

however, limit the accuracy of some of the results for fast reactions which necessarily would involve trace quantities of the reactants. The deviations from constancy in the gas composition and its accurate determination, for example, is solely responsible for the general scatter of the results in the case of nitrogen and water mixtures. For oxygen mixtures where this problem did not exist, the scatter of the data is small and the accuracy of the relevant cross sections are higher (standard deviation = 10%). Thus, it is apparent that, for practical purposes, the technique which has been described is specially suited to ion-molecule re-

actions of cross sections less than approximately 100 \AA^2 . For faster reactions, the accuracy of composition determination is essential and probably requires the use of gas chromatographic equipment to supplement the analysis of the reactant gas.

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Compressibility of Solid Iodine*

R. GROVER, A. S. KUSUBOV, AND H. D. STROMBERG

Lawrence Radiation Laboratory, University of California, Livermore, California

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A large discrepancy exists between the recently published, static, x-ray-determined compressibility of solid iodine and previously published shock-wave compression data. In order to resolve this discrepancy, static piston displacement compression measurements have been made on iodine up to 40 kbars. The agreement of these measurements with shock data indicates that compressions calculated from x-ray data on iodine are in error.

In a recent paper on the compression of solid iodine at high pressures as measured by an x-ray method,¹ the existence of previously measured shock-compression data on iodine² was overlooked, and in consequence a striking disagreement with shock data was not realized. With the recent development of different, potentially more accurate experimental techniques of measuring P - V relations (x-ray³ and ultrasonic methods⁴) it is important to evaluate the consistency of data from different techniques. In addition, these x-ray data raised serious questions about the interpretation of electrical conductivity measurements on shock-compressed iodine performed at this laboratory.⁵ It is the purpose of this article to review the shock data, for the most part above 100 kbar, and to present new static compression data at lower pressures for the purpose of making a more complete evaluation of iodine compression data.

The data to be compared are summarized in Fig. 1. The room-temperature isotherm determined from x-ray

density measurements lies considerably above the measured shock Hugoniot of iodine. It should be noted that x-ray densities for iodine were calculated from the shift of only two x-ray lines instead of the necessary three. However, the resultant uncertainty in the density determinations, according to Ref. 1, is likely to be less than the $\pm 1\%$ brackets drawn on the x-ray line. The shock data points show a larger than usual scatter in the P - V plot, but when they are displayed in the usual plot of the shock velocity U_s versus the velocity of the shocked material U_p , the relation is linear up to about 600 kbar. The raw shock data are contained in a report⁶ issued by this laboratory and is a recalibrated version of the original data.² The Hugoniot curve in Fig. 1 is calculated from a least-squares fit to the velocity data and corresponds to the linear relation

$$U_s = 0.141 + 1.56U_p \quad (\text{velocities in cm}/\mu\text{sec}) \quad (1)$$

for iodine at theoretical density, 4.95 g/cc. The relation (1) includes a correction for the 1% average porosity of the samples used in the shock-wave experiments. The shock speed (1) extrapolates to a value in excellent agreement with a bulk sound velocity of 0.140, calculated from measured longitudinal and transverse sound velocities, and is consistent with old values of the

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¹ R. W. Lynch and H. G. Drickamer, *J. Chem. Phys.* **45**, 1020 (1966).

² B. J. Alder and R. H. Christian, *Phys. Rev. Letters* **4**, 450 (1960).

³ H. G. Drickamer, R. W. Lynch, R. L. Clendenen, and E. A. Perez-Albuerno, *Solid State Phys.* **19**, 135 (1966).

⁴ O. L. Anderson, *J. Phys. Chem. Solids* **27**, 547 (1966).

⁵ R. Grover (unpublished).

⁶ *Compendium of Shock Wave Data*, M. van Thiel, Ed. (UCRL-50108, June 1966), distributed by C.F.S.T.I., Natl. Bur. Std. (U.S.), U.S. Dept. Commerce, Springfield, Va.

isothermal compressibility.⁷ This is characteristic of nearly all well-behaved solids in the absence of phase transitions, and indicates that Eq. (1) is a reliable interpolation formula below 150 kbar.

