

pression is small, perhaps less than 1%, which can of course correspond to quite high pressures for very incompressible materials. Since the velocity of sound in a material can be determined to an accuracy of 0.1% or better and this uncertainty enters the volume calculations as a relatively small additive term, volume results to better than 0.01% may be obtained. A significant advantage of this method is that it yields elastic constants and compression results simultaneously.

A disadvantage of Cook's approach is the restriction to small compressions. In this paper we develop a method which will allow the determination of accurate volume data at high pressure from elastic wave-velocity experiments regardless of the amount of compression involved. To use this method, sonic-velocity data as a function of both pressure and temperature are required; and the temperature dependence of the thermal expansion, heat capacity, and density at room pressure must be known. To illustrate the application of the method, precision sound-velocity measurements have been made in mercury over a range of temperature and pressures and used, in conjunction with available thermodynamic data, in a precision determination of volume as a function of pressure and temperature.

#### EXPERIMENTAL APPARATUS AND PROCEDURE

The velocity of sound in liquid Hg is determined as a function of pressure and temperature by a variant of the pulse-echo technique originally developed by Pellam and Galt.<sup>26</sup> The liquid Hg is placed in a stainless-steel sample holder, and the holder placed in a cylindrical pressure vessel. Pressure is generated by driving a piston into the vessel and is transmitted to the Hg by a liquid pressure-transmission medium. Electrical leads are brought into the vessel through the base-plug pressure closure. The pressure in the vessel is determined by monitoring the resistance of a coil of Au-2.1% Cr wire, which is calibrated as a function of pressure vs a free-piston gauge. Experiments on the variation of sonic velocity in Hg with pressure were performed at three temperatures; 21.9°, 40.5°, and 52.9°C.

A pulsed oscillator, balancing network, preamplifier, and amplifier obtained from the Arenberg Ultrasonic Laboratory, Inc. are arranged as shown in Fig. 1. A 5-Mc/sec pulse of 10- $\mu$ sec duration at a 60-cps repetition frequency is used, and the pulse and sample echoes are displayed on a Tektronix 547 cathode-ray oscilloscope (CRO). It is somewhat difficult to make highly accurate, absolute wave-velocity measurements by the simple pulse-echo technique since it is difficult to account for the relative phase shift between echoes. Therefore, in this work the change in transit time relative to the transit time at 1 atm is measured using

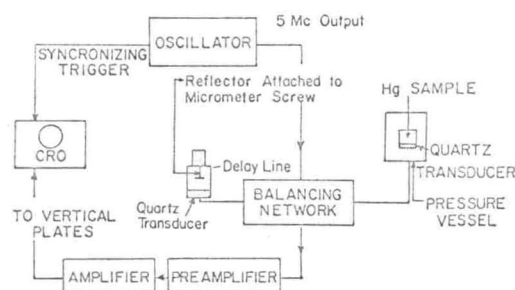


FIG. 1. The high-frequency-pulse equipment.

the first echo only. The initial transit time is computed from the 1-atm sonic-velocity data for liquid Hg of Hubbard and Loomis<sup>27</sup> (accurate to 0.02%) and the known length of the sample. Correction for the change in sample length due to  $T$  and  $P$  was made using the measured linear-expansion coefficient for the Type 303 stainless steel used for the sample holder<sup>28</sup> [ $16.2 \times 10^{-6} (\text{°C})^{-1}$ ] and Bridgman's linear-compression data for Fe<sup>11</sup> [ $-\Delta l/l_0 = 1.904 \times 10^{-7} P - 0.22 \times 10^{-12} P^2$  (for  $P$  in bars)]. Since the magnitude of the length change is small, high accuracy is not needed in making these corrections.

The change in transit time was determined using a variable-Hg delay line consisting of a pot of Hg with a quartz transducer at its bottom and a steel reflector inserted into it from the top. The reflector is connected to a micrometer screw so that changes in its position can be accurately determined. At the outset of each particular high-pressure experiment, a convenient cycle of the unrectified first echo from the specimen and from the delay line is placed in phase on the CRO by adjusting the level of the reflector in the delay line. With the unrectified signals the cycles can be matched to within  $\pm 1.4$  nsec. With application of pressure to the sample a change in transit time results causing a shift in position of the sample echo on the CRO. By adjusting the reflector height in the delay line the same cycles were again brought into coincidence. The change in transit time is then given by  $\Delta t = 2\Delta d/c$ , where  $\Delta d$  is the change in micrometer reading and  $c$  is the sonic velocity in Hg at room temperature and 1 atm. After application and release of pressure, the transit time is found to return to its original value to within 1.4 nsec. In each pressure run half the data points were taken with increasing pressure, and half, with decreasing pressure. Since the delay-line micrometer permits the transit-time change to be determined on the average to about 0.06% and since the sample length can be measured to about 0.03%, the change in velocity is determined to about 0.09%. The absolute velocity itself, however, is determined to 0.04%, including the

<sup>27</sup> J. C. Hubbard and A. L. Loomis, *Phil. Mag.* 5, 1177 (1928).

<sup>28</sup> *Metals Handbook*, T. Lyman, Ed., (American Society for Metals, Cleveland, Ohio, 1948), p. 555.

<sup>26</sup> J. R. Pellam and J. K. Galt, *J. Chem. Phys.* 14, 608 (1946).