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COMPRESSIBILITY OF LIQUID HYDROGEN
TO 40,000 ATMOSPHERES AND 1100°K

Livermore, California

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ABSTRACT

Liquid hydrogen with an initial density of 0.0710 g/cm^3 at 20.5°K was compressed to a density of 0.192 g/cm^3 . Using available thermodynamic data, a calculation of the Hugoniot path was made which showed that the compressibility is higher than would be expected from the commonly useful linear extrapolation of the Hugoniot curve in the shock-particle velocity plane. Further calculations of the melting lines in the PV plane and the heat capacity showed that the Hugoniot path was completely in the liquid phase and that the temperature of the compressed fluid was 1100°K . Uncertainties in estimating thermodynamic data in the range where measurements are lacking are discussed in line with these calculations, and further experimentation is suggested.

INTRODUCTION

The postwar years have seen great strides in the development of explosive shock-wave techniques used in the compression of solids and liquids. While static methods are older, they have some disadvantages not shared by dynamic experiments. The strength of the sample containers and anvils limits the temperature and pressures that can be reached. This limitation is specially restrictive in the case of liquids and gases that leak through seals at pressures considerably below the yield point of the hardest anvil materials. This problem is especially severe in the case of hydrogen which readily penetrates metals due to its small molecular size. Nevertheless, some excellent work was done in the Netherlands¹ on gaseous hydrogen which was compressed to nearly 3000 atm. At lower temperatures in the

liquid,² the pressures have not been as high, and neither of these contemporary investigators (refs. 1 and 2) have managed to reach the pressures obtained by Bridgman,³ whose work unfortunately was much less accurate. The highest pressures reached thus far were obtained by Stewart⁴ on the 4.2°K solid. It is the purpose of this paper to show that this data range can be extended by using a shock-wave technique. A single experiment performed on the liquid supplemented the data enough to allow us to sketch out the thermodynamic region of interest.

The pressure and compression behind a plane shock wave were calculated using the Rankine-Hugoniot conservation equations. The technique has been well discussed by Walsh et al.⁵ The two parameters needed are the velocity of the shock wave (U_s) through the sample and the mass or particle velocity (U_p) behind the shock wave. As discussed by Walsh et al.,⁵ adiabatic decompression paths of metals can be calculated using the solid state models of Slater or Dugdale and McDonald.

These decompression paths were calculated for the sample container used here. The particle velocity behind the shock in the container could, therefore, be obtained from the "free surface" velocity (U_{fs}), which is the sum of the particle velocity caused by initial compression and the velocity gained by decompression at the surface of the sample container (see Fig. 1). A measurement of the shock velocity in the liquid sample can then be used to obtain the container-sample interface condition on the decompression adiabat of the container. This yields pressure (P) and particle velocity (U_p) in the sample. The volume and energy change can then be obtained from the conservation equations.

EXPERIMENTAL

Configuration of the sample holder, insulation, and explosive is schematically indicated in Fig. 1a. Details, such as electrical leads, sample and vacuum lines, and thermocouples, have been left out. The sample holder is machined from a single block of magnesium alloy.* The configuration is cylindrically symmetric. The cavity α contains the sample. Surrounding the space α , there is an annular space (β) where the shock velocity and free surface velocity of the magnesium container (A) are measured. Cover plate B holds several probes (p) and isolates the sample from

* The alloy used was AZ31B magnesium with a density of 1.775 ± 0.003 g/cc.

(b) PIN

Fig. 1. Experimental assembly.

the evacuated space β , which again is isolated by c from the atmosphere.

The general configuration of the barium titanate shock-wave detector (p) used in this experiment is sketched in Fig. 1b. The detector consists of a cylindrical shield closed off by an 0.05-mm metal shim at the bottom. An axially polarized BaTiO_3 crystal is clamped between a central conductor and this shim. The central conductor and the sides of the crystal are insulated from the cylindrical shield. All probes had this general shape. Those which were used to measure the shock properties in magnesium were either spring-loaded on the surface or suspended from a holder with set screws. Only the probes suspended in the sample were soldered in the holder.

All seals were made with Teflon gaskets. The outer area (Y) provides space for the coolant. The cylindrical assembly A is mounted on a cylindrical steel spacer (S), which together with the 5-mm brass plate D forms a 2.5-cm gap which was found necessary to obtain the desired temperature in the sample. The assembly is mounted in a wooden box of which the bottom K is shown. The ring R provides a means of supporting the spacer S in such a way that the bottom surface of D is at the same level as the bottom surface of K. The remaining space inside the box is filled with Styrofoam insulation. A 2-in. layer of Styrofoam below D, covered by a Teflon sheet, is remotely removed. The spaces marked "void" are flushed with helium to prevent air condensation. The lower void between the explosive and box was sealed with a flexible polyethylene membrane. A 2- to 3-sec induction period was followed by a rapid rise in the vapor pressure of the liquid hydrogen sample after plate D and the high explosive were brought into contact. The total operation, from removing the insulation to detonation of the explosive, was, therefore, automated to limit delays. The estimated delay between contact of D and the H. E. and detonation was thereby reduced to less than 0.1 sec.

