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-HYDROGEN ISOTOPE MEASUREMENTS AND THERMODYNAMIC
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SUBMITTED TO: Invited Review Paper submitted for
the 6th AIRAPT, Boulder, Colorado, July 25-29, 1977
and to be published in conference proceedings by
the Plenum Press.

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EQUATION-OF-STATE FOR FLUIDS AT HIGH DENSITIES -HYDROGEN
ISOTOPE MEASUREMENTS AND THERMODYNAMIC DERIVATIONS*

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ABSTRACT

Hydrogen isotopes play an important role in our energy technologies, in particular the compression to high densities for initiation of controlled thermonuclear fusion energy. At high densities the properties of the compressed hydrogen isotopes depart drastically from ideal thermodynamic predictions. We review the measurement of accurate data including our own recent measurements of n -H₂ and n -D₂ in the range 75-300 K and 0.2-2.0 GPa (2-20 kbar). An equation-of-state of the Benedict type is fit to these data with a double-process least-squares computer program. We review the results and compare with existing data and with a variety of theoretical work reported for fluid hydrogens. A new heuristic correlation is presented for simplicity in predicting volumes and sound velocity at high pressures.

*Work performed under the auspices of the U.S.E.R.D.A.

INTRODUCTION

The high density properties of the molecular hydrogen isotopes (H_2 , D_2 , T_2) are of current interest in energy programs. At Los Alamos we have been developing techniques for static measurements of high accuracy in the hydrogens to support the ERDA energy program^[1-3]. These light isotopes provide an example of a high density fluid and molecular hydrogen, because of its basic nature - the simplest molecule - is a useful material for intercomparison between accurate experiment and theory. Specifically excluded from this report are measurements in solid, liquid, and gaseous states and only the region bounded by the melting curve and above the critical temperature will be treated. A summary of measurements in this region is easily completed because only a very few results have been obtained. For hydrogen there are accurate measurements by Michels and coworkers^[4] between 100 K to 423 K at pressures to 2.6 kbar, a study by Tsiklis et al.^[5] between 300 K and 423 K at pressures from 0.5 to 6.5 kbar, a crude pioneering measurement by Bridgman^[6] up to 13 kbar at 338 K, and finally our own recent measurements^[7] in the range 75-300 K and 2-20 kbar. An indication of the coverage in the PT plane is shown in Fig. 1. For deuterium an even shorter summary may be given, the results of Michels et al.^[4] in the same pressure and temperature regime as for hydrogen and our own recent results^[8] again covering the range 75-300 K and 2-20 kbar. In addition to the measurement of P, T, and V we have made simultaneous measurements of sound velocities over this same surface in order to provide a set of data that over defines the thermodynamic system and that we use to improve the accuracy of the resultant equation-of-state (EOS) fit. The data have an accuracy estimated to be no worse than 0.5% for the fitting to an EOS.

Theory is more plentiful for dense fluids, borrowing from gas, solid, and liquid theory as a starting point. Neither the ideal gas law nor the van der Waals equation provide for qualitative features of high density fluid data. We select several of these theories to discuss and compare. The virial expansion equations can be made complete, we will examine the Benedict-Webb-Rubin equation that Heber^[9] adapted to hydrogen. The

Benedict^[10] type of equation we have used for higher density fluid has a regular behavior at extrapolated densities a factor of more than 5 greater than the measured range. The van der Waal type of equation of state has been struggled with for dense fluids; it is a bridge between the virial and statistical mechanical models and we examine results from the equation of Haar and Shenker^[11] that we have applied to hydrogen. Potential theory has been carefully treated and compared recently by Barker and Henderson ^[12] although an interesting vignette is provided by a heuristic model we develop here. Ashurst^[13] has recently developed a simple potential theory that we will compare. Statistical mechanical equations such as used by Baker and Swift^[14] will be compared. Mixing together of these theoretical models to arrive at an EOS consistent at low pressures with earlier existing data and with theory at higher densities Kerley^[15] at Los Alamos has obtained results that are in good agreement with our new data. We will complete the survey of molecular theory with a remark about the metallic state formation and will avoid references to higher density atomic, neutronic and hadronic equations of state.

The hydrogen and deuterium data will form the basis for the comparison of these several equations-of-state.

