

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

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

conservation of mass

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

conservation of momentum

and

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

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

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

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