RESULTS

The parameters obtained in this experiment, which are summarized in Table I, are ρ_0 , U_{fs} , and U_s of the magnesium sample and ρ_0 and U_s of the hydrogen sample. The remaining quantities listed in Table I are obtained from the conservation conditions and the interfacial pressure and mass velocity continuity at the sample-metal interface. The deviations given in the table are believed to have a confidence level of 90%. The absolute accuracy is, of course, difficult to establish on a single experiment.

Table I. Shock-wave parameters of magnesium container and hydrogen sample.

Material	T ₀ (°K)	P ₀ (atm)	ρ ₀ (g/cc)	U _s (cm/μsec)	U _{fs} (cm/μ sec)	U _p (cm/μsec)	ρ ₀ /ρ	P (Mbar)
Mg	20.45 ± 0.05		1.803	0.842 ± 0.007	0.640 ± 0.003	0.312 ± 0.0015	0.629 ± 0.0025	0.474 ± 0.006
H ₂	20.45 ± 0.05	1.8 ± 0.05	0.0710	0.940 ± 0.011		0.592 ± 0.003	0.370 ± 0.01	0.040 ± 0.0005

Confidence in the deviations given rests on experience gained with 13 similar experiments done with liquid argon. In addition, some uncertainty still exists in the equation of state of magnesium in this pressure range.

FURTHER CALCULATIONS

A. Available Data

It is of interest to explore the available data to evaluate what further contributions can be made, as well as to obtain an estimated Hugoniot going through the measured point. The volumetric properties of hydrogen have been investigated by a number of people. The best static compressibility measurements taken to date in the region of interest here were reported by Michels *et al.*,¹ and by a number of investigators at the Bureau of Standards² in Boulder, Colorado. The regions covered by these investigators are displayed in the pressure volume plane in Fig. 2. The data from these two sources are internally self-consistent. In an earlier report, the NBS group admitted some difficulty in establishing their errors. Problems showed up in the estimation of the volume dependence of the heat capacity.

$$\partial C_v / \partial V)_T = T \cdot \partial^2 P / \partial T^2 |_V$$

This problem was later solved by introducing additional heat capacity data which greatly reduced the errors in entropy and heat capacity. The NBS group² feels, however, that first derivatives can be obtained from this data to a nominal accuracy of about 0.3 to 0.5%. Maximum errors of 5%, do however, occur in first derivatives. Michels' isotherms were fitted with an accuracy of ± 0.01% with a five parameter expansion. Here no peculiarities are found in $(\partial^2 P / \partial T^2)_V$.

Fig. 2. Range of the available data considered in the PV plane.

Two isotherms measured by Bridgman³ at 30° and 60°C are also included in Fig. 2. Unfortunately, the large deviation of these data from Michels' measured compressibility places doubt on their accuracy.

One more set of high pressure points is available from an isotherm measured by Stewart⁴ at 4.2°K. These latter points bound the PV plane of hydrogen at the low volume end.

B. Estimates of the Hugoniot Curvature

The Hugoniot locus passes through the region of the NBS data and can be calculated directly in this range using the condition that

$$\Delta E = \frac{1}{2} (P_0 + P) (V_0 - V).$$

In the limit of 1 atm, the shock velocity must approach the sound velocity measured by Van Itterbeek.⁶ This made it possible to smooth a spurious but small fluctuation in earlier NBS data. Above 300 atm, Michels' and Bridgman's data may be used. Rather large extrapolations of Michels' data have to be made to reach these Hugoniot conditions. For convenience, the fitted isothermal paths were used. For isotherms between -175° and -160°C, the pressure extrapolation is tenfold. At room temperature, this extrapolation is more than fourfold.

In the course of this work, it was noted that relatively large errors in the energy estimated along an isotherm changed the pressure at which the calculated Hugoniot intercepts it, without appreciably changing the Hugoniot slope $(dU_s/dU_p)|_H$ in the U_s, U_p plane. Pressure errors are relatively important. A large difference in this Hugoniot slope was, therefore, obtained by comparing Michels' data to the data of Bridgman. While the positive sign of the high-order terms in Michels' P vs V expansion suggests that the extrapolations would yield high values of pressure, the Bridgman isotherms were even stiffer. In Fig. 3, the Hugoniot is drawn in the shock-particle velocity plane. This representation was chosen because it yields a relatively slowly curving Hugoniot locus. It may be noted that the Hugoniot points obtained from Bridgman's isotherms force us into a considerably higher order fit than do Michels' data. The most reasonable Hugoniot (Table II) is the one obtained by giving the most weight to Michels' data.

Fig. 3. Hydrogen Hugoniot in the shock vs particle velocity plane.

Table II. Pressure-volume curves of hydrogen.

