

THE QUANTUM BEHAVIOUR OF COMPRESSED GASES

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The pressure-volume relationships of hydrogen and deuterium have been studied at 64.5° K and 78.9° K and at pressures between 150 and 1250 atm. The results show a marked quantal inflation of the pressure which is in good agreement with the predictions of a quantized Lennard-Jones and Devonshire theory of the gases.

The p - v - T behaviour of the lighter gases is affected by the quantization of the translational motion of their molecules. In an earlier paper¹ this effect was calculated approximately for a Lennard-Jones and Devonshire² (LJD) gas. In the LJD treatment each pair of molecules in a gas has a mutual interaction potential energy

$$\epsilon(r) = 4\epsilon^*[(D/r)^{12} - (D/r)^6], \quad (1)$$

where D and ϵ^* are characteristic molecular parameters and r is the distance between the centres of the interacting molecules.

It was concluded¹ that the pressure of the gas is higher than it would be if the molecules behaved classically, by an amount

$$\Delta p = \frac{NkT}{v_0} \left[\frac{v_0}{v} + \frac{3}{2} \frac{d \log y^*}{d(v/v_0)} \right] \left[\frac{2(2\pi mkT)^{\frac{1}{2}} \sigma}{h} \left(\frac{4\pi}{3} \right)^{\frac{1}{2}} - 1 \right], \quad (2)$$

where N is the number of molecules in the volume v , m is the molecular mass, k is Boltzmann's constant, h is Planck's constant and T is the absolute temperature. The parameter v_0 is a characteristic volume equal to ND^3 ; y^* is a function only of v/v_0 (given in eqn. (4)), and σ depends on v/v_0 and D .

Some calculations from eqn. (2) suggested that compressed hydrogen and deuterium should show significant quantum effects at temperatures below 100° K. For example, the pressure of hydrogen at 80° K and a density of 0.04 mole cm⁻³ would be 470 atm deduced from the classical LJD theory † and 830 atm from the quantal theory.

In this paper we describe some pressure-density measurements to determine which of the two theories better describes the behaviour of H₂ and D₂ under such conditions. It must be emphasized that no high accuracy was sought in these measurements because the pressures predicted by the two theories were so strikingly different.

EXPERIMENTAL

For making pressure-density measurements at low temperatures the constant volume method of Holborn and Schultze⁴ was considered most convenient. An apparatus of this type had previously been used in this laboratory.⁵ The general arrangement can be seen from fig. 1. A 1 ml steel pipette A, mounted in a simple cryostat, was connected through a needle valve B to a manifold leading on one side to the mercury gas compressor⁶ C, and on the other to a gas burette D in each case through a high pressure

† This figure was found by interpolation in the extensive tables of the properties of a classical LJD gas compiled by Wentorf, Buehler, Hirschfelder and Curtiss.³

needle valve E, F. The pressure of gas in the pipette was adjusted to the desired value by means of the compressor and the pipette sealed by closing the needle valve B. The manifold was then closed to the high-pressure system and opened to the gas burette and pumping system to evacuate the connecting lines. After this had been done the burette was sealed from the pumping system by mercury and the gas enclosed in the pipette was expanded into the burette which was maintained at constant temperature in an oil bath. Here its pressure was measured, using a mercury manometer. From volume and pressure measurements with the burette the number of moles of gas initially enclosed in the pipette was found and hence its density at the high pressure calculated. The gas burette had been calibrated previously⁵ but a correction was applied in these measurements for the fact that 1 ml of the gas was at the cryostat temperature.

The cryostat consisted of a Dewar flask containing liquid nitrogen and fitted with a rubber bung through which passed the steel connecting line to the pipette. Temperatures were measured by a platinum resistance thermometer in a pocket immersed in the liquid nitrogen adjacent to the pipette. A connection to a vacuum pump was also provided

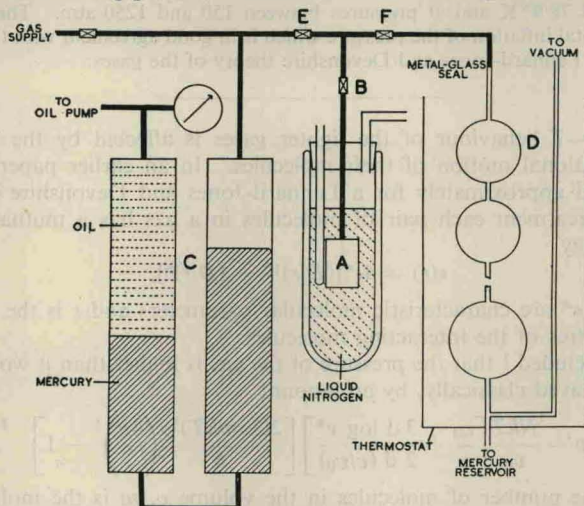


FIG. 1.—Schematic diagram of apparatus.

to reduce the pressure on the liquid nitrogen and so obtain temperatures below the normal boiling point.