EXPERIMENTAL

Experimental results for hydrogen have already been published and our new results for deuterium will be published so that this section is devoted to a survey of the experimental results.

The paucity of hydrogen data at high pressures and low temperatures is related to hydrogen embrittlement of high strength steels and at low temperatures to martensitic brittleness of high strength steels. Bridgman had recognized the former problem and used a metal bomb containing the hydrogen to insert into a kerosene bath in the piston cylinder in order to protect the walls of his cylinder from direct contact with hydrogen.

During compression corrections for the crushing of the bomb as well as compressibility of kerosene and bomb material had to be made so it is not surprising that his reported hydrogen volumes are too large by over 2% at 4 kbar and by 10% and 17% at his highest pressure of 13 kbar and 303 and 338 K respectively. Vodar and Saurel^[16] remark on the latter difficulty "The low temperature study of highly compressed gases is subject to many difficulties of which by no means the least is the fragility of reservoirs." The strengths of steel limited an unsupported pressure vessel to about 7 kbar although only at low temperatures are these pressures realized by Mills and Grilly in melting curve measurements. Early methods of measurement are summarized by Levelt-Sengers^[17]. Much recent improvement in materials and the knowledge of materials properties has made it possible for us to construct a piston cylinder apparatus that is able to directly seal and compress hydrogen and deuterium to over 20 kbar. This equipment is shown in Fig. 2, a tungsten carbide cylinder to contain the hydrogen is supported with tapered segmented anvils pressed into a belt. Axial support is provided by the flanges to the inner cylinder. Bridgman unsupported area seals are used on both the movable piston and fixed plug. A quartz crystal transducer is mounted on the unsupported area of the fixed plug and sound pulses are propagated into a fixed path in the fluid and reflected to the transducer through the buffer rod. This design has removed the necessity for leads into the high pressure chamber. Pulses of 10 MHz or 30 MHz sound are timed with a Tektronic scope to ± 5 ns. Volume changes are determined from measurement of the piston travel with a dial gauge of 0.0025 mm sensitivity and corrections applied for measured compressibility of the piston-cylinder components. Lower temperatures are achieved by enclosing the piston cylinder in a cryostat and cooling with precooled nitrogen gas. Pressures are obtained with Dake press and are determined with an Ashcroft free-piston gauge reading of the hydraulic fluid. The initial charging of the cell is accomplished with the piston retracted to expose a capillary opening in the cap of the tungsten carbide cylinder. An initial pressurization at over 3 kbar is provided from an American Instrument Company mercury-piston compressor. The gas has 99.995% purity and is normal hydrogen or deuterium initially and thought to remain so in the absence of a catalyst due to a slow self conversion rate and the time frame of our experiments at reduced temperatures.

The apparatus, procedures, and accuracies are completely discussed in earlier references^[1,7]. The average errors for hydrogen are; $\pm 0.4\%$ in volume, $\pm 0.5\%$ in sound velocity, ± 0.5 K in temperature or less at room temperature and liquid nitrogen temperatures, and $\pm 0.5\%$ in pressure or less at the pressures less than 20 kbar. The errors for deuterium measurements of volume and sound velocity are slightly reduced.

RESULTS

For H_2 we measured 1952 complete sets of P, V, T, v_s points along 60 isotherms up to 20 kbar pressure^[7]. To these we added the 26 points of Michels et al.^[4] determined ≥ 1 kbar in our temperature range 75 - 307 K. Additional data sets of P, V, T , or P, T, v_s were obtained due to accidents, leakage and the vagaries of high pressure equipment; these data have been used for comparisons.

The range of data is shown in Fig. 3 for hydrogen by plotting $\ln V$ vs T for five isobars between 3 - 18 kbar. Along an isotherm the sound velocity measurements, including the calculated lower pressure data points of Michels et al. are shown in Fig. 4. Although the measured volumes are normalized to Michels data at the pressure where the piston seals off the fill capillary there is no further normalization of the absolute sound velocity measurements to the calculated values of Michels. An interesting feature of the data should be noted: at lower pressures (below the region of validity for our published EOS) there is an inflection point in the v_s vs P data, $(\partial^2 v_s / \partial P^2)_T = 0$, which the EOS to be described does not reproduce. Such a behavior is also noted from the nitrogen data as obtained by A. Lacan^[18]. The least square fit of a power law relation

$$v_s = B_1 + B_2(P + B_3)^n \quad (1)$$

where B_1, B_3 are often set to zero is shown as the solid line fit to this data in Fig. 4. The temperature dependence of B and D can be determined by comparison of the 60 isothermal fits and in the case of hydrogen this smooth representation of the data set was used together with graphically smoothed volume data to determine a matrix of 114 values in the temperature and pressure range restricted to < 20 kbar by the melting curve at lower temperatures.

