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-