4.2° Isotherm			H ₂ Hugoniot				
E (cal/g)	P (atm)	V (cc/g)	E (cal/g)	U _s (mm/ μsec)	U _p (mm/ μsec)	P × 10 ³ (atm)	V (cc/g)
-86.445	0.968	11.233	-62.9	<u>1.122</u>	0.000	0.001	14.087
-86.34	54.28	10.911	-62.7	<u>1.2</u>	<u>0.045</u>	<u>0.0388</u>	<u>13.56</u>
-85.12	193.4	10.415	-60.4	<u>1.4</u>	<u>0.1455</u>	<u>0.1437</u>	<u>12.62</u>
-81.97	386.9	9.919	-55.4	<u>1.6</u>	<u>0.250</u>	0.281 ₂	11.88 ₆
-76.24	636.6	9.423	-35.9	2.0	0.475	<u>0.655</u>	<u>10.74</u> ₁
-67.13	958.3	8.927	+65.05	3.0	1.035	2.176	9.227
-53.65	1392.0	8.431	+83.0	<u>3.145</u>	<u>1.105</u>	<u>2.436</u>	<u>9.137</u>
-33.78	2033.0	7.935	+256.5	4.0	1.635	4.583	8.329
- 4.78	2971.0	7.439	+569.1	5.0	2.300	8.058	7.607
37.64	4313.0	6.943	1041.0	6.0	3.040	12.78	6.949
99.36	6198.0	6.448	1070.5	<u>6.10</u>	<u>3.08</u>	<u>13.16</u>	<u>6.974</u>
188.55	9011.0	5.952	1699.0	7.0	3.840	18.83	6.359
318.37	13130.0	5.456	2554.0	8.0	4.680	26.23	5.846
515.92	20430.0	4.960	3617.0	9.0	5.550	35.00	5.400
			4124.0	<u>9.40</u>	<u>5.92</u>	<u>38.99</u>	<u>5.215</u>

NOTE: Double lines indicate experimental and single lines calculated points. The other points were read from a large scale smoothed plot in the U_s, U_p plane.

C. The Thermal Pressure and the Grüneisen Approximation

We noted above that relatively large uncertainties in the energy extrapolations along Michels' isotherms did not affect the Hugoniot path appreciably. These errors do show up, however, in the pressure-temperature plane. It was, therefore, decided to attempt temperature calculations along a constant volume path. To be considered here are the effects of the two-phase region and the volume dependence of the heat capacity. Let us first investigate the validity of Grüneisen's rule to evaluate its usefulness in further calculations.

Mie and Grüneisen proposed that the equation of state of a condensed material can be written as

$$PV = V \cdot \partial U / \partial V + \gamma E \quad (1)$$

if we assume that all vibrational states have the same volume dependence.⁷ In Eq. (1) U is the potential energy and E the kinetic energy of a system of oscillators. Use of γ in the calculation of equation of state properties of solids has been found quite useful, for the thermodynamic value

$$\gamma = V \cdot \partial P / \partial E \big|_V \quad (2)$$

shows only a slight temperature dependence. This result can be obtained theoretically if not all states have the same γ . In that case, appropriate averages can be taken⁸ that show some temperature dependence. Furthermore, a semi-empirical result of the application of the theoretical Dugdale and McDonald or Slater expressions for γ to measured Hugoniot curves⁵ is that $\gamma/V \simeq \text{constant}$.⁹

If the above conditions hold for hydrogen, we can readily determine the energy change along Stewart's isotherm using

$$dE = \left[T \gamma C_V / V - P(V) \right] dV, \quad (3)$$

while

$$\partial P / \partial T \big|_V = C_V \gamma / V$$

defines the thermal pressure change between the 4.2°K isotherm and the solidus temperature.

Values for the Grüneisen γ may be calculated over wide conditions of volume and temperature using Michels^{1,10} and NBS's data for the gas and liquid. Figure 4 shows at high temperatures the expected approach to the ideal gas value of 0.4. The high-temperature Levelt data does not extrapolate smoothly to the NBS curves, but the deviations are within the error limits discussed in section A.

The significance of the NBS values near the liquid gas interface can be checked from other sources. Johnston et al.,¹¹ measured the compressibility of the liquid as a function of temperature. Volume expansion along the vapor line and vapor pressures were obtained by Scott and Brickwedde¹² and White et al.,¹³ respectively. The heat capacity (C_s) was obtained by

Fig. 4. Variation of $V(\partial P/\partial E)_V = \gamma_G$ of hydrogen as a function of temperature at various volumes. Solid lines indicate data range. Dashed lines show extrapolated range. NBS data is at $T < 100^{\circ}\text{K}$. Michels' data is at $T > 100^{\circ}\text{K}$.

