apparent that with appropriate changes in design such a gage can be built and operated using proper extrapolation procedures. When one reaches pressures of this magnitude, nonlinear terms in the elastic coefficients of the piston become significant and must be considered. Such effects give uncertainties of approximately 0.01 percent at 10 kbar.

c. Similarity Method

Dadson and coworkers (1955, 1958, 1965) have developed two methods for evaluating the elastic distortion in regular free-piston gages based upon an underlying assumption that the functional variation of the gap width along the length of the crevice will be closely related for two different free-piston gages, even though neither is known. They assume this relationship between the two systems can be related to dimensions and elastic parameters for known systems of specific construction as discussed below. Dadson names these two methods the "similarity" method and the "flow" method. He has carried out extensive work using the former method and has used the flow method only as a supporting measurement.

The similarity method assumes that two idealized piston-cylinder systems constructed of isotropic elastic material, having perfect cylindrical and concentric geometry, and with selected known elastic moduli can be constructed such that the functional variation of the gap width along the length of the crevice is proportional at all pressures. The proportionality constant in this case is the inverse ratio of the elastic moduli of the assemblies. To satisfy this condition, the dimensions of the assemblies must be nominally equal, but the initial gap width must be in the inverse ratio to their elastic moduli. Dadson has shown, however, that this latter condition on the initial width is not particularly critical, probably due to the fact that the initial gap is small compared to the gap at higher pressures.

Using these assumptions, which are very sound provided adequately precise assemblies can be constructed and idealized conditions met, one can write an expression for the effective areas A_P (and) B_P of the two assemblies in the form:

$$A_P = A_0\,[1+\lambda_A f(P)] \text{ and } B_P = B_0\,[1+\lambda_B f(P)] \quad (9)$$

where $f(P)$ is an unknown function of pressure to be determined experimentally. Because of the principle of completely similar distortion, λ_B and λ_A are related by $\lambda_B = k\lambda_A$ where the constant k is the ratio of the two Young's moduli E_A and E_B or, alternately, the shear moduli G_A and G_B. In equation form:

$$k=\frac{E_A}{E_B} \quad \text{or} \quad k=\frac{G_A}{G_B}. \quad (10)$$

This clearly implies the ratios of the two sets of moduli are equal or, in other words, that the Poisson ratios of the two materials are equal. Since the term $\lambda_A f(P)$ and $\lambda_B f(P)$ are very small, one can write

$$\frac{A_P}{B_P}=\frac{A_0}{B_0}\,[1+(\lambda_A-\lambda_B)f(P)]$$

$$=\frac{A_0}{B_0}\,[1+\lambda_A(1-k)f(P)]. \quad (11)$$

Two balances can be compared experimentally with sensitivity of a few parts in 10^6. The ratio A_P/B_P is thus measurable to a high degree of accuracy, and the quantity $\lambda_A f(P)$ can be extracted from equation (11) provided k is known. The quantity $\lambda_A f(P)$ is precisely the desired change in effective area of system A. When this function is known, the free-piston gage A is calibrated at high pressures, and the change in area of system B or any other system is readily available. Since the sensitivity to errors or uncertainties in k becomes very high if $(1-k)$ is small, it is desirable to construct the two systems with highly different elastic moduli but with equal Poisson ratios and also to know accurately the elastic moduli of both materials. These restrictions, coupled with the strength requirements and the need for precise machining properties severely limit the possible materials usable in such a study. The first two metals used by Dadson and coworkers were steel and an aluminum bronze known as "hydurax". In later work they also used a tungsten alloy "GEC heavy metal" to provide a three-way intercomparison as a self-consistent check on the method. The elastic constants of these materials are given in table 2. Since errors in elastic constants give a first-order error in λ, it is essential to obtain the best values possible for the elastic constants of both materials. Dadson used static values for the shear moduli and ultrasonic values for Poisson ratios and gave detailed reasons for this decision.

TABLE 2. Elastic parameters for metals in similarity intercomparison

	Young's modulus (E) (dyn/cm^2)	Modulus of ridgidity (G) (dyn/cm^2)	Poisson's ratio
Steel (K9)	20.5×10^{11}	7.86×10^{11}	0.295
"Hydurax" aluminum bronze	14.3×10^{11}	5.45×10^{11}	0.333
CEC heavy metal—tungsten alloy	36.7×10^{11}	$13.5_5\times10^{11}$	0.286_5

It is significant to note that the functional variation of effective area with pressure is still preserved in the similarity method. This is the only method for which this functional relation is experimentally available above the pressure available to the differential mercury manometer. Although elastic theories suggest a linear variation of area with pressure, nonlinear effects might be expected to be associated with changes in viscosity along the length of the gap due to this pressure variation of the viscosity. Such nonlinear variations were actually observed by Dadson using liquid paraffin as a fluid. However, when light mineral oil or castor oil was used as a transmitting fluid, the data agreed with a linear relationship such that disagreement in effective area of less than one part in 10^5 was demonstrated at measured pressures up to two kilobars. This linear relationship was thus assumed in later analysis. A further significant and surprising result of Dadson's work was the dependence of the distortion constant of a single piston cylinder assembly on the transmitting fluid used even when the linear relationship existed. The values of λ from equation (11) were, for example, approximately ten percent higher when using light mineral oil than when using castor oil. The magnitude of the effect was approximately the same for two different sized piston assemblies. These results are in marked contrast to the earlier work mentioned above at lower precision and lower pressures wherein the effective area was reported as not depending on the viscosity of the fluid.

It will be noted from table 2 that the condition for the Poisson ratio used in a "similarity" pair of metals is not well satisfied when the aluminum bronze is used in conjunction with either of the other two metals. Assuming the functional relationship $f(P)$ in equation (9) is simply P, Dadson has given an analysis indicating how this discrepancy in the Poisson ratio can be accounted for using elastic theory. The use of elastic theory in determining a correction term here is in contrast to the approach of Zhokhovskii and others given above where elastic theory is used to evaluate the total change in effective area of the assembly. To obtain these correction terms, Dadson defines

$$k=\frac{G_A}{G_B}\neq\frac{E_A}{E_B}$$

and shows that correction terms

$$\Theta_A=\frac{3\sigma_A-1}{2E_A}\text{ and }\Theta_B=\frac{3\sigma_B-1}{2E_B}\tag{12}$$

must enter the determination of λ as indicated:

$$(1-k)\lambda_A=(\lambda_A-\lambda_B)_{\mathrm{meas}}+(\Theta_B-k\Theta_A).\tag{13}$$

It is interesting to note that these correction terms are of the same form and of approximately the same magnitude as the total change in area of the controlled-clearance free-piston gage described above.

The extension of the similarity method to three metals allows three separate experimental combinations yielding two direct determinations of λ for each individual piston-cylinder assembly and one indirect determination. Since the purpose of the investigation is to establish a primary scale, a determination of the distortion coefficient for the steel assembly is the only important quantity. The similarity method thus gives three measurements of this quantity although the indirect determination does have some dependence on the other two. Four to six independent sets of measurements were made on each of two piston-cylinder assemblies of identical design but with different nominal areas. Similarity measurements were made on one assembly to 500 bar and on the other to 1200 bar although the calibrated assembly was capable of 3000 bar. Similar measurements were also made on a piston-cylinder assembly of a different design capable of pressures to 6000 bar. The total dispersion of the λ values determined for the two low-pressure assemblies was approximately four percent, the largest errors of which appeared to be associated with intercomparisons with the bronze assembly, which has an unfavorable Poisson ratio comparison. A brief error analysis indicated better reliability of selected data, and a final value of $4.0_6\times10^{-7}$/bar was reported for λ associated with the steel piston-cylinder assembly with an estimated accuracy of two percent. The 6000 bar assembly exhibited a value of $3.0_6\times10^{-7}$/bar due to its different construction.

Two additional internal checks were also available. The λ value for each assembly was independently determined; therefore, an intercomparison of any two steel assemblies so calibrated yields a direct measurement of the differences in the values of λ so determined. For the two lower pressure assemblies, the difference in λ determined by the similarity method agreed within 1.5 percent compared to a direct intercomparison measurement of one percent. A similar intercomparison of a high-pressure gage with the low-pressure assemblies over the range possibly gave agreement of approximately two percent in λ. All internal checks thus indicate precision of the order of two percent in λ as measured by this method. This implies the accuracy of approximately one part in 10^5 in effective area at one kbar and one part in 10^4 at 10 kbar provided A_0 is known this well. It was also noted that the variation of effective area with pressure was linear to the maximum value of 6 kbar.

Dadson and coworkers developed the flow method as an independent check on the changes of effective area with pressure as measured with the similarity method. The flow method is based on the concept that a change in effective area associated with pressure distortion could be related to a known difference in area between two piston-cylinder assemblies similarly constructed but of slightly different zero pressure effective areas. Since the fluid flow in the crevice between the piston and cylinder is very sensitive to the gap width, the flow rate can be used as an indicator of changes in effective area. The most severe problem is obtaining a simple relationship between the measured flow rate and the effective area. This difficulty is associated with the varying viscosity along the crevice as well as the changes in pressure profile and gap width along the gap length. Dadson assumed the pressure profile along the gap length to be similar in the two systems and the width of the gap at any point to be proportional to the pressure at the point. Further details will not be given since the method is not of primary significance. Measurements were made to 1500 bar and to this pressure agreement with the similarity method of approximately three percent in the determination of λ was obtained. The dispersion of the measured points was slightly larger than in the similarity method.

d. Summary

Following the above survey of the three major approaches used to evaluate or eliminate the elastic distortion error in a free-piston gage it is appropriate to evaluate the relative merits of the three approaches. The independent determination of the freezing pressure of mercury at 0 °C gives a very good intercomparison between techniques. The results reported for these measurements are given in table 3 of section 3 on fixed points. Although the error flags of all measurements before and including that of Newhall, et al. (1963) overlap, there is an obvious overconfidence in the evaluation of systematic errors or theoretical uncertainties in at least one of the last four measurements indicated in table 3. With current understanding, one can only suggest possible weak points in each measurement and indicate areas for improvement.

As pointed out above and as indicated by the error flags associated with Zhokhovskii's determination of the mercury freezing pressure, his theoretical approach is not sufficiently reliable to be competitive with either the similarity method or the controlled-clearance gage. On reading Dadson's papers one is impressed with the care in construction and analysis which characterizes his work using the similarity method. His work on the determination of the mercury point shows the same care and precision techniques. This experimental integrity adds considerable confidence to this measurement. The similarity method, however, is subject to much greater fundamental uncertainty when compared with the controlled-clearance gage, especially at the higher pressures. For example, the correction terms for use of metals with differing Poisson ratios in the similarity method as indicated above are of the same order as the total elastic corrective terms in the controlled-clearance gage. Furthermore, the use of two measurements in the similarity method rather than the one in the controlled-clearance gage tends to give error accumulation. In the calibration of the mercury freezing pressure, the determination of Newhall, et al. using the controlled-clearance gage involved only one measurement and lacked adequate sensitivity in the determination of the transition point due to the use of the change in volume as an indicator of the transition. The lack of repeated measurements reduces confidence in the error flag.

In contrast, Yasunami's work, using the controlled-clearance gage, appears to be of very high quality. The work was characterized by very high sensitivity of detection, a large number of repeated measurements, and the use of a relatively large diameter piston (1.1 cm). Unfortunately, the large piston required the use of a lever (of rather large arm ratio) which throws a serious uncertainty into the mercury-point determination. It is interesting to note that Yasunami's higher value differs from the other measurements in the direction explainable on the basis of friction. One limitation common to a different degree in all recent determinations of the mercury point is the lack of knowledge of the temperature or temperature effects on the piston. For example, temperature gradients within the piston have not been considered at all.

In the selection of a standardized instrument upon which a primary pressure scale can be based, the controlled-clearance piston gage has several rather strong features to recommend it in preference to other presently available techniques. First, the instrument can be used over a very wide pressure range. Second, the change in effective area with pressure is of the order of 20 percent of that exhibited by regular free-piston gages. This implies that errors in elastic constants with pressure will not be as serious. Third, sensitivity of the system does not decrease drastically at the higher pressures due to excessive fluid leakage. Fourth, the analysis of the variation of effective area with pressure is well based with assumptions and idealizations involved in only minor correction terms. Fifth, special materials involving appropriate elastic parameters are not required.

The fact that no other workers have attempted to compete with Dadson and coworkers indicates a feeling among others in the field that his analysis has been extended nearly to its limit. This is not the case for the controlled-clearance gage. Several rather obvious but time-consuming studies need to be carried out using a controlled-clearance gage. First, in light of Dadson's measured variations of the values of λ depending on fluids used, measurements should be made using a controlled-clearance piston with different fluids in order to see if the assumptions involved in the extrapolation to the "zero-leak" condition are valid for low and high viscosity liqiuds. This, of course, is the most serious uncertainty in the controlled-clearance technique. Second, the use of pistons of different elastic properties would give an internal check on the change of elastic parameters with pressure. Third, a reliable pressure multiplier (perhaps of the type used by Zhokhovskii and coworkers) needs to be developed. Such a multiplier would allow the use of larger diameter pistons at the higher pressure, thus making initial area measurements more precise and also decreasing the percentage error associated with uncertainties in gap width. Fourth, a more careful analysis of the piston-temperature problem should be made.

It appears from the work of Johnson and Heydemann that such a primary scale can be extended to pressures of at least 26 kbar, and since fluids with reasonable viscosity are available above this pressure, it appears possible that with appropriate technical development the primary scale could be extended well above 30 kbar.

2.2. The Mercury Manometer

Historically the mercury manometer has been considered by most workers as the most suitable fundamental pressure standard due to its inherent simplicity. The height of the column, the density of the mercury, and the gravitational field at the geographical point are the only fundamental quantities involved, and since all three could be measured with rather high accuracy at a rather early date, the mercury manometer became a very natural standard. The simplest manometers used a column open to the atmosphere, and the temperature of the mercury which influences the density was simply measured at one point and assumed constant throughout. A significant number of such columns were constructed and operated to heights of 300 meters during the period from 1840 to 1900. Present-day columns a few meters in height use the highest purity mercury, well-controlled temperature baths, and elaborate height-measuring techniques. Since the pressure is low, all pressure heads associated with connecting lines must also be considered, and care must be taken to measure accurately the position of the mercury meniscus and to minimize surface tension effects. Serious problems with temperature control are associated with manometers for pressures above a few atmospheres due to their inherent height.

As early as 1894 Stratton (1894) proposed the use of a multiple-tube manometer which consisted of a number of alternating columns of mercury and a low-density liquid (water or some suitable organic). In 1915 Holborn and Schultze (1915) first described the differential mercury manometer which consists of a single mercury column, to each end of which is attached a free-piston gage. Since a free-piston gage can reproduce a given pressure with a precision and order of magnitude better than its inherent accuracy, known pressures can be transferred from the top to the bottom of a mercury manometer using the free-piston gage, and higher pressures can be developed while maintaining the accuracy of the mercury manometer. The compactness, relative convenience, and suitability for temperature control of either the multiple manometer or the differential manometer allowed the extension of the mercury manometer to higher pressures while maintaining the accuracy of the small open-column manometers.

As mentioned above, extensive intercomparisons with free-piston gages using this type of mercury manometer as a standard instrument led to the rather thorough understanding of the free-piston gage. Notable developments and refinements in these manometers were made by Wiebe (1897), Crommelin and Smid (1915), Keyes and Dewey (1927), Meyers and Jessup (1931), Roebuck and Ibser (1954), and Bett and Newitt (1963).

Keyes and Dewey (1927) built a differential manometer usable to approximately 600 bar with reported accuracy of approximately one part in 10^4. Meyers and Jessup in a rather extensive work described a five-column multiple manometer useable to 15 bar with an accuracy better than one part in 10^4. Operation of the five columns as a unit in a differential manometer extended the pressure range to 75 bar with a precision of a few parts in 10^3. No mention of accuracy was made. Roebuck and Ibser (1954) were able to measure pressures to 200 bar with an accuracy better than one part in 10^4 using a multiple manometer consisting of nine columns 17 meters in length with temperature controlled to approximately 0.3 °C. The most recent and by far the most extensive use of a mercury manometer to calibrate free-piston gages is the work of Bett, Hayes, and Newitt (1954) and Bett and Newitt (1963) using a differential manometer constructed to operate at 2500 bar with a column nine meters high. Temperatures were controlled to approximately 0.02 °C, and extreme care was taken to determine density and purity of mercury, and other variables influencing pressure heads.

Intercomparison with free-piston gages yielded the first definitive quantitative measurements of the change of effective area with pressure in a free-piston gage. Anticipated accuracies were approximately three parts in 10^5 at 500 bar and six parts in 10^5 at 2500 bar. Calibrations of free-piston gages were carried out to 700 bar using a cumulative method of transferring each pressure from the bottom to the top of the mercury column (60 to 70 transfers). Measurements to 1400 bar were made using a differential method in which the effective area of the free-piston gage was assumed to vary linearly with pressure as was indicated in the cumulative method. In this differential technique, the differential manometer measures only a change in pressure associated with a change in effective area of the piston but has the advantage that errors are not cumulative.

Coefficients λ for the change of effective area of the piston gage with pressure of 3.55×10^{-7}/bar and 2.83×10^{-7}/bar were obtained using the cumulative and differential methods respectively for the same free-piston gage, which corresponds to a difference of approximately one part in 10^4 at 1400 bar. The difference was attributed to error accumulation, and the result of the differential technique was given preference by the authors. No such discrepancy was observed for a gage calibrated to approximately 100 bar. This coefficient for the change of effective area with pressure is compared with a value of 4.2×10^{-7}/bar given by Dadson (1955, 1958) for a similarly constructed free-piston gage. This discrepancy in the determination of λ between the mercury manometer and the similarity method of Dadson cannot be traced to a single effect. Bett and Newitt seriously questioned the current data on compressibility of mercury.

Recent data by Davis and Gordon (1967) on the compressibility of mercury indicate a discrepancy from previous data much less than that needed to explain the different values of λ obtained by the two different methods. It is not unreasonable that some of the discrepancy in λ can be due to Dadson's similarity approximations. The extension of a differential manometer to higher pressures using the well-constructed and well-designed apparatus of Bett and Newitt demonstrated some rather serious limitations of the mercury manometer at the higher pressures. First, the knowledge of the compressibility of mercury and any other liquids in the manometer and the variation with pressure of these compressibilities represent a serious limitation to increased accuracy. Second, the error accumulation due to a large number of transfers is not completely understood. This of course, is associated with the free-piston gages used for transfer and perhaps indicates a weakness in our analysis of free-piston gages given before. Third, the inherent human factor involved in numerous transfers is questionable.

While free-piston gage construction and understanding have improved due in large measure to studies using mercury manometers, the improvement in accuracy of the mercury manometer and its extension to higher pressures have not kept pace. As stated previously, agreement between piston gages and mercury manometers is approximately one part in 10^5 at a few bar. Mercury manometers operating in this range are reaching an accuracy of a few parts in 10^6.

Above what pressure one should use the free-piston gage is not clear, but due to convenience it appears that the mercury manometer will seldom be used above 10 bar in future calibration and standardization.

2.3. Piston-Cylinder Gage

The use of a piston-cylinder system with either piston packing or a solid-medium pressure environment represents the best approximation to a primary scale at pressures above 25 kbar. Although some work using such a system in calibration studies of the Bi I-II transition pressure has been done, notably by Kennedy and Lamori (1962), and by Boyd and England (1960), it appears that the future usefulness of this technique in calibration will be limited to higher pressures.

Two dominant effects are of significance: first, the friction between the piston and cylinder or packing, and second, the internal friction associated with the solid-medium environment. Both these effects give rise to irreversible load-pressure curves with attendant uncertainties as to both magnitude and direction. Although the total double-valued friction is seldom less than ten percent of the total load, there is strong evidence that both types of frictional forces are nearly symmetrical, and pressures can be estimated to ± one to two percent with proper care. Uncertainties of this magnitude are comparable with indirect extrapolation techniques and represent a serious restriction to the universal acceptance of the piston-cylinder as a primary standard.

Boyd and England (1960) calibrated the Tl II-III transition pressure at approximately 37 kbar with a reported accuracy of 3.5 percent. Haygarth, et al., (1967, 1969) have carried out two rather extensive studies to calibrate the Ba I-II and the Bi III-V transition pressures at nominal pressures of 55 kbar and 77 kbar respectively. They reported accuracies of 0.5 kbar and 2.0 kbar respectively at these pressures. Extension to pressures above 50 kbar required a shortening of the unsupported portion of the piston to a value less than the diameter of the piston.

2.4. Galvanic Cell as a Primary Pressure Indicator

Pressure can be defined by thermodynamic relationships as discussed in an earlier section. One such relationship which offers the possibility of making direct primary determinations of pressure is

$$\left[\frac{\partial G}{\partial P}\right]_T = V \tag{14}$$

where G is Gibbs free energy, P is pressure, and V is molar volume. It follows that

$$\left[\frac{\partial \Delta G}{\partial P}\right]_T = \Delta V. \tag{15}$$

There is a direct relationship between the electromotive force (E) of a galvanic cell and the Gibbs free energies of the reactants and products:

$$\Delta G = -nFE \tag{16}$$

where F is a Faraday and n is the number of equivalents per mole. By substituting (16) into (15) we obtain

$$nF(\partial E/\partial P)_T = -\Delta V = V_{\mathrm{react}} - V_{\mathrm{prod}} \tag{17}$$

and by integration

$$P = -nF \int (dE/\Delta V)_T. \tag{18}$$

Pressure may then be calculated from the molar volumes of the reactants and products and the potential of the cell.

Bridgman (1958) suggested the use of a cell for such a purpose and Lloyd and Giardini (1964) report that a cell consisting of $\mathrm{Au/AgI + MnO_2|AgI/Tl}$ has a power output showing a maximum at 6500 bar. Bradley et al. (1966) conducted tests with $\mathrm{Pb/PbCl_2|AgCl/Ag}$ cells under pressure to determine the feasibility of measuring pressure by such a cell. Up to 15 kbar they obtained potentials which increased with increasing pressure in agreement with the reaction volume change. At higher pressures, however, the measured potential fell with increasing pressure. They attribute this effect to slow diffusion of ions during the cell reaction and an electronic component of conduction acting as an external shunt.

The molar volume measurements can easily be made by x-ray diffraction as described in section 4 of this report.

Thus, this technique seems to offer a very simple and rigorously defined means of determining absolute pressure but at present cannot be put to practical use because of the experimental difficulties. There is no basis whatever for eliminating the possible use of this technique. Continued research on solid state electrolytes may result in a cell that is feasible for primary pressure measurement.

3. Fixed Points on Pressure Scale

By analogy with the temperature scale as discussed in section 1 it appears appropriate for pressure calibration to pick certain points as fixed points for a practical pressure scale. A discussion as to how to choose such points and to evaluate their usefulness is also given.

3.1. Criteria for Selection

The fixed pressure points on the high-pressure scale are based upon either liquid-solid or solid-solid transformations in pure substances. The basis for the selection of a particular substance will naturally depend on the existence of a polymorphic transition at some suitable pressure and must satisfy several additional conditions which are discussed below.

a. Detectability

The parameter which is to be measured should have a large change at the transition in order to be easily detected by some standard measurement procedure.

Phase transitions in solids have been detected by numerous methods. They include measurements of:

- (a) electrical resistance (Bridgman, 1952; Balchan and Drickamer, 1961).
- (b) volume (Bridgman, 1942).
- (c) optical properties (Balchan, 1959) such as refractive index (Weir, et al., 1962), absorption (Klyuev, 1962), and reflectance (Bassett, et al., 1967).
- (d) crystal-structure change by x-ray (Jeffery, et al., 1966; Jamieson, 1963) and neutron diffraction (Brugger, et al., 1967, Bennion, et al., 1966).
- (e) differential thermal analysis (Kennedy, et al., 1962).
- (f) magnetic properties (Cleron, et al., 1966).
- (g) ultrasonic velocities (Hagelberg, et al., 1967).

Of the above list, probably the electrical resistance and volume measurements have been the most useful and most accurate determinations of the transition points. Differential thermal analysis (DTA) signals have also been used extensively, especially for mapping out phase diagrams, and have value for determination of high-temperature triple points and high-temperature phase boundaries where transition times are small. With the use of counting techniques, x-ray diffraction techniques become a useful tool in detecting phase changes.

b. Kinetics

Phase transition kinetics must be favorable. Hysteresis and transformation time should be small. The items to be considered here are nucleation energy, strain energy, and grain size.

In reviewing the literature, very little has been said with regard to equilibrium transition pressures. There are some cases where transition points determined on the increasing pressure cycle are compared to accepted equilibrium pressure values noting a discrepancy but failing to clarify the reason for it. In view of the previous discussion on this subject, it would be very desirable to find a substance with a small nucleation energy for both the forward I → II and the reverse II → I transitions. Substances with high shear strength do not make good calibrants since they produce strained regions in the sample. In pressure systems where high strains are present, localized regions may exist where the pressure and/or density is sufficient to nucleate a critical volume and initiate the transition before the average pressure over the sample has reached the thermodynamic equilibrium value. The result is a transition which broadens with respect to pressure.

Corll, in a study of the effect of sample encapsulation (Corll and Warren, 1965; Corll, 1967) on pressure enhancement, reports experimental results on a ferroelectric ceramic which undergoes a transition from the ferroelectric state to the antiferroelectric state at 2.7 kbar. The experiment consisted of measuring the pressure-induced transition in two samples, one of which was encapsulated in epoxy. Both samples were run simultaneously in a liquid system. The results indicate that the encapsulated sample transformed at lower applied pressure than an unencapsulated sample in all cases. The author concludes that a 15 percent pressure enhancement had taken place and that "these effects must be considered in the interpretation of pressure-induced phenomena as well as for accurate pressure-calibration experiments." Good measurement practice requires passage through a transition at a constant but small pressurization rate. The kinetics of the transformation give rise to variations in the calibration point, the sharpness of the transition, and the width of the nucleation hysteresis. Davidson and Lee (1964) measured such variations for the Bi I–II transition. The effects will be more severe in materials which are characterized by slow transformation rates.

