

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:

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

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/cm².

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 similar 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, appa-

ratus, 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 adaptations have been proposed and used rather widely as a basis of a primary pressure² 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

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