The temperature dependence of the sound velocity clarifies the problem of fitting the gas-like equations-of-state to these data. In Fig. 5 we have plotted the temperature variation of sound velocity at pressures between 0.5 - 2.0 kbar as obtained for deuterium from our extrapolated EOS and the calculated values of Michels. In this region at the lowest pressure, deuterium shows a gas-like behavior, that is, the sound velocity increases with temperature as required from kinetic gas theory - although the quantitative behavior is not correct. At higher pressures and low temperatures, progressively closer to the melting line, the sound velocity has the liquid-like characteristic of decreasing with increasing temperature. Corresponding results for the lower pressure isobar for hydrogen are also shown for calculated values of Michels and our own EOS extrapolated to these lower pressures. These curves indicate that isotherms of v_s vs P will cross each other at lower pressure. This feature of the data is well described by the EOS fit we have developed for both hydrogen and deuterium. This graph allows the further comparison of sound velocity at 0.5 kbar between hydrogen and deuterium, found to be in the approximate ratio of $\sqrt{M_{D_2}/M_{H_2}} : v_s(H_2)/v_s(D_2)$.

For n -D₂, 1340 data sets of P , V , T , v_s were measured over the ranges 75 - 300 K and 2 - 20 kbar^[3]. A representative set of volumetric and sound velocity data versus pressure along one isotherm is shown in Figs. 6A and 6B. The statistical error of these data was sufficiently small so that good convergence to the least-squares fitted equation-of-state was possible with the full data set expanded to 1404 data sets including the lower pressure data (> 1 kbar) from Michels et al.^[4].

EQUATION-OF-STATE DEVELOPMENT

For ease of manipulation we have considered an EOS of the form,

$$V = f(P, T). \quad (2)$$

Many types of closed-form expressions for the EOS of fluids have been given. Benedict^[10] found that an equation of the form

$$V = \sum_{n=1}^3 \sum_{m=-2}^2 \Lambda_{nm} T^{n/2} P^{-m/3} \quad (3)$$

could be simplified, when highly correlated terms were eliminated, to give the following equation which he used for nitrogen:

$$V = (A+BT+CT^{-1/2})P^{-1/3} + (D+ET)P^{-2/3} + (F+GT+HT^{-1/2} + JT^{-1})P^{-1} \quad (4)$$

We used this equation for our hydrogen and deuterium data, all of which were obtained well into the supercritical fluid region^[20]. The equation has a form that is amenable to use with the double-process least-squares fitting method.

To use P-V-T and v_s data together in a double-process least-squares fitting process, we write the thermodynamic relation

$$\frac{1}{v_s} = \left[\left(\frac{\partial v}{\partial P} \right)_s \right]^{1/2} \frac{M}{V}^{1/2} \left\{ - \left(\frac{\partial v}{\partial P} \right)_T - \frac{T \left[\left(\frac{\partial v}{\partial T} \right)_P \right]^2}{C_p} \right\}^{1/2} = g(P, T) \quad (5)$$

and, as discussed^[2], minimize the sum S for n sets of points in the following equation:

$$S = \sum_n [V_{\text{exp}} - f(P, T)]^2 + \sum_n \left[\frac{1}{v_s} - g(P, T) \right]^2. \quad (6)$$

In addition to our own data we need the value of C_p at our normalization pressure over the full temperature range. The lower pressure data of Michels^[4] (and recently tabulated Russian values^[21] for hydrogen only) were used to obtain $C_p(T)$ at our lowest pressure $P = 2$ kbar over the 75 - 307 K temperature range. Then the heat capacity

$$C_p = C_{p_0}(T) - T \int_{P_0}^P \left(\frac{\partial^2 v}{\partial T^2} \right)_P dP \quad (7)$$

can be directly calculated for use in Eqs. (5) and (6). The expression for $\underline{n}\text{-H}_2$ is

$$C_{p_0}(\tau) = 1.1239\tau + 61.463\tau^{1/2} + 1259.3 \\ - 10512\tau^{-1/2} + 31638\tau^{-1} \text{ [J/mole-K]}. \quad (8)$$

The resultant fits to Eq. (4) for $\underline{n}\text{-H}_2$ and $\underline{n}\text{-D}_2$ are listed in Table I.