Very little is known about the effect of grain size on polymorphic transitions. Heydemann (1967) determined the Bi I → II point with two samples of different purity and grain size. Sample A (99.8% pure) had an average grain size of about 0.15 cm as compared to about 0.03 cm in Sample B (99.999% pure). The transition pressure at 20 °C for Sample B (smaller grain size and higher purity) was found to be 25.499 kbar while that for Sample A (larger grain size and lower purity) was 25.481 kbar with an uncertainty of ±60 bar. In this instance there is no measurable effect due to the difference in grain size. In the study of minor effects on phase transitions, such as this, studies should be made by comparison or differential techniques and not on an absolute basis, while the calibration study should be made on the highest purities available.

Careful calibration studies should state grain size of the material used. Cycling a sample through a transition several times probably has some effect on grain size. In studying the Cs II–III, III–IV transitions, large crystallites are very much in evidence when one tries to obtain an x-ray diffraction pattern. At the same time very sharp electrical resistance traces are found. After cycling through these points several times in order to get an x-ray pattern, the electrical resistance trace becomes more sluggish. In silver iodide the grain size was observed to increase through repeated cycling while that of iron decreased (Bassett, private communication).

c. Sample Purity

The substance should be obtainable with high and readily reproducible purity. It should also be chemically stable and relatively easy to handle. There is no general relation regarding the effect of sample impurities on a transition pressure. Transition pressures of some materials are relatively unaffected by impurities while others are relatively sensitive.

In work by Zeto, et al. (1968) on bismuth, the equilibrium transition pressure was essentially independent of purity (six 9's vs two 9's), microstructure (single-crystal vs extruded polycrystal), and thickness of the samples.

Gschneidner, et al. (1962) studied the cerium $\gamma-\alpha$ transformation pressure as a function of rare-earth impurity. The effect of lanthanum, praseodymium, dysprosium, and lutecium additions is to increase the $\gamma-\alpha$ transformation pressure. Lanthanum, the largest solute atom, raised the transformation pressure the most while lutecium, the smallest atom, raised it the least.

Brandt and Ginsburg (1963) studied the effects of antimony and lead impurities on the Bi I–II, II–III transition pressures. Lead atoms which are about the same size as bismuth atoms did not appreciably affect the nature of the phase diagram in concentrations up to 1.26 percent.

Antimony, however, at increased concentrations caused the width of Bi II to become more narrow until at solute concentration of 0.8 percent it disappeared. The Bi I–III phase transition then produced a volume change of 7.5 percent equal to the sum of the changes (4.5%, 2.9%) of the Bi I–II and Bi II–III transitions.

Bundy (1965) reports that the addition of cobalt or vanadium impurities to iron increases the Fe $\alpha-\epsilon$ transition pressure. The rate of increase was much greater with vanadium (whose size is larger than iron) than with cobalt (whose size is almost identical to iron).

Work by Darnell (1965) indicates that with alkali halides, anionic impurities have little effect on the transition pressure while the cationic seem to have a very marked effect. It is interesting to note that in all of the work cited above, the effects are negligible at impurity levels of less than 0.1 percent.

While chemical stability is of little problem with most calibrants, the oxidation problem encountered with cesium and barium can be minimized through more careful handling procedures.

d. Transformation Characteristics

The temperature dependence of the transition pressure dP/dT should be small. Where this is not possible, dP/dT should be known to good accuracy, which condition implies that temperature be measured to consistent accuracy.

The transition should take place at a sharply defined equilibrium pressure with a small region of indifference as defined in section 1. In the work of Bridgman (1940a), the region of indifference of the Bi I–II transition was 60–100 bar at 30 °C. Dadson and Greig (1965) found a point at which pressure changes of 0.1 bar in either direction reversed the mercury transition. This phenomenon illustrates the superiority of liquid-solid transitions. It has been common to select the midpoint of the region of indifference as the thermodynamic equilibrium point, which condition is not necessarily true. It can be seen that a wide region of indifference places a large uncertainty on the transition point.

The materials presently employed as pressure calibrants do not possess all the desirable characteristics discussed. In cases where a poor characteristic exists, it is of greater importance to understand the implication of the constraints imposed. As pointed out previously, the constraints of the pressure-transmitting medium must be better understood if conditions deviate from hydrostatic assumption.

3.2. Error Analysis

In high pressure work where calibration studies for a particular material seem to be giving a convergent trend toward some particular value, a 'best value' has been evaluated for the point. The 'best value' for the transition pressure of calibrants discussed in this review is determined on the basis of a weighted average of the significant published values. The weight used for a particular value is the square reciprocal of the standard deviation. This approach requires that each author make a complete analysis of all possible sources of systematic error associated with his work and estimate properly the accuracy. If an author has failed to do this, a best value which is unduly biased toward the work of this particular author results. In situations where this analysis has not been made, the error has been re-evaluated by the reviewers in order to make an equitable comparison. We emphasize the fact that for calibration studies, past or future, a detailed evaluation of the possible sources of systematic error is as important as the determination of the measured value itself.

One of the difficulties in intercomparing various papers is the fact that authors often present insufficient data and descriptive detail for the reviewer to make an objective evaluation of errors. Furthermore, the uncertainties presented in some calibration papers are uncertainties in the reproducibility of the experimental point and do not represent a realistic evaluation of the absolute accuracy. In order to present worthwhile data, an author needs both to discuss and evaluate all possible sources of systematic error. If, in addition to experimental measurements, one makes use of some theory, he must take into consideration the uncertainty introduced in the theory.

3.3. Fixed Points Below 30 Kbar

Early in his work Bridgman (1911a) recognized the value of using manganin wire resistance gages to measure hydrostatic pressure. Bridgman measured the effect of pressure on manganin wire and found that there was no appreciable temperature effect between 0 °C and room temperature. (In order for these gages to be reliable they must be annealed and then calibrated against a standard.) Bridgman's (1911b) first manganin gages were calibrated against the free-piston gage up to a pressure of 12 kbar. The sensitivity of the free-piston gage used was about 8 bar and that of the manganin gage about 2 bar. The results of this calibration demonstrated that the change of electrical resistance of manganin is nearly linear with pressure enabling it to be calibrated by a single pressure at some fixed point.

a. Mercury

The freezing point of mercury at 0 °C was selected for this calibration point. Pressures were measured with a manganin gage which had been previously calibrated against a free-piston gage. The data published at this time (1911) presented the value of 7620 kg/cm^2 (7.472 kbar)[4] for the liquid-solid transition pressure at 0 °C. In later years (1940) he states that this point "was measured in the first place with an absolute gage and taken in all my work to be 7640 kg/cm^2 (7.492 kbar)" (Bridgman, 1940b). According to Babb (1963) the final value (7640 kg/cm^2) was the average of the six determinations; two detected by volume change and the other four by electrical resistance.

Bridgman's work on mercury, as reported in 1911, was never re-examined until the work of Johnson and Newhall in 1953. These investigators developed a controlled-clearance piston gage as opposed to the re-entrant type cylinder of Bridgman, as discussed in section 2. Pressures were determined with a gold chromium gage, a manganin resistance gage, and by the F/A (force/area) method. The transition pressure in this determination is 109, 760 ± 750 psi (7.568 kbar) compared to Bridgman's value of 7.492 kbar. In consequence of an unusually large experimental error of ±0.7 percent, these two values are in fair agreement.

The next calibration study of Hg was made by Zhokhovskii (1955). He felt that though the fixed point of Hg at 0 °C was convenient due to its reproducibility, it was insufficient for calibration purposes. Consequently, he determined the melting curve of mercury up to 10 kbar. For this purpose the pressure cell is placed in a liquid bath to guarantee stable temperatures. The temperature of the interior of the cell was measured by a thermocouple which had sensitivity of 0.005 °C. For the determination at $t = 0$ °C, the bath was filled with melting ice. The measurement of pressure was accomplished by the use of a manganin gage which had been previously calibrated against a free-piston gage. The method of detecting the phase boundary was based on changes of pressure and temperature at the transition.

The temperature at the ice point turned out to be 0.035 °C due to the flow of heat into the cell, while the pressure at this point was 7722 kg/cm^2 (7.573 kbar). For greatest accuracy this one measurement was made with the free-piston gage. The experimental data were then represented by the empirical Simon-type equation with three empirical constants:

$$\log (P + 37663) = 1.21458 \log T + 1.69765, \qquad (1)$$

where P is in kbar and T is in kelvins. From the slope of this smoothed curve he extrapolated the pressure from its value at $T = 0.035$ °C to 0 °C and obtained an equilibrium transition pressure for the mercury liquid-alpha transition of 7715 kg/cm^2 (7.566 kbar). No precise limits of error or evidence as to the dispersion of the data on which this result is based are given.

In later investigations Zhokhovskii, et al. extended the melting curve of mercury up to 20 kbar (1957) and to 25 kbar (1959a). In this work they have fitted 64 experimental points to equation (1) over the range up to 25 kbar, which corresponds at 0 °C to the smoothed value of 7719 kg/cm^2. Values of P/P_c were calculated for each of the experimental points. The majority of the deviations lie within ±0.3 percent to ±0.5 percent. In the region below 15 kbar the observed deviations ΔP_i tend to be mostly positive, while above this value they are distributed mostly on the negative side, which distribution indicates a systematic discrepancy.

In 1963, Newhall, Abbot, and Dunn, using an improved version of the controlled-clearance piston gage, arrived at the value of 7.5654 kbar for the mercury point at 0 °C. The temperature was at 0.002 °C; however, no details of temperature measurement are given. The value given is based on a single determination so no details are available as to the reproducibility of the data or the dispersion within a series of measurements.

In 1965, Dadson and Greig (1965) of the Standards Division of the National Physical Laboratory in England published the results of a very thorough and careful investigation on the freezing pressure of mercury. While most of the previous workers utilized the volume change of mercury to identify the transition point, these measurements employed the change of electrical resistance of the mercury sample. The magnitude of this change is of the order 4:1 at 0 °C. This method has the advantage of using very small quantities of mercury so that the effect of volume changes at the transition point is significantly minimized.

The constant temperature bath used was of the type employed for the calibration of precision thermometers

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[4] In this section the actual numbers *and units* reported by the original sources are given to indicate the intended number of significant figures. The value transferred to kbar units will be shown in parentheses.

at the ice point. The ice-water mixture was contained in a Dewar flask, which in turn was enclosed in a thermally insulated container. The temperature of the bath was checked periodically by a platinum resistance thermometer and was found to remain constant within ±0.002 °C. The interior of the pressure vessel exceeded the temperature of the bath by about 0.005 °C.

In the range of the transition the pressure was changed in increments of 0.1 bar (contrast with bismuth and barium). Changes of this magnitude on either side of the equilibrium point were found to give almost instantaneously a recognizable drift in electrical resistance. The mean value of a series of 74 measurements is 7.5692 kbar. The dispersion of the data is reproduced in a histogram and appears to be distributed normally about the mean. The total uncertainty is reported as ±1.2 bar.

A report of a determination of the mercury point has recently been published by K. Yasunami (1967 a, b). He used a lever-type controlled-clearance gage and detected the freezing pressure of mercury by a latent-heat detector. This detector was constructed of 16 pairs of semiconductor thermal elements having a sensitivity of 400 μV/°C/pair. Temperature was controlled to ±0.001 °C. The use of the lever-type piston gage allows the use of a piston whose area is one cm^2, which is 15.5 times the area of pistons used by other investigators. Yasunami reports the value of 7.5710 kbar ±1.2 bar within 99.7 percent statistical confidance limits.

All the recent studies of the mercury transition include excellent discussions of the sources of error. The 'best value' selected for the mercury transition pressure at 0 °C is 7.5692 kbar ±1.5 bar. The 7.5692 value is based upon a weighted average of all the data of table 3, and the 1.5 bar error represents the rms deviation from the average of all the weighted values (except that of Bridgman, whose value is definitely low.)

TABLE 3. Mercury (liquid $-\alpha$) at 0 °C

Researcher	Transition pressure (kbar)	Error (bar)	Method of detection
Bridgman (1911b)[a]	7.492	72	Volume
Johnson and Newhall (1953)	7.568	50	Volume
Zhokhovskii (1955)	7.5658	3	Pressure drop as transition initiates
Zhokhovskii, Razuminkhin, Zolotykh, Burova (1959)	7.5697	23	
Newhall, Abbot, and Dunn (1963)	7.5662	3.4	Volume
Dadson and Greig (1965)[b]	7.5692	1.2	Electrical resistance
Yasunami (1967a, 1968)[c]	7.5710	1.2	Latent heat
Cross (1968)	7.5674	1.6	Electrical resistance
Best Value (Weighted Average)[d]	7.5692	1.5[e]	

[a] This value is the average of two volume and four electrical resistance determinations.

[b] 74 experimental determinations.

[c] 16 experimental determinations.

[d] Each value is weighted proportional to 1/(Error)^2.

[e] RMS deviation of weighted values (excluding Bridgman's).

b. Bismuth I–II

Three polymorphic transitions occur in bismuth at room temperatures, two of which are important pressure-calibration points (i.e., Bi I–II, Bi III–V). The Bi II–III transition, being so close to the Bi I–II point, is of little value as an additional calibration point.

At the time Bridgman began making compressibility measurements in the 30 kbar region, he felt that more precise measurements were desirable. As to his approach he states: "One would naturally first try to merely extend the former procedure to higher pressure, but this is not feasible because the free piston had about reached its limit at 13,000 due to rapidly increasing viscosity of the pressure-transmitting medium, demanding forces to rotate the piston great enough to break it, and also due to the rapidly increasing distortion, the correction for which can only be calculated by the methods of the theory of elasticity in a range in which the fundamental assumptions of the theory are becoming rapidly inapplicable. However, the fundamental idea of the free-piston gage, namely, the measurement of pressure by measurement of the thrust on a piston in equilibrium with the pressure, appears to remain the simplest and perhaps the only method. The errors to which this is subject are two: those arising from friction and those arising from geometrical distortion. If these two sources of error could be overcome, then an extension of the same procedure as before could be used, namely, direct measurement of some easily determined pressure fixed point against which the manganin gage could then be calibrated and used thereafter as a secondary gage" (Bridgman, 1940b).

Using the approach mentioned and taking into account corrections for friction and distortion of the apparatus, Bridgman experimentally determined the pressure of the solid-solid Bi I–II transition. The value reported for the transition was 25,420 kg/cm^2 (24.930 kbar) at 30°C, which can be transferred for comparison to 25.155 kbar at 25 °C using the later measured slope of the phase line. With the transition pressure of the bismuth point and mercury point known, manganin wire gages were calibrated in terms of both. These experiments were carried out in liquid systems and yielded a workable calibration scale up to 30 kbar.

A great deal of experimental work has been done on the re-examination of the Bi I–II transition and other fixed points of interest to the calibration of high-pressure apparatus. Babb (1963) published a correction to Bridgman's 30-kbar pressure scale on the basis of the new determination of the freezing point of mercury at 0 °C by Dadson and Greig. Included with this work was a corrected value of 25.375 kbar for the Bi I–II transition at 25 °C.

Boyd and England (1960), using a simple piston-cylinder apparatus which they describe as based on the Coes-Hall design, arrived at the value 25.200 ± 0.4 kbar at 30 °C. The hysteresis of the electrical trace was 11.6 percent. "By balancing on the transition with phases I and II present, increasing the pressure until I → II and releasing the pressure until II → I, it was possible to reduce the hysteresis to 3.1 percent about a mean value of 25.2 kbar." The 25.2 value at 30 °C corresponds to 25.4 kbar at 25 °C.

Kennedy and LaMori published two papers (1961, 1962) in which they employed a piston-cylinder (not a free-piston gage) with a solid-media sample chamber and measured the Bi I–II transition. They rotated the piston through an angle of a few degrees at each pressure to reduce frictional effects in the piston device on the up and down stroke. They reported a value of 25.380 ± 0.020 kbar at 20 °C in their 1962 paper. The error flag in this work represented a repeatability flag and did not include any systematic error analysis. The pressure corresponding to the midpoint of the interval between the up and down stroke was selected as the equilibrium pressure. Since both nucleation hysteresis and the "region of indifference" growth hysteresis, as well as the apparatus frictional effects, are all undetermined in this experiment, the absolute uncertainty is obviously much greater than 20 bar. Heydemann (1967a) has estimated an uncertainty of approximately ± 175 bar for the Kennedy-LaMori measurement, which estimate is smaller than the concensus of the present reviewers.

Vereshchagin, et al. (1966) published the value of 25.4 kbar ± 0.1 percent for the Bi I–II transition pressure but gave insufficient details to make an evaluation of their work possible.

Johnson and Heydemann (1967) describe a dead weight, free-piston gage with a range up to 26 kbar (see section 2). Using this apparatus Heydemann (1967a) published the results of determinations of the Bi I–II transition pressure on samples of two different purities. This measurement was carried out in a true hydrostatic medium where nucleation and growth rate effects could be studied, which allows a much more meaningful statement of thermodynamic equilibrium to be made. Correction errors due to friction are also virtually eliminated. With a bismuth sample purity of 99.999 percent the transition pressure was 25.499 ± 0.060 kbar and for 99.8 percent pure bismuth a pressure of 25.481 ± 0.060 kbar was determined.

The determinations discussed above are given in table 4 for quick reference. Two shock measurements are also presented for interest, one by Duff and Minshall (1957) and one by Larsen (1967). The shock measurements are not directly comparable due to nucleation and other sample hysteresis and non-equilibrium effects. By the very nature of the measurement techniques used in the determinations shown, the measurement of Heydemann (1967a) uniquely meets the requirements for a standardization measurement of a fixed point since only this measurement is referred to the primary free-piston gage. For this reason we have selected as a best value for the Bi I–II equilibrium transition pressure the value 25.499 ± 0.060 kbar reported by Heydemann.

It is of interest to note from table 4 that the average of all the values except Heydemann's centers around 25.4 kbar or approximately 100 bar below Heydemann's value and outside his error flag. Although this may be simply statistical error in the previous measurements, all of which have error flags greater than 100 bar, there is an explanation for this effect. Zeto, et al. (1968)

TABLE 4. Bismuth I–II transition at 25 °C

Researcher	Transition pressure (kbar)	Error (kbar)	Method of detection	Sample purity
Bridgman (1940a) [a]	(e) 25.155		Volume	
Duff and Minshall (1957)	(s) 25.580	0.13	Shock	
Boyd and England (1960) [a]	(a) 25.400	.4	Volume	99.99% Electrolytic Bi
Kennedy and LaMori (1961)	(a) 25.410	See text	Volume	99.999%
Kennedy and LaMori (1962)	(a) 25.380	See text	Volume	
Babb (1963) (correction of Bridgman)	(e) 25.375		Correction	
Heydemann (1967)	(e) 25.499	.060	Volume	99.999%
	(e) 25.481	.060		99.8%
Vereshchagin, et al. (1966)	25.4	.25		
Larsen (1967)	(s) 25.4	.8	Shock	
Best Value [b]	25.499	.060		

(e) equilibrium; (s) shock; (a) average of increasing and decreasing cycle.

[a] Measurement made at 30 °C.

[b] Heydemann's (1967) value accepted (see text).

have shown that the equilibrium pressure is located near the upper part of the nucleation hysteresis for the Bi I–II transition, and since all work previous to Heydemann took the center of some hysteresis interval and Heydemann measured the equilibrium pressure, Heydemann's value would be higher but correct.

3.4. Fixed Points Between 30 and 80 Kbar

In a quest for higher pressures Bridgman developed a supported piston-cylinder system capable of 50-kbar pressure and later a two-stage piston-cylinder system capable of 100-kbar pressure (Bridgman 1935, 1941). The 100-kbar apparatus was essentially a $^1/_{16}$ inch diameter piston-cylinder assembly totally immersed in a larger piston-cylinder liquid-containing vessel operating at pressures of 25 to 30 kbar. The piston material was tungsten carbide, which had a compressive strength of 45 kbar at one bar. The compressive strength increases due to the confining pressure and allows pressures of over 100 kbar to be reached.

Using this two-stage apparatus Bridgman (1942, 1945, 1948) measured the compression ($\Delta V/V_0$) of numerous solids to 100 kbar. Many phase transformations were indicated by discontinuities in the volume at specific indicated pressures. Such routinely measured transitions were not intended as fixed points but as exploratory work. Later workers began to use transitions in Tl, Cs, Ba, and Bi reported by Bridgman at 40,000 kg/cm^2 (39 kbar), 45,000 kg/cm^2 (44 kbar), 60,000 kg/cm^2 (59 kbar), and 90,000 kg/cm^2 (88 kbar) as fixed-point calibration values as discussed below.

Using a different technique, Bridgman (1952) measured the electrical resistance on many metals and alloys to reported pressures of 100 kbar. The apparatus employed two opposed anvils with truncated ends press-fitted into steel support rings, and is commonly known as Bridgman anvils. The sample was encased in silver chloride surrounded by a 0.010-inch thick ring of pipestone, all of which was compressed between the flat center portion of the anvils. Pressure in the anvil apparatus was determined from the ratio of the applied force to the area of the anvil with no regard to pressure gradients. The method of pressure determination was assumed valid due to correlation of the observation of the known bismuth transition at 25 kbar.

Determining pressures in this manner, Bridgman reported electrical-resistance measurements on many metals and alloys, a number of which showed discontinuities indicating phase transformations. Transitions in Tl, Cs, and Ba were reported at 45,000 kg/cm^2 (44 kbar), 54,950 kg/cm^2 (54 kbar), and 80,000 kg/cm^2 (78 kbar) respectively, but no transition was reported in bismuth above the Bi II–III transition. The study was intended as a routine exploratory resistance study of a large number of materials. Bridgman (1952) assumed that the transitions indicated by volume change and by resistance were manifestations of the same transformations and was not surprised at the pressure discrepancies. He attributed the lack of detection of the higher Bi transition in the resistance study to a negligibly small change in resistance. Later, as other workers began using these transitions to establish pressures, a great deal of discussion was generated as to whether the volume and resistance measurements actually indicated different transformations.

Since electrical resistance discontinuities were relatively easy to measure in the solid-media systems such as the "belt" and the multi-anvil devices made popular by the diamond synthesis, Bridgman's resistance transition pressures were used as fixed points, and a so-called "resistance scale" came into general use. It is apparent from Bridgman's writing that neither his volume measurements nor his electrical resistance measurements were intended as calibration experiments, but it is also obvious that the volume measurements were made with much greater care.

Bundy (1958) did measure an electrical transition in Bi at very high pressures. Using an extrapolation of a load vs pressure curve for the belt apparatus in which pressures were determined using the Bridgman resistance scale, Bundy placed the high-pressure Bi transition at 122.5 kbar.

By 1961 it became apparent to the scientific high-pressure community that the pressure calibration above 25 kbar was very uncertain and that the points being used as fixed points had never been well-characterized. Bridgman's volume measurements were generally accepted as more accurate than the resistance measurements, and reference was often made to Bridgman's "volume scale." One confusing item in the literature requires clarification. Bridgman in his volume measurements on bismuth reported five (5) discontinuities below 100 kbar. As a result eight (8) phases were designated on tentative phase diagrams for Bi. The high-pressure transition measured by electrical resistance was designated as the V–VIII transition and was so referred to in the literature of the early sixties. More recent work has failed to confirm two of the volume discontinuities, and this transition is now designated as the III–IV transition.

Vereshchagin, et al. (1966) have reported calibration pressures for several transitions in the 30 to 100 kbar range. They claim the use of a "free-piston gage to 100 kbar", but the description of the apparatus is so meager that no meaningful evaluation can be made. From the description given it is obvious that the use of the term "free-piston gage" is out of order, and the stated accuracy of the measurements is questionable.

a. Thallium

The earliest work dealing with the Tl II–III transition pressure was that of Bridgman (1935, 1941). His first published value of 41,000 kg/cm^2 (40 kbar) was the result of routine volumetric measurements in which it was noted that the "band of indifference" was fairly wide. His next published value for the Tl II–III transition pressure was

45,000 kg/cm^2 (44 kbar) in the electrical resistance study mentioned. This value was obtained on the increasing pressure cycle, and apparently no attempt was made to find an equilibrium pressure as appears to be the case in the volumetric study. In this 1935 work, ΔV determinations were obscured by plastic yield of the pressure cylinder in the region of the transition pressure. It is also interesting to note that Bridgman examined shear stress in a large number of materials and reported a transition at a mean pressure of 25,000 kg/cm^2 (24.5 kbar) in thallium.

Boyd and England (1960) made the first thallium "calibration"-type measurement in a piston-cylinder device of the Coes-Hall design. It could be operated up to 50 kbar and 1750 °C. These authors initially found a total hysteresis of about 11.6 percent between the increasing and decreasing pressure cycles. By cycling about the transition so phases II and III were both present, it was possible to reduce the hysteresis. The author did not state how much this region was decreased. The equilibrium transition pressure was taken as the midpoint of this region. Corrections made for the frictional components gave an average transition pressure of 37.1 ± 3 kbar at 30 °C. The transition was detected by the electrical resistance discontinuity of thallium which was enclosed in silver chloride. The frictional effects were a result of piston friction as well as reversible effects in the pressure environment.

