

Shock wave measurements on solid hydrogen and argon*

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(Received 10 May 1973)

Hugoniot data for solid argon (initially at 77°K and 1 bar) and solid hydrogen (initially at 5°K and 1 bar) have been obtained to 143 kbar and 6.4 kbar, respectively, using the projectile impact method. The argon data (at volumes of 15.28, 14.84, and 14.64 cm³/mole) are in fair agreement with previous shock data, and in excellent agreement with the most recent theoretically predicted Hugoniot. The hydrogen data (at volumes of 17.10, 15.32, 15.27, 15.11 cm³/mole) are compared with Hugoniot calculated from published isothermal compression data. For both argon and hydrogen, the shock and isothermal data are self-consistent under the assumption γ/V is constant. To compressions of $V/V_0 \approx 0.65$, the previous isothermal compression measurements on solid hydrogen are consistent with the present shock data.

I. INTRODUCTION

As early as 1939 Megaw¹ measured the compression of solid molecular hydrogen to pressures of 100 kg/cm². Stewart² has extended these measurements to 20×10^3 kg/cm² utilizing a static dilatometric technique. Stewart's 4°K isotherm is the only experimental pressure-volume datum which theoretical models have attempted to reproduce.³⁻¹⁰

Comparatively more work has been undertaken on solid argon. Static compressibility measurements have been reported by Stewart^{2,11} at 38, 65, and 77°K to pressures of 20×10^3 kg/cm². Urvas *et al.*¹² obtained a value for the zero pressure bulk modulus of 12.7 ± 0.6 kbar (at 77°K) using data over a pressure range of 0-20 bar. Hugoniot measurements on solid argon to pressures of 640 kbar are reported by Dick *et al.*¹³ With the exception of one datum point, at 19 kbar, their measurements are not directly comparable with static compression measurements, since the pressures involved in their Hugoniot experiments are higher than those for the static data.

II. EXPERIMENTAL TECHNIQUE

An expendable high-vacuum shroud surrounded the sample target. The target itself was connected to an external sample gas manifold by means of Swagelok type vacuum feed-throughs (see Fig. 1). To impact the target, a gun accelerated flyer plate (2.5 mm thick) entered the chamber by penetrating a thin (0.001") stainless steel foil. Thus, the sample is exposed to a warm environment for times which are less than 0.1 msec. The configuration used in these experiments allows continuous visual inspection of each sample target until shortly before impact. This assures that each sample is free of voids, cracks, and inclusions.

Both target (3 cm in diam) and striker plate (4 cm in diam) were machined from type 304 stainless

steel. A copper flange was soldered to the open lip of the target. A 1.5 mm thick, flat, fused silica window was mounted on the copper flange by means of silicone rubber adhesive (GE type 108) [see Fig. 2(a)].

The present technique employs a thin reflecting foil which is placed within the target substance at a known angle with respect to the shock propagation direction. Upon arrival at the foil, the shock wave rotates the foil slightly and thereby alters the amount of light reflected by it. This provides a redundant set of measurements of the shock transit time through the substance. Initially a thin (0.001") mylar film was bonded to a stainless steel ring of known dimensions. Reflecting aluminum bands 1 mm wide, spaced 1 mm apart, were vacuum deposited on the mylar film. This ring was securely bonded to the inside bottom surface of the target. In later experiments, a microscope slide cover glass (0.007" thick) with gold bands was used in place of the mylar film. Two flat, 1 mm thick, half-silvered mirrors were also bonded to the bottom surface, one on each side of the ring [see Fig. 2(b)].