Table I. Fitted Constants to Eq. (4) as Determined by a Double-process Least-square Fit to the $\underline{n}\text{-H}_2$ Smooth Data Set and the 1340 Data Point Set of $\underline{n}\text{-D}_2$

	$\underline{n}\text{-H}_2$	$\underline{n}\text{-D}_2$
A	35.715	35.283
B	0.0033903	0.00094703
C	-22.479	3.2843
D	-17.174	-25.090
E	-0.021393	0.0063917
F	-8.9486	13.650
G	0.11061	0.069563
H	19.233	-159.29
J	-31.395	720.00

Average deviation over the range of temperature and pressure from the sound velocity data and values calculated by the equation of state are $\pm 0.53\%$ and between measured and calculated volumes are $\pm 0.22\%$ for deuterium. Tables of calculated thermodynamic properties are available for hydrogen^[19] and will be similarly published for deuterium. In Fig. 7 the sound velocity surface $v_s(P, \tau)$ is plotted from the EOS for

hydrogen.

DIRECT COMPARISONS

As we have discussed there is little data with which our measurements can be directly compared. For hydrogen we have seen that data of Bridgman were not in good agreement. Recently, Tsiklis et al.^[5] made static volume measurements at pressures up to 5 kbar at 298.2 K and a careful comparison shows average deviation of + 0.72% from our EOS values. There are no similar measurements for deuterium. Our sound velocity measurements for both hydrogen and deuterium are completely new. The only comparison possible is by extrapolation to low pressure with a few calculated values of Michels in a region of overlap.

The potential theory has been recently applied to hydrogen by Ashurst^[13] to obtain thermodynamic and transport properties. While the theoretical fit was based only upon the earlier lower-pressure data, the model was extended by Ashurst up to the freezing pressure or to 20 kbar over a range of temperatures 98.2 - 3273.2 K. In the region of direct comparison the molar volumes deviate at the lower temperatures and pressures by 1 - 5% and for temperatures between 200 - 300 K are less than 1% at 2 kbar and > 6% at 20 kbar. The sound velocities calculated show a much larger deviation, up to 17%, in this range. We anticipate that, with our new data of 0.5% accuracy these calculations may be refined and provide an improvement of the calculated transport properties as well.

The model developed by Kerley^[15] for deuterium and modified for the case of hydrogen has been compared with the present measurements. A variety of data was used to parameterize this theory and the results of our comparison show a very encouraging level of agreement in a range where no previous data existed. In Fig. 4 we show the volume vs pressure along the 100 K and 300 K isotherms. The differences between the measured and theoretical values are at most 2.4% at the freezing point for 100 K and the average deviation is less than 1% throughout the range of our data.

The comparison of sound velocity data is only a little less satisfactory. A comparison is shown in fig. 9 along the two isotherms 155 K and 300 K. Average deviation over the temperature and pressure range of our measurements are 1 - 2%. This agreement can be considered very good.

EXTRAPOLATED COMPARISONS OF EOS

The EOS developed for para-hydrogen by Heber^[3] is based, at higher densities, upon a 14 parameter surface of a modified Strabridge form:

$$P = RT \left[1 + (A_1 T^2 + A_2 T + A_3 + A_4/T) + (A_5 T^2 + A_6 T + A_7 + A_8/T + A_9/T^2) + (A_{10} T^2 + A_{11} T + A_{12})^2 + (A_{13} T^2 + A_{14} T)^3 \right] \quad (9)$$

and covered data up to 1 kbar in the temperature range of 20 - 300 K. The earlier 17 constant equation of McCarty and Heber^[22] extended up to 0.7 kbar. Extrapolation to smaller volumes gives pressures that are too high by over 50% at 20 kbar and 300 K. Sound velocities calculated with this equation disagree with those of Michels by up to 3.5% and only a small fraction of these differences can be ascribed to differences between normal and para-hydrogen.