The next determinations on the Tl II–III point were those of Kennedy and LaMori (1961 and 1962) using a piston-cylinder device in which the piston could be rotated slightly in order to reduce frictional effects. It would be difficult to analyze the actual effect of this rotation since according to a comment by F. Dachille "only a few (couple of) *very* short strokes were used at each pause in the running of the transition . . ." The piston was not completely free to rotate as in the free-piston gage. In both the above cited studies the equilibrium transition pressure was reported to be 36.69 ± 0.1 kbar. The error flag represents repeatability and does not reflect systematic errors. It is felt that the uncertainty of Kennedy and LaMori (1961, 1962) does not adequately reflect an appraisal of possible errors; thus, an error flag of ± 0.5 kbar has been assigned to this work. Vereshchagin, et al. (1966) reported a value of 39.9 ± 0.4 kbar using their so-called "free-piston" gage. The "best value" cited in table 5 for the transition pressure of the Tl II–III transition is 36.7 ± 0.5 kbar. This value represents a weighted average of the studies by Boyd and England with the study by Kennedy and LaMori. Bridgman's work on thallium does not represent an attempt to calibrate this point, and Vereshchagin, et al. give insufficient detail to evaluate their work. The error flag is the estimate of the reviewers of the error in the Kennedy and LaMori study.

b. Cesium

The Cs I–II transition was first detected by Bridgman (1938b) by electrical resistance methods using an improved modification of his 50 kbar apparatus. He noted that the transition was very rapid and had little hysteresis. In a later measurement by volume methods, this same fact was noted, but the transition pressure was determined to be 23,000 kg/cm^2 (22.5 kbar, Bridgman, 1938a).

Kennedy and LaMori (1961, 1962) made the only other calibration study of this point and placed the transition at 22.6 ± 0.6 kbar at 25 °C.

The second transition in cesium was first reported by Bridgman (1949) at 45,000 kg/cm^2 (44 kbar) as a part of the series of volumetric measurements. Later Bridgman (1952) measured a sharp "cusp"-type peak in the electrical resistance which he reported at 54,950 kg/cm^2 (54 kbar). The shape of this resistance curve caused Bridgman and others a great deal of concern since there was no discontinuity present. This transition was referred to as the cesium II–III transition and used as a fixed point value. Work by Hall, Merrill, and Barnett (1964) has shown that there are actually two closely spaced transitions associated with this point, i.e., Cs II–III and Cs III–IV. These transitions are separated by about 0.5 kbar, and both are sharp discontinuities in resistance. Through simultaneous monitoring of electrical resistance and x-ray diffraction measurements,

TABLE 5. Thallium II–III transition

Researcher	Transition pressure (kbar)	Error (kbar)	Temp.	Method of detection	Sample purity
Bridgman (1935)	(e) 40		30 °C	Volume	Highly purified
Bridgman (1952)	(c) 44		Room temp.	Resistance	Highly purified
Boyd and England (1960)[a]	(e) 37.1	3	29 ± 1 °C	Volume	99.99% Electrolytic
Kennedy and LaMori (1961)[a]	(e) 36.69	See text	25 °C	Volume	99.95%
Kennedy and LaMori (1962)[a]	(e) 36.69	See text	25 °C	Volume	99.95%
Vereshchagin, et al. (1966)	36.9	0.4			
Best Value	36.7	0.5	25 °C		

(e) equilibrium; (c) compression.

[a] Used to calculate best value.

it was demonstrated that Bridgman's (1952) electrical resistance transition of 54 kbar is the same one that he observed at 44 kbar by volume methods.

Kennedy and LaMori (1961, 1962) reported a pressure of 41.8 ± 1 kbar for the Cs II–IV transitions using volume-type measurements. The uncertainty here should undoubtedly be enlarged since the investigators were not even aware of the two closely spaced transitions and did not observe them. On the compression cycle the initiation pressure of the Cs II–III point was measured, while on the decompression cycle the initiation pressure of the Cs IV–III point was measured. Considering the fact that the range of existence of Cs III is about 0.5 kbar wide at 25 °C, a better value for the Cs II–III equilibrium transition pressure is 41.5 ± 1.2 kbar using the Kennedy and LaMori data. This value places the Cs III–IV transition pressure at 42.0 ± 1.2 kbar, indicating an increase in the observed hysteresis by 0.5 kbar, and increases the uncertainty slightly.

At the present time not enough work has been done on the calibration of the cesium transition to recommend a best value. It appears that either the Cs II–III or Cs III–IV point might serve as a better calibration point than the Tl II–III points as they exhibit much less nucleation hysteresis and are very nearly midway between the Bi I–II and Ba I–II points. The chief disadvantage of using cesium for calibration is its high chemical activity. This can be overcome by careful handling procedures, but it is generally difficult to maintain a high purity.

c. Barium I–II

Bridgman (1941, 1942) in his volumetric studies reported two transitions in Ba, one at approximately 17 kbar and one at 60,000 kg/cm^2 (59 kbar). These became known as the Ba I–II and the Ba II–IV, respectively. In 1952 he located an electrical resistance discontinuity which he placed at 80,000 kg/cm^2 (78 kbar). Bridgman suggested that this transition may be associated with the former one at 59 kbar. The fact that these are actually the same transition was suggested by Kennedy and LaMori (1961) and was later proved by Barnett, Bennion, and Hall (1963) using simultaneous x-ray and electrical resistance measurements. No workers other than Bridgman ever observed the transition at 17 kbar, and its existence is uncertain. Bridgman's 59 kbar transition is presently referred to as the Ba I–II transition. The accurate determination of this point is of prime importance in high-pressure calibration since all extrapolation procedures to higher pressures depend strongly upon it. Kennedy and LaMori (1962) in the first calibration-type measurement obtained a preliminary value of 59.6 kbar from a single experiment during which a piston broke at the initiation of the transition. Later LaMori (1963) published the value of 59.1 ± 1.6 kbar using a double stage piston-cylinder device in which the polymorphic transi-

TABLE 6. Cesium transitions

Researcher	Transition pressure (kbar)	Error (kbar)	Temp.	Method of detection
	Cesium I–II			
Bridgman (1938a)	(e) 21.63		30 °C	Electrical resistance
	(e) 21.59		25 °C	
Bridgman (1938b)	(e) 23.0		Room temp.	Volume
Kennedy and LaMori (1962)	(e) 22.6	0.6	25 °C	Volume
	Cesium II–IV			
Bridgman (1948)	44		10 °C	Volume
Bridgman (1952)	(c) 54			Electrical resistance
Kennedy and LaMori (1961)	(e) 41.8	1	Room temp.	Volume
Kennedy and LaMori (1962)	(e) 41.725	1	Room temp.	Volume
	Cesium II–III			
Revised (1967)[a]	41.5	1.2	25 °C	Calculations
	Cesium III–IV			
Revised (1967)[a]	42.0	1.2	25 °C	Calculations

(e) equilibrium; (c) compression.

[a] Transition pressure calculated from data of Kennedy and LaMori (1962) using data of Hall, Merrill, and Barnett showing the existence of two separate closely spaced transitions.

Highest sample purity stated in any of the above experiments was 99 percent.

tion was detected by the electrical resistance discontinuity. A very large hysteresis was reported. On compression the transition initiated at 67.4 ± 0.6 kbar and on release at 54.4 ± 0.6 kbar resulting in an overall hysteresis of 13 kbar. With a hysteresis of this magnitude, the assumption that the friction of the up and down stroke is symmetrical about the equilibrium pressure is not necessarily valid.

Using the lattice constant of NaCl as a pressure gage and referring to the semi-empirical equation of state of Decker (1965), Jeffery, et al. (1966) reported a value of 53.3 ± 1.2 kbar for the equilibrium pressure of the Ba I–II transition. Later improvement of the input data for Decker's theory (1971) coupled with the NaCl compression data of Jeffery, et al., yield an improved equilibrium pressure of 54.7 kbar for this barium transition.

The pressure of the Ba I–II transition has been determined to be 55.0 ± 0.5 kbar at 22 °C by Haygarth, Getting, and Kennedy (1967) using a "modified single-stage piston-cylinder apparatus". These investigators used a piston whose unconstrained length to diameter ratio was less than unity. Under such a condition the compressive strength of the tungsten carbide piston increases and extends the pressure range of the piston-cylinder apparatus. The barium sample was in the form of a strip confined in a AgCl or AgBr pressure medium. The transition was detected by electrical resistance measurements. Samples of three purities were used indicating a small but detectable effect upon the transition point. The average transition pressures for the three different purities are given below:

Purity	Transition pressure	Average hysteresis	Number of determinations
99.5%	54.7 ± 0.5 kbar	5.6 kbar	11
High Purity 1	54.9 ± 0.5 kbar	5.1 kbar	1
High Purity 2	55.0 ± 0.5 kbar	5.7 kbar	6

Zeto, et al. (1968) made a determination of the Ba I–II point in a hydrostatic environment. The pressure-transmitting fluid was a 50–50 mixture by volume of pentane and iso-pentane, whose hydrostaticity at that pressure was demonstrated by viscosity measurements (Barnett and Bosco, 1969). The pressure calibration is based upon the extrapolation of the relative resistance change of a manganin gage by means of a quadratic equation whose coefficients are determined by a two-point calibration at the Hg L–I at room temperature and the Bi I–II transition. The equilibrium transition pressure was taken as the center of the region of indifference and is reported at 56.27 kbar.

The "best value" for the barium transition pressure is based on an average of the published values of Jeffery et al. (1966; Decker, 1968), Haygarth et al. (1967), and Zeto and Vanfleet (1969). The low-purity value of Haygarth is used since 99.5 percent purity is the material readily available and generally used. The errors discussed by these authors in each case represent errors in experimental reproducibility. Jeffery et al. (1966) report one standard deviation of 0.6 kbar, Haygarth et al. (1967) 0.5 kbar, and Zeto et al. (1969) 0.52 kbar.

A few comments are in order concerning systematic errors in these three studies. Jeffery, et al. (1966) and Haygarth, et al. (1967) were forced to use the midpoint of the transition in up and down pressure cycles. For Jeffery, et al. this involved only sample hysteresis of 2.6 kbar; for Haygarth, et al. it involved both apparatus and sample hysteresis totaling approximately 5.4 kbar, while Zeto, et al. performed an equilibrium experiment. If one takes the center of the region of indifference as the calibration point, uncertainties due to hysteresis are small in the work of Jeffery, et al. (1966), large in the work of Haygarth, et al. (1967), and non-existent in the work of Zeto, et al. (1969).

Jeffery's work involves error due to uncertainty in the theory of approximately two percent. Zeto's work involves a serious and unknown extrapolation error which could be of the order of 2 kbar. In view of these comments, the following are estimates of uncertainties for each measurement:

Jeffery, et al. (1966)	Reproducibility	0.6 kbar
	Theory	1.1 kbar
	Hysteresis	1.3 kbar
Haygarth, et al. (1967)	Reproducibility	0.5 kbar
	Hysteresis	2.7 kbar
	Corrections	0.2 kbar
Zeto, et al. (1969)	Reproducibility [5]	0.52 kbar
	Extrapolation	2.0 kbar

Since the uncertainties in the three cases are of approximately the same magnitude and are in large measure just estimates, it appears illogical to give greater weight to any one of these measurements in calculating a "best value".

The various reported values for the Ba I–II transition are given in table 7. The commonly available barium used for calibration is approximately 99.5 percent pure. The "best value" of 55.3 kbar is given for this material and represents the average of the values reported by the three groups mentioned. The other work is not felt to be of comparable validity. The value for the initiation of the transition on compression will vary in each piece of equipment and must be calibrated in terms of the equilibrium point. The error flag for the best value represents a judgment by the reviewers.

d. Bismuth III–V

As discussed above, the so-called "high Bi point" now known as the Bi III–V was reported in routine

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[5] This error involves uncertainties in the mercury and bismuth points and uncertainties in temperature.

TABLE 7. Barium I–II transition at 25 °C

Researchers	Transition pressure (kbar)	Temp.	Method of detection
Bridgman (1942)	(e) 59	23 °C Room temp.	Volume
Bridgman (1952)	(c) 78	Room temp.	Electrical resistance
LaMori (1963)	(e) 59.1	25 °C	Electrical resistance
Jeffery, et al. (1966)	(e) 53.3	25 °C	X-ray diffraction and electrical resistance
Jeffery, revised (1968)[a]	(e) 54.7[b]	25 °C	
Vereshchagin, et al. (1966)	(c) 58.5		
Haygarth, Getting and Kennedy (1967)	(e) 54.7[b] (e) 55.0	22 °C	Electrical resistance
Zeto and Vanfleet (1969)	(e) 56.273[b]	25 °C	Electrical resistance
Best Value	55.3 ± 1.2	25 °C	

(e) equilibrium; (c) compression; (s) shock.

[a] Based on NaCl compression data of Jeffery, et al. (1966); pressure obtained from Decker's (1968) revised equation of state for NaCl (Decker, 1971).

[b] Best value an average of these three values.

studies at pressures from 88 kbar to 129 kbar. In the early nineteen sixties more serious attempts were made to determine this transition pressure.

As a result of a series of measurements, Balchan and Drickamer (1961) reported the Bi III–V transition at 89–92 kbar and used the value of 90 kbar as the accepted value. Using the pressure scale of Kennedy and LaMori (1962), Klement, Jayaraman, and Kennedy (1963) determined the phase diagram of bismuth up to 70 kbar and 460 °C. Four points were located by DTA methods on the Bi III–V boundary. From linear extrapolation through these four experimental points, a pressure of 82 kbar at 25 °C was estimated, but allowing for curvature in the phase boundary such as was indicated, the authors estimated a transition pressure of 78–82 kbar at 25 °C. Giardini and Samara (1965) re-examined the upper bismuth point using a "manganin gage with multiple-event resistance cell". Using an extrapolation based on the value of 59 kbar for the fixed point of barium, they concluded that the upper limit for the Bi III–V transition was no higher than 81–82 kbar. These measurements all refer to the initiation of a resistance transition on the increasing pressure cycle.

Stark and Jura (1964) used a unique method in an attempt to approach thermodynamic equilibrium for several high-pressure transitions. Due to the fact that the transition pressure observed under compression is always higher than the thermodynamic equilibrium transition pressure, a method of heating the sample by an electrical pulse of millisecond duration was employed to thermally activate the transition. In order for this method to work, dP/dT must be negative. When an electrical pulse is sent through the sample, it is heated high enough to transform some of the material to the higher pressure phase. When the pressure is not in the region of a phase boundary, the resistance returns to its initial value in a time less than a minute. The transition point is determined when the resistance returns to its value in the high-pressure phase. It is important *that the material studied have no thermally activated* metastable state. The Bi III–V transition was reported at 82 ± 4 kbar by this method while a value of 88 kbar was reported with conventional measurement on the compression cycle.

With the use of x-ray diffraction and Decker's (1966, 1971) NaCl pressure scale, Jeffery, et al. were able to isolate the nucleation hysteresis and report an equilibrium transition pressure of 73.8 kbar for the Bi III–V point. The equilibrium value was taken as the midpoint of the nucleation hysteresis interval. Later, improved measurements of the zero-pressure compressibility data used in Decker's semi-empirical equation of state revised the transition pressure value to 76.0 ± 1.3 kbar. (See section 4 of this review.)

Vereshchagin, et al. (1966) published a value of 89.2 kbar ± 1 percent and stated that the measurement was made in a free-piston gage. Since little description of the technique and virtually no experimental details were given, no meaningful evaluation of this work can be made. Haygarth, et al. (1969) reported a value of 77.5 ± 1.0 kbar for Bi III–V equilibrium transition pressure. This value was based on a short extrapolation of the Bi III–V phase line as measured in the piston-cylinder system used for the Ba I–II calibration and one unrepeated direct measurement of the transition point at 25 °C. Equilibrium was taken as the average of increasing and decreasing cycle in which both apparatus and sample hysteresis were present.

The work of Jeffery, et al. (1966) and Haygarth, et al.

represent the only two studies which are not dependent on an extension of an apparatus calibration referred to the Ba I–II transition. These other studies used a value of 59 kbar for the Ba I–II transition from Bridgman's volume work, and the lowering of this value as discussed above naturally will reduce the reported values for the Bi III–V transition. Jeffery, et al. have better means of eliminating apparatus hysteresis and thus determining the true sample hysteresis, but the use of a theoretical equation of state leads to uncertainty. The method of Haygarth, et al., is more direct, but uncertainties associated with hysteresis effects and extrapolation are more serious. As in their work on barium, Haygarth, et al. report only reproducibility flags and not absolute accuracy error flags. For these reasons the reviewers conclude that only the results of the two studies mentioned be used in the evaluation of a "best value" and that an error of 1.8 kbar be used for each of the studies. This approach equally weights the two studies and yields a value of 76.7 ± 1.8 kbar for the Bi III–V transition.

3.5. Fixed Points Above 80 Kbar

Just as the calibration studies of the Hg L–α and the Bi I–II transformation points differ in nature from the calibration studies in the 30–80 kbar range, the calibration of points above 80 kbar differs from the studies below 80 kbar. Historically, calibration of points has been based upon extrapolated load vs pressure curves and on comparisons with shock data, both of which are much less reliable than the methods previously discussed.

Several reference points have been identified, and values have been established for the increasing pressure cycle. The severity of the hysteresis in transitions in this pressure region has not been studied systematically.

a. Tin

Stager, Balchan, and Drickamer (1962) were the first to detect and measure the Sn I–II transition, and they published a value of 113–115 kbar on the basis of thirteen determinations.

Barnett, et al. (1966) reported the value 92 ± 3 kbar for the initiation of this transition on the compression cycle. On the basis of Decker's (1971) equation of state for NaCl, a new value of 94.0 ± 3 kbar is calculated. Since measurements were taken only on the compression cycle, no value for the equilibrium transition pressure of tin was calculated.

Stark and Jura (1964) obtained a transition pressure of 99 ± 4 kbar using their method of thermal shock.

b. Iron

The pressure-induced phase transition in iron was discovered by means of shock-wave techniques and was reported to occur at 130 kbar (Bancroft, et al., 1956; see table 10). When corrected to the hydrostat, the pressure would be about 128 kbar. Bancroft, et al. also observed some effect of sample thickness, indicating that the shock times are possibly shorter than or of the same order of magnitude as the transition time. Later shock measurements (Loree, et al., 1966) gave 127 ± 1 kbar after the strength-of-material correction. These measurements are probably not reliable for calibration of static systems as discussed in section 5.

The iron phase transition has also been studied by static techniques (Balchan and Drickamer, 1961; Takahashi and Bassett, 1964; Clendenen and Drickamer, 1964; Bundy, 1965; Mao, et al., 1967; Millet, 1968; Takahashi, et al., 1968; Stark and Jura, 1964; Takahashi, unpublished). Pressure measurements resulting from the shock and static work are reviewed in table 10.

The principal disadvantage of iron as a fixed point on

TABLE 8. Bismuth III–V transition at 25 °C

Researcher	Transition pressure (kbar)	Error (kbar)	Method of detection
Bridgman (1952)	(e) 88		Volume
Bundy (1958)	(c) 122		Electrical resistance
Balchan and Drickamer (1961)	(c) 89–92		Electrical resistance
Klement, Jayaraman, and Kennedy (1963)	(x) 78–82		
Stark and Jura (1964)	(e) 82	4	Electrical resistance
Giardini and Samara (1965)	(c) 82		Inductive coil
Jeffery, Barnett, Vanfleet, and Hall (1966)	(e) 73.8	1.3	X-ray diffraction electrical resistance
Jeffery, revised (1968)[b]	(e) 76.0[a]	1.8	
Vereshchagin, et al. (1966)	(c) 89.3	0.9	
Haygarth, Ludemann, Getting, and Kennedy (1969)	(e) 77.5[a] 78.2	1.0 1.0	Electrical resistance
Best Value	76.7	1.8	

(e) equilibrium; (c) compression; (s) shock; (x) extrapolation of phase diagram.

[a] Values used to determine best value.

[b] Pressure obtained from Decker's (1968) revised equation of state for NaCl (Decker, 1971).

the pressure scale is the sluggishness of the phase transition. Takahashi, et al. (1968) report that at room temperature the high-pressure phase appears at 127 kbar, that the low-pressure phase persists to a pressure of 152 kbar with increasing pressure, and that the high-pressure phase persists to 83 kbar with decreasing pressure. Stark and Jura (1964) found that short thermal pulses to a sample of iron at pressures above 118±6 kbar would drive the transition towards the high-pressure phase while thermal pulses to an iron sample at pressures below 118±6 kbar would drive the transition towards the low-pressure phase.

TABLE 9. Tin I–II transition at 25 °C

Researcher	Transition pressure (kbar)	Error (kbar)	Method of detection
Stager, Balchan, and Drickamer (1962)	(c) 113 115		Electrical resistance
Barnett, et al. (1966)	(c) 92	3	X-ray diffraction and electrical resistance
Barnett, revised (1968)[a]	(c) 94	4	
Stark and Jura (1964)	(c) 99	6	Electrical resistance

(c) compression.

[a] Based on NaCl compression data of Barnett, et al. (1966); pressure obtained from Decker's (1971) revised equation of state for NaCl.

Considerable caution should be exercised in the use of iron as a fixed point for pressure calibration. The sluggishness of its transition appears to make it time-dependent, temperature-dependent, and possibly even stress-dependent. As yet, the thermodynamic transition pressure at room temperature has not been adequately established.

c. Barium II–III

The high barium transition has been determined only by electrical resistance methods by Balchan and Drickamer (1961). The pressure calibration was based on the Ba I–II point at 59 kbar to 144 kbar where a resistance increase of 42 percent was observed. This value is the average of four determinations, all on the compression cycle. The reported value of 144 kbar for the Ba II–III transition is undoubtedly high in view of the more recent values for the Ba I–II and Bi III–V transitions. Further calibration work needs to be done.

TABLE 11. Barium II–III transition at 25 °C

Researcher	Transition pressure (kbar)	Method of detection
Balchan and Drickamer (1961)....	144	Electrical resistance.

d. Lead

The phase transition in lead has been suggested as a calibration point (Drickamer, 1963). Balchan and Drickamer (1961) reported a pressure of 161 kbar for the transition in lead, basing their measurements on an extrapolation from fixed points below 100 kbar (Ba I–II, 59 kbar; Bi III–V, 90 kbar). Subsequently, the lead transition has been used by several workers as a calibration point at 161 kbar.

Takahashi, et al. (1969) found that in the diamond-anvil x-ray press, the high-pressure phase of lead (hexagonal close-packing) appears at 130±10 kbar with increasing pressure at room temperature. This value was based upon the lattice parameter of iron mixed with the lead to serve as a pressure calibrant. The iron compression data used for this purpose are those of Takahashi, et al. (1968), who based their measurements upon an NaCl scale that does not differ significantly from that of Decker (1968). NaCl was not used directly with lead because of a chemical reaction between the two. Vereshchagin, et al. (1969), using a supported Bridgman anvil apparatus similar to the Drickamer cell, found that

TABLE 10. Iron $\alpha-\epsilon$ transition

Researcher	Transition pressure (kbar)	Temp.	Method of detection	Remarks
Bancroft, et al. (1956)	130		Shock	
Bancroft, et al. (1956)	128		Shock	Corrected to hydrostat.
Balchan and Drickamer (1961)	133±2	20 °C	Electrical resistance	Bridgman anvils. Increasing load.
Takahashi and Bassett (1964)	130	(R.T.)	X-ray diff. Diamond cell	Represents maximum pressure. First observed ϵ with increasing load.
Stark and Jura (1964)	118±6	(R.T.)	Electrical resistance	Transition driven by short thermal pulses. Resistance measured at R.T.
Loree, et al. (1966)	127±1		Shock	Corrected to hydrostat.
Takahashi, et al. (1968)	127	23 °C	X-ray diff. Diamond cell	Represents *maximum* pressure. First observed ϵ with increasing load.
Takahashi, et al. (1968)	83	23 °C	X-ray diff. Diamond cell	Represents *minimum* pressure. Last appearance of ϵ with decreasing load.
Takahashi (unpublished)	125±10	23 °C	Electrical resistance Drickamer cell	Calibration based on extrapolation from fixed points (Jeffery, et al. 1966) using Decker's revised NaCl scale.

iron showed a resistance jump at a load slightly less than that of lead. Although they interpreted this as indicating that the iron transition should be revised to a higher pressure to conform with the lead transition, there is evidence that the pressure of the lead transition should be revised downward to be consistent with the iron transition. They calibrated their device assuming the following pressures for transitions on the fixed point scale: Bi I–II (24.5 kbar), Bi III–V (88 kbar), and Pb I–II (161 kbar). These calibration points are based on linear extrapolation of a pressure-load relationship established at lower pressures by force/area calculations and are subject to error by loss of efficiency with increasing load.

The loss of efficiency in Bridgman anvil devices can be attributed to two factors: (1) the compressibility and amount of extrusion of the gasket material decrease with increasing pressure, and (2) deformation of the anvils causes a decrease in the ratio of maximum pressure to applied pressure. The latter has been observed to take place in diamond anvils. Since the anvils employed by Bridgman (1940b, 1942, 1952), Balchan and Drickamer (1961), and Vereshchagin, et al. (1969) are larger than the diamond anvils and are constructed of tungsten carbide, they probably deform more and at lower pressures than the diamond anvils. This deformation results in a greater loss of efficiency at pressures above 100 kbar. Recent work by Vereshchagin (verbal communication) indicates that he feels that the pressures for the transitions in iron and lead should be revised downward. His new values are more consistent with those based on x-ray diffraction (Takahashi, et al., 1969; Mao, et al., 1969).

In light of the discrepancies for the lead transition pressure, we recommend caution in the use of lead as a fixed point on the pressure scale. In addition, we feel that further investigations on the subject should be made.