The target was carefully aligned with the axis of the barrel, of the propellant gun used for shock loading,¹⁴ after which the high-vacuum shroud was put into place. A lucite window in the shroud allowed the target to be viewed during the course of an experiment. After evacuating and then flushing the target chamber with the appropriate gas, target samples were grown in situ, by condensation of the gas and subsequent freezing of the resultant liquid. Sample gases were obtained from the Linde Corporation and had a stated purity of 99.996% and 99.999% for the argon and hydrogen. Growth and retention of the solid was continuously monitored visually up to 1 min before impact [see Fig. 2(c)]. Cooling was accomplished by passing the appropriate cryogen (liquid nitrogen in the case of argon

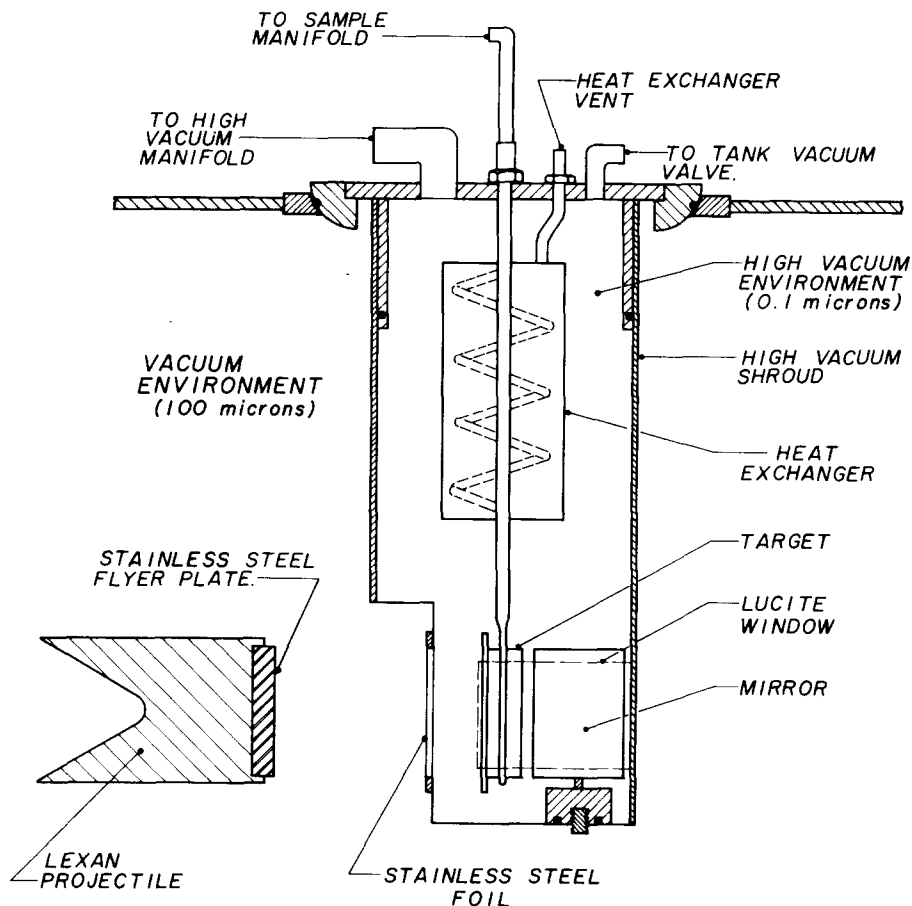


FIG. 1. Experimental configuration (cross section) showing target position and vacuum shroud.

and liquid nitrogen followed by liquid helium in the case of hydrogen) through a copper coil which was attached with pure tin to the outside of the stainless steel sample chamber. For the hydrogen, but not argon, experiments a liquid nitrogen heat exchanger was incorporated into the target immediately above the sample chamber to precool the hydrogen gas.

In Fig. 2(d) we show a typical streak camera record of a hydrogen shot. The extinction of the two outermost lines corresponds to the arrival of the shock at the base of the solid gas sample. The angled break apparent in the five streaked images of the reflecting bands corresponds to the arrival of the shock at the foil. The interval between extinction of the outside mirrors and the interruption of the grid lines gives five measures of the shock velocity within the sample. Such a record is the optical analog of the shorting-pin method for detecting shock arrivals utilized by Dick *et al.*¹³ in solid argon and van Thiel and Alder¹⁵ in liquid argon. The mirror positions can be correlated with the streak lines in the target picture. The bright line crossing the diameter of the target corresponds to the slit position used in obtaining the streak

record. All usable data for these experiments were chosen on the basis of sharp extinction of the outside mirrors, and a definite break in the grid lines on the foil.