Smith et al.¹⁴ To correct derivatives taken along the liquid-vapor phase line to constant volume and pressure, the following expressions may be used:

$$\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial V}{\partial T}\right)_S - \left(\frac{\partial V}{\partial P}\right)_T \cdot \left(\frac{\partial P}{\partial T}\right)_S = 0.2217 \frac{\text{cc}}{\text{g} \cdot ^\circ\text{K}},$$

$$C_P = C_S + T \left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial P}{\partial T}\right)_S = 9.72 \frac{\text{cal}}{\text{mole} \cdot ^\circ\text{K}},$$

$$C_V = C_S + T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_S = 5.84 \frac{\text{cal}}{\text{mole} \cdot ^\circ\text{K}}.$$

Three ways of defining γ yield

$$\gamma = \frac{V}{C_V} \cdot \left(\frac{\partial P}{\partial T}\right)_V = 2.02,$$

$$\gamma = \left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial P}{\partial V}\right)_T \cdot \frac{V}{C_V} = 2.13,$$

and

$$\gamma = \frac{1}{V} \cdot \left(\frac{\partial V}{\partial T}\right)_P \cdot c \cdot \frac{1}{C_P} = 2.03,$$

in complete agreement with Fig. 4. Furthermore, the value of 2 is in line with those quoted for a large number of solids.¹⁵

If, however, for the solid, the expansion coefficient obtained by Megaw from her measurements of $C_P - C_V$ are used with her compressibility¹⁶ and a Debye temperature (θ_D) of 122°K, a rather large value for γ is calculated.

$$\gamma_{4.2^\circ} = \frac{\alpha_P V}{\beta_T C_V} = \frac{(2.4)10^{-3} \text{ } ^\circ\text{K}^{-1}}{(6.9)10^{-10} \frac{\text{cm}^2}{\text{dyn}}} \cdot \frac{22.6}{(0.0794)10^7} \frac{\text{cc/mole}}{\text{ergs/mole } ^\circ\text{K}} = 100.$$

This value gets even larger if Stewart's compressibility of $5.0 \times 10^{-10} \text{ cm}^2/\text{dyne}$ is used. Now, if one makes the reasonable approximation that β/V is a constant, Stewart's compressibility, combined with the volumes of ref. 16, and $C_P - C_V$ of ref. 17, yields somewhat smaller values. At 13, 10, 7, and 4 °K, we respectively obtain the values 4.3, 6.0, 25, and 55. The disagreement here is essentially due to the uncertainty of the difference between the constant pressure and constant volume heat capacities given by Megaw.

We have seen, therefore, that in the liquid the value of $V \partial P / \partial E|_V$ (aside from some lack of quantitative agreement) shows a gradual temperature-volume behavior and incidentally is not out of line with values for other elements.¹⁸ The rapid rise of this value in the solid, however, is anomalous. This may be further emphasized by considering heat capacity measurements. For a lattice the Grüneisen constant can be written as $\gamma = \partial \ln \nu / \partial \ln V$, with ν being a lattice frequency and the assumption being that $\partial \ln \nu_i / \partial \ln V = \partial \ln \nu_j / \partial \ln V$ for all i and j . This can then be applied to the Debye lattice to yield

$$\gamma_D = \frac{\partial \ln \theta}{\partial \ln V}.$$

Measurements of C_V made by Guenter Ahlers at the University of California¹⁷ suggest that $\gamma_D = 2.5 \pm 0.1$. But the same data combined with C_V of para-hydrogen confirm Megaw's measured expansion between 4.2 and 13.9 °K. Therefore, it must be concluded that Grüneisen's rule does not hold for low-temperature solid hydrogen.

D. Phase Line Calculations

Because of the rapid variations in γ , an attempt to use the assumption that γ/V is a constant yields large deviations between experimental and calculated phase lines at low pressures. A better assumption is that $\partial P / \partial T|_V$ is constant. This reduces the error but still causes inconsistencies between calculated Hugoniot and phase line energies above the range where phase lines were measured. We are, therefore, forced to make $\partial P / \partial T|_V$ a function of volume. The values listed in Table III are essentially based on the volume dependence in the liquid. Using Michels' and NBS's data, $\partial P / \partial T|_V$ was extrapolated to low temperatures at various volumes. This volume dependence $\partial / \partial V \cdot \partial P / \partial T|_V$ was adopted after scaling the 11.235-cc/g value down to the value of the solid. With the pressures and temperatures of melting given by Goodwin's equation¹⁹

$$(P - 0.071)/(T - 13.947) = 30.3310 \cdot \exp(5.693/T) + 2T/3$$

the solidus in Fig. 5 may then be obtained. The two liquidus curves were obtained by alternately assuming the entropy ($\Delta s_m = 0.995$ cal/g-°K) and the enthalpy of melting ($\Delta H_m = 13.89$) to be constant. The determination of the heat capacity is discussed below.

Table III. The phase line obtained assuming that $\left. \frac{\partial P}{\partial T} \right|_V$ varies as in column 6.