Recent results by Drickamer (1970) and Vereshchagin, et al., (1970) on calibration in the higher pressure range are of particular interest to this report. Drickamer gives the transition pressures Bi(III–V) = 73 – 75 kbar, Fe($\alpha-\epsilon$) = 110–113 kbar, Pb = 128–132 kbar, Ba = 118–122 kbar, while the values of Vereshchagin, et al. are Bi(III–V) = 79 kbar, Fe($\alpha-\epsilon$) = 129 kbar, Pb = 138 kbar, and Ba = 125 kbar.

4. Interpolation and Extrapolation Methods and Their Calibration

Once a set of fixed points has been chosen it is then necessary to devise manometers to measure pressure at intermediate points. There are many pressure gages which have been used for this purpose, several of which will be discussed in this section. It is also desirable to consider systems for determining pressures above that at which one can measure the pressure in a fundamental way since our present capabilities allow us to generate pressures in excess of our ability to accurately measure them. Thus, we will also consider extrapolation techniques in this chapter.

TABLE 12. Lead I–II transition at 25 °C

Researcher	Transition pressure	Method of detection
Balchan and Drickamer (1961).	161 kbar........	Electrical Resistance.
Takahashi, et al. (1969), Mao, et al. (1969).	130±10 kbar.	X-ray Diffraction.

4.1. Theoretical Equations of State

There are many uses of equations of state in high pressure calibration, the most prominent of which are as interpolation and extrapolation formulas. They are also useful in determining pressure changes due to temperature differences, and also possibly even to aid in establishing a high pressure scale. Temperature effects will be mentioned both here and in section 6.

a. Proposed Isothermal Equations

There are several types of interpolation equations relating pressure and volume along a given isotherm, the simplest of which is a simple power series

$$V/V_0 = 1 - aP + bP^2 + \ldots \tag{1}$$

This is the form in which Bridgman (1958) represented his results and is called the Bridgman equation. The next step involves semi-empirical equations which have been derived using certain approximations. The most common of these are the Murnaghan equation (Murnaghan, 1944),

$$P = \frac{B_0}{k}\,[y^{3k} - 1] \tag{2}$$

the Birch equations (Birch, 1947)

$$P = 3\,\frac{B_0}{2}\,(y^7 - y^5) \tag{3}$$

and

$$P = \frac{3B_0}{2}\,(y^7 - y^5)\,[1 - \xi(y^2 - 1)] \tag{4}$$

and the Tait equation (Tait, 1898)

$$V/V_0 = 1 - \left[\frac{\ln\left(1 + \dfrac{rP}{B_0}\right)}{r}\right] \tag{5}$$

There are also various modifications of these equations.

In the above equations, B_0 is the initial bulk modulus at atmospheric pressure, $y = (V_0/V)^{1/3}$ where V_0 is the volume at $P=0$, and k, ξ, and r are parameters which can be related to B'_0, the pressure derivative of the bulk modulus at $P=0$, i.e.,

$$k=r-1=B'_0 \text{ and } 4\xi=12-3B'_0. \tag{6}$$

Of these equations, the Tait equation allows the volume to go to zero at a finite pressure (MacDonald, 1966). Because of this and because it generally does not fit experimental data on solids at high pressures as well as some of the other equations, it will not be developed further, except to say that it follows from an integration assuming that the isothermal bulk modulus is a linear function of pressure (Anderson, 1966), i.e.,

$$B=-V_0\left(\frac{\partial P}{\partial V}\right)_T=B_0+B'_0P. \tag{7}$$

A more detailed analysis of the Tait equation has been recently given by MacDonald (1966).

The Birch equation has been used in the form of equation (3) with one arbitrary parameter or in the form (4) with two arbitrary parameters. This equation is derived from the theory of finite strain under the assumption that the total strain energy can be expanded as $E=\Sigma a_n\epsilon^n$, where ϵ is the hydrostatic strain in an isotropic solid. Equation (4) follows if $a_n=0$ for all $n\geqslant 4$ and equation (3) follows for $a_n=0$ for all $n\geqslant 3$. This assumption, as well as the use of finite strain theory, has been discussed by Knopoff (1963). The equation should be a rather good representation of the pressure volume isotherm at $T=0$, for a cubic crystal in a hydrostatic environment for not too large a strain. Birch estimates that it can give good results for relatively large strain for materials in which ξ is small (Birch, 1952). Bernardes and Swenson (1963) observe that the experimental data for the alkali metals at low temperatures fit the Birch equation with small values of ξ, but that slight deviations from this equation appear along higher temperature isotherms. Gilvarry (1957) notes that equation (3) requires that the initial value of the Gruneisen constant at zero pressure must equal 11/6, which, of course, is not satisfied by all solids. This indicates that the two parameter equation (4) is necessary to insure that the $P-V$ relation has the correct initial curvature at zero pressure. This second constant is related to the third-order elastic constants and should be kept in Birch's equation for often the third-order elastic constants are comparable to the second-order elastic constants. Recent high pressure measurements (McWhan, 1967) indicate $\xi=-0.40$ for MgO, $\xi=-1.02$ for NaCl, and $\xi=-1.74$ for alpha-quartz. We will hereafter consider only equation (4) when referring to the Birch equation.

The Murnaghan equation, derived by Murnaghan from the theory of finite strain (Murnaghan, 1937) is an approximation in which the instantaneous bulk modulus $B=-V\left(\frac{\partial P}{\partial V}\right)_T$, where $V=V(P)$, is assumed to vary only linearly with pressure. Murnaghan refers to it as integrated linear theory (Murnaghan, 1951). It also involves the assumptions that the strain is small and isotropic and the pressure is hydrostatic. The parameters B_0 and $k=B'_0$ can be determined from measurements at zero pressure or they can be left arbitrary and chosen to give the best fit to a set of measurements of P versus V. The best fit to measured data is obviously obtained if both parameters are allowed to be arbitrary. Quite reasonable fits can be obtained, however, by using ultrasonically determined values of B_0 leaving only one arbitrary parameter to vary to give the best fit. The value k has been related to the Gruneisen parameter; i.e., $k=2\gamma+1/3$, or the initial pressure derivative of the bulk modulus, B'_0. Rarely does one find the relation between k and γ to hold but recently Anderson (1966) has shown that precise ultrasonic measurements at rather low pressures will give values of B_0 and B'_0 which allows Murnaghan's equations to represent high pressure isotherms fairly well if the compression is not too large. Many authors (see MacDonald, 1966; and Cook and Rogers, 1963) have proposed equations of state that are nothing more than Murnaghan's equation in a different form and with different labeling of the parameters.

Murnaghan allowed both parameters to vary arbitrarily and was able to fit Bridgman's compression measurements to 100 kbar on Na to within 1.5 percent in V/V_0. He also observed that the arbitrary coefficients varied considerably depending upon the region of the data used to determine them. He concluded that this indicates that the equation is only an approximation to the truth and that higher order approximations should be considered. A second order theory was also given by Murnaghan (1951) which allows the pressure derivative of the bulk modulus to vary with pressure. He also concluded that this was not accurate enough for the large compression of Na and concluded that the third order elastic constants were very important for large compression.

Recently Rose (1967) extended the expansion of the instantaneous bulk modulus to terms of order P^2.

$$B=\left(-V\frac{dP}{dV}\right)_T=B_0+B'_0P+B''_0P^2/2. \tag{8}$$

Integrating (8) along on isotherm yields the equation of state

$$P=\frac{-2B_0\tan\left[\sqrt{\dfrac{2B_0B''_0-B'^2_0}{2}}\left(\ln V/V_0\right)\right]}{\sqrt{(2B_0B''_0-B'^2_0)}+B'_0\tan\left[\sqrt{\dfrac{2B_0B''_0-B'^2_0}{2}}\ln V/V_0\right]}. \tag{9}$$

The coefficients in (8) can be expressed in terms of 2nd, 3rd, and 4th order single crystal elastic constants as defined by Brugger (1964). For a cubic ($m3m$ symmetry) crystal one obtains (Ghate, 1966; Thurston, 1967)

$$\begin{aligned} B_0 &= (c_{11}+2c_{12})/3 \\ B_0' &= -(c_{111}+6c_{112}+2c_{123})/9B_0, \text{ and} \\ B_0'' &= (c_{1111}+8c_{1112}+6c_{1122}+12c_{1123}-2c_{11}-15B_0 \\ &\quad -9B_0B_0')/27B_0^2. \end{aligned} \quad (10)$$

The bulk moduli must be converted from adiabatic to isothermal to use in static equations of state. Experimental pressure dependence of the elastic constants have been measured for several materials (Lazarus, 1949; Hughes and Kelly, 1953; Bateman, et al., 1961; Daniels and Smith, 1963; Miller and Smith, 1964; Chang, 1965; Bogardus, 1965; Bartels and Schuele, 1965; Chechile, 1967; Koliwad, et al., 1967).

In principle, Bridgman's equation, equation (1), can fit any analytic compression curve if the expansion is carried out to enough parameters. However, the use of several terms may cause the curve to have anomalous variations related to the scatter in the data and not to fundamental compressibility. One should not use more parameters than is justified by the accuracy of the data. For rather incompressible materials two parameters seem sufficient to fit the data. But an equation of four parameters is not good enough for the alkali metals (Bridgman, 1958).

Gilvarry (1957, 1956) has given an equation of state which will generate many of the proposed isothermal equations of state for solids

$$P=(n-m)^{-1}B_0[(V_0/V)^n-(V_0/V)^m] \qquad (11)$$

where n and m are constants. There is no theoretical basis for this equation but it can be made to fit a wide class of $P-V$ relations by varying the parameters m and n and is equivalent to equations (2) and (3) for given choices of m and n.

Comparisons of these empirical equations of state with experiment are not always too conclusive in that there is often a great deal of scatter and experimental uncertainty in the experiments. *In many cases any or all of these equations of state might be argued as valid representations because they fit the data to within the experimental accuracy.* The experimental techniques are being improved so that experimentally we are just now beginning to be able to discriminate among the proposed equations. There is a more serious problem, however, and that is the accuracy in the pressure measurement itself in the experimental equations of state. Over the years the proposed pressure scale has changed considerably and there are still large differences between the pressure scales used by some experimenters and considerable uncertainty in the pressure measurement. It is hoped that some of the guess work can be removed by the use of equations of state.

Recent work (McWhan, 1967), using x-rays to detect volume change, indicates that the bulk modulus is not linear with pressure and that the simple two-parameter, Murnaghan equation, equation (2), will always yield too large a pressure for a given compression. This equation, however, will yield reliable pressure to within 3 percent for $V/V_0>0.9$, i.e., where terms of higher order than linear in equation (8) can be neglected. However, for these small compressions, equations (2) and (4) will give the same results and the Birch equation appears to be valid to higher compression and is thus preferable. One advantage of the Murnaghan equation is its simple form, while still making a valuable interpolation tool at low pressures. A comparison of pressure differences determined from the Birch and Murnaghan equations versus compression for several values of B_0' is given in figure 3. It will be noted that the Murnaghan equation always predicts a larger pressure than the Birch equation for any value of B_0'. If one expands the bulk modulus calculated from (4) in a power series of P, one finds $B_0''=-(B_0'^2-7B_0'+143/9)/B_0$, which is always negative and never zero.

Two experiments which definitely favor the Birch equation (4) over the Murnaghan equation (2) have recently been completed (McWhan, 1967; Weaver, et al., 1967). In these experiments, MgO and NaCl, two materials with very different compressibilities, were intimately mixed in a high pressure x-ray cell and their lattice parameters simultaneously measured at various pressures. If the pressure was then calculated from the MgO compression using (2) or (4), which agreed to within 1 percent to 300 kbar, the $P-V$ relation of NaCl agreed with (4) to within 10 percent but definitely disagreed with (2). McWhan used results of Bartels and Schuele (1965) for B_0 and B_0' for NaCl. Better agreement with (4) would follow if the results of Chang (1965) were used for B_0', i.e., isothermal $B_0'=5.18\pm.09$.

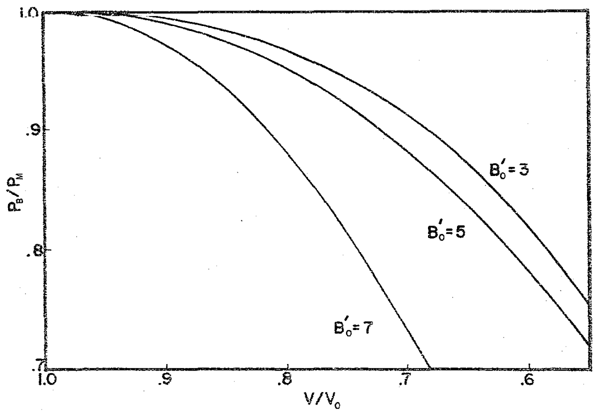

FIGURE 3. Ratio of pressures from the Birch to the Murnaghan equations.

It was concluded that the Birch equation (4) was the most reliable of these two parameter equations considered. It should also be added, however, that all the equations based on the theory of finite strain are valid only for cubic crystals in hydrostatic media.

Two other equations of state might be considered here, the Thomas-Fermi equation and the Hugoniot equation. The former is appropriate for a degenerate Fermi gas and will not be discussed since its range of validity is in the megabar region. The Hugoniot equation will be considered in section 5.

b. The Equation of State Including Temperature

In all of the above equations, the parameters must in general be considered as functions of temperature. The temperature-dependent equation of state has been discussed by Gilvarry (1957) and Bernardes and Swensen (1963). Gilvarry concludes that the above isothermal equations should be quite good along any isotherm as long as the appropriate parameters are chosen for that isotherm. He also points out that n and m in equation (11) are essentially independent of T and then using the Mie-Gruneisen theory determines the temperature dependence of B_0 and V_0 and proposes a generalized Birch equation of state. This equation is then compared to Swensen's P, V, T results for the alkali metals with quite good agreement. Swensen points out that in general the thermal contribution to the free energy is small and thus the compressibility is approximately dependent on volume only. Since the thermal pressure in most cases will be small compared to the lattice pressure, an approximate temperature equation of state is quite satisfactory once the pressure along an isotherm is well established.

The most common equation of state including temperature is the Mie-Gruneisen equation (Gruneisen, 1926)

$$P=-\frac{dU}{dV}+\frac{\gamma_e E}{V} \tag{12}$$

where U is the lattice potential energy, E the vibrational energy, and γ_e a parameter defined by

$$\gamma_e=\frac{\Sigma\gamma_i E_i}{E} \tag{13}$$

in which

$$E=\Sigma E_i,$$

$$E_i=\frac{\hbar\omega_i}{2}+\frac{\hbar\omega_i}{e^{\hbar\omega_i/kT}-1}, \tag{14}$$

and

$$\gamma_i=-\frac{d\ln\omega_i}{d\ln V}. \tag{15}$$

These equations follow from the quasi harmonic approximation in which the thermal energy of the crystal is taken as that of a set of weakly coupled harmonic oscillators with ω_i the angular frequency of the ith normal mode of vibration. The parameter γ_e is not identical to the γ defined by the Gruneisen relation

$$\gamma=\frac{\alpha V}{C_v K} \tag{16}$$

where α is the volume thermal expansion, K is the isothermal compressibility, and C_v the specific heat at constant volume. Pautamo (1963) shows that the γ in (16) is given by

$$\gamma=\frac{\Sigma\gamma_i C_{vi}}{C_v} \tag{17}$$

where

$$C_{vi}=\left(\frac{\partial E_i}{\partial T}\right)_V. \tag{18}$$

He also demonstrated that γ_e is nearly temperature independent while γ is quite temperature dependent at low temperature. For $T>\Theta/2$, $\gamma_e=\gamma$ for the materials studied by Pautamo.

Equation (12) is the Mie-Gruneisen vibrational equation of state. If the first term in (14), which is the zero point energy, is assumed independent of temperature and lumped with the potential energy, then

$$P=-\frac{dU'}{dV}+\frac{\gamma_T E_T}{V} \tag{19}$$

follows which is the thermal Mie-Gruneisen equation (Fumi and Tosi, 1962). The value γ_T is now defined by

$$\gamma_T=\frac{\Sigma\gamma_i E_{Ti}}{E_T} \tag{20}$$

where E_{Ti} is the second term on the right hand of (14). In general γ_T will not be the same as γ_e.

The Hildebrand equation (Hildebrand, 1931)

$$P+\frac{dU}{dV}=\frac{T\alpha}{K} \tag{21}$$

has also been suggested as a reliable approximation for an equation of state. Fumi and Tosi (1962) argue that the approximations leading to the Hildebrand equation are not as accurate as those of equation (12) except at very high temperatures. Since the Mie-Gruneisen equation is always better than or as good as the Hildebrand equation, the Hildebrand equation will not be considered further.

The vibrational energy in (12) can be calculated using a Debye model for the distribution of normal modes. Above the Debye temperature this should be a rather good approximation. The only major problem is to determine the dependence of γ_e upon T and V. It is often considered to be a constant but a better approximation to the correct equation of state is obtained if an estimate of the volume dependence of γ_e is found (Pautamo, 1963). The parameter γ is related to the anharmonicity of the lattice potential and can break down for an extremely anharmonic potential. Pastine (1967), however, argues that the lattice potential becomes more harmonic at elevated pressures making the Mie-Gruneisen equation even a better approximation at high pressures.

Leibfried and Ludwig (1961) have derived the Mie-Gruneisen equation from the approach of lattice dynamics. They demonstrate that this equation follows if one truncates the expansion of the lattice potential after fourth order terms. This limits the usefulness of their approach to that of low compression where the potential can be reasonably approximated by four terms in the expansion. As was pointed out earlier, the potential energy is more prominent than the vibrational kinetic energy in determining the relation between P and V at temperatures which are not excessive. Thus, it is imperative to use the best possible potential energy term in the Mie-Gruneisen equation and estimate the kinetic energy contribution using the quasi harmonic approach. Thomsen and Anderson (1969) have demonstrated that a consistent approach using the fourth order expansion for the potential is not sufficient for NaCl above 70 kbar.

c. Equations of State for Specific Materials

The equations discussed above were based on macroscopic measurements of the bulk modulus and its derivatives but were not concerned directly with interatomic forces. There are, however, certain materials for which the predominant interaction forces are simple enough to allow a calculation of an equation of state from an atomic viewpoint. These are the alkali metals and the alkali halide ionic crystals. The alkali halides are much easier to use experimentally but the alkali metals provide a more stringent test of the theory because they are highly compressible.

d. Alkali Metals

These metals can be approximated by a model consisting of closed shell, positively charged ions distributed in a negative charge sea of nearly free electrons. The cohesive energy contains the terms (Bardeen, 1938a, 1938b)

$$E=E_0+E_f+E_c+E_I. \qquad (22)$$

E_0 is the kinetic energy of the conduction electrons in their lowest-energy momentum state. E_f, the Fermi energy, is the interaction energy of the electron sea and the discrete positive charges. E_c is the correlation energy of the interaction of an electron with the space charge density of the negative sea and accounts for the fact that the electrons tend to avoid each other. E_I comes from the ion-ion overlap and van der Waals terms. E_0 is calculated by solving the Schroedinger wave equation in a Wigner-Seitz cell (1934). The volume dependence of E_f is quite straightforward and can be found in any solid state text (Kittel, 1966).

The two other terms in (22) have either been ignored or empirically estimated. Since these last two terms are relatively small for the alkali metals, the cohesive energy versus volume can be determined quite accurately. Temperature effects are included in the theory by using a Debye model for the free energy of the lattice vibrations. At room temperature and above, the procedure should be quite accurate for sodium.

Bardeen (1938a, b) calculated $E(V)$ and then differentiated to get the compressibility as a function of volume for sodium and lithium. The results agree with experiment for sodium but are consistently low in the case of lithium.

Bardeen (1938a, b) also proposed a semi-empirical equation of state for the alkali metals at absolute zero by combining Frolich's (1937) formula for E_0 with an expression for E_f which assumed the effective number of free electrons per atom remains constant. This equation is

$$E=Ay^3+By^2+Cy \qquad (23)$$

where $y=(V_0/V)^{1/3}$. The parameter A is purely empirical but B and C can be determined theoretically. The equation can be reduced to one parameter with the requirement that E is a minimum at $y=1$ and by using the measured value of the initial bulk modulus B_0 (Bernardes and Swenson, 1963).

$$P=B_0y^4(y-1)\left[3+\frac{A}{B_0V_0}(y-1)\right] \qquad (24)$$

where V_0 is the zero pressure volume. The fit to experimental data (Swenson, 1955; Beecroft and Swenson, 1961) is well within experimental error for all the alkali metals if A is left arbitrary.

Since the correlation term is better understood now (Kittel, 1963), the new calculation for these materials carried out by Pastine (1968) is welcomed. Pastine also gives a good description of the origin of the various contributions to the $P-V$ isotherm and his results agree quite well with experiment. It is hoped that more accurate experimental work will be done on sodium to better evaluate the theory.

e. Ionic Compounds and in Particular NaCl

The Born model (Born and Goeppert-Mayer, 1933) has given very good results for the cohesive energy of alkali halides. This model assumes the solid is composed of closed shell positive and negative ions of integer charge. The largest contribution to the energy is the coulomb energy of the ionic charge configuration. This energy is well understood. This attraction term is balanced by an overlap repulsion term as the ion shells are forced against each other. The approximation assumes a given empirical form for the overlap term, in that it arises from two-body central forces. In addition to these terms, van der Waal's dipole-dipole and dipole-quadrupole interaction terms may also be included (Mayer, 1933). Tosi (1964) has shown that the inclusion of these terms, even though there is no accurate expression for them, definitely improves the results. Koliwad, Ghate, and Ruoff (1967) seem to disagree with this conclusion, however. Several good review articles are written on this subject;

see, for example, Tosi (1964) and Born and Huang (1954) each of which have an extensive bibliography.

Again, temperature effects are included by adding a "thermal pressure", i.e., a vibration energy term is included in the free energy. The Mie-Gruneisen equation is most common with γ assumed as a function of volume only. The appropriate γ in the Mie-Gruneisen equation is essentially temperature independent as shown by a direct calculation of the volume dependence of frequencies of the modes of vibration (Arenstein, et al., 1963).

Decker (1966) applied this theory for NaCl specifically to the problem of pressure calibration, particularly when the high pressure system was to be used at high temperatures. His equation was not considered as a "calibration" but was hopefully to be used to make temperature corrections to the pressure calibration once a room temperature isotherm was known. However, the calculated pressure versus volume agreed very well with Bridgman's (1945) isothermal measurements on NaCl and also with high pressure shock data (Alt'shuler, et al., 1960; Christian, 1957). More recently, it has been shown to give pressures accurate to 3 percent to 300 kbar (McWhan, 1967; Weaver, et al., 1967) when NaCl is compared with MgO for which the pressures can be confidently calculated from the equations of finite strain. The agreement is even better when the recent value of the initial compressibility of NaCl is used in the theoretical calculation (Decker, 1971; Chang, 1965; Slagle and McKinstry, 1967).

Because of the wide use of NaCl as a pressure standard, we give a comparison of various experimental and theoretical equations of state for this substance in the following section.

Compression data for NaCl have been based on: (1) shock compression studies by Christian (1957), Alt'shuler, et al., (1960), Lombard (1961), and Fritz, et al., (1968); (2) theoretical equation of state (based on the Mie-Gruneisen equation of state) by Decker (1971); (3) the Murnaghan equation of state employing ultrasonic bulk modulus data by Anderson (1966); (4) x-ray diffraction measurements by Perez-Albuerne and Drickamer (1965); (5) comparisons of molar volumes of NaCl and MgO by x-ray diffraction (McWhan, 1967; Weaver, et al., 1967). The results of these studies are not all in good agreement as shown in table 13. Therefore, some evaluation of these data are required before NaCl can be used as a pressure standard.

1. The shock Hugoniot data of Christian, Alt'shuler, et al., and Lombard are in fair agreement. Isothermal compression values based on shock data by Christian and Fritz, et al., differ by only 3 percent at 200 kbar. The recent data by Fritz, et al. can probably be considered the most reliable.

2. Decker's equation of state is sensitive to the zero pressure compressibility of NaCl. The values for pressure versus compression which he reported in his 1966 paper were based on a zero pressure isothermal compressibility of 4.27×10^{-3} kbar^{-1}. The recent determinations of the zero pressure compressibility of NaCl by Chang (1965), Slagle and McKinstry (1967), and Drabble and Strathen (1967) indicate that the best value is $4.22 \pm 0.01 \times 10^{-3}$ kbar^{-1}. Decker (1971) has recalculated pressure versus compression based on this new value. (See table 14.)

Weaver, et al. (1968) have also calculated the volume-pressure relationship of NaCl using the Hildebrand and Mie-Gruneisen equations of state. They evaluated

TABLE 13. Reported pressure-volume relationships for NaCl (pressure in kbar)

Reference and temperature	Specific volume (V/V_0)	1.00	0.95	0.90	0.85	0.80	0.75	0.70	0.65	
Christian (1957)	Hug[a]	0			61	100	152	221	(310)	
	20[b]	0			58	93	138	194	(260)	
Alt'shuler, et al. (1960)	Hug[a]	0			62	98	149	214	316	
Lombard (1961)	Hug[a]	0				102	154	224	340	
Decker (1966)	25	0	13.6	31.7	55.8	88.2	131.6	192.1	275.0	
Anderson (1966)	25	0	14	33	61	100	160	252	394	
Perez-Albuerne & Drickamer (1965)	25	0	14	32	58	93	141	202	(290)	
Weaver, et al. (1968a)	25	0	13.8	32.3	57.2	90.9	136.6	199.2	286	
Decker (1968)	25	0	13.8	32.2	57.1	90.5	135.8	199.4	287.3	
Fritz, et al. (1968)	25[b]	0	14.0	33.1	59	94	140.9	203.2		Q
	25[b]							203.7	292.1	L

[a] Shock Hugoniot uncorrected for temperature.