III. RESULTS

Particle velocities in the sample were obtained by an impedance match solution.¹⁶ The Hugoniot for stainless steel was taken from McQueen *et al.*¹⁷

$$U_s = 4.569 + 1.490 u_p \quad (1)$$

using a density of $\rho_0 = 7.896 \text{ g/cm}^3$. This Hugoniot was corrected to 77 and 5°K using the thermal expansion data of Coruccini and Gniewek¹⁸ and a Grüneisen parameter of 2.170.¹⁷

In Table I we present Hugoniot data for solid argon and solid hydrogen. Figure 3 shows our argon data plotted along with the data of Dick *et al.*¹³ We note, that at a given compression our data lie at a slightly higher pressure than do those for Dick *et al.*,¹³ however, they agree within the error bars. Ross¹⁹ has recently constructed theoretical Hugoniot curves for solid argon utilizing an exponential-six interaction potential. He fit the potential to the liquid

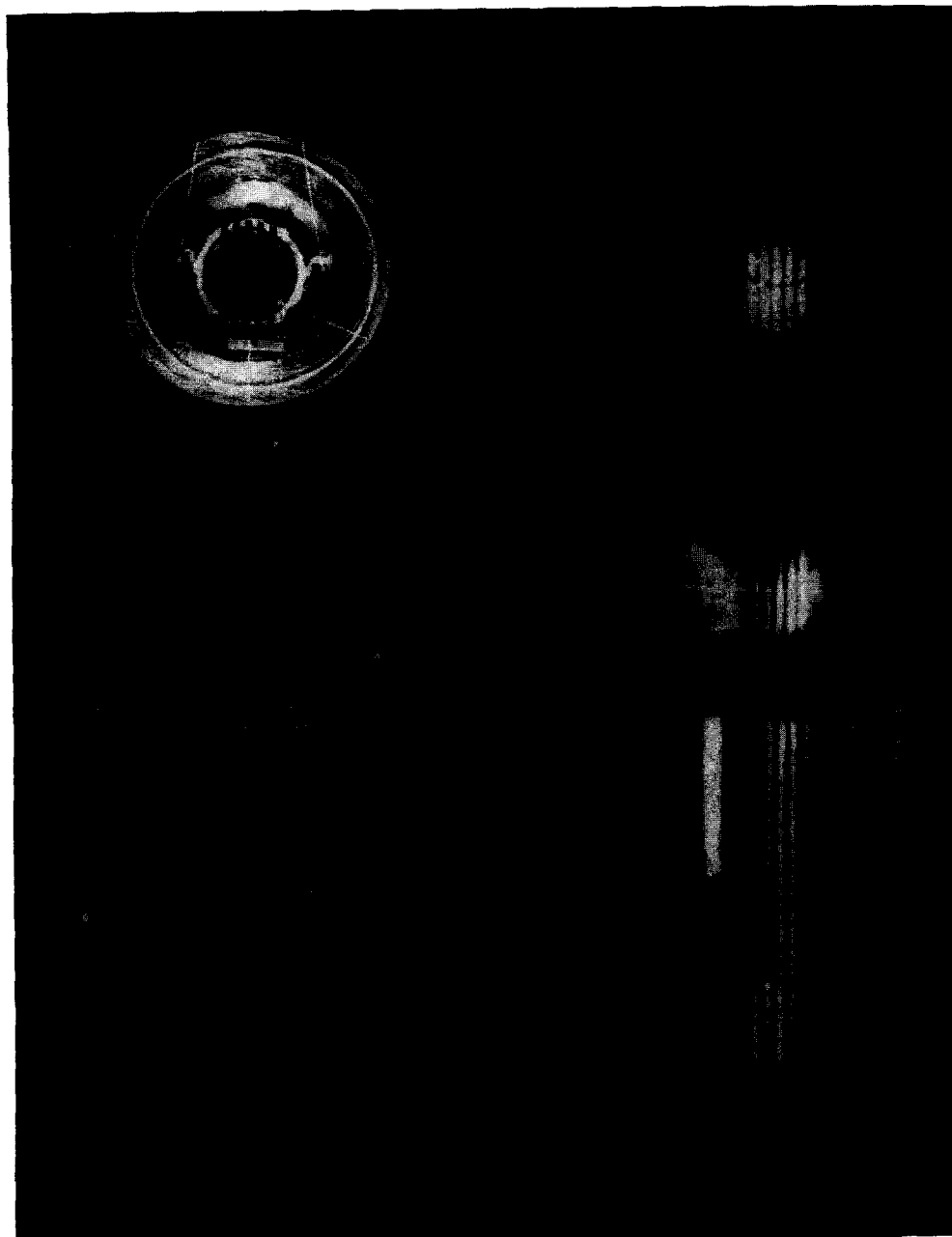


FIG. 2. (a) Solid hydrogen target. (b) Cross section of target showing position of foil and mirrors. (c) Half grown solid hydrogen crystal, showing liquid-solid interface. (d) Target prior to experiment, with a typical streak camera record below. Next to the record is the time calibration.

argon Hugoniot of van Thiel and Alder¹⁵ and then calculated a Hugoniot based on the solid density. His best theoretical model does not reproduce the Dick *et al.* data well. He concludes that the data of Dick *et al.* on solid argon and van Thiel and Alder on liquid argon are consistent within the error bars, but they are not in excellent agreement. Kerley²⁰ has presented a Hugoniot for solid argon calculated on the basis of Debye theory which appears to agree with that calculated by Ross. In Fig. 3 we plot the Hugoniot for solid argon using Ross' best fit to the interaction potential,²¹ as well as the theoretical Hugoniot of Kerley. The agree-

ment with our data is excellent.

We interpret the essential agreement between the two sets of data, and the excellent agreement with the theoretical Hugoniot to mean that the immersed foil technique is a viable and useful method for measuring shock velocities in transparent solid gas samples.