It was necessary that the valve B used for sealing the gas pipette be outside the cryostat and it was therefore inevitable that a small proportion of the enclosed gas was approximately at the ambient temperature instead of that of the cryostat. Care was taken to ensure that this amount should be as small as possible; it was about 10% of the total. The temperature of the needle valve B was noted at each density determination and the number of moles of gas at this temperature calculated from the compressibility data of Michels and Goudek⁷ and subtracted from the total to find the number of moles at the cryostat temperature.

The total volume of the pipette and the fraction of this volume which was immersed in the cryostat were calculated from the dimensions of the apparatus. These volumes were checked by comparing the results of some measurements of the compressibility of hydrogen at 293° K and 79° K with the data of Michels and Goudek⁷ and of Johnston and White⁸ respectively.

High pressures were measured by Budenberg standard test gauges of the Bourdon tube type, the accuracy of such gauges being sufficient for the purpose of the investigation.

Commercial (electrolytic) hydrogen was purified by the method of Hainsworth and MacInnes.⁹ Gas from a cylinder was passed at a pressure of 100-150 atm through a tube containing platinized asbestos heated to 110° C and then through a steel trap immersed in Dry Ice and alcohol to the gas compressor.

Deuterium was prepared from 99.7% D₂O by a method similar to that used by Schiff and Steacie.¹⁰ A 500 ml steel reaction vessel was immersed in Dry Ice and alcohol, evacuated and then filled with dry nitrogen. It was next opened and 50 ml of D₂O

introduced. The reactor was closed and returned to the Dry Ice bath for about 20 min to ensure "deep freezing" of the D_2O . After this period it was opened and 100 g of calcium turnings added. The vessel was again evacuated, then sealed and the Dry Ice bath removed. After a short while an extremely rapid exothermic reaction took place, the pressure rising to 100 atm in about half a minute. The deuterium was then passed at about 40

TABLE 1.—ISOTHERMS OF HYDROGEN

$T = 64.5^\circ \text{K}$		$T = 78.9^\circ \text{K}$	
pressure (atm)	density (mole cm^{-3})	pressure (atm)	density (mole cm^{-3})
350	0.0344	300‡	0.0299‡
500	0.0387	500	0.0358
790	0.0440	600‡	0.0385‡
1000	0.0467	700	0.0404
1250	0.0493	800‡	0.0422‡
		950	0.0442
		1250	0.0478

‡ measurements using hydrogen prepared by reaction of H_2O with calcium.

TABLE 2.—ISOTHERMS OF DEUTERIUM

$T = 64.5^\circ \text{K}$		$T = 78.9^\circ \text{K}$	
pressure (atm)	density (mole cm^{-3})	pressure (atm)	density (mole cm^{-3})
150	0.0265	150	0.0215
200	0.0296	200	0.0258
300	0.0348	300	0.0313
350	0.0369	350	0.0335
400	0.0381	400	0.0352
500	0.0408	500	0.0380
700	0.0446	700	0.0424
900	0.0474	900	0.0456

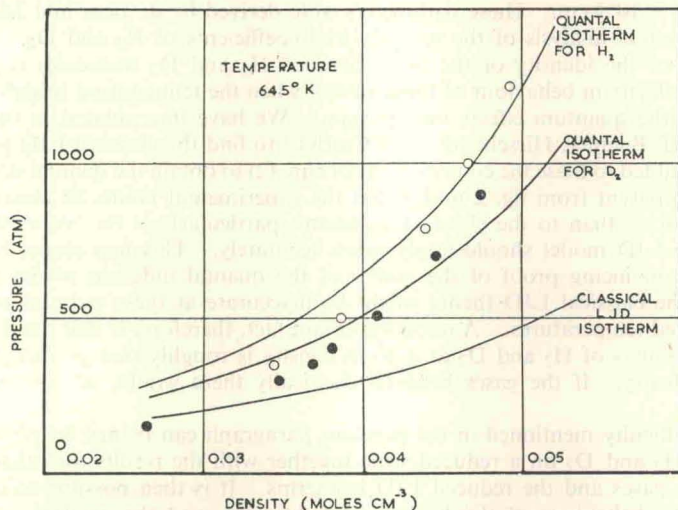


FIG. 2.—Theoretical and experimental isotherms at 64.5°K . The open circles are the experimental points for H_2 , the filled circles are for D_2 .

atm through a liquid nitrogen trap into the gas compressor. It is, perhaps, noteworthy that Schiff and Steacie¹⁰ carried out the reaction at 260°C ; in our case the reaction started while the reactor was still below 0°C . A few density measurements were made on a sample of hydrogen prepared by the same method, using H_2O instead of D_2O .