[b] Shock Hugoniot corrected to isotherm.

(   ) Extrapolated values.

Q Quadratic fit.

L Linear fit.

TABLE 14. Calculated pressures vs. compression for NaCl at 25 °C

Compression		Pressure (kbar)	Compression		Pressure (kbar)
Linear $-\Delta a/a_0$	Volume $-\Delta V/V_0$		Linear $-\Delta a/a_0$	Volume $-\Delta V/V_0$	
0.001	0.0030	0.71	0.068	0.1904	83.79
0.002	0.0059	1.44	0.070	0.1956	87.72
0.004	0.0119	2.93	0.072	0.2008	91.75
0.006	0.0178	4.46	0.074	0.2059	95.90
0.008	0.0238	6.04	0.076	0.2111	100.17
0.010	0.0297	7.67	0.078	0.2162	104.57
0.012	0.0355	9.36	0.080	0.2213	109.08
0.014	0.0414	11.09	0.082	0.2263	113.72
0.016	0.0472	12.88	0.084	0.2314	118.50
0.018	0.0530	14.72	0.086	0.2364	123.40
0.020	0.0588	16.62	0.088	0.2414	128.45
0.022	0.0645	18.58	0.090	0.2464	133.64
0.024	0.0702	20.60	0.092	0.2513	138.97
0.026	0.0759	22.68	0.094	0.2563	144.45
0.028	0.0816	24.82	0.096	0.2612	150.85
0.030	0.0873	27.03	0.098	0.2661	155.08
0.032	0.0929	29.30	0.100	0.2710	161.83
0.034	0.0985	31.64	0.102	0.2758	167.95
0.036	0.1041	34.05	0.104	0.2806	174.24
0.038	0.1097	36.53	0.106	0.2854	180.70
0.040	0.1152	39.09	0.108	0.2902	187.35
0.042	0.1207	41.72	0.110	0.2950	194.17
0.044	0.1262	44.43	0.112	0.2997	201.19
0.046	0.1317	47.22	0.114	0.3044	208.40
0.048	0.1371	50.09	0.116	0.3091	215.81
0.050	0.1426	53.04	0.118	0.3138	223.42
0.052	0.1480	56.08	0.120	0.3185	231.25
0.054	0.1534	59.21	0.122	0.3231	239.29
0.056	0.1587	62.43	0.124	0.3277	247.55
0.058	0.1641	65.74	0.126	0.3323	256.03
0.060	0.1694	69.15	0.128	0.3369	264.76
0.062	0.1747	72.66	0.130	0.3414	273.72
0.064	0.1799	76.26	0.132	0.3460	282.92
0.066	0.1852	79.97	0.134	0.3505	292.38

the parameter in the Born-Mayer repulsive potential using the zero pressure compressibility given by Slagle and McKinstry. Their results are virtually the same as those of Decker. Weaver (1968) has compared the three NaCl pressure scales of Fritz, et al. (1968), Decker (1968), and Weaver, et al. (1968) and suggests some explanations for the discrepancies between them. However, these discrepancies are at most the same order of magnitude as the uncertainties due to the determinations of the lattice parameters by x-ray diffraction.

3. Anderson (1966) used the Murnaghan equation of state with the bulk modulus and its pressure derivative based on sonic velocity measurements up to 3 kbar by Bartels and Schuele (1965). The Murnaghan equation, which is valid when the bulk modulus is a linear function of pressure, yields results that deviate drastically from direct experimental data at compressions exceeding $V/V_0=0.85$. Therefore, the Murnaghan equation should not be used for compressions exceeding $V/V_0=0.85$.

4. Perez-Albuerne and Drickamer (1965) determined the compression of NaCl by x-ray diffraction employing silver and molybdenum as pressure standards. They used the shock compression data to calculate pressure from the molar volume of the silver and molybdenum. The compression data for NaCl thus obtained are in agreement with the Hildebrand equation of state employing parameters evaluated at low pressure.

TABLE 15. Reported pressure-volume relationships for MgO (pressure in kbar)

Reference and temperature \ Specific volume (V/V_0)		1.000	0.950	0.925	0.900	0.875
Perez-Albuerne & Drickamer (1965).	25	0	103	161	229	308
Anderson & Schreiber (1965)	25	0	96	154	220	298
Anderson & Andreatch (1965)	25	0	92	149	215	292
McQueen & Marsh (1966)	Hug[a]	0	....	....	212	292

[a] Shock Hugoniot uncorrected for temperature.

5. Weaver, et al. (1967) used MgO as a pressure internal standard to determine the compression of NaCl by x-ray diffraction. MgO was chosen because compression data from four different sources (table 15) show much less scatter than the NaCl compression data. Shock compression results of McQueen and Marsh (1966) agree within 2 percent with data calculated by the Murnaghan equation in which the bulk modulus and its derivative were obtained by sonic velocity measurements on a single crystal (Anderson and Andreatch, 1965) and a polycrystalline sample (Anderson and Schreiber, 1965). Perez-Albuerne and Drickamer (1965) used niobium as a pressure standard to obtain compression data for MgO by x-ray diffraction. Their values are consistently higher than those from the other methods. The method by which the niobium shock data were corrected from the Hugoniot to the 25 °C isotherm is not discussed in their paper and it is possibly the source of the discrepancy.

Weaver, et al. (1967) chose to use the MgO compression data based on the polycrystalline sonic velocity measurements for their pressure determination. It is interesting to note that had they chosen the single crystal determination of Anderson and Andreatch (1965) or the shock data of McQueen and Marsh (1966), their pressures would be about 2 percent lower but would still agree within 1 percent with the NaCl pressure values of Decker (1971) and Fritz, et al. (1968).

McWhan (1967) also made molar volume comparisons between MgO and NaCl by high pressure x-ray diffraction up to 135 kbar. These are in excellent agreement with the measurements by Weaver, et al.

4.2. Experimental Techniques for *P-V-T* Measurements

This section deals with experimental techniques capable of determining and utilizing relationships among the three quantities, pressure, molar volume, and temperature. Equations of state which express relationships among these three quantities have been discussed in the previous section. Both the acquisition of $P-V-T$ data and the utilization of $P-V-T$ relationships for determination of pressure from volume and temperature are discussed. There are four major types of instrumentation which are used for these purposes: (1) dilatometry, (2) high pressure-temperature x-ray and neutron diffraction, (3) sonic velocity methods, and (4) dynamic shock methods. (These will be discussed in a separate section.) All of these techniques are able to detect phase transformations and, hence, can be calibrated by means of fixed points. The purpose of this section, however, is to discuss these techniques in relation to the continuous changes in volume as a function of pressure and temperature.

a. Dilatometry

The most direct means of determining molar volume as a function of pressure and temperature is by the measurement of the external dimensions of a block or rod of material while it is being subjected to hydrostatic pressure. This technique is known as dilatometry. The term, dilatometry, however, has come into common usage only as other methods for determining $P-V-T$ relationships have been developed.

Although attempts to measure compressibility by dilatometry date back to 1880, (Buchanan) the first really accurate measurements were made in 1923 (Bridgman). A comprehensive description of the techniques of dilatometry and their development may be found in Chapters V and VI of *The Physics of High Pressure*, (Bridgman, 1958). Bridgman determined the compressibility of iron by measuring the shortening of a rod of iron as it was subjected to hydrostatic pressure in a containing cylinder. The relative change in dimensions of the rod and the cylinder was measured by resistance of a wire extending from the rod across a contact attached to the cylinder. A correction for the change in the cylinder length based on external measurements of the cylinder was then made. Once he had obtained the compressibility for iron in this manner, he proceeded to determine compressibilities for other solids by the method of differential linear compressibility. This consists of placing a rod of sample inside of an open cylinder of iron and placing this whole assembly under hydrostatic pressure in a high pressure vessel. A slide wire extending from the rod across a contact attached to the iron cylinder is then used to indicate the relative changes in the lengths of the rod and cylinder. In order to increase his sensitivity for some determinations, he installed a lever at the end of the sample rod to amplify the motion by a factor of seven.

With these devices, Bridgman claimed that he could detect changes in length of 1.5×10^{-6} cm. or a fraction of a wavelength of visible light. He felt, therefore, that his method for detecting changes in length was as good as interferometry. He reports a mean deviation of about 0.16 percent for his determinations of the iron compressibility.

Another dilatometric technique for measuring changes in volume as a function of pressure is the piston displacement method. Bridgman developed this method for determination of compressibility of fluids. It was adopted, however, by investigators at the Geophysical Laboratory as a means of measuring the compressibility of solids. (Adams, et al., 1919). A solid sample is placed in a liquid (e.g., kerosene) in a high pressure vessel and pressure is applied by an advancing piston. The compressibility of the solid is found by comparison with a sample of known compressibility. Most dilatometric measurements are in the range 1 bar to 60 kbar and have been a valuable source of $P-V-T$ data in that range.

The aneroid might be considered an application of dilatometry to the measurement of pressure. However, the authors know of no case in which dilatometry has been utilized to measure high pressures by means of the compressibility of a solid. The major contribution of dilatometry to the technology of pressure measurement has been $P-V-T$ data which have led to formulations of equations of state for solids.

b. High Pressure-Temperature X-ray Diffraction

X-ray diffraction is one of the most accurate methods presently used for determining molar volume of a crystalline solid. In recent years, several devices have been designed for making x-ray diffraction measurements of samples under a wide range of temperature, pressure, and combined temperature-pressure conditions. Thus, these devices provide a valuable source of experimental data relating pressure, temperature, and molar volume. Discussions of the acquisition of x-ray diffraction data at high and low temperatures have appeared elsewhere in the literature (see, for instance, Peiser, et al., 1955), thus the following sections are devoted to the acquisition of x-ray data for samples under conditions of high pressure and combined high pressure and high temperature.

The determination of lattice constants from x-ray diffraction data is discussed in many books on x-ray diffraction (see, for instance, Klug and Alexander, 1954). The accuracy of molar volume determinations by x-ray diffraction depends on the accuracy of the measurement of 2θ which is normally good to 4 significant figures.

Several methods for making x-ray diffraction measurements of samples under pressure are in use today. Nearly every type of device for achieving static high pressure has been modified for making high pressure x-ray diffraction studies. The modifications consist either of constructing a portion of the device of a material which is transparent to x-rays or using a gasket material that is transparent to x-rays.

The earliest use of a high pressure device for obtaining x-ray diffraction data of a sample under pressure was reported by Cohn (1933). Using a Bridgman bomb, he provided an x-ray window of beryllium for the entering beam and a window of Bakelite or glass for the exiting window. By placing a photographic film outside the exit window, he was able to make photographic records of diffraction patterns of samples under pressures up to 3 kbar. Frevel (1935) reported making successful high pressure diffraction patterns at pressures up to 1 kbar by placing a sample under pressure in a capillary glass tube at the center of a Debye-Scherrer camera.

Jacobs (1938) showed that diffraction patterns of samples under pressures up to 5 kilobars could be obtained by filling a specially designed Debye-Scherrer camera with helium under pressure. The helium produced the desired pressure in the sample without adversely affecting the film as long as care was taken to release the pressure slowly. Jacobs was able to determine the structure of a high pressure phase of silver iodide and to compare the change in molar volume at the transition with Bridgman's (1915) determination by dilatometry.

Lawson and Riley (1949) reported the use of a coarsely crystalline beryllium bomb up to pressures of 15 kbar. The pressure transmitting medium was oil. A film placed outside the beryllium bomb recorded the diffraction pattern. A major disadvantage was the superposition of the beryllium pattern on the sample patterns. Lawson and Tang (1950) found that using a bomb consisting of a single crystal of beryllium greatly decreased the interference from the beryllium but that the beryllium became too plastic above 10 kbar. A bomb consisting of two single crystals of diamond with a hole drilled along the interface between them proved to be even more satisfactory. By squeezing a sample between two steel pistons in the hole they were able to achieve pressures as high as 25 kbar.

In the late 1950's and early 1960's, interest in x-ray diffraction of materials under pressure increased rapidly with the result that a large variety of techniques were developed. These can be classified into five general categories:

1. Piston and cylinder in which the cylinder or a portion of it is constructed of diamond or beryllium (Vereshchagin, 1965; Jamieson, 1961; Bradley, et al., 1964; and Kasper, 1960).

2. Bridgman anvils arranged so that the x-rays enter and leave the sample through the space between the anvil faces. Most instruments of this design use an annular gasket of material transparent to x-rays (Jamieson and Lawson, 1962; McWhan and Bond, 1964; Perez-Albuerne, et al., 1964; and Owen, et al., 1963).

3. A pair of Bridgman anvils, one of which is transparent to x-rays so that the x-ray beam may be bounced off the sample in a parafocusing geometry (Jamieson, 1961; and Davis and Adams, 1962).

4. A tetrahedral press in which gasket material transparent to x-rays is used. The beam may enter through a hole in one of the anvils and exit through the slots between anvils or it may both enter and exit through slots between anvils (Barnett and Hall, 1964).

5. Bridgman anvils of diamond arranged so that the x-rays enter and leave the sample through the anvils themselves (Piermarini and Weir, 1962; Bassett and Takahashi, 1964; and Bassett, et al., 1967).

The highest pressure x-ray diffraction measurements have been achieved with the Bridgman anvil types in both geometries. The most hydrostatic x-ray measurements have been achieved in the tetrahedral press. *Precision and accuracy for individual instruments are* discussed in a later section.

Although there is now a large body of data for volume as a function of temperature and volume as a function of pressure, there are very few data for volume as a function of simultaneous temperature and pressure for solids above 10 kbar and 100 °C. Barnett and Hall (1964) report that their tetrahedral press is capable of achieving 1000 °C and 75 kbar simultaneously by means of an internal heater. Bassett and Takahashi (1965) have made optical observations in their diamond anvil press up to 250 °C at 100 kbar and have the capability of making x-ray diffraction measurements at those conditions. There is a program under way at Battelle Memorial Institute for obtaining volume data at high pressure and temperature employing a belt high-pressure apparatus with a portion of the belt transparent to x-rays (Freud and Sclar, 1969).

The molar volume of zinc as a function of simultaneous pressure and temperature has been measured by Snyder (1967) using a tetrahedral press. All the volume determinations at room temperature and at high temperature have employed an internal standard in the manner described in the following sections.

Each type of device described in the previous section has been used to measure continuous change in unit cell dimension and molar volume as a function of change in pressure, thus making it possible to determine pressure by means of an equation of state for the material under pressure. The use of lattice parameter (molar volume) has several advantages over the use of fixed point calibration when x-ray diffraction is being employed (Jeffery, et al., 1966).

1. It provides a means of determining pressure at any point throughout the whole range of pressure of which static high pressure devices are capable.

2. The lattice parameter is a single valued function of pressure. Thus, pressures determined in this way are just as reliable during decrease as during increase of load.

3. The calibrant can be mixed intimately with the sample thus allowing observations of local effects on pressure as well as the effect of load.

Cubic substances have been used for internal pressure standards not only because of the greater simplicity of calculation but because of the elimination of axial ratio as a variable as well. Some cubic materials which have been used are NaCl, MgO, Ag, Mo, Al, and Nb (Perez-

Albuerne and Drickamer, 1965). Of these, the one which has been used the most is NaCl (Jamieson and Lawson, 1962; Bassett, et al., 1967; Jeffery, et al., 1966; McWhan, 1967). NaCl has several properties which make it desirable as an internal standard.

1. It is cubic.
2. It has a high compressibility resulting in a more sensitive standard than the other materials which have been used.
3. It flows plastically thus providing a pressure transmitting medium.
4. It is not as heavy an absorber as some of the other materials and therefore can be used in larger abundances.
5. It has no phase changes up to 300 kbar. (Johnson, 1966; and Bassett, et al., 1968).
6. It is ionic and so the principal terms in lattice energy are easily treated theoretically.
7. There is a great deal of experimental data on NaCl.

The tetrahedral high pressure x-ray diffraction apparatus has been used for volume determinations at simultaneous high pressure and high temperature (Snyder, 1967). The temperature was measured by thermocouple, the volume by x-ray diffraction, and the pressure was calculated by means of Decker's equation of state for NaCl (Decker, 1966). A disadvantage in the use of NaCl for pressure determination at high temperatures is the tendency for recrystallization to take place resulting in large single crystals which cause spotty diffraction lines and Laue spots that reduce the accuracy of the diffraction measurements. This seems to become a serious problem only at temperatures above 300 °C.

McWhan (1964) discusses two sources of error in his high pressure x-ray method employing a gasketed sample between Bridgman anvils with an x-ray beam traversing the space between the anvils and producing a diffraction pattern on a photographic film. The first of these is line measurement, the second is physical. Using a cylindrical film of diameter 114.6 mm with the sample at the center, he reports that he is able to measure the diffraction angle θ to $\pm 0.01°$. His overall average error in d-spacing due to reading is approximately 0.1 percent.

He breaks the physical sources of error down into five categories: (1) film shrinkage, (2) effective camera diameter, (3) absorption, (4) sample eccentricity, and (5) pressure distribution. The use of a printed scale on the film helps minimize error due to film shrinkage. Careful machining should result in an error less than 0.01 percent due to camera diameter. Dilution of the sample can reduce the source of error due to absorption to the range, 0.1 percent to 0.3 percent. Error due to eccentricity can be kept to 0.1 percent in d-spacing by very careful positioning of the sample at the center of the anvil faces. Pressure gradient which is considerable in an opposed anvil device can lead to line broadening of from 0.04° to 0.1° θ at 150 kbar. Taken together, these errors result in a minimum absolute error in d-spacing of about 0.5 percent.

McWhan estimates that by using a Guinier focusing geometry which eliminates absorption as a source of error, he is able to reduce his error to 0.2 percent. However, an advantage which the Debye-Scherrer geometry has over the Guinier geometry is the camera symmetry which allows measurement of both sides of a diffraction line, thus providing a means of checking sample centering for each determination. McWhan concludes that with a correction curve and careful work the minimum realistic error in d-spacing, hence lattice parameter, that can be obtained with molybdenum radiation in the Debye-Scherrer geometry is 0.1 percent and in the Guinier geometry is 0.07 percent. For a given equation of state for NaCl, an error of 0.1 percent in lattice parameter leads to an error of 2 percent in pressure at 100 kbar.

Mao, et al. (1967) discuss four sources of error in their high pressure cell in which a sample is placed between two opposed diamond anvils, and an x-ray beam passes perpendicular to the anvil faces and produces a diffraction pattern on a cylindrical film of 100 mm diameter (Bassett, et al., 1967). These are: (1) reading error, (2) change in film dimension, (3) change in sample-to-film distance, and (4) change in x-ray wavelength due to change in monochromator orientation. Repeated readings of the same pattern show a standard deviation of 0.03 percent for d-spacings. Sources (2), (3), and (4) taken together result in a standard deviation of 0.15 percent for d-spacings. The sample-to-film distance is calculated from the diffraction data of a sample of known lattice parameter at one bar pressure between the anvil faces. Since the same errors are involved in the sample-to-film distance determination as in the high pressure lattice parameter determinations, these errors are cancelled out as long as they are constant. By placing a polycrystalline platelet of NaCl or MgO on the film side of the back diamond anvil, it is possible to mark the film with a known diffraction pattern even while the sample is under pressure. In this way, corrections can be made for changes in both film and camera dimensions. Since this external polycrystalline sample is able to clearly resolve $MoK_{\alpha 1}$ and $MoK_{\alpha 2}$, it provides a means for determining the spectrum of radiation being used. All photographs for which a monochromator was used show that the radiation was pure $K_{\alpha 1}$. Therefore, variation of wavelength, (4) may be eliminated as a source of error. Absorption is not considered to be a serious source of error because of the very thin (5 microns) tabular shape of the sample. Line broadening indicates a pressure range of approximately 10 kbar in the x-ray beam at 150 kbar. However, if the diffraction lines are always read at the center, the pressure distribution does not introduce a serious error.

Since sample-to-film distance is determined in such a way as to cancel errors and a means for correcting for film shrinkage is used, the accuracy is probably approximately equal to the precision. Thus, the diamond anvil cell can be expected to produce data with a minimum error of 0.15 percent in average d-spacing or lattice parameter and 3 percent in pressure at 100 kbar for a given equation of state of NaCl.

One of the principal advantages discussed by Jeffery, et al. (1966) of the tetrahedral press over opposed anvil designs is the homogeneity and hydrostaticity of pressure throughout the sample. This permits a pressure resolution of 0.5 kbar or better. They estimate their precisions for lattice parameter measurements to be approximately 0.1 percent or less than 2 kbar when pressure is determined by means of an NaCl compression curve up to 100 kbar. In repeat runs of actual measurements of pressure phase transformations in Bi and Ba using the NaCl internal standard, they found errors between 1 percent and 2 percent in pressure thus confirming their estimates of the precision of their technique.

In conclusion, three analyses of instrumental error in the application of x-ray diffraction to the measurement of pressure by means of an equation of state for NaCl have been reviewed. They were found to be in remarkably good agreement on the sources and magnitude of error for such diverse geometries. It should be remembered, however, that in each analysis the equation of state of NaCl was assumed to be correct and so it was not considered as a source of error.

c. Neutron Diffraction

Although very little work in high pressure neutron diffraction has been undertaken, the technique clearly has some advantages over high pressure x-ray diffraction (Bennion, et al., 1966; Brugger, et al., 1967; Smith, et al., 1966). One is able to detect ordering of the magnetic spins, since scattering is by the nucleus and the scattering powers differ from those for x-ray diffraction and scattering powers are not dependent on scattering angle. Bennion, et al. (1966) and Brugger, et al. (1967) report that by means of a piston and cylinder high pressure vessel and a fixed angle of time-of-flight detector they were able to achieve an accuracy of 0.0002 Å (0.1% to 0.2% of their d-values), a capability comparable to that of x-ray diffraction, and to resolve peaks to 0.020 Å apart, a resolution far superior to that of x-ray diffraction. They have used NaCl as an internal pressure standard in the same manner that it has been used in high pressure x-ray diffraction. With their accuracy, the use of an internal standard is as satisfactory as it is in the x-ray techniques. The accuracy reported by Smith, et al. (1966) is also 0.1 percent to 0.2 percent for the more conventional goniometric measurements and should also permit reliable use of an internal pressure standard.

d. Sonic Velocity Measurements

In the preceding sections, we considered two types of techniques, dilatometry and diffraction, which yield data on molar volume as a function of pressure and temperature. Sonic velocities, however, yield data from which we may calculate the first derivative of volume with respect to pressure (compressibility) or the reciprocal of compressibility (bulk modulus). When sonic velocities are measured over a range of pressures, the first and second derivatives of bulk modulus may be calculated. The pressure range over which sonic velocity measurements can be made with reasonable accuracy is limited by the need for hydrostatic conditions. As a result, most measurements have been made in the one bar to 10 kbar range. However, equations of state based on measurements of bulk modulus and its derivatives at low pressure can be used to predict $P(V)$ along an isotherm to much higher pressures with fairly good accuracy (Anderson, 1966).

Frequencies for making sonic velocity measurements are chosen so that wavelengths are smaller than sample thicknesses. Thus, ultrasonic frequencies in the range of tens of megacycles per second are used.

Ultrasonic velocities in solids are usually measured by cementing a quartz crystal transducer to a block of the material being studied and applying an electric signal of the desired frequency to the quartz. In turn, the quartz produces sound waves of the same frequency which traverse the sample and are reflected from the far surface. The travel time for a pulse of sound can be measured by picking up the reflected pulse with the same transducer. The more bounces the pulse makes within the sample, the greater the effective path length and the greater the accuracy. Lazarus (1949) made ultrasonic measurements by this technique up to 10 kbar by placing the sample and transducer in a hydrostatic fluid medium inside a high pressure vessel.

The accuracy of ultrasonic measurements has further improved with the use of phase comparison or interferometry for measuring the travel time of the sound through the sample (McSkimin, 1950).

In both of the methods described above, longitudinal or transverse waves may be produced in the sample by the choice of x or y cut quartz crystals cemented either directly to the specimen or with a buffer rod of quartz or fused silica between the quartz driver and the specimen. By various combinations of longitudinal and transverse waves with different orientations of a single crystal of sample, it is then possible to obtain the various second order elastic constants for the sample.

McSkimin and Andreatch (1964) further refined the techniques for ultrasonic velocity measurements by designing a device in which they can place the sample under a uniaxial stress while sonic velocities are being measured. This is done by squeezing a cube of sample between two very flat stainless steel surfaces, and at the same time bouncing sound waves between two of the exposed surfaces of the sample cube.

In addition to the hydrostatic and intentionally stressed systems described so far, measurements have been made in a solid system up to forty kbar using ridgman anvils (Katz and Ahrens, 1963). In this appa-atus, an x cut quartz crystal is attached to the back f one anvil and a y cut quartz crystal is attached to the ack of the other. This makes it possible to introduce ither longitudinal or transverse waves through an anvil and into the sample by activating one or the other.

An important result of ultrasonic work is the determination of isothermal bulk modulus, B_T, and its pressure derivatives, B'_T, B''_T:

$$B_T = -V\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{\beta} \qquad (25)$$

where β is the isothermal volume compressibility. Since in acoustical measurements there is insufficient time during compression for dissipation of heat, the values which can be derived directly from the measurements are the adiabatic bulk modulus B_s and its pressure derivatives B'_s and B''_s:

$$B_s = -V\left(\frac{\partial P}{\partial V}\right)_S. \qquad (26)$$

The relationship between the adiabatic and isothermal bulk moduli is given by:

$$B_s = B_T\,(1+\alpha\gamma T) \qquad (27)$$

where α is the volume coefficient of thermal expansion and γ is the Gruneisen ratio.