Temperatures along the argon Hugoniot were calculated with the method of Walsh and Christian²² by combining both sets of data. Using these temperatures, a 77°K isotherm was calculated. The agreement between the calculated isotherm and

TABLE I. Hugoniot data for solid argon and solid hydrogen.

Shot number	u_p (mm/ μ sec)	U_s (mm/ μ sec)	P (kbar)	V (cm ³ /mole)	T ($^{\circ}$ K)
ARGON					
Initially at 77 $^{\circ}$ K and 1 bar		$V_0 = 24.21$ cm ³ /mole	$\rho_0 = 1.65$ gm/cm ³	Lawrence and Neal (1965)	
246	1.425 \pm 0.009	3.86 \pm 0.17	90.8 \pm 4.5	15.28 \pm 0.75	1367
248	1.650 \pm 0.010	4.27 \pm 0.18	116.1 \pm 5.8	14.84 \pm 0.74	1883
249	1.850 \pm 0.011	4.68 \pm 0.20	143.0 \pm 7.2	14.64 \pm 0.73	2444
HYDROGEN					
Initially at 5 $^{\circ}$ K and 1 bar		$V_0 = 22.65$ cm ³ /mole	$\rho_0 = 0.089$ gm/cm ³	Megaw (1939)	
275	0.801 \pm 0.005	3.31 \pm 0.13	2.36 \pm 0.11	17.10 \pm 0.60	38
254	1.496 \pm 0.010	4.63 \pm 0.21	6.16 \pm 0.32	15.27 \pm 0.79	71
282	1.515 \pm 0.011	4.71 \pm 0.20	6.36 \pm 0.32	15.32 \pm 0.76	73
283	1.525 \pm 0.008	4.62 \pm 0.16	6.27 \pm 0.27	15.11 \pm 0.79	72

the experimentally determined isotherm is excellent. This agreement suggests that the assumptions implicit in the Walsh and Christian method (γ/V is constant and C_V is constant) are valid to compressions of $V/V_0 \approx 0.6$ for solid argon. The values for the specific heat, $C_V = 5.76$ cal/mole \cdot $^{\circ}$ K, and for the Grüneisen parameter, $\gamma = 2.50$ at a volume of 24.2 cm³/mole where taken from the data of Lawrence and Neal.²³ In the $U_s - U_p$ plane, the zero particle velocity intercept for our data is 1.10 ± 0.07 km/sec (for the combined sets it is 1.05 km/sec). This is consistent with the bulk sound speed of 1.05 km/sec calculated from the data of Lawrence and Neal.²³ Dick *et al.*¹³ calculated that the Hugoniot crossed the melting line at 250 kb with a temperature of 5900 $^{\circ}$ K. Using the Walsh and Christian method we calculate a temperature of ~ 4900 $^{\circ}$ K at this pressure. On this basis it appears that the present Hugoniot data lie within the solid phase.