Melting Line (ref. 12)		Solidus				Liquidus With $\Delta S_m \equiv \text{constant}$			Liquidus With $\Delta H_m \equiv \text{constant}$		
T (°K)	P (atm)	V^s (cc/g)	E^s (cal/g)	$\bar{Y}^s$	$\left. \frac{\partial P}{\partial T} \right _V^s$ (atm/°K)	V^l (cc/g)	E^l (cal/g)	$\bar{Y}^l$	V^l (cc/g)	E^l (cal/g)	$\bar{Y}^l$
19.25	187.8	10.911	-82.23	8.56	8.87	11.923	-67.67	1.91	11.645	-71.68	2.18
24.1	405.9	10.415	-76.60	6.28	10.68	11.247	-60.79	0.77	10.897	-67.44	1.75
29.6	703.1	9.9192	-70.6	5.92	12.45	10.628	-53.9	0.36	10.253	-62.0	1.58
36.0	1099.0	9.4232	-59.8	5.23	14.53	10.035	-41.5	0.65	9.660	-51.9	1.64
42.8	1587.0	8.927	-45.8	4.65	16.28	9.464	-25.6	0.98	9.102	-38.4	1.55
50.45	2219.0	8.4313	-26.4	4.13	17.88	8.9	-4.2	1.29	8.561	-19.4	1.68
60.1	3123.0	7.9353	+1.0	3.65	19.5	8.362	+26.8	1.43	8.0301	+7.9	1.58
71.86	4396.0	7.4394	+44.0	3.21	21.06	7.793	74.3	1.36	7.5083	50.7	1.42
85.9	6161.0	6.9434	+102.4	2.85	22.62	7.247	137.9	1.22	6.9928	108.9	1.25
102.4	8578.0	6.4475	+188.1	2.57	24.33	6.709	230.8	1.07	6.4831	194.6	1.08
122.1	12053.0	5.9515	+308.2	2.29	25.8	6.176	359.4	0.90	5.9771	314.7	0.92
145.85	16969.0	5.4555	+479.0	2.03	27.1	5.647	541.4	0.75	5.4738	485.5	0.77
182.40	25455.0	4.9596	+746.7	1.75	28.2	5.1156	825.2	0.59	4.9715	753.2	0.62

Superscript s indicates solid values.

Superscript l indicates liquid values.

$\bar{Y}$ is a temperature average between isotherm and solidus for the solid; and liquidus and Hugoniot for the liquid.

Fig. 5. The pressure-volume plane of hydrogen: I_1 - 4.2°K isotherm, I_2 - -175°C isotherm, I_3 - 30°C isotherm, I_4 - 60°C isotherm, S_1 - calculated solidus, l_1 - calculated liquidus with $\Delta H_m = \text{constant}$, l_2 - calculated liquidus with $\Delta S_m = \text{constant}$, H_P , H_R - Hugoniots with initial conditions at 14.1 and 10.7 cc/g, $\circ$ - NBS liquidus.

Several significant observations may be made here. First of all, the Hugoniot with initial conditions at 28.4 cc/mole and 20.1°K does not cross the phase line as is apparent from Fig. 5. The liquid phase line volumes are known accurately to 340 atm from direct measurement.² These data are indicated by the circles and favor the liquidus obtained by assuming a constant enthalpy of fusion. The initial decrease of γ in column 9 of Table III is, therefore, readily interpreted as an overestimate of the pressure along the liquidus. One would, indeed, be tempted to say that $\gamma/V = \text{constant}$ is a good approximation for the liquid if the initially rapid decrease in the last column of Table III is ignored.

E. The Value of C_V and Hugoniot Temperatures

Before the Hugoniot temperature can be calculated, an estimate must be made of C_V . It is well known that an assembly of harmonic oscillators has a value of $3R$ in the high temperature limit and leads to a Debye-type curve at lower temperature. But it is also realized that the repulsive part of the two-particle potential is considerably larger than quadratic. It is, therefore, possible that at any volume and sufficiently high temperature the interparticle potential can be effectively represented as a step function. The heat capacity is then again that of an ideal gas. Fortunately, heat capacities can be derived from the accurate data taken by deGraaf.^{10,20} Figure 6 shows the calculated heat capacities from this source as solid lines together with the zero density (or ideal gas) value for the rigid rotor. While it is clear that compression has increased the value of C_V by $0.35R$ at 13.22 cc/g, the rate $\partial C_V / \partial \rho$ does not change much over the measured range. Neither $\partial C_V / \partial T$ nor $\partial C_V / \partial \rho$ seem to decrease with density. The latter quantity is plotted in Figs. 7 and 8. Figure 7 can be obtained directly by differentiating the data in refs. 10 or 20. While the trend is not clear cut, the data suggest that the rate of change approaches a constant. Data published by Rabinovitch²¹ (Fig. 8), however, predict an increasing rate of rise of $\partial C_V / \partial \rho$ with density. As further support for the contention that hydrogen at smaller volumes vibrates in a more harmonic potential, we note in Fig. 6 that the NBS data also show a higher heat capacity at smaller volumes. While lack of quantitative agreement is deplorable, the trend is consistent with data.

Fig. 6. The heat capacity of hydrogen from various sources.

- Michels (ref. 20) or Levelt (ref. 10)
- Ideal gas-rigid rotor value.
- AIP Handbook with $\theta_D = f(V)$ estimated here.
- NBS Circular 7987 data.

Fig. 7. Dependence of the density derivative of the heat capacity on temperature and volume [Michels et al., *Physica* 25, 1097 (1959)].

Fig. 8. Dependence of the density derivative of the heat capacity on temperature and volume [V. A. Rabinovitch, Inzhenerno-Fizicheskiy Zhurnal 5, No. 5, 30 (1962)].

