

Bridgman? The first evidence in favor of this hypothesis is the work of COOK<sup>(13)</sup> who has found that many complex substances, such as explosives, follow Tait's Law upon isothermal compression, although he did not recognize that the equation he was using was indeed Tait's Law. Further, BEECROFT and SWENSON<sup>(17)</sup> have determined compressibilities on sodium up to 20,000 atm. at various temperatures and have found that they could fit their data fairly well with a three-term alternating pressure series. Essentially, they are truncating the series in equation (4) at the third term and empirically adjusting the constants. These two bits of evidence point towards the idea that Tait's Law should be valid for solids, for which the simple Bridgman approximation is insufficient. What is needed to define the whole validity of the law are sets of data over wide ranges of temperature and pressure on substances which do not obey the simple law.

Such data is available in the literature on the alkali metals. Bridgman reports several different runs on the alkali metals, some of which go up to 100,000 kg/cm<sup>2</sup>. This work was done around room temperature. The various sets of data that Bridgman gives are contradictory. The latest of these<sup>(10)</sup> are entitled "The compression of 39 substances to 100,000 kg/cm<sup>2</sup>", here called Br III, and "Rough compressions of 177 substances to 40,000 kg/cm<sup>2</sup>",<sup>(14)</sup> here called Br II. These two sets of data were reported simultaneously although the work was done on different apparatus. An earlier set of values, called here Br I, also range to 100,000 kg/cm<sup>2</sup>.<sup>(15)</sup> The results of SWENSON<sup>(16)</sup> giving the values of the compressibilities to 10,000 atm. at 4.2°K have been analyzed. Swenson also reports work at 77°K but the details given in the paper are not sufficient for a complete analysis. In some recent work BEECROFT and SWENSON<sup>(17)</sup> have given results for sodium at various temperatures for pressures up to 20,000 atm. Analysis of this data has not been included. Much data on substances other than alkali metals is available and will be reported in a subsequent paper.

### 3. CALCULATIONS

The calculations were done on an IBM 1620 computer. The data was all converted to pressure-specific volume data. Since the number of points was generally limited and unequally spaced, the

data were converted by Lagrangian interpolation<sup>(18)</sup> (5 or 7 point) to a table of equally spaced values; Newton's interpolation formula<sup>(19)</sup> did not yield as consistent a set of data. From this table of data the value of  $(\partial P/\partial v)_T$  was determined numerically using a 7 point Lagrangian differentiation.<sup>(20)</sup> If the Tait equation [equation (4)] is rewritten as

$$(\partial P/\partial v)_T = -\frac{L}{J} - \frac{P}{J} \quad (8)$$

then determining the best straight line of  $(\partial P/\partial v)_T$  versus  $P$  will give us  $L/J$  and  $1/J$  from which  $L$  and  $J$  can be computed readily. This was accomplished by a least squares technique, minimizing the mean square deviation in  $(\partial P/\partial v)_T$  and considering the error in  $P$  to be negligible. This technique was tested on values determined from an analytic curve and gave excellent agreement. One point needs to be mentioned; since the values of  $(\partial P/\partial v)$  are part original data and part interpolated data, the curve of these combined data will systematically reproduce the random variations of the original data. The derivatives derived from this data will accordingly mirror these systematic deviations in a magnified fashion giving rise to a curve that crosses the straight Tait line several times in a seemingly systematic way. The systematic portion of this curve is however a computational artifice and should not be considered a systematic deviation.

#### The lithium data

Figure 1a presents the graph of the derivative versus the pressure for the Bridgman work. The straight line is the least squares fit using the combined Br II and Br III data. The two sets of data do not seem to form a thoroughly consistent straight line. Apparently the derivatives of the Br II set are lower than those of the Br III data, in agreement with the findings of Bridgman who stated that the 40,000 kg/cm<sup>2</sup> apparatus gives a somewhat greater compressibility in the range 25,000 to 40,000 kg/cm<sup>2</sup> than the 100,000 kg/cm<sup>2</sup> apparatus.<sup>(10)</sup> This discrepancy is found with all the alkali metals considered here and is greatly amplified by the use of the derivative rather than the volume.

In addition to the variations due to the use of two different apparatus, the disagreement between