A correction for the irreversible heating occurring in shock compression must be made to the shock Hugoniot in order to find the normal isotherm at high pressures. The conventional method⁸ was used in which the thermal pressure of the solid due to shock heating is given by a Mie-Grüneisen equation of state.⁷ The thermal pressure is proportional to the Grüneisen coefficient, $\gamma_G = V(\partial P/\partial E)_V$, which is found from the Dugdale-MacDonald formula.⁸ According to this formula, γ_G equals 2.12 at normal conditions, whereas the thermodynamic value determined from handbook thermal data⁹ and the above bulk sound velocity is 2.37. This disagreement is typical of shock data for metallic elements. Although the calculated isothermal pressure for iodine in Fig. 1 is thus somewhat uncertain, its large displacement from the x-ray-determined isotherm ($\sim 40\%$) is an order of magnitude larger than typical offsets of shock and static data^{3,4} ($\sim 5\%$). It is furthermore surprising that the x-ray isotherm lies above the Hugoniot, since the normal thermal pressure correction is always negative.

After communicating with Drickamer and confirming this discrepancy, we considered ways of resolving the disagreement. A possible cause of the differing compressibilities could have been the high temperatures produced by shock compression. For instance, at 45 kbar the calculated shock heating is 340°C. The fact that solid iodine is a very anisotropic, weakly bound molecular crystal suggests that a high-temperature phase transition to a higher density phase may have taken place in the shock experiments.

It was decided that a convenient starting point for investigating this possibility would be a conventional static P - V measurement with an available piston-displacement apparatus.¹⁰ Such data had not been previously published, although Bridgman¹¹ had reported evidence of a phase transition with a 2% volume change in the vicinity of 15 kbar. An end-loaded press capable of volume measurements up to 40 kbar was used to obtain data shown in the right portion of Fig. 1.

⁷ E. Grüneisen, *Handbuch der Physik* (Julius Springer-Verlag, Berlin, 1926), Vol. 10, p. 1.

⁸ M. H. Rice, R. G. McQueen, and J. M. Walsh, *Solid State Phys.* 6, 1 (1958).

⁹ *American Institute of Physics Handbook*, D. E. Gray, Ed. (McGraw-Hill Book Co., New York, 1963), 2nd ed. Sec. 4.

¹⁰ D. R. Stephens, *J. Phys. Chem. Solids* 25, 423 (1964).

¹¹ P. W. Bridgman, *Collected Experimental Papers* (Harvard Univ. Press, Cambridge, Mass., 1964), Article No. 113.

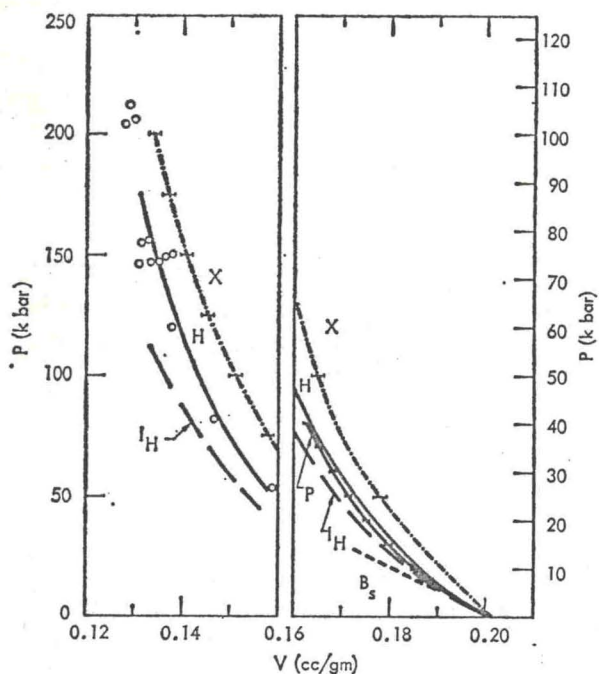


FIG. 1. Compressibility data of solid iodine. Pressure scales on right and left ordinate scales refer to right- and left-half of graph, respectively. Letters refer to different types of data as follows: X—x-ray compression; H—shock Hugoniot; P—piston displacement; I_H —normal isotherm calculated from shock data; B_s —slope of normal adiabat according to acoustic data.

With such a press, phase transitions with 0.5% or less volume change are generally detected. The line P in Fig. 1 represents the average of four runs, two each with the iodine in lead and gold capsules to check the effects of possible reactivity with the capsules. The brackets indicate the spread of the P - V data among the four runs (~ 0.001 cc/g).

The static volume displacement was found to vary continuously over the whole pressure range as indicated in Fig. 1, and thus shows no evidence of the transition reported by Bridgman.¹¹ These volume changes are substantially in agreement with the shock isotherm I_H at low pressure, indicating also that a phase transition does not occur upon shock compression of iodine. We thus conclude that the compressibility of solid iodine given by shock data is correct and much larger than indicated by x-ray data up to 200 kbar.

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