Comparing results of Baker and Swift^[14] with extrapolations of our EOS for hydrogen at $T \sim 1000$ K, their molar volumes are larger by 10 - 20% in the pressure range 20 - 100 kbar. On the other hand a virial type of equation devised by Grigor'ev et al.^[23] yields molar volumes near freezing that are smaller than those extrapolated from our EOS by 5, 13, 27 and 31% at pressures of 26, 167, 3440, 4660 kbar respectively. A measured point at 1 kbar (estimated temperature 1200 K) during isentropic, dynamic compression gave $V = 3.0 \text{ cm}^3/\text{mole}$ compared to value $4.4 \text{ cm}^3/\text{mole}$ extrapolated from our EOS.

The useful correlation we have shown of the sound velocity and volumetric data with a power law dependence on pressure,

$$v_s, V = B_0 p^n \quad (10)$$

where B_2 and n are constants along an isotherm can be correlated with a high density potential model^[19]. The Lennard-Jones 6, 12 potential in the limit of high density can be simplified,

$$\phi(R) = 4 \epsilon \left[\left(\frac{R_0}{R} \right)^{12} - \left(\frac{R_0}{R} \right)^6 \right] \quad (11)$$

in terms of the volume with repulsive forces only,

$$\phi(V) = 4 \epsilon \left(\frac{V_0}{V} \right)^4 \quad (12)$$

and since $P = -\left(\frac{\partial F}{\partial V}\right)_T$ we obtain $P = 16 \epsilon \frac{V_0^4}{V^5}$ and $P = A\rho^5$ where ρ is the density. Using the sound velocity as $v_s^2 = V \left(\frac{dP}{dV} \right)_T$, $v_s^2 \sim 5 A\rho^4$ so that $v_s \propto \rho^{2/5}$ and $V \propto \rho^{-1/5}$. Since we have also determined experimentally that the product $v_s V \sim \text{const}$ (independent of pressure) as shown in Table II we compare this potential model and find $v_s V \propto \rho^{1/5}$. However, by choosing the repulsive term exponent as 9 rather than 12 we obtain

$$\begin{aligned} v_s &\propto \rho^{3/8} \\ V &\propto \rho^{-1/3} \end{aligned} \quad (13)$$

and $v_s V \propto \rho^{1/24}$ which exponents are each in satisfactory agreement with the measurements. We have compared this result in Table II and the results for two other heuristic theories, Rao's model for a liquid and the free volume model.

Rao's law states that the 'constant' $R_a = v_s^{1/3} \frac{M}{\rho}$ where M is the molecular weight. R_a can be interpreted as the molar velocity of sound in analogy with molar refraction. We compare the product $v_s^{1/3} V$ and find large variations in both temperature and pressure.

The free volume model has an interpretation that in the spaces between molecules a gas kinetic velocity of propagation for sound waves is valid and that through the molecule an infinitely fast propagation occurs. The

resulting correlation was obtained by following Eyring as discussed by Van Dael and van Isterbeek, to become $v_s v^{1/3} = \text{constant}$ and values are tabulated in Table II. Reasonable temperature independence is obtained.

In summary we have studied the molecular hydrogen isotopes both because they are important materials of present energy programs and because they have fundamental theoretical significance. We examine the status of our knowledge of molecular matter at high densities. Our measurements that extend in the range 75 - 300 K and 2 - 25 kbar for $n\text{-H}_2$ and $n\text{-D}_2$ provide P, V, T, v_s data sets of about $\pm 0.5\%$ accuracy. We have used our new data in a double-process least-squares fit to a Benedict type equation-of-state that is shown to reproduce that data with good accuracy over the full range of conditions and to provide reasonable extrapolations to both low and high pressures and have established satisfactory comparison with existing sparse data. Several types of equations-of-state were compared to these data, the agreement being generally far outside the accuracy limits. However, the theoretical model by Kerley compared most satisfactorily with the measurements over the full temperature and pressure range. Heuristic models were evaluated and a new correlation presented that should prove useful in extrapolating these results for volume and sound velocity to higher pressures.

Study of these useful hydrogen isotopes is far from complete. At present we are seeking to adapt higher pressure technology to these questions and obtain additional experimental data against which refined theory can be evaluated.