However, in the previously mentioned paper of Ross¹⁹ a melting point of 50 kbar at 700 $^{\circ}$ K is calculated for the solid argon Hugoniot. This would imply that our Hugoniot points are in the liquid phase. Resolution of this dilemma awaits the direct experimental measurement of temperatures on the Hugoniot.

Calculation of temperature in hydrogen is not as straightforward as in the case of argon, since it is initially at a temperature where the specific heat changes rapidly as a function of temperature. Therefore, we first calculated a theoretical Hugoniot for hydrogen from the Stewart data utilizing a Grüneisen parameter which varied as

$$\gamma = \gamma_0 (V/V_0)^A. \quad (2)$$

In Fig. 4 we show our Hugoniot data with Stewart's 4 $^{\circ}$ K isotherm, and theoretical Hugoniot calculated using values of A equal to 1.0, 1.25, and 1.50 in Eq. (2). A value of γ_0 equal to 2.34 at a

reference volume of 21.19 cm³/mole²⁴ was used. Good agreement between the calculated and measured Hugoniot was found for the case $A = 1.0$. This corresponds to the assumption that γ/V is constant.

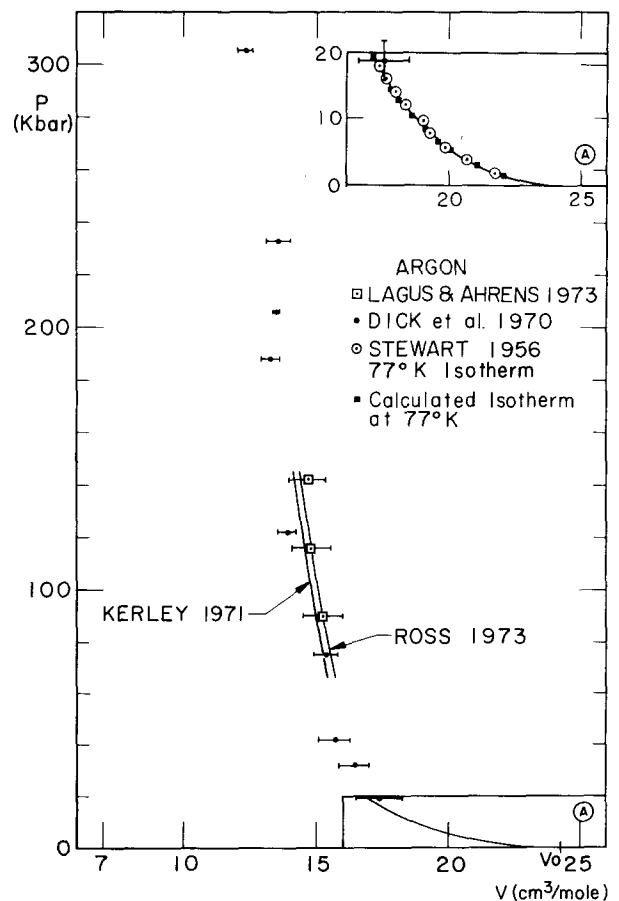


FIG. 3. Solid argon Hugoniot data. The insert displays the calculated and experimentally determined 77 $^{\circ}$ K isotherm at an expanded pressure scale.