The excitation of the rotational motion does not seem to be visibly impeded by compression to 840 amagats. It seems, therefore, reasonable to assume a Debye model with a superimposed free-rotor heat capacity to yield a gradual rise of C_V to 8 cal/mole-°K. The energy-temperature curves for this model are represented in Table IV. Here E_t is the sum of the Debye lattice energy (E_D), the energy of the diatomic rigid rotor (E_r), and the energy of the diatomic harmonic oscillator. The Debye temperature is designated by θ . An estimate of the range of the Debye temperatures to be used may be obtained from the solid-state heat capacity measurements.¹⁷ These indicate a γ_D value of 2.5. If γ_D is independent of volume, we obtain a θ_D of 800°K at 5 cc/g. If γ_D decreases with volume as do the Dugdale, McDonald, or Slater forms, a constant γ/V value of 2.5/21.2 mole/cc and a value of 450°K, at 5 cc/g are more reasonable. This latter value of $\gamma_D/V = d \ln \theta_D / d \ln V$ was used in the calculation of the temperature. The Debye model was assumed to hold over the entire volume range.

Table III values were used in the Hugoniot temperature calculations. Part of this table is reproduced in Table V to aid the calculation and is tabulated together with the Hugoniot conditions at the listed liquid volumes. Table Va gives the low pressure Hugoniot conditions consistent with NBS Circular 7987.² Figure 9 shows the temperature obtained with both the constant enthalpy and constant entropy assumptions on the phase line. The two extremes probably should be averaged if the variation of entropy and enthalpy of melting as measured by Bartholome²² holds true at higher temperatures. He found that the enthalpy of melting increased, but the entropy change decreased with pressure. It may be of interest to note, however, how close the extrapolated values of temperature obtained from Michels' data (horizontal lines) compare to the above method of calculation.

F. Discussion

Further experimentation on hydrogen could most profitably be done in the region of the phase line. In the first place, the thermal variation of energy and pressure can be expected to be a very nonlinear function in this region. It does not need to be emphasized that this makes theoretical estimation difficult.

The other reason is the current uncertainty about the character of the melting transition at high pressures. The question still exists: At what pressure does this first-order phase transition cease to exist,²³ if at all?

Table IV. Energy of the hydrogen harmonic oscillator (E_{vib}), rigid rotor (E_{rot}) and Debye lattice energy (E_D), as well as the total energy of the lattice (E_t) for different Debye temperatures (θ).

T(°K)	E_{vib}	E_{rot}	$E_D(\theta=105)$	E_t	$E_D^I(\theta=200)$	E_t^I	$E_D^{II}(\theta=300)$	E_t^{II}	$E_D^{III}(\theta=400)$	E_t^{III}	$E_D^{IV}(\theta=450)$	E_t^{IV}
0		0	0		0		0		0		0	
25		0	24.83		5.48		1.68		0.71			
50		0	125.69		54.60		23.09		10.98		8.19	
75		2.6	254.9	257.5	146.81	149.4	81.91	84.5	45.79	48.4	34.63	37.2
100		9.5	400.9	410.4	262.66	272.2	168.73	178.2	109.21	118.7	87.33	96.8
150		49.2	680.4	729.6	539.1	588.3	393.99	443.2			253.09	302.3
200		116.4	972.9	1089.3	803.4	919.8	651.84	768.3	525.32	641.7	471.06	587.5
250		200.8	1267.8	1468.6	1089.4	1290.2	923.8	1124.6			716.00	916.8
300		294.6	1563.0	1857.6	1379.4	1674.0	1205.0	1499.6			977.76	1292.4
350		392.2	1859.2	2251.4								
400		490.9	2156.4	2647.3	1965.2	2456.1	1778.8	2269.7	1606.7	2097.6		
500		689.6	2750.0	3439.6	2555.0	3244.6	2337.7	3027.0	2178.9	2868.5	2093.1	2782.7
600		888.4	3343.5	4231.9			2947.8	3836.2			2668.2	3556.6
700		1087.1	3937.0	5024.1								
800		1285.8	4532.0	5817.8	4334.0	5619.8			3930.4	5216.2		
900	11.18	1484.5	5125.5	6621.2							4421.7	
1000	22.60	1683.2	5744.5	7450.3	5519.5	7225.3	5312.0	7017.8	5110.0	6815.8	5012.0	6717.8
1100	40.24	1882.0	6318.0									
1200	65.08	2080.7	6915.0									
1300	97.85	2279.4	7513.0									
1400	138.84	2478.1	8103.0									
1500	188.34	2676.8	8699.0	11564.0			8280.0	11145.0			7968.0	10833.0
1600	246.43	2875.6	9295.1	12417.0					8667.2	11789.0		
1800	386.39	3273.0	10487.2	14111.0							9750.6	13374.0
2000	555.97	3670.4	11679.3	15906.0	11466.0	15692.0	11250.0	15476.0	11039.0	15265.0	10980.0	15206.0
2500	1061.75	4663.9	14659.7				14220.0		14010.0			
3000	1613.6	5657.4	17640.0				17199				16875.0	
3500	2470.5	6650.9	20620.4									

Table V. Values used to calculate Hugoniot temperatures with a Debye model approximation (V in cc/g, E in cal/g, T in °K, P in atm).