ACKNOWLEDGEMENTS

We thank L. C. Schmidt (IASI) for the construction and assembly of the piston-cylinder apparatus. We are indebted to R. H. Johnson (IASI) for programming and early computation for hydrogen of the double-process least-square fitting routines. Conversations with many colleagues have been stimulating and we thank R. D. McCarty for information regarding the heat capacity of hydrogen.

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FIGURE CAPTIONS

- Fig. 1 Log T vs log P In the higher density $n\text{-H}_2$ fluid region ($P \gg 0.5$ kbar) and above the freezing line the areas denoted regions in which measurements have been made and compilations published. The heavy dotted area is the region covered by the present author's measurements, Ref. [7]; the light dotted area by measurements of Michels et al., Ref. [4]; the open region by measurements of Tsiklis, Ref. [5]; and the two lines the early measurements by Bridgman, Ref. [6]. Two compilations are shown as cross hatched regions, that by Weber, Ref. [9] as the solid line cross hatch and that by Vargaftik, Ref. [21], by the dotted line cross hatch. Dissociation of the molecule occurs at the higher temperatures.
- Fig. 2 Cutaway drawing of the piston-cylinder belted anvil apparatus. Major components are identified and the inserts show the upper movable piston seal, retracted so a charge can be admitted through the fill capillary, and the lower seal with the coaxial lead in to the sound transducer on the unsupported area of the Bridgman seal.
- Fig. 3 Plot of log V vs $1/T$ for five isobars in fluid $n\text{-H}_2$. Experimental points (interpolated) are shown by square, 3 kbar; cross, 5 kbar; triangle, 8 kbar; plus, 12 kbar; circle, 18 kbar. At the lowest temperature the points are terminated at the freezing line.
- Fig. 4 Sound velocity in $n\text{-H}_2$ vs P along the 300 K isotherm. The closed circles are from Michels et al., Ref. [4]. The closed triangles are measurements by the present authors, Ref. [7], at higher pressures.
- Fig. 5 Sound velocity in $n\text{-H}_2$ and $n\text{-D}_2$ vs T along several isobars. The crosses refer to $n\text{-D}_2$ calculations from the EOS Eq. (4), the plus refer to calculations by Michels et al., Ref. [4]. The lowest values are at a constant pressure of 0.5 kbar and by steps 1.0, 1.5 and 2.0 kbar. The single isobar at $P = 0.5$ kbar for $n\text{-H}_2$ is plotted and

the filled circles are data by the present authors, Ref. [7], the open circles from a compilation by Vargaftik, Ref. [21] and the triangles data from Michels et al., Ref [4].

Fig. 6A Log molar volume vs log pressure for deuterium at $T = 295.3 \pm 0.8$ K based on data for nine experimental runs and 332 points. Circles, $T = 294.5$; triangles, $T = 294.9$; plus, $T = 296.0$; s, $T = 296.1$; diamond, $T = 295.7$; inverted triangle, $T = 296.0$; x in square, $T = 296.1$; asterisk, $T = 295.3$; plus in diamond, $T = 295.6$. The first and last run were separated by about four months.

Fig. 6B Log sound velocity vs log pressure for deuterium at $T = 295.3 \pm 0.8$ K based on 332 pts and nine isothermal runs; symbols as in Fig. 6A. The smooth curve is a least-squares fit on Eq. (1) to the data.

Fig. 7 Sound velocity in $n\text{-d}_2$ vs T, P . At lower temperatures this surface is truncated by the freezing line.

Fig. 8 Molar volume vs pressure. The full line is the calculation by Kerley, Ref. [15] at 300 K and results from the EOS, Eq. (4) are shown as circles. The dashed line is from Kerley and triangles from our EOS at $T = 100$ K.

Fig. 9 Sound velocity vs pressure. The full line is the calculation by Kerley, Ref. [15] at 300 K and the results from the EOS, Eq. (1) are shown as circles. The dashed line is from Kerley and triangles from our EOS at $T = 100$ K.

Fig. 1

Figure
2

BELTED ANVIL DEVICE

Fig 3

Fig. 6 A

Fig. 6 B

HYDROGEN Sound Velocity vs T and P

Figure 7

Fig. 8

Fig. 9