For a cubic crystal at zero pressure the adiabatic bulk modulus is derived from the adiabatic elastic moduli by:

$$B_s(0) = \frac{c_{11}+2c_{12}}{3} \qquad (28)$$

where c_{11} and c_{12} are the elastic moduli oriented parallel and perpendicular respectively to the applied normal stresses and (0) indicates zero pressure.

The elastic moduli of a crystal may be derived from he velocities of longitudinal and transverse acoustic waves propagating through the crystal in different directions. These relationships for a cubic crystal are iven in table 16.

The first pressure derivative of the bulk modulus an be determined from two types of sonic velocity measurements, (1) the variation of elastic moduli as a unction of pressure in a hydrostatic system (Anderson, 966) and (2) the third order elastic moduli calculated rom acoustic velocities in a uniaxially stressed sample (Thurston, 1967; McSkimin and Andreatch, 1964). The relationship of the first pressure derivative of bulk modulus to the third order elastic moduli for a cubic ($m3m$) substance at zero pressure is given by:

$$B'_s(0) = -\frac{1}{9B_s(0)}\,(c_{111}+6c_{112}+2c_{123})\,. \qquad (29)$$

Fourteen different combinations of stress, propagation, and vibration directions are necessary to acquire enough data to calculate the third order elastic constants. McSkimin and Andreatch (1964) give the equations relating the velocities to the third order elastic constants.

TABLE 16. Relationship of elastic moduli to acoustic wave velocities in cubic crystals

Velocities	Propagation direction	Vibration direction	Mode
V_1	(001)	(001)	Long
V_2	(001)	(110)	Trans
V_3	(110)	(110)	Long
V_4	(110)	(001)	Trans
V_5	(110)	(110)	Trans

Elastic moduli

$c_{11} = \rho V_1^2$
$c_{11} = \rho(V_5^2 + V_3^2 - V_4^2)$
$c_{12} = \rho(V_1^2 - 2V_5^2)$
$c_{12} = \rho(V_3^2 - V_5^2 - V_4^2)$
$c_{44} = \rho V_2^2$
$c_{44} = \rho V_4^2$

The conversion from B'_s to B'_T is given by:

$$B'_T(0) = B'_s(0) + T\alpha\gamma\left(\frac{B_T(0)}{B_s(0)}\right)\left[1-\frac{2}{\alpha B_T(0)}\left(\frac{\partial B_T(0)}{\partial T}\right)-2B'_s(0)\right]+\left[T\alpha\gamma\left(\frac{B_T(0)}{B_s(0)}\right)\right]^2\left[B'_s(0)-1-\frac{1}{\alpha^2}\cdot\left(\frac{\partial\alpha}{\partial T}\right)_P\right]. \qquad (30)$$

The second pressure derivative of bulk modulus can be calculated from the fourth order elastic moduli. For a cubic ($m3m$) substance at zero pressure the relationship is given by:

$$B''_s(0) = [-2c_{11}-15B_s(0)-9B_s(0)B'_s(0)+c_{1111}+8c_{1112}+6c_{1122}+12c_{1123}]/27B_s^2(0). \qquad (31)$$

The authors know of no experimental determinations of the fourth order elastic constants, and the conversion of adiabatic values to isothermal ones has not been worked out.

Anderson (1966) in a discussion of precision of ultrasonic velocity measurements estimates that the change of velocity with pressure in a hydrostatic system can be known to at least four significant figures provided the pressure also can be measured to four figures. This can be realized in measurements employing a dead weight loader for a primary pressure standard. He concludes that B_s can be measured to five figures, B'_s to three and possibly four figures, and B''_s to two and possibly three figures.

McSkimin and Andreatch (1964) estimate that their measurements of velocities as a function of stress have a possible error of five parts in 10^5. The third order elastic constants which are utilized in the calculation of B_s' have errors which would result in an error of approximately 2 percent in the B_s'.

By substituting any combination of equations in table 16 into the equation for the adiabatic bulk modulus of a cubic substance, we obtain:

$$B_s(0)/\rho = v_p^2 - 4/3(v_s^2) \qquad (32)$$

where v_p is the velocity of longitudinal waves and v_s is the velocity of transverse waves. This equation is also valid for a perfectly isotropic substance (Katz and Ahrens, 1963). Thus the ratio of bulk modulus to density may be found directly from the longitudinal and transverse sonic velocities in either a properly oriented single cubic cyrstal or a polycrystalline sample (which is essentially isotropic if the wavelength is long compared with the crystallite size.) Anderson and Schreiber (1965) have determined the bulk modulus and other elastic constants of MgO from sonic velocities in a polycrystalline sample under hydrostatic pressure up to 4 kbar. Katz and Ahrens (1963) have made velocity measurements on polycrystalline KCl and $CaCO_3$ between Bridgman anvils at pressures up to 40 kbar.

Pressure as a function of the ratio of bulk modulus to density at a given temperature is easily found from an equation of state. Thus, it is possible to find the pressure of a sample from its sonic velocities when its equation of state is known.

The high sensitivity of ultrasonic measurements suggests a possible secondary pressure gage in hydrostatic systems. Heydemann (1967b) has studied the feasibility of such a gage and proposes the use of fused quartz as the gage material. Indications are that such a gage would be more repeatable, more accurate, and more convenient than the manganin gage. In solid systems, a technique such as that employed by Katz and Ahrens (1963) is potentially useful as a means for determining pressure. Some advantages which it has to offer are: (1) sonic waves do not require special materials as windows or plugs for access to the sample; the source can be attached to the outer surface of a pressure chamber or anvil as in the apparatus of Katz and Ahrens, and (2) it is possible that in a carefully designed system the use of various geometries could yield information on the anisotropic strain within the sample. On the other hand, it has some disadvantages which make it generally less attractive than other methods. These are: (1) the sample must be homogeneous thus not allowing an intimate mixture of a sample with a calibrant as in high pressure x-ray diffraction, (2) the sample must be contained between two very parallel faces and the distances between the faces must be well known, and (3) lack of hydrostaticity may introduce a serious error in the calculations.

Studies indicating the potential use of ultrasonic measurements to characterize liquid media to 50 kbar have been made by Heydemann and Houck (1968).

4.3. Resistance Gage

Secondary pressure gages based upon interpolation and extrapolation methods can be constructed using any physical parameter which varies monotonically with pressure. Criteria for selection of a particular phenomenon in preference to others are convenience, simplicity, reliability, and sensitivity. The resistance gage based upon the change of electrical resistance of a given length of metallic wire offers a very convenient and straightforward measurement consistent with a relatively high degree of reliability and sensitivity.

The possible use of such a gage for hydrostatic-pressure systems was first realized by Lisell (1903), who had measured the change of resistance with pressure for several metals. For most metals the very small change, a few parts per million for a pressure change of one bar, requires a very accurate measurement of the resistance. Earlier Palmer (1898) and later Bridgman (1909b) used the resistance of liquid mercury in a glass capillary, since for liquid mercury the change in resistance with pressure is almost two orders of magnitude greater than for most solid metals. Lisell proposed the use of manganin wire and when Bridgman (1911a) extended his measurements to pressures above the freezing pressure of mercury at room temperature, he adopted manganin as a resistance gage and studied its properties sufficiently to develop a secondary standard as reproducible and as sensitive as his primary free-piston gage in its stage of development at that time. Based upon continued development by Bridgman (1940a, b; 1946) and by Michels and Lenssen (1934) and careful studies by Adams, Goranson, and Gibson (1937) the manganin resistance gage became the accepted secondary gage for use in hydrostatic systems.

With significant increases in the precision, reliability, and range of the primary free-piston gage, re-evaluations of the resistance gage have been made (Newhall, 1962). The increased precision in both the primary and the resistance gages indicated limitation of the gages as discussed below. The significant considerations in selecting a suitable material for a resistance gage and the inherent advantages of this gage in contrast to other interpolation devices will be discussed before presenting the recent developments.

a. Requirements of an Acceptable Resistance Gage

One can enumerate those properties of a metal which would be desirable for use as a resistance gage: (1) high sensitivity of resistance to pressure, (2) low sensitivity of resistance to temperature, (3) a high degree of reproducibility from gage to gage (i.e., low sensitivity to chemical composition and manufacturing techniques), (4) a stable value of resistance with time or past history, (5) linear or nearly linear response with pressure, (6) high resistivity, and (7) lack of a phase transition in the pressure range of interest. Some of these desirable features tend to be mutually exclusive. For example, those materials with high sensitivity to pressure and high resistance tend to be nonlinear and often have phase transformations at relatively low pressures. Mercury and bismuth are good illustrations. Item three above suggests the use of a metallic element which can be obtained in very high purity, but a perusal of likely candidates indicates relatively large variations of resistance with temperature as discussed below. If all of the above properties are desired, the possibilities become greatly restricted. Ease of construction along with items three and four suggest the use of chemically inert metals sufficiently malleable to draw wire to form coils. The use of a high resistivity metal, although not necessary, simply reduces size and improves accuracy since it tends to lessen the effects of contact resistances and contact emfs.

In addition to convenience and simplicity, one of the significant features of the resistance gage as compared to other commonly used gages, both primary and secondary, is the relatively constant absolute sensitivity of the gage over all currently-available hydrostatic pressures. This feature means that the percentage detectable variation in pressure decreases at the higher pressures and makes the gage very appealing in this range.

The dominant reason for the selection of manganin as a suitable gage is the low sensitivity of resistance to temperature. Manganin is a Cu-Mn-Ni alloy specially prepared for use in precision resistors to have a high resistance with a low temperature coefficient of resistance at room temperature. A gold-chromium alloy (2.1 percent Cr) has been used for precision resistors and also considered as a pressure gage (Darling and Newhall, 1953).

A graph of resistance as a function of temperature at atmospheric pressure for manganin, Au-2.1 percent Cr, and Advance (a trade name for a particular constantan alloy) is shown in figure 4 for comparison. In contrast to these three and to similar alloys, pure metals such as copper, aluminum, platinum, and silver have temperature coefficients between 0.003 and 0.004 $^{\circ}C^{-1}$, which means that on the scale of figure 4 they would be off the graph when less than one degree from room temperature. The seriousness of this problem can be seen by considering the use of aluminum wire for which the relative resistance changes for one degree elevation in temperature would offset a one kbar pressure increase. Both Advance and Au-2.1 percent Cr wire, as seen in figure 4 have a significantly lower temperature coefficient than manganin over the temperatures of interest, but when the other items listed above are considered they appear less favorable. The seriousness of the temperature variation drastically restricts the possible gage materials. Schultz (1943) suggested the use of a 15.0 percent Mn-84.1 percent Ag alloy because of a high pressure coefficient and relatively low temperature coefficient,

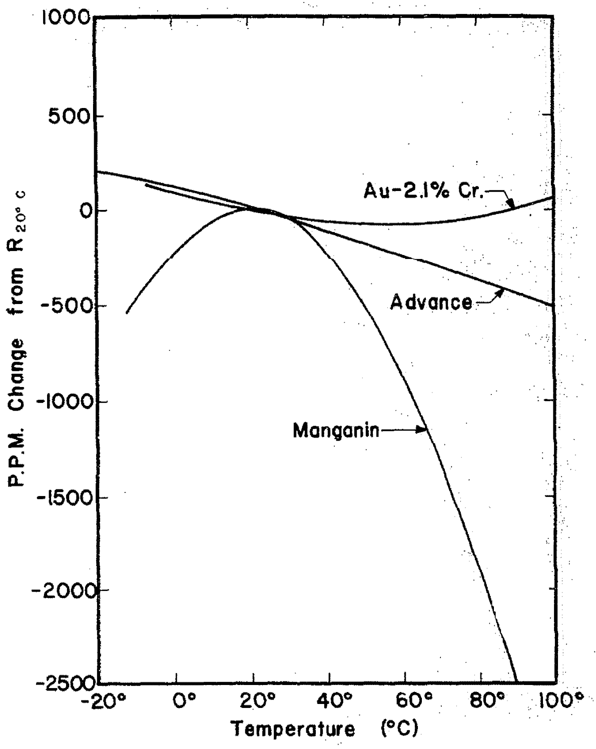

FIGURE 4. Variation of resistance with temperature for typical sample of manganin, Advance, and Au-2.1 percent Cr.

Ebert and Gielessen (1947) measured the pressure and temperature coefficients of a large number of alloys, and indicated how the pressure coefficient varies with concentration for several alloys. They also indicated the possible use of Ag-Mn alloys and report data on at least two alloys which show promise: 78 At percent Ag-22 At percent Mn with a pressure coefficient of 3×10^{-6}/bar and a temperature coefficient of 1×10^{-5}/°C, and 82 At percent Ag-10 At percent Mn-8 At percent Sn with a pressure coefficient of 0.9×10^{-6}/bar and a temperature coefficient of 2.5×10^{-6}/°C. Darling and Newhall (1953) proposed the use of Au-2.1 percent Cr, and several studies have been directed to its use as discussed below.

Reference to tables of low temperature coefficient alloys (1961, Metals Handbook) reveals at least three new alloys (76% Ni, 17% Cr, 4% Si, and 3% Mn; 75% Ni, 20% Cr, 3% Al, and 2% Cu; and 72% Fe, 23% Cr, 5% Al, and 0.5% Co) which show promise and are different from those above. Of course, pressure data must be obtained to determine the pressure coefficients of resistivity, stability, and related properties.

b. The Manganin Gage

The term "manganin" is a generic term which refers to one of several closely related compositions of copper-manganese-nickel alloys which, in their widest variations range between 67–87 percent Cu, 10–27 percent Mn, and 0–20 percent Ni. The wire generally used for wire-wound resistors and used in high-pressure gages is simply referred to as commercial manganin and is approximately 84 percent Cu, 12 percent Mn, 4 percent Ni, and varies somewhat depending upon the manufacturer. The use of an alloy of rather specific and critical concentrations has inhibited the development of a universal pressure calibration curve for manganin similar to the standard thermocouple calibrations. In practice each resistance coil is individually calibrated to form a pressure gage, and differences in composition and heat treatment involved in manufacturing have not been carefully reported or discussed in previous work. A calibration curve would be feasible to within an accuracy of at least one percent if a specific alloy and wire manufacturing process were specified and appropriate procedures were outlined for coil winding and seasoning. Since the change in resistance is nearly linear, a universal calibration accurate to one or two percent to 20 kbar would be obtained by simply specifying a universal pressure coefficient. Fractional pressure coefficients of resistance reported in the literature most recently are near 2.3×10^{-6} bar^{-1}, but a survey of past reported values beginning with Bridgman yields values ranging from $2.1-2.5 \times 10^{-6}$ bar^{-1}, and individual workers often report variations of one to two percent in gage coils constructed in different ways using wire from the same spool. Due to improved uniformity in currently available commercial wire, similarly constructed and seasoned coils using wire from the same spool can now be expected to have pressure coefficients equal to within a small fraction of one percent.

Since relative resistance can be measured without excessive difficulty to a few parts in 10^6 using either a precision Mueller bridge, a Carey-Foster bridge, or potentiometric techniques, pressure sensitivity of one to two bars is not difficult to obtain if adequate care is taken. To assure long-term accuracy in this range is more difficult, of course. With this type of sensitivity available, the question of stability, reversibility, and changes of the zero-pressure resistances as well as the pressure coefficient with temperature become significant when applied to an individually calibrated gage.

c. Stability and Reversibility

Bridgman (1911a) in his early work reported a drift of both the zero-pressure resistance and the pressure coefficient with time unless an appropriate "seasoning" or "artificial aging" procedure was followed. This type of procedure is common practice when manufacturing precision wire-wound resistors from manganin or other resistance alloys and is effectively a low-temperature annealing of the strains induced in the wire by the winding process. For manganin a temperature of 140 °C is generally recommended for 48 hours or more. Longer anneals at 125 °C are also effective. The initial resistance generally decreases by one to two percent during this temperature anneal and is then stabilized to at least a few parts in 10^6. To stabilize the pressure coefficient the gage must be exposed to pressure as high as one expects to use the gage at least once and preferably two or three times. For the temperature anneal Bridgman (1940a, b) used a cycle of heating to 140 °C for several hours followed by quenching to dry-ice or liquid-nitrogen temperature repeated several times and claimed that this procedure improved stabilization. The temperature cycling apparently relieves localized strain regions and thus improved uniformity.

Boren, Babb, and Scott (1965) report short-term stability (before and after pressure excursions) of the order of one part per million on appropriately wound and seasoned manganin gages to 25 kbar when using the Bridgman temperature season and only one pressure season. If the gage is not pressure seasoned, a significant nonreversible resistance change generally referred to as pressure hysteresis is observed, but following appropriate seasoning this hysteresis is of the order of one bar or less. The manner in which the coil is wound is important if minimal creep and hysteresis are to be obtained. Tightly wrapped close-pack winding causes straining of the wire during a pressure excursion and results in non-reproducible effects due to the difference in compressibility of the coil form and the resistance wire, and relaxation of these strains with time. Bowman and Johnson (1957) have described a practical, strain-free mounting in which the wire forms a helical coil of small radius, which in turn is placed in helical grooves around an insulating form. Boren, Babb, and Scott (1965) report that coils so constructed have good short-term stability and reproducibility on increasing and decreasing pressure of approximately one ppm. Coils wound loosely around a bobbin which are not close-packed yield instabilities and hysteresis of only a few ppm and are very adequate for all but the most exacting work. This is the type of coil generally used by early workers who often reported no hysteresis or creep due to lack of sensitivity in the resistance measurement. Stability and reversibility appear to be uninfluenced by extremely high pressure according to Barnett and Bosco (1967), who reported stability to within the accuracy of their measurements after excursions to over 50 kbar. In practice, most workers wind coils non-inductively. This precaution decreases noise level if any electronic amplifiers are used in the null detection system and also allows use of low-frequency resistance-bridge measurements if desired. Whether dc or ac techniques are used, it is imperative that a four-lead measurement of resistance be made.

One of the two most serious problems with state of the art manganin gages is the long-term stability. Good quality commercial resistance standards made of manganin are stable to approximately one ppm per year. To attain this high stability, relatively large wire and surface coating are used to reduce oxidation and similar surface deterioration which changes the conduction cross section of the wire. Surface deterioration of a fraction of a micro-inch will drastically affect resistance. Low-strain configurations and careful annealing also reduce drift. If such care is taken the only major residnal drift should be long-term low-temperature strain annealing. Similar precautions must be taken in pressure gages, but the allowable size places a serious restriction in this regard. It is significant to realize that a drift in the zero-pressure resistance of a coil does not necessarily imply a loss of calibration of the coil since the pressure coefficient indicates only the percentage change. Conversely, it is possible, but not as logical, that a change in pressure coefficient could occur without a zero drift occurring. Johnson (1963) reported a change of one ppm/week in the zero resistance value, but less than one bar effective difference in eight kbar over a period of 100 days.

Although earlier work (Bridgman, 1911a) implied manganin coils exhibit good long-term stability, later work with improved sensitivity demonstrated the limitations of these coils. Bridgman (1940a, b) reported changes in the pressure coefficients of a few parts in 10^3 over a period of two months, and Adams, Goranson, and Gibson (1937) reported constant coefficients "to one part in 10^3" for several months. Boren, Babb, and Scott (1965) reported a drift of the zero-pressure resistance of slightly less than one part in 10^4 for a well-seasoned coil in two months. Definitive work has not been reported and appropriate effort has not been made to determine and improve the long-term stability of manganin gages when changes in the ppm range are considered.

d. Variation of Resistance and Pressure Coefficient with Temperature

The variation of the resistance with temperature for a typical sample of manganin is shown in figure 2. Since manufacturers generally will guarantee only a room temperature coefficient of less than 20×10^{-6} °C^{-1}, a temperature control of at least 0.1 °C must be used for high-pressure work to be reproducible to at least one bar if one assumes that the shape and position of the resistance vs. temperature curve is not dependent upon pressure. It is desirable to have the maximum of the resistance curve at room temperature or the operating temperature of the gage. Commercially available manganin is manufactured with this principle in mind. Adams, Goranson, and Gibson (1937) have indicated, however, that a seasoning treatment of 140 °C for ten hours increased the maximum by approximately 10 °C. Johnson (1963) has reported an increase of 10 °C in the position of the maximum with an applied pressure of eight kbar, and Wang (1967) has reported a shift of approximately 3 °C at four kbar with little change in shape of the curve. Assuming that the shift is linear with pressure and that the shape of the curve does not change, a gage operating at 50 kbar and room temperature would be operating 40 °C–60 °C from the maximum, which would result in a temperature coefficient of approximately 50×10^{-6} °C^{-1} at 50 kbar. This result suggests temperature control of approximately 0.02 °C is necessary to maintain repeatability of one bar. This simple approximation illustrates the need for a material with a lower temperature coefficient than manganin over a larger temperature and pressure range.

If a coil is calibrated at a given controlled temperature and used only at that temperature, the complete pressure and temperature dependence of the resistance is not required, only the pressure variation. In practice, however, the complete function would be desirable. As indicated by Wang (1967); by Adams, Goranson, and Gibson (1937); by Michels and Lenssen (1934); and by Bridgman (1940a, b) the pressure coefficient is almost independent of temperature below 10 kbar. These workers report changes of 0.01 percent, 0.013 percent, 0.013 percent, and 0.022 percent in the pressure coefficient for a one-degree change in temperature, and each indicates that their value is only approximate. These quantities are so small they require resistance measurements in ppm to observe. Since the manganin gage is currently being used to pressures of 50 kbar (Barnett and Bosco, 1967), further work on the complete functional relationship of resistance with pressure and temperature at higher pressures is needed.

e. Linearity of the Resistance Change

There is, of course, no fundamental reason that the resistance change in manganin is linear with pressure. Bridgman and Lisell simply observed this fortuitous result to be true within the accuracy of their original measurements. As primary gages were improved and extended to pressure above a few kilobars the extent of nonlinearity became apparent. Bridgman (1940a, b) reported a discrepancy of approximately two percent in pressure between a linear extrapolated calibration and a primary measurement at 25 kbar and introduced a calibration curve in which pressure is expressed as a second-order variation with change of resistance:

$$P=A\Delta R+B(\Delta R)^2. \qquad (33)$$

Bridgman determined the constants A and B using the mercury freezing point at 0 °C and the Bi I–II room-temperature solid-solid transition. Such a two-point calibration technique is now generally considered necessary if accuracies better than one or two percent in pressure are desired, especially above ten kbar. Even below ten kbar Babb (1963) has shown the need for a two-point calibration and has discussed variations from the previous linear calibrations used by Bridgman. The best study of linearity is that of Boren, Babb, and Scott (1965), who used five fixed points (H_2O I–III–L, Hg L–I at −25 °C, Hg L–I at +20 °C, and Bi I–II with nominal pressures of 2090, 2525, 7450, 11500, and 25100 bar respectively) to overdetermine the two coefficients A and B. They found a fit which agreed at all five points to within three bars. These data indicate that there is no need for a third-order term in the calibration expression until greater accuracy is obtained in the fixed-point calibration pressures. At 25 kbar the second term in the expression contributes approximately 0.8 kbar, approximately three percent, to the pressure value for the particular coil. If a single-point calibration were made using the mercury-0 °C calibration point, the calibrated pressure would have deviated from the accepted pressure by only two percent. The authors report uncertainties on the coefficient A in equation (33) of 0.035 percent and on B of 1.2 percent based on statistical analysis of a least-square fitting to a given set of five calibration values. If one includes the variation due to the uncertainty of the reported calibration pressures, the values of A and B are less well-defined. The B coefficient is highly dependent upon the value used for the Bi I-II point since it is rather far removed from the other points. The coefficient B is uncertain to approximately ten percent as a consequence of the 60 bar uncertainties in the Bi point reported by Heydemann (1967).

Since a manganin gage has recently been used to 60 kbar in a hydrostatic environment by Barnett and Bosco (1967), the curvature and shape of the calibration curve above 25 kbar is now becoming of interest. Zeto and Vanfleet (1969) have made calibration intercomparisons between manganin and the fixed transition pressures, Hg I–L (20 °C), Bi I–II Tl I–II and Ba I–II at nominal pressures of 11 kbar, 25 kbar, 37 kbar, and 55 kbar respectively. The main thesis of these authors was an argument that the Ba I–II transition was significantly lower than the previously accepted pressure of 59 kbar. Since their paper was published, a lower value for the barium transition has been widely accepted (see section 3 of this review). It is thus now possible to use their data to evaluate the behavior of a manganin gage at pressures to 60 kbar based upon the independently determined transition pressure of Ba.