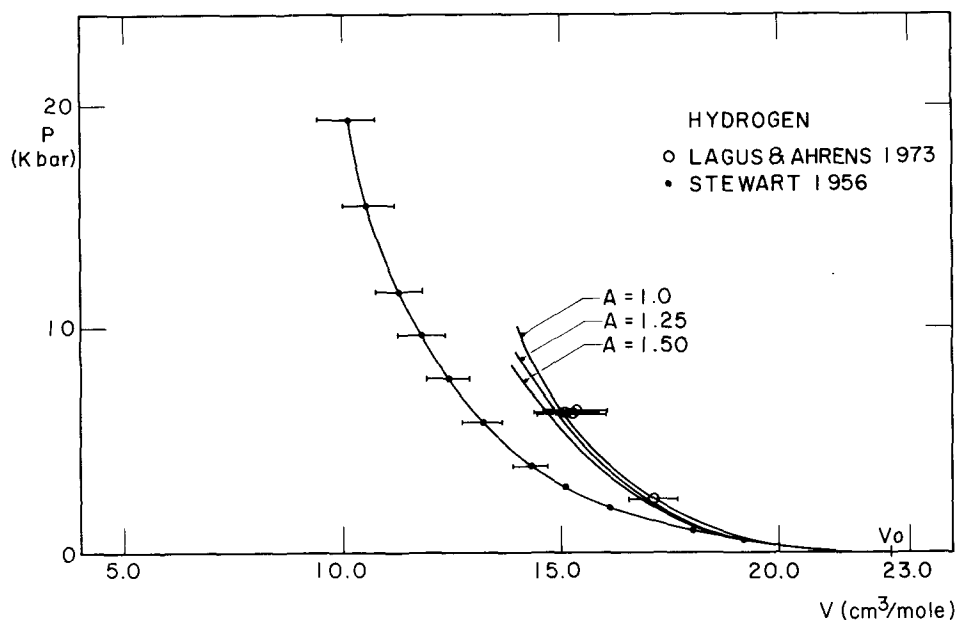


FIG. 4. Solid hydrogen Hugoniot data. Also plotted are the experimentally determined 4°K isotherm, and theoretical Hugoniot calculated from the isotherm (see text).

Temperatures along the hydrogen Hugoniot were calculated by the method of Ahrens *et al.*²⁵ The variation of specific heat was taken from Ahler²⁴ up to 15°K. A Debye model was used to extrapolate to higher temperatures. The melting line of hydrogen has been measured by Mills and Grilly²⁶ to 3500 kg/cm². Extrapolation to 6.3 kbar using their melting line parameters gives a melting point of 86°K. We conclude that the hydrogen was still solid, but just barely.

It might be argued that the agreement between our zero particle velocity intercept and the measured bulk sound speed for the solid augers well for the present data to correspond to the solid phase. However, in shock wave experiments on alkali metals, Rice²⁷ has shown that extrapolation of $U_s - u_p$ data from a region in which shock melting has definitely occurred, results in agreement with bulk sound speeds measured for the solid phase.

IV. CONCLUSIONS

The agreement between the 77°K isotherm calculated from the Hugoniot data for argon and the experimentally determined 77°K isotherm implies that the method of Walsh and Christian for reducing Hugoniot data, assuming γ/V is constant, is a viable technique for argon (at least to compressions of $V/V_0 \approx 0.6$). The excellent agreement between the three argon Hugoniot points and the theoretical Hugoniot of Ross suggests that there may be a systematic error in the data of Dick *et al.*, and that further work on argon utilizing our more direct technique should be undertaken.

For hydrogen, the consistency between the mea-

sured Hugoniot points and the Hugoniot curves calculated from the isothermal compression data, leads us to conclude that the assumption of γ/V is constant is also a reasonably good one. The agreement further suggests that at least to compressions of $V/V_0 \approx 0.65$ the Stewart isotherm is valid.

Due to the moderate uncertainties ($\sim 5\%$ – 6%) extant in the shock wave measurements presented, these data cannot be used to differentiate between various proposed forms of the equation of state. Reduction of the uncertainties by a factor of 2 or 3 should allow such data, when used in conjunction with isothermal compression data, to provide quantitative information on the thermal contribution to the equation of state.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the invaluable assistance in the design and construction of these experiments rendered by Sol Giles and Professor James Westphal. The execution of the experiments was undertaken with the aid of Harold Richeson and David Johnson. This research was supported by National Science Foundation Grant GP-39483.

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