

viously, 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 \pm 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

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

where G is Gibbs free energy, P is pressure, and V is

molar volume. It follows that

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

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

$$\Delta G = -nFE \quad (16)$$

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

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

and by integration

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

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 $\text{Au/AgI} + \text{MnO}_2|\text{AgI/Tl}$ has a power output showing a maximum at 6500 bar. Bradley et al. (1966) conducted tests with $\text{Pb/PbCl}_2|\text{AgCl/Ag}$ 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 \rightarrow II and the reverse II \rightarrow 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 \rightarrow 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 μ m as compared to about 0.03 μ m in Sample B (99.999% pure). The transition pressure at 20 $^{\circ}$ 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