As discussed in section 3 of this review, the Hg I–L, Bi I–II, and the Ba I–II transitions appear to be the best-known calibration pressures in their respective pressure regions. Taking values of $\Delta R/R$ from the work of Zeto and Vanfleet with pressures from Zhokhovskii (1957), Heydemann (1967a), and Haygarth, et al. (1967), as shown in table 17 a one-point, a two-point, and a three-point calibration can be made and yields the equations for the pressure in kbar:

$$P_1 = 426.82 \left(\frac{\Delta R}{R}\right)$$

using Hg I–L only (34)

$$P_2 = 417.61 \left(\frac{\Delta R}{R}\right) + 338.2 \left(\frac{\Delta R}{R}\right)^2$$

using Hg I–L, and Bi I–II only (35)

$$P_3 = 412.61 \left(\frac{\Delta R}{R}\right) + 606.9 \left(\frac{\Delta R}{R}\right)^2 - 3131 \left(\frac{\Delta R}{R}\right)^3$$

using Hg I–L, Bi I–II and Ba I–II. (36)

TABLE 17. Fixed point vs manganin gage intercomparison values

Transition	Pressure (kbar)	$\frac{\Delta R}{R} \times 100$	Temperature
Hg I–L	11.627	2.7241	20.36°
Bi I–II	25.608	5.8545	23.5°
Tl I–II	36.564	8.2806	23.5°
Ba I–II	54.7	12.3317	22.0°

Figure 5 illustrates the differences of $(P_2 - P_1)$, $(P_2 - P_3)$, and $(P_3 - P_1)$ for comparison as they vary with a nominal pressure P_3. If the Tl I–II transition with manganin data from Zeto and Vanfleet is used, a third-order least square fit yields coefficients in equation 36 only slightly different from those given which implies the Tl I–II value used is consistent with the Bi I–II value of Heydemann. The rather strong third-order term and divergence from the second-order equation suggests either (1) the above third-order equation is not a good form of the resistance-pressure relationship, (2) the pressure calibration values used are still not reliable, or (3) the data of Zeto and Vanfleet are in serious error. At this writing it appears that the first of these alternatives is the most probable. The precise calibration of the manganin gage in the region between 25 and 50 kbar will require extensive work due to unknown nonlinear terms. This nonlinearity may well be associated with a change

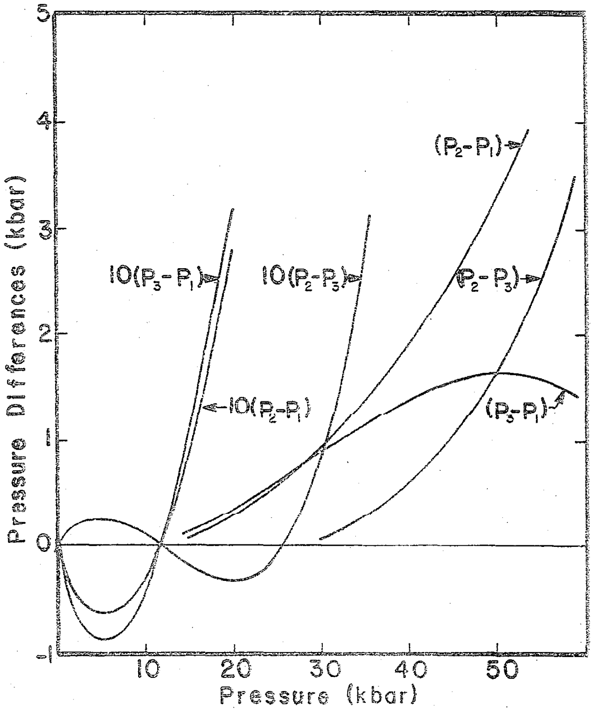

FIGURE 5. Variation between a linear (P_1), quadratic (P_2) and cubic (P_3) calibration curve for a manganin gage using Hg I–L: Hg I–L with Bi I–II; and Hg I–L, Bi I–II and Ba I–II respectively.

in position of the maximum in the temperature-resistance curve for manganin at these very high pressures.

Of passing interest is the use of a manganin coil as a pressure gage in a non-hydrostatic environment by Montgomery, et al. (1963), and by Samara and Giardini (1964). Use of a manganin coil in non-hydrostatic media has been tried by others in the field but not extensively reported since the pressure coefficient is non-reproducible and the resistance is irreversible, at least on the sensitivity scale discussed above. Furthermore, the coefficient is drastically different from that measured using hydrostatic pressure. For qualitative interpolation between known pressure calibration points as used by these authors it has utility.

f. Gold-2.1 Percent Chrome Gage

As mentioned above, Darling and Newhall (1953) proposed the use of an Au-2.1 percent Cr alloy as an improvement to replace the manganin gage due to the improved temperature-resistance variation. Boren, Babb, and Scott (1965) and more recently Davis and Gordon (1967) have evaluated this gage in terms of its stability, reversibility, and general adaptability to use. They report a rather serious irreversible hysteresis loop, in no case being less than five bars wide according to Boren, et al. Davis and Gordon report a very serious resistance variation with temperature at high pressure even though a rather low variation is obtained at low pressure. Both authors report serious difficulty in stabilizing the resistance gage with appropriate seasoning techniques. Although significant stabilization occurs, it requires greater care and control than does manganin according to Davis and Gordon, and the final stability is much poorer than manganin. A further practical problem of making electrical connections to the gage wire is encountered as reported by Darling and Newhall. The improved resistance vs temperature characteristic gives improved response when changing pressure rapidly and gives added stability with respect to temperature at the lower pressures, but the material appears to have several rather serious drawbacks when considering its use as a secondary standard.

g. Conclusion

In the ever continuing search for better calibration and measuring techniques, several areas for future work appear significant.

1. It seems meaningful for the high-pressure community to specify and accept a particular specific manganin alloy and perhaps a manufacturer with appropriate specifications for general use as a pressure gage and also to specify a standard technique of winding and seasoning coils. If this were agreed upon, pressure calibration to within one percent could be assured without independent calibration of each gage.

2. To facilitate intercomparisons of gages as calibrated by independent workers, a two-point calibration should be reported of the form:

$$P=A\left(\frac{\Delta R}{R}\right)+B\left(\frac{\Delta R}{R}\right)^2$$

for pressures less than 25 kbar.

3. As new alloys become available from the manufacturers of precision resistors, these alloys along with others not previously studied should be tested to see if improved resistance-temperature characteristics can be obtained consistent with other stability requirements and appropriate pressure coefficients.

4. Additional work needs to be carried out to increase the long-term stability of manganin coils. The use of coated manganin to prevent oxidation appears feasible and promising.

5. Additional data on manganin at higher pressures to increase our knowledge of the $R(T, P)$ function is significantly important for use of the gage at the higher pressures.

4.4. Other Pressure Gages

This section deals with additional properties of materials which vary continuously with pressure and therefore offer possible methods for pressure determination. All of them are capable of detecting phase transformations and hence, can utilize the fixed point pressure scale for pressure determination. The purpose of this section, however, is to discuss the continuous changes of these properties as a means of interpolating and extrapolating pressures.

a. Optical Absorption as a Pressure Gage

Many substances have absorption edges or bands within the visible, ultraviolet, or infrared which shift as a function of pressure. The direction and rate of shift vary greatly from material to material. However, there are some that shift rapidly across the visible spectrum and once calibrated provide remarkably sensitive and convenient methods for determining pressure.

Two types of instruments have been used for the study of absorption spectra of substances under pressure: (1) piston and cylinder with NaCl windows in the walls of the cylinder (Drickamer, 1961; Fitch, et al., 1957), and (2) diamond anvil press in which the diamond anvils serve as windows (Weir, et al., 1962). Drickamer has constructed two versions of the piston cylinder device. One has flat piston ends and a fairly large sample volume which can go up to 55 kbar. The other, which has tapered pistons with flats 0.090 inches in diameter, can achieve 200 kbar with occasional excursions to higher pressures. The pressure transmitting medium surrounding the sample is NaCl. Opaque masks of pipestone or aluminum are embedded in the NaCl along with the sample. Light enters and exits from the sample chamber through pressed NaCl plugs filling tapered holes in the cylinder wall.

In the diamond anvil press, a sample is squeezed between flat diamond anvil faces which are mounted on the ends of pistons driven together by a lever and screw assembly. Axial holes in the pistons permit light to enter and leave the sample by way of the diamond anvils. In the piston-cylinder design, the whole high pressure unit is placed in the sample location of a spectrophotometer. In the case of the diamond press, the sample area can be imaged and photographed, or the image can be masked and small portions of it measured successively with a microspectrophotometer. An ungasketed sample within a diamond press sustains a large pressure gradient, thus the imaging and selection of portions of the image is necessary. With the use of a gasket, however, the diamond press can be placed directly in a spectrophotometer.

Drickamer (1963, 1965) and his coworkers have studied the effects of pressure on the absorption spectra of many substances. Many of these would be satisfacory for calibration for pressure determination; Lippincott and Duecker (1964) selected nickel dimethylglyoxime as a pressure gage in a study of pressure distribution in a diamond anvil high pressure cell. Zahner and Drickamer (1960) reported that the absorption maximum at 19,000 cm^{-1} for nickel dimethylglyoxime shifts toward lower frequencies with pressure with an initial slope of -80 cm^{-1}/kbar. The slope decreases with pressure and at 100 kbar, the frequency f the absorption band is approximately 13,000 cm^{-1}. Thus, the absorption band of nickel dimethylglyoxime raverses most of the visible spectrum between 1 bar nd 100 kbar.

Lippincott and Duecker using mixtures of nickel dimethylglyoxime with alkali halides in the diamond anvil press, were able to detect the effect of pressure on the absorption spectrum by three different methods. They observed a color change with pressure under a microscope in white light, they photographed the sample in monochromatic light of various frequencies thus identifying the portion of the sample at the pressure for which there is the maximum absorption for that frequency, and finally, they made step scans across the sample area by microscope spectrophotometer. They also used TlBr which has an absorption edge at 23,950 cm^{-1} and which according to Zahner and Drickamer (1959) shifts -115 cm^{-1}/kbar. This material is particularly suitable for the photographic technique since its absorption edge shows particularly well in a photograph.

Neither Zahner and Drickamer (1960, 1959) nor Lippincott and Duecker (1964) discuss precision or sources of error in their measurements. Zahner and Drickamer (1960), however, give a plot of experimental points having a spread of approximately 10 percent in pressure for three different runs. One gets the impression that if optical absorption is to be used seriously for pressure determination, the precision can be made much better than this. Since the optical absorption method is only a means of interpolation and extrapolation, the accuracy of the method must depend upon the accuracy of the calibration of the standards.

The broadening of the absorption band in nickel dimethylglyoxime with increasing pressure may also be a serious source of error at higher pressures. Perhaps other substances would prove to be more suitable for higher pressures.

One of the chief advantages of this method is the rapidity with which it can give the pressure. One can make instantaneous observations of the color of the sample by microscope. Spectrophotometer measurements or photographic techniques take only minutes longer. Another advantage is that the method can give the pressure at a point in the sample even when a large gradient is present. Of all the methods of pressure determination described here, the optical absorption method is probably capable of determining pressure within the smallest volume of sample. An estimate of the lower limit of that volume is 50 cubic microns. By contrast, the smallest volume of sample under pressure for which an x-ray diffraction pattern has been obtained is of the order of 5,000 cubic microns.

The chief disadvantage of the absorption technique is that the samples which can be mixed with the pressure indicator without obscuring it are limited to those which are transparent and have refractive indices close to those of the pressure indicator.

b. Refractive Index as a Pressure Gage

Many aspects of the study of refractive index as a function of pressure are similar to those found in the study of sonic velocities as a function of pressure. This is true because refractive index is the normalized velocity of light. As in the case of sonic velocity measurements, refractive index can be calculated from the thickness of the sample and the time required for a signal to travel to the far side of a sample and back again. Also, as in sonic velocity measurements, the most precise way of measuring the travel time is by interferometry. Vedam and his coworkers (Vedam and Schmidt, 1966; Vedam, et al., 1966) have designed a liquid high pressure chamber with an alumina window which permits continuous observation of the interference between light reflected from the front and back faces of a block of sample hydrostatically compressed within the liquid medium. With this device, they have measured refractive indices for a number of materials up to 7 kbar. This technique is similar to the liquid systems used in the sonic velocity methods.

Bassett (unpublished) has attempted to measure refractive index as a function of pressure in a diamond anvil press by a method analogous to the one used by Katz and Ahrens (1963) for measuring sonic velocities. The time for the light to travel from the upper diamond-sample contact to the bottom one and back again is determined by interferometry using the same relationships as used in ultrasonic interferometry. The frequency and number of wavelengths in the sample can be measured with a high degree of accuracy but the sample thickness is very poorly known because of distortion of the anvil faces.

As in the case of sonic velocity measurements, refractive index in the liquid system serves no purpose as a means of measuring pressure because pressure in liquids is more accurately measured by piston. Refractive index in the solid system where it could be useful, suffers from the uncertainty of the sample thickness.

c. Phase Boundaries as Pressure Gages

Two types of phase boundaries offer possible means of pressure determination, (1) a phase boundary that has a finite and non-zero slope in a pressure-temperature plane, (2) a phase boundary that has a finite and non-zero slope in a pressure-composition plane. In the former case, pressure might be determined from a sample with a known phase boundary by placing that sample under pressure and then changing the temperature until the phase transition is detected. From the phase diagram, the pressure of transition for that temperature could be read. This method, however, suffers from the fact that there would be no freedom to make measurements along an isotherm, isobar, or adiabat. One would be restricted to the set of temperature-pressure values characteristic of the phase boundary of the reference material being used.

The second type of phase boundary, however, holds much more promise as a means of determining pressure, since unlike temperature, the composition of a pressure indicator can be adjusted without influencing the system or the sample being studied. Solid solution series of alkali halides offer the most interesting possibilities for pressure indicators. Darnell (1965) has determined the pressure of phase transition for solid solution series of RbCl-KCl and KBr-KCl as a function of composition. The RbCl-KCl samples have transitions at pressures ranging from 5.3 kbar for pure RbCl to 19 kbar for pure KCl. A plot of pressures versus mole fraction departs slightly from linearity. The KBr-KCl series ranges from 17 kbar to 19 kbar and also departs somewhat from linearity. Jamieson (1965, 1966) prepared solid solution samples of KCl-NaCl in spite of a large immiscibility gap between a few percent NaCl and a few percent KCl. He did this by melting the two salts together in desired ratios, cooling to 650 °C where the salts are completely miscible in the solid state and holding the temperature there for several hours, and finally air quenching the samples to room temperature. In spite of the fact that these samples were metastable, he found that they transformed from the $B1$ to the $B2$ structure with the application of pressure just as if they were stable solid solution samples. By high pressure x-ray diffraction, he measured the effect of mole fraction on the pressure of phase transformation and found that the pressure rises from 19 kbar for pure KCl to approximately 150 kbar for 15 percent KCl–85 percent NaCl. He was unable to go to higher pressures with his apparatus. Bassett (unpublished) using visual observations in a diamond anvil press was able to follow the phase transformation by small increments from 150 kbar at 85 percent NaCl all the way to 300 kbar in pure NaCl (Bassett, et al., 1968).

No systematic effort has been made to accurately determine the pressures of transition for any of the intermediate compositions in the KCl-NaCl series, yet this particular series has some features which make it particularly attractive as a pressure indicator.

1. Salts have come to be used by many investigators as pressure transmitting media. In this respect, KCl-NaCl solid solutions have properties similar to those of pure NaCl.
2. The pressures covered by this series, 19 to 300 kbar, represent the range in which nearly all high pressure static solid systems are operated.
3. The phase transition, unlike other properties, can be detected by a wide variety of detectors.
4. The composition series, unlike the fixed point calibration transitions can be prepared to produce a phase transition at any pressure between 19 and 300 kbar.
5. The $B1$-$B2$ phase transition can be detected optically in almost as small a volume as the optical absorption gage, approximately 100 cubic microns.
6. The volume change accompanying the $B1$-$B2$ transition has the effect of diminishing a pressure gradient and of stabilizing the pressure while the transition is in progress.
7. The transition has the effect of relieving shear strain within the sample.

Some of the unattractive features of this proposed pressure gage are:

1. Although the sluggishness and hysteresis seem small, these are problems that are shared with the fixed point transitions.
2. Because the samples are metastable, they tend to separate into nearly pure KCl and NaCl with time and especially with humidity. Annealing at 650 °C for a few hours before use, however, is a simple remedy for this.

The AgCl-NaCl solid solution series offers another interesting possibility for a pressure gage. It would cover the range from 80 kbar to 300 kbar and would not have the problem of immiscibility.

Fe-Co and Fe-V alloys have been suggested by Bundy (1967) for calibration purposes in a manner analogous to the salt solid solutions discussed above. He finds that under static conditions in a Drickamer type cell "the pressure of initiation of the transformation increases with the alloy content; from 131 kbar for pure iron up to 290 kbar for 20 wt percent Co. The V alloys rise much faster: 280 kbar at 6 wt percent."

Since the transformation is readily detected by resistance measurements in these alloys, they seem well suited for calibration in certain types of apparatus. Bundy has determined the pressures given above on the basis of a pressure scale which relies heavily upon the lead phase transition reported at 161 kbar.

Recent comparisons of the Pb and Fe transitions with the NaCl compression scale (Decker, 1968) by Mao, et al., (1969), however, indicate that the lead transition may be as low as 110 kbar and the iron transition as low as 115 kbar. These data are discussed in more detail under the headings of lead and iron in section 3. Thus, it may be necessary to revise the value of pure iron and the values for the Fe-Co and Fe-V alloys downward by different amounts. When this is done a curve passing through Bundy's points and the new value for pure iron still shows a remarkably good fit.

5. Dynamic Pressure Methods

Workers using static techniques in the pressure range above 100 kbar have commonly used results of dynamic shock data to determine the pressure in their experiments (Perez-Albuerne and Drickamer, 1965). The dynamic measurements, which have been useful for such calibrations have been equation of state data (Walsh, et al., 1957).

5.1. The Hugoniot Equation of State

The results of shock wave compression yield pressure-volume internal energy (P–V–E) data along the Hugoniot, which is a curve in the P–V plane that is reached by shocking a material to various pressures from fixed P–T conditions. With the assumptions listed below, these results can be used to calculate P–V relations along an adiabatic line or an isothermal line. The latter is most useful for comparison with static measurements. There are several recent review articles discussing the theoretical interpretation and experimental techniques used in this work (Rice, et al., 1958; Deal, 1962; and Duvall and Fowles, 1963). The P–V–E relations are obtained from the measured shock and particle velocities, using the equations of conservation for mass, momentum, and energy

$$V(U_s-u_{p0})=V_0(U_s-u_p) \qquad (1)$$

conservation of mass

$$P_x-P_{x0}=(U_s-u_{p0})(u_p-u_{p0})/V_0 \qquad (2)$$

conservation of momentum

and

$$E-E_0=1/2(P_x+P_{x0})(V_0-V) \qquad (3)$$

conservation of energy

where the subscript ($_0$) refers to the state preceding the shock front and the other terms are for conditions immediately following the shock front. U_s is the shock velocity measured relative to the material in front of the shock, u_p is the particle velocity, V is the specific volume or the reciprocal of the density, and P_x is the forward stress component. These equations were developed under the following assumptions: (1) equilibrium is established in the material in times short compared to the duration of the pressure pulse, (2) the shock pressure profile is steady in time, (3) the pressure is discontinuous at the shock front, and (4) heat transport by thermal conduction can be neglected for times involved in the shock measurements. The validity of these assumptions is attested by the experimental results. P_x is not exactly the same as the "pressure" because the stress is not hydrostatic.

P_x, V, and E are determined along the Hugoniot if u_{p0}, V_0 and P_{x0} are initially known and U_s and u_p are measured. The measurement of U_s is straightforward and can be done with an accuracy of about 1 percent. It is not easy to directly measure u_p but rather the free surface velocity, u_{fs}, is measured; this is the velocity imparted to the particles at the free surface at the end of the shocked specimen. One then commonly assumes that

$$u_{fs}=2u_p \qquad (4)$$

which is a very good approximation for low energy shock waves (Goranson, et al., 1955) and apparently accurate to within better than 3 percent in general (Rice, et al., 1958). Rice and Goranson discuss an iterative technique for determining u_p with greater precision than possible using equation (4). This method involves the additional assumption that the material is relieved from the shocked state along an isentrope, i.e., a line of constant entropy. The overall accuracy in the determination of u_p is about 2 percent. Thus, the accuracy in the determination of P_x along the Hugoniot varies from about 2.2 percent for $V/V_0=1.0$ to 3.2 percent for $V/V_0=0.5$.

The first correction that we will discuss is that due to the strength of materials. This amounts to estimating the hydrostatic pressure that would result in the same volume change as that arrived at by the one dimensional stress along the Hugoniot. Thus, we shift from the Hugoniot curve to a shock hydrostat. This distinction is primarily important for measurements at lower pressures, that is, those comparable to the yield strength of the material. Fowles (1961) has experimentally demonstrated that the Hugoniot stress exceeds the shock hydrostat by 2/3 the yield strength in simple tension when measured on material with the same plastic strain as at the appropriate point on the Hugoniot. This result can be derived theoretically from the elastic model (Fowles, 1961) but needed experimental verification because strain-rate effects may invalidate this model (Lundergan and Herrmann, 1963). With this correction, quite accurate low pressure equations of state for Cu, Pb, and Al have been measured (Munson and Barker, 1966). At higher pressures, this correction is not too significant as is demonstrated experimentally by the lack of any measurable anisotropy in the Hugoniot curves for single crystal Zn between 200 and 400 kbar (Walsh, et al., 1957).

The P-V-E results along the Hugoniot or shock hydrostat can be converted to P-V results along other lines in the pressure-volume plane by employing an equation of state. Generally the Mie-Gruneisen equation is used. This equation was discussed in section 4 and arguments presented to show that it is quite reliable at temperatures above the characteristic Debye temperature of the material. The most critical term in this equation of state is the volume dependence of the Gruneisen parameter, γ (V) (Duvall and Fowles, 1963). In general, this expression is estimated from Slater's formula for the Debye theory extended for an isotropic continuum (Slater, 1939).

$$\gamma=-\frac{V}{2}\left(\frac{d^2P/dV^2}{dP/dV}\right)-2/3 \qquad (6)$$

Dugdale and MacDonald (1953) have modified this formula for cubic lattices to read

$$\gamma=-\frac{V}{2}\left(\frac{d^2(PV^{2/3})/dV^2}{d(PV^{2/3})/dV}\right)-1/3 \qquad (7)$$

The Dugdale-MacDonald formula seems to give better results (Rice, et al., 1958; Chang, 1967) than the Slater formula, in spite of the fact that one of the assumptions in its derivation has been shown false. The usual approach is to transform the P-V relations along the Hugoniot to the isotherm passing through the initial value P_0, V_0, by assuming $(\partial P/\partial T)_V$ is independent of pressure or equivalently that $\gamma C_v/V$ is a constant (Birch, 1968). C_v is the specific heat at constant volume. This relation is very likely inexact but for small enough changes in V, i.e., low energy shocks, it should be a satisfactory approximation.

In order to interpret dynamic shock measurements of phase changes, one must know the temperature as well as P and V at the transition. Again, for relatively low energy shocks, it is sufficient to approximate the temperature from the relation along an isentropic compression (Walsh and Christian, 1955).

$$T=T_0\exp\left[-\left(\frac{\partial P}{\partial T}\right)_V\frac{(V-V_0)}{C_v}\right] \qquad (8)$$

where C_v and $(\partial P/\partial T)_V$ are assumed independent of pressure. This equation gives the temperature for isentropic compression but neglects the extra rise in temperature due to the shock. The temperature along the Hugoniot can also be calculated in a more elaborate manner by using the Mie-Gruneisen equation of state (Goranson, et al., 1955).

Even with all the above assumptions, one would expect the P-V relations along an isotherm to be correct to within a few percent if the work is done carefully. There still remains the question as to whether these results, after transforming to the isotherm, should be expected to compare with static pressure measurements. Work hardening and strain rate effects may alter the pressure distribution, especially in the low pressure region. Since there is a disparity between dynamic and static yield strength (Duvall and Fowles, 1963), one might also expect a difference in the static and dynamic equations of state. Recently there have been some comparisons between static and dynamic measurements in the low pressure range with very good agreement (Lundergan and Herrmann, 1963; Munson and Barker, 1966). Munson and Barker compared their results with static measurements by calculating best fit a and b coefficients along their isotherm using Bridgman's equation. (Equation (1) section 4.) They compared these with the same coefficients determined from static compression and ultrasonic measurements. Ruoff (1967) shows that the agreement with the ultrasonic work is very satisfactory especially if the a and b for the ultrasonic data are not taken from B_0 and B_0' but rather determined again from a least squares fit to the ultrasonic measurements. This is necessary because the two-coefficient Bridgman equation is not a good representation of an equation of state.

The shock measurements give values of $P(V, T)$ along the Hugoniot which agree, to within the uncertainty of the measurement, with Decker's (1965, 1966, 1971) equation of state for NaCl; this in turn agrees with static measurements along the room temperature isotherm to better than 2 percent in pressure for a given volume.

5.2. Phase Transitions Via Shock Measurements

There are a few phase transitions that have been observed both in the static and dynamic measurements. Since the pressure in the dynamic case can be determined experimentally with an accuracy of 2 to 3 percent, this could help establish the pressure at these transitions. A number of problems arise, however. The temperature at the dynamic measurement is greater than the initial starting temperature. Thus, the measured transition pressure must be corrected to the same temperatures as that of the static measurement. This requires a knowledge of dP/dT along the phase line. A more difficult problem is centered in the question of rates of transition and possible nucleation problems. In general, there will be a tendency to exceed the equilibrium pressure before a new phase can nucleate, and then one wonders if the rapid changes in pressure in the shock front might not tend to overshoot the phase transition pressure. In fact, if the transition is not rapid enough, it may not even occur at all. This is the case for melting of bismuth (Duff and Minshall, 1957). Duvall and Fowles (1963) claim that melting is a slow transition. One must also consider the slow nature of many solid state reactions (Roy and Dachille, 1967). In determining the pressure at the transitions, a correction for the strength of material must be applied before comparing with static data. There is also the question as to whether the plastic shear strain in the shock might not alter the transition pressure.

a. Bismuth I–II Transition

Duff and Minshall (1957), Hughes, et al. (1961) and Larson (1967) have all measured the Bi I–II transition by shock techniques. The observed break in the Hugoniot was identified as the Bi I–II transition by Duff and Minshall who measured the temperature dependence of the phase transition and found excellent agreement with the slope of the static phase line. Duff and Minshall observed the dynamic transition pressure to be about 2.7 kbar above the accepted static equilibrium value. They assumed that u_p was half the measured free surface velocity when the plastic wave reflected from the free surface. They observed no elastic wave and made no strength of material correction to account for non-hydrostatic compression. Hughes, et al., used the same assumption concerning the particle velocity but their technique, which was quite different, had too much scatter from sample to sample. Their best estimate of the transition pressure would be 26±3 kbar after correcting to 25 °C and for strength of material (Larson, 1967). Larson measured the pressure using an impedance matching technique between Bi and a piezoelectric quartz gauge. After the appropriate corrections, Larson's value for pressed Bi is 25.4 ± 0.8 kbar and for cast Bi is 25.9±1.2 kbar, in good agreement with static equilibrium measurements. (The values given in table 18 are uncorrected.) None of these measurements showed any variation of the transition pressure for shock transit times between 10^{-6} to 10^{-8} seconds.