V_s	E'_s	T_m	ΔS_m		E_H	P_H	T_H	ΔH_m		E_H	T'_H	P'_H
			V_ℓ	E_ℓ				V'_ℓ	E'_ℓ			
9.9192	-70.6	27.30	10.673	-53.9	-34.0	720	37.3	10.305	-62.0	-20.8	48.8	920
9.4232	-59.8	32.22	10.080	-41.5	-8.4	1120	53.7	9.710	-51.9	+16.0	70.8	1490
8.9272	-45.8	37.8	9.514	-25.6	+34.7	1760	71.8	9.144	-38.4	+81.4	97.5	2410
8.4313	-26.4	44.35	8.960	-4.2	108.5	2760	104.5	8.598	-19.4	182.8	134.5	3700
7.9353	+1.0	52.70	8.389	+26.8	238.2	4360	140.	8.055	+7.9	357.4	186.	5755
7.4394	+44.0	63.15	7.830	74.3	439.0	6625	199.	7.526	50.7	595.2	250.	8285
6.9434	+102.4	75.9	7.281	137.9	772.3	10140	288.	7.006	108.9	990.3	355.	12280
6.4475	+188.1	91.2	6.736	230.8	1247.0	14720	402.	6.492	194.6	1528.0	498.	17300
5.9515	+308.2	110.3	6.197	359.4	1930.0	20900	574.	5.982	314.7	2288.0	678.	24000
5.4555	+479.0	133.7	5.662	541.4	2946.0	29500	804.	5.477	485.5	3400.0	934.	33200
4.9596	+746.7	167.75	5.128	825.2	4456.0	41700	1168.	4.974	753.2	4992.0	1288.	45800

Table Va. Hugoniot conditions given in NBS Circular 6791.

P	E	T
39	-62.7	21.8
144	-60.4	25.6
281	-55.4	29.1

Fig. 9. Temperature variation along the Hugoniot.

A first reaction might be that a solid-fluid critical point exists simply because all first-order transitions are analogous from the thermodynamicist's point of view and a liquid-gas critical point does exist. Lennard Jones and Devonshire²⁴ and Karase and Pople²⁵ have shown that a transition can be theoretically produced with a relatively simple model that allows the existence of interstitial atoms and two rotational orientations. The critical point they calculated is too low. The models are thus far highly qualitative, and no adequate theory of the solid state exists to resolve the problem.

In Fig. 5, we note that a Hugoniot (H_R) calculated from a sample initially compressed to 100 atm at 4.2°K, crosses the phase line at 3400 atm. Figure 10 shows the U_s vs U_p plot of H_R with the liquid-phase Hugoniot (H_P) (Table II). Table VI lists the pressure and volume as well as the particle and shock velocity of H_R . The first thing we may note is that this Hugoniot probably does not have a two-wave structure in the two-phase region because of the large slope of the adiabat at this point. To determine the slope of the adiabat, we can write

$$\left. \frac{\partial P}{\partial V} \right|_S = - \left. \frac{\partial P}{\partial S} \right|_V \left. \frac{\partial S}{\partial V} \right|_P$$

since $\left. \frac{\partial P}{\partial T} \right|_m = \frac{\Delta S}{\Delta V}$ (Clapeyron Clausius equation)

$$\left. \frac{\partial P}{\partial V} \right|_S = - \left. \frac{\partial P}{\partial S} \right|_V \left. \frac{\partial P}{\partial T} \right|_m,$$

and since in the two-phase region $\left. \frac{\partial P}{\partial T} \right|_V = \left. \frac{\partial P}{\partial T} \right|_m$

$$\left. \frac{\partial P}{\partial V} \right|_S = - \frac{T}{C_V} \left(\left. \frac{\partial P}{\partial T} \right|_m \right)^2.$$

Subscripts S, V, P, and m refer to partials at constant entropy, volume, and pressure and along the melting line. At the conditions of Table III and Fig. 10, we get for the sound velocity: $C = 3.8 \times 10^5$ cm/sec. The condition that needs to be satisfied to obtain a two-wave structure is that

$$C + U_P \leq U_s.$$

We note that this does not hold here, although the conditions of Table II come close to it. It may also be noted from Fig. 10 that the change of slope of the Hugoniot at the solidus is likely to be small in this region, as may be inferred from the solidus and liquidus intersections and also from the observation that

Fig. 10. Hugoniot paths in the shock vs particle velocity plane. Hug R - Initial conditions: 100 atm, 10.71 cc/g, and 4.2°K. Hug P - Initial conditions: 1 atm, 14.09 cc/g, and 20.1°K. Dashed section on Hug R is approximate path in the two-phase region.

Table VI. Hugoniot H_R with starting conditions on Stewart's 4.2°K isotherm.