A comparison of these three measurements is given in table 18. P_{HY} is the pressure in the elastic wave, U_{21}, u_{p2}, P_2, and V_2/V_0 are the shock velocity, particle velocity, pressure and relative volume in the first plastic wave. T is the temperature behind the first plastic shock. The particle velocity of Duff and Minshall is probably too large which could be due to experimental error as discussed by Larson. The following paragraph shows that generally the appropriate particle velocity is less than half the free surface velocity when an elastic wave precedes the plastic wave. This also would indicate that the first two values of u_{p2} in the table may be large.

TABLE 18. Bi transition by shock measurements

P_{HY}	U_{21}	u_{p2}	P_2 (kbar)	V_2/V_0	T	Reference
	2.049	0.135	27.15	0.943	42 °C	Duff & Minshall (1957)
	2.054	.128	25.7	.938		Hughes, et al. (1961)
2.0	2.060	.126	25.55	.939		Larson (1967) cast
2.4	2.060	.125	25.2	.941		Larson (1967) pressed

This would increase his measured pressure by 0.7 kbar.

Let us consider the corrections mentioned in the above paragraph. From (1) and (2)

$$u_{p1} = \sqrt{P_1(V_0 - V_1)} \tag{9}$$

for the elastic precurser wave and for the following plastic shock

$$u_{p2} = \sqrt{(P_2 - P_1)(V_1 - V_2)} + u_{p1}. \tag{10}$$

Now assume an elastic decompression wave reflects from the free surface and moves back into the material with essentially the same velocity as the initial elastic wave. This decompression wave interacts with the plastic shock before it strikes the surface, slightly lowering the density behind the shock giving:

$$u'_{p2} = \sqrt{(P_2 - P_1)(V_0 - V'_2)} > u_{p2}. \tag{11}$$

The appropriate specific volumes in the above equation are pictured in figure 6. In fact, from the interaction

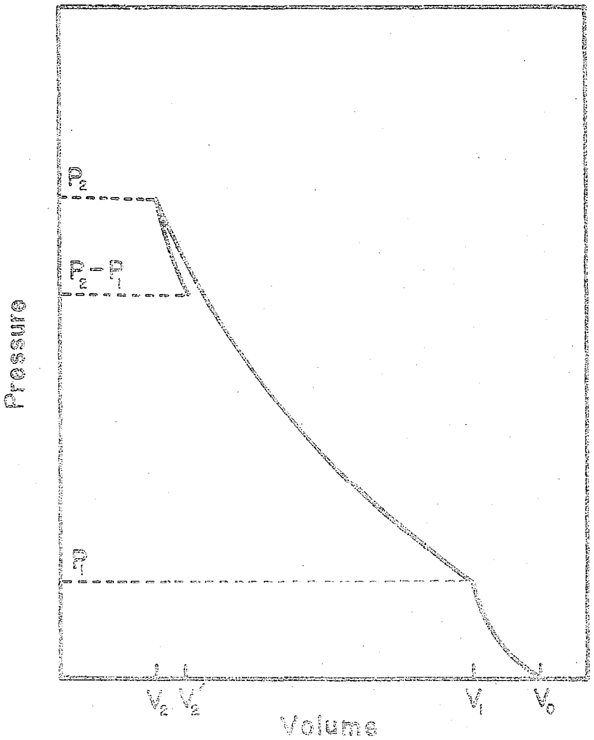

FIGURE 6. The elastic and plastic Hugoniot showing the effect of the returning elastic wave on the forward plastic compression wave.

$$u'_{p2} = u_{p2} + \sqrt{P_1(V'_2 - V_2)}. \tag{12}$$

$V_0 - V'_2 > V_1 - V_2$ because the elastic wave Hugoniot is steeper than the plastic wave Hugoniot and the volume change for a given pressure change is less at higher pressures. This altered shock then interacts with the free surface imparting to it a velocity $2u'_{p2} > 2u_{p2}$. We have neglected thermal effects that tend to expand the lattice behind the shock again making $u'_{p2} > u_{p2}$.

Let us also consider the impedance technique of Larson. Following Larson, we will assume a linear relation between P and u_p in the low pressure region as shown in figure 7.

A shock of pressure P_Q in the quartz will be generated by a shock of pressure P_{Bi} striking the Bi-quartz boundary. A rarifaction wave of magnitude $P_{Bi} - P_Q$ will be reflected back into the Bi. Conserving pressure at the boundary and using equation (2) and figure 7 we find

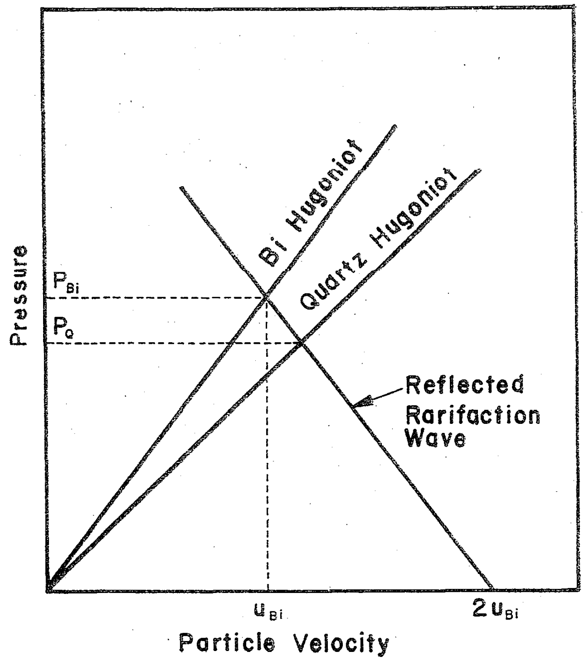

FIGURE 7. Pressure vs particle velocity curves for a Bi plate against a quartz crystal with the shock progressing from Bi into quartz.

$$P_{Bi} = \frac{(\rho_Q U_Q + \rho_{Bi} U_{Bi})}{2\rho_Q U_Q} P_Q \tag{13}$$

where ρ and U stand for the density behind the shock and shock velocity in the two media. For the elastic wave one would estimate the rarifaction wave returning into the Bi to be about 0.7 kbar. This wave interacts with the plastic wave lowering the pressure by this amount before it strikes the surface. Thus, the "measured" pressure in the plastic wave should be increased by 0.7 kbar.

The above correction would bring Larson's measurements into excellent agreement with the static work of Vanfleet (1967). In this hydrostatic measurement, Vanfleet observed transition rates for Bi I–II which show that if nuclei of the Bi II phase are present, the transition is very rapid for an overpressure of ½ to 1 kbar. It is quite possible that the shock wave will nucleate all possible phases and thus the only criterion for a rapid change of phase is to have enough excess pressure above the equilibrium value.

b. Transition in Iron

Another transition, measured in shock work, that might be useful for pressure calibration is the α-ϵ Fe transition above 100 kbar. This transition was measured as 130 kbar at 37 °C by Bancroft, et al. (1956). Corrected to the hydrostat, the pressure would be about 128 kbar. They also observed some effect of sample thickness indicating that the shock times are possibly shorter than or of the same magnitude as the transition time. Later measurements (Loree, et al., 1966) gave 127 ± 1 kbar after making the strength of material correction. These measurements assumed the free surface velocity was twice the particle velocity behind the shock. As discussed above, this may give a calculated pressure which is slightly high. The temperature dependence of this transition has been measured between 78 K and the α-γ-ϵ triple point, which has been set by shock data as 110–115 kbar and 500 °C (Johnson, et al. (1962)). These measurements could not accurately determine the absolute pressure and thus the pressures were adjusted to agree with the values of Bancroft, et al., for shock in iron at room temperature. The α-ϵ transition has been measured in static work by Balchan and Drickamer (1961) at 133 kbar but they used calibrants whose pressure was determined by shock data. However, this measurement shows not only that shock pressures agree with each other but also that transition pressures may not be greatly altered by the plastic shear strain in the shock front.

To conclude this section, we comment that it appears that one should be very cautious in using the pressures from shock measurements as calibration points for static measurements. The major problems are the strength of material corrections, which can be reasonably well approximated but have not always been included, and rate effects on transition pressures for which very little is known.

6. Pressure Scale at Elevated Temperatures

Many measurements have been made at elevated temperatures and high pressures. These include melting curve determinations, detection of solid-solid and other types of phase lines, chemical reactions, effects of temperature and pressure on electrical resistance, and diffusion measurements. With very few exceptions, the pressure in these experiments has been taken from a room temperature calibration of the apparatus. In a few cases, experimenters have tried to estimate the effects of elevated temperatures upon the pressure calibration. These estimates vary greatly. Bundy (1964) proposed a 16 kbar rise in pressure when internally heating his pressure chamber to 500 °C at 100 kbar. Lees and Williamson (1965) conclude that the effect of temperature on the load/pressure calibration is less than 3 kbar at 50 kbar and 1000 °C. Decker and Vanfleet (1965) felt that the effects of temperature might depend strongly upon the nature of the gasket formation while Millet (1968) proposed that the pressure might even decrease when internally heating a specimen at pressures where the gaskets have not completely formed. Millet's argument centers around the relieving of pressure gradients at elevated temperatures.

Because of the difficult nature of this problem, very little definitive research has been done. With our present technology, however, it is possible to attack the problem. A few experiments have been reported which give preliminary answers to some of these questions. These experiments will be briefly discussed here. In that the effect may depend considerably upon the nature of the experimental apparatus, we will discuss each general type separately.

A problem which is related to that above is the effect of pressure upon the e.m.f. of thermocouples and their calibration. This problem will also be discussed in the present section and we will then conclude by mentioning some techniques which have been proposed to calibrate presses at elevated temperatures. In multianvil devices, the anvils are forced against the faces of a three dimensional pressure cell made of materials such as pyrophyllite or a thermo-setting plastic mixed with boron, etc. (Barnett and Hall, 1964). As the pressure cell is compressed, some of the material extrudes between the anvils forming gaskets. When the friction between the cell material and the anvils is sufficiently large, the flow of material in the gasket region ceases and the pressure within the cell rises as more load is applied. The gasket regions are also compressed as the load increases and eventually assume a large share of the total load, thus limiting the useful pressure at the center of the cell. Large pressure gradients will be present in the gaskets and much smaller pressure gradients are set up in the bulk of the pressure cell.

It is not practical to heat the entire apparatus because of its large mass. Neither is it desirable to do so, in that high temperatures would weaken the anvils, etc. Thus, the heating must be accomplished internally and the cell material must also serve as a good thermal insulator between the high temperature furnace region and the anvils, which will remain near room temperature.

As the temperature of the furnace region is increased, the heated material will expand against the colder surrounding material. This outer region, being composed of solid material, will resist the expansion until a sufficient pressure gradient is set up to force material outward. Thus, the pressure in the furnace area would be expected to increase. The new distribution of pressure through the solid medium pressure cell might cause more material to move into the gaskets and also possibly drive the anvils back, increasing the oil pressure behind the rams. Another fact that complicates th problem is that the mechanical properties of the heate material may change, i.e., become less viscous, and relieve pressure gradients in the furnace region. Becaus of these latter effects, one cannot be certain as to whether the pressure at the sample monotonically increases with rising temperature or not.

Upon cooling the furnace area, the inner materia will contract but will probably not return to the initial state prior to heating. The high temperature may also have irreversibly altered the nature of the cell material. Because of these two changes, the entire process may not be repeatable from one heating cycle to the next. However, one would suppose that after a number of such cycles, the pressure-temperature relation would settle down to a repeatable cycle. The above effects of temperature on the sample pressure are likely different for each different cell material and will also depend upon the relative volume of the furnace region to the total sample.

Lees and Williamson (1965) concluded that the effect of temperature on their pressure calibration was less than 3 kbar at 50 kbar and 1000 °C, because of the agreement between their measured melting curves for zinc and aluminum and a linear extrapolation of those measured by Butuzov (1957) in a hydrostatic system. Decker and Vanfleet (1965) observed that an increase of 4 kbar at 70 kbar and 1400 °C and no increase when heating below 15 kbar was required to make the melting curve of gold best fit a Simon's equation. A more direct approach to this problem is that taken by Young and Barnett (private comm. 1968) in which they measured the lattice parameter of NaCl, using x-rays, while heating the sample to 400 °C, beginning at several different initial pressures. The pressure at the sample was then calculated from the measured temperature and lattice parameter using Decker's (1971) equation of state. For a 50–50 boron-plastic tetrahedron with preformed gaskets and using $^5/_{16}''$ double tapered anvils, they found the pressure to increase with temperature but not monotonically. At 60 kbar and 400 °C their measured increase was about 4.5 kbar.

The basic principles of the belt and girdle apparatus are very similar to those of multianvil systems and thus we would expect similar effects of temperature on pressure. The principal differences would come from different geometries and thus also different pressure gradient patterns.

Bundy (1964) proposed a 16 kbar rise in pressure in a belt apparatus when heating to 500 °C near 100 kbar. His conclusion was reached by comparing the difference between the triple point of iron measured in his apparatus and that obtained by shock techniques. Bundy's Bi III–V point in these measurements was higher than that presently accepted. A 26 kbar increase would be required using more recent calibrations to bring his measurements into coincidence with the shock work. The problem here may stem from the inappropriateness of the comparison of shock and static phase lines and not an increase in pressure due to heating. In contrast, Strong (1962) concluded that a pressure change of 3–5 kbar took place when heating a specimen to 400–600 °C at 70 kbar in a belt apparatus.

The calibration of the piston cylinder apparatus at elevated temperatures is quite different from the pressure systems in which a gasket is formed from the pressure transmitting material. However, there are some similarities in that to attain high temperatures, the sample is internally heated and the furnace region must be thermally insulated from the cylinder walls by some pressure transmitting material. For these systems, the pressure can be estimated from F/A (force on the piston over the piston area) if one can determine the appropriate corrections for friction between the piston and the cylinder walls and for internal friction in the pressure transmitting medium (usually talc). Kennedy and coworkers (1963) have assumed the internal friction to be negligible and that the friction forces on the piston are symmetric with in-stroke and out-stroke. Pistorius, et al. (1967) has shown that the KCl transition at 19.2 kbar using Kennedy assumptions at room temperature is 3 kbar higher with the KCl contained in a talc pressure medium than when the KCl completely fills the cylinder. He suggests that this is an unsymmetrical friction term from elasticity of the talc.

Kennedy and Newton (1963) have measured the increase in pressure, in their apparatus, with temperature due to thermal expansion in the furnace area. They found, for the particular geometry used, a pressure increase equal to the double value of friction at 275 °C and an increase of 9 kbar at 30 kbar when heating to 1100 °C. In spite of this measurement, they claim that normally the pressure rise due to heating just about cancels out pressure losses due to friction. This might be valid for a small temperature rise but it would appear that the pressure in a measurement at temperatures above 300 °C should be roughly given by F/A plus half the double value friction. This latter statement must be modified when considering the different sequences of pressure and temperature application. In many articles on the measurement of phase transitions, the actual historical sequence is not stated clearly, but in the article by Sterrett, et al. (1965) it is stated that "the pressure is adjusted upward just before melting so that the sign of the friction correction was known." It might be that this precaution is always taken by Kennedy and his coworkers. The relative volume of the furnace region to the total volume should make considerable difference in the pressure increase. Schamp, et al. (1963) compared F/A at the melting point of various alkali halides to the pressure at these points measured by Clark (1959) in a hydrostatic medium. There was considerable scatter in their results, probably due to different history of pressure cycling before the measurements, but most of the values of F/A, uncorrected for any friction effects, lay within ±7 percent of Clark's pressure values.

Generally, the double value friction is not measured, but a phase line is determined on increasing and decreasing pressure cycles assuming $P=F/A$, and the average of the two measurements assumed to be the correct phase line. Recent measurements by Pistorius, et al. (1967) show that this technique is incorrect except at temperatures above 500 °C since the nature of temperature effects on the friction correction depends upon the history of the pressure and temperature changes, these should be carefully controlled and defined in the measurement.

The last general type of high pressure system that we will discuss is the liquid chamber using the resistance of a manganin wire as a pressure indicator. The resistance as a function of pressure for manganin at room temperature is nearly linear and can be accurately fit by a polynomial of order P^2. The manganin resistance is normally calibrated by measurements at two known phase transformations, usually the melting point of Hg and Bi I–II for high pressure work. One is still left with the problem of how well this calibration might serve at elevated temperatures.

Wang (1967) measured the resistance of a manganin coil to 7 kbar and 200 °C and noted a 2 percent increase in the pressure coefficient of resistance from 25 °C to 200 °C. If one knows the temperature of the manganin pressure gage and corrects the resistance, assuming the atmospheric pressure resistance versus pressure curve, the pressure at 4 kbar will be accurate only to about 2 percent.

It is also possible to circumvent this problem by locating the manganin coil in a part of the liquid system removed from the heater such that the coil remains essentially at room temperature (Birch, 1968). In using this technique, one should allow sufficient time, after changing the pressure or temperature, for the system to attain pressure equilibrium throughout.

The thermocouple is by far the most convenient device for measuring temperature in a high pressure cell. The major problem, which is still not satisfactorily solved, is that of the effect of pressure on the thermal e.m.f. of thermocouples. Comparisons of different thermocouples in the same high pressure environment (Bundy, 1961) (Hanneman and Strong, 1965) show that the pressure effects are a serious problem at high temperatures. These comparisons are direct measurements which, for the most part, are easily interpreted but the published results are not in good agreement. The later work of Hanneman and Strong (1965) and Peters and Ryan (1966) are probably more reliable than that of Bundy (1961). The absolute pressure effect measurement is a much more difficult problem and direct measurements have been successfully carried out only up to 100 °C (Bridgman, 1918; and Bundy, 1961). These measurements are adequate for corrections up to 100 °C but, as is verified by the thermocouple comparison measurements, cannot be extrapolated to higher temperatures. Hanneman and Strong (1965 and 1966) have made some indirect estimates of the effect of pressure on thermocouple calibration to higher temperatures by comparing measured phase lines with theoretical calculations. The comparisons are not clear cut and a large uncertainty still exists, probably considerably larger than that estimated by Hanneman and Strong. They also discuss other corrections that must be considered and have corrected their data for temperature and pressure gradients in the cell. Getting and Kennedy (1970) have made some measurements on the effect of pressure on the thermal emf which indicate a much smaller correction for Pt−PtRh and even an opposite sign for the correction for chromel-alumel at high pressure.

Several authors have suggested that high pressure calibration at elevated temperatures could be accomplished by determining the load along a known high temperature phase line. Some of the phase lines that have been suggested are the α-γ phase line of iron (Clougherty, 1963a, 1963b), the calcite-argonite transition (Sclar, et al., 1963) melting curves of the alkali halides (Schamp, et al., 1963), and other elements (Jayaraman, et al., 1963). Of these, the melting curves are probably more sharply defined. The ideal situation would be to have a very steep phase line with a negative slope dT/dP. The best of the above suggestions is that of Schamp, et al. because the comparison is against a phase line measured in a hydrostatic system where the pressure is quite accurately known. One drawback is that such phase measurements are only available at low pressures. All other phase lines to date are of questionable assistance in pressure calibration until one has solved the problems of pressure effects on thermal e.m.f. and temperature effects on pressure due to expansion of the heated cell and sample.

7. Summary

Within the past few years sufficient experimental results have become available to obtain some cross checks on the calibration of static pressures in the region up to 80 kbar. The results of several different researchers using both direct and indirect methods are showing a convergent trend in pressure calibration in this range. Furthermore, improved techniques in the free piston gage have improved the reliability in the 0–10 kbar range. The maximum accuracies now attainable in the determination of pressure are of the order of 0.02 percent at 8 kbar, 0.25 percent at 25 kbar, 2 percent at 50 kbar, and 4 percent at 100 kbar.

We conclude that the controlled clearance free piston gage is the best approach to the primary pressure scale at pressures above 10–20 bars. A direct measure of pressure using this method is a fairly standard operation to 10 kbar, but can be extended up to 25 kbar with considerable effort. The simplest and most practical technique for pressure calibration is the use of fixed points on the pressure scale, in close analogy to the fixed points of the International Practical Temperature Scale. The major problem then is to settle on the pressure to be assigned to the fixed points and techniques for uniquely reproducing the points.

Since the pressure fixed points are based upon polymorphic transitions in selected materials, the elimination of both pressure and temperature gradients is of prime importance to maintain sharpness of the transition. These points can only be consistently reported in terms of the equilibrium transition pressure which requires a knowledge of hysteresis and transformation kinetics within the calibrating apparatus. Such measurements have been only crudely attempted in the 50 to 80 kbar range. When one uses fixed points to calibrate high pressure equipment, either equilibrium between the phases should be established or the transition pressure should be corrected for sample hysteresis since it is affected by a non-hydrostatic environment.

In the 0–80 kbar range the polymorphic transitions in mercury, bismuth, thallium, and barium are the best known and therefore the most useful calibration points. Kinetic studies on the bismuth I–II and thallium II–III transitions have shown appropriately small regions of indifference, but the rather large hysteresis and region of indifference for transitions studied above 40 kbar represent serious limitations to improved precision in this range. We recommend that studies be initiated to select materials with transitions which can be more precisely defined in this pressure range. In the 25 kbar range, or what has generally been considered the hydrostatic range, the fixed points are calibrated against the free piston gage, but points above this region are subject to greater uncertainty.

The fixed point calibrations above 80 kbar (based on extrapolation of bismuth and barium transitions) have been measured only on the compression cycle. There is a marked lack of consistency in values reported by various workers and some lack of reproducibility in similar apparatus in different laboratories. At the Symposium on the Accurate Characterization of the High Pressure Environment sponsored by the Carnegie Institution and the National Bureau of Standards, it was decided by those present to adopt a temporary working pressure scale which should represent the best values known to date for the 80 kbar range and the fixed points above 80 kbar. It is important to note that the values agreed upon are in good agreement with the results of this study (see section 3). The temporary working scale adopted at the Carnegie Institution-NBS Conference on High Pressure is presented in table 19.

7.1. Interpolation Methods

The need for some means of interpolation to determine intermediate pressures is obvious. It is recommended that a manganin wire resistance gage be used as the interpolation device whenever a hydrostatic environment is used. These gages should be calibrated at the mercury and bismuth points.

TABLE 19. Temporary working pressure scale

Material	Pressure (kbar)	Temperature
Mercury	7.569	0 °C
Bismuth I–II	25.50	25 °C
Thallium II–III	36.7 ± 0.3	25 °C
Cesium II–III	42.5 ± 1.0	25 °C
Cesium III–IV	43.0 ± 1.0	25 °C
Barium I–II	55 ± 2	25 °C
Bismuth III–V	77 ± 3	25 °C
Tin	100 ± 6	25 °C
Iron $\alpha - \epsilon$	126 ± 6	25 °C
Barium	140	25 °C
Lead	120 – 160	25 °C

Above 30 kbar the shape of the manganin calibration curve is very uncertain. It is recommended that a specific manganin alloy with appropriate specifications be adopted for use in pressure measurements and also that a standard technique for winding and seasoning gages should be specified. This would insure pressure calibration of one percent without further intercomparison of each gage.

Using solid medium systems in the pressure range below 300 kbar, the NaCl scale based on the theoretical equation of state of NaCl is presently the best interpolation technique. It also has the capability of pressure calibration at elevated temperatures. In the 300 kbar region, the theoretical sodium chloride equation of state is in agreement with experimental compression data from shock measurements within about one percent. It is also important to note that the piston cylinder data is in agreement with the experimental sodium chloride equation of state data within one percent at 77 kbar.

Sodium chloride is recommended both in this report and by those in attendance at the Symposium on the Accurate Characterization of the High Pressure Environment as the most suitable substance for high pressure calibration by continuous change in the volume-pressure relationship. The theoretical 25 °C compression data is summarized in section 4 along with a value predicted at the fixed points from x-ray volume measurements coupled with the theory.

For many studies, the only interpolation device will be a calibration of the oil line pressure (press load) against a smoothed curve through the fixed points on the compression cycle. One serious limitation of the accuracy using this method is that the shape of the calibration curve is different for different types of high pressure apparatus. Various types of encapsulation materials and sample geometries further complicate this situation. In order to achieve a fairly accurate calibration using this method, great care must be taken with the details of the calibrant, sample chamber, and how the pressure experiment is carried out. Assuming proper care has been exercised in these items this type of interpolation instrument has a maximum accuracy of 2 to 3 percent and much less on an extrapolation. Although this is the least desirable type of interpolation gage for solid pressure transmitting systems, it is, however, generally the most practical and a fair reproducibility can be achieved in an isothermal experiment.

7.2. Dynamic Pressure Studies

Dynamic shock measurements provide another method of measuring pressure. Actually these measurements give the component of stress in the direction of motion of the shock front but the hydrostatic pressure can be estimated after making strength-of-material corrections. In order to compare with static work the temperatue in the shock front must be determined and then using some appropriate equation of state the results converted to pressure-volume data along an isotherm. Recent volumetric comparisons from various laboratories are in rather good agreement with each other, and in spite of the uncertainties in the corrections involved these results in general agree with static pressure measurements. Uncertainties in rate and nucleation effects attending phase transformations make this technique unsuited to highly accurate fixed point measurements and comparison with static fixed points is not reliable.

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