P (atm)	V (cc/g)	U_p (mm/ μ sec)	U_s (mm/ μ sec)
100	10.71	0	1.84
194.5	10.42	0.0531	1.93
394	9.92	0.153	2.08
667	9.42	0.272	2.26
1072	8.93	0.419	2.52
1720	8.43	0.612	2.87
2443	8.10	0.787	3.23
2932	7.94	0.892	3.44
3435	7.80	0.992	3.65
Two-phase region			
5120	7.40	1.298	4.20
5753	7.25	1.408	4.36
6910	6.99	1.602	4.61
8600	6.71	1.856	4.97
11560	6.30	2.263	5.50
12740	6.18	2.410	5.69

Stewart's isotherm implies a sound velocity at $V = 8.7 \text{ cm}^3/\text{g}$ of 3.8×10^{10} cm/sec which is equal to that in the two-phase region, within the error of the calculations. There is, however, an adequate break in the Hugoniot curve at the liquidus, which should make detection possible.

Higher pressures can, of course, be reached if we stop the mass motion behind the shock front by reflecting the shock from a dense material. Reflected Hugoniot paths were calculated from several principal Hugoniots, but none was obtained that clearly crossed the phase line either from the solid or from the liquid side. This is probably a fortuitous situation caused by the particular form of the melting line equation, which may be inadequate above the statically measured (P, T) range of 0-3600 atm and 14-65 °K. It is not unreasonable, however, to assume a slower entropy increase along the phase line than is indicated by the equation used here. For it must be noted that for metals the exponent C in the Simon equation

$$P - P_t = P_0 \left[(T/T_T)^C - 1 \right]$$

is larger and the metallic state is approached in compression. In that case, a Hugoniot reflected from a principal Hugoniot in the solid phase may cross the phase line at a pressure as much as twice as high as the latter.

Further work should be designed primarily to obtain more accurate information on $\partial P/\partial E \Big|_V$ as a function of volume and temperature. A study of the phase region by techniques that measure shock and free surface velocities only is likely to be limited to detection of the phase at higher pressures, but will not necessarily yield a density difference between solid and liquid. It is, however, possible to aid the latter investigation by light scattering and conductivity measurements.

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REFERENCES

- ¹A. Michels, W. deGraaf, T. Wassenaar, J. M. H. Levelt, and P. Louwerse, *Physica* 25, 25 (1959).
- ²H. M. Roder, L. A. Weber, and R. D. Goodwin, NBS Circular 7987 (1963).
- ³P. W. Bridgman, *Proc. Am. Assn. of Arts and Sciences* 59, 173 (1924).
- ⁴John W. Stewart, *J. Phys. Chem. Solids* 1, 146 (1956).
- ⁵M. H. Rice, R. G. McQueen, and J. M. Walsh, *Solid State Phys.* 6, 1 (1958).
- ⁶A. van Itterbeek, W. van Dael, and A. Cops, *Physica* 27, 111 (1961).
- ⁷E. Grüneisen: Handbuch der Physik (Verlag J. Springer, Berlin, 1926), Vol. 10, p. 22.
- ⁸T. H. K. Barron, *Ann. Phys.* 1, 77 (1957).
- ⁹M. Van Thiel, unpublished results.
- ¹⁰W. deGraaf, Thesis, University of Amsterdam, June 1960.
- ¹¹H. L. Johnston, W. E. Keller, and A. S. Friedman, *J. Am. Chem. Soc.* 76, 1482 (1954).
- ¹²R. B. Scott and F. G. Brickwedde, *J. Chem. Phys.* 5, 736 (1937).
- ¹³A. D. White, A. S. Friedman, and H. L. Johnston, *J. Am. Chem. Soc.* 72, 3927 (1950).
- ¹⁴A. L. Smith, N. C. Hallett, and H. L. Johnston, *J. Am. Chem. Soc.* 76, 1486 (1954).
- ¹⁵J. C. Slater, Introduction to Chemical Physics (McGraw-Hill, N. Y., 1939), p. 451.
- ¹⁶H. W. Woolley, R. B. Scott, and F. G. Brickwedde, *J. Res. NBS* 41, 379 (1948).
- ¹⁷G. Ahlers, UCRL-10757.

¹⁸Slater's and Dugdale and McDonald's equation for γ applied to Hugoniot's of metals yield values decreasing with volume. Furthermore if $(-\partial P/\partial V)_s$ and $(\partial^2 P/\partial^2 V)_s$ are positive, γ must decrease.

¹⁹R. D. Goodwin, Cryogenics 2, 353 (1963).

²⁰A. Michels, W. deGraaf, G. J. Wolkers, Physica 25, 1097 (1959).

²¹V. A. Rabinovich, translation FTD 62-1569 from: Inzhenerno-Fizicheskiy Zhurnal 5, No. 5, 30 (1962).

²²E. Bartholome, Z. Physik. Chem. (B) 33, 387 (1936).

²³F. E. Simon, Z. Elektro Chem. 35, 618 (1929); Trans. Farad Soc. 33, 65 (1937).

²⁴J. E. Lennard Jones and A. F. Devonshire, Roy. Soc. (London) Proc. A169, 317 (1939); A170, 464 (1939).

²⁵F. E. Karase and J. A. Pople, Phys. Chem. Solids 18, 28 (1961); 20, 294 (1961).

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