The results of these investigations are given in tables 1 and 2 in the form of pressure-density isotherms, and are shown graphically in fig. 2 and 3.

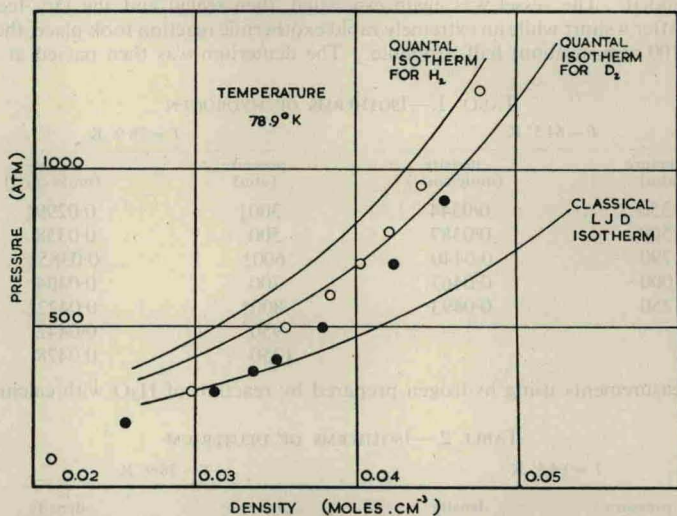


FIG. 3.—Theoretical and experimental isotherms at 78.9°K. The open circles are the experimental points for H₂, the filled circles are for D₂.

DISCUSSION

In the figures, our results are compared with the classical LJD and quantal isotherms for H₂ and D₂ at 64.5°K and 78.9°K. The theoretical curves have been calculated assuming that the potential energy between a pair of molecules of either H₂ or D₂ is represented by eqn. (1) with $\epsilon^* = 50.75 \times 10^{-16}$ ergs, and $D = 2.92 \times 10^{-8}$ cm. These parameters were derived by de Boer and Michels¹¹ from a quantal analysis of the second virial coefficients of H₂ and D₂. The assumption of the identity of the fields between H₂ and D₂ molecules is justified by the similarity in behaviour of these gases⁷ when the temperature is high enough to render the quantum effects unimportant. We have interpolated in the tables of Wentorf, Buehler, Hirschfelder and Curtiss³ to find the classical LJD pressures and have added to these the contributions of eqn. (2) to obtain the quantal isotherms.

It is apparent from fig. 2 and 3 that the experimental points lie closer to the quantal curves than to the classical isotherms, particularly at the higher densities where the LJD model should apply more accurately. This fact alone, however, is not a convincing proof of the reality of the quantal inflation of the pressure because the classical LJD theory might be inaccurate at these reduced pressures and reduced temperatures. A more significant fact, therefore, is that the difference in the pressures of H₂ and D₂ at a given density is roughly that predicted by the quantal theory. If the gases behaved classically there would, of course, be no difference.

The difficulty mentioned in the previous paragraph can be met by plotting the data for H₂ and D₂ on a reduced scale together with the results for other simple non-polar gases and the reduced LJD isotherms. It is then possible to compare directly the behaviour of the heavy and light gases and the predictions of the classical and quantal theories. To do this, we introduce the quantities:

$$\begin{aligned} \text{reduced pressure,} & \quad p^* = pv_0/N\epsilon^* = pD^3/\epsilon^*, \\ \text{reduced volume,} & \quad v^* = v/v_0 = v/ND^3, \\ \text{reduced temperature,} & \quad T^* = kT/\epsilon^*, \end{aligned}$$

defined by Wentorf, Buehler, Hirschfelder and Curtiss.³ It is also convenient to write the quantal correction (2) in terms of the dimensionless parameter

$\Lambda^* = h/D(m\epsilon^*)^{\frac{1}{2}}$ which de Boer^{11,12} showed occurs in the general expression for the reduced equation of state in quantum statistics. Eqn. (2) then becomes

$$\Delta p^* = T^* \left[v^{*-1} + \frac{3}{2} \frac{d \log y^*}{d v^*} \right] [9.0710 y^{*\frac{1}{2}} T^{*\frac{1}{2}} v^{*\frac{1}{2}} \Lambda^{*-1} - 1]^{-1}, \quad (3)$$

where y^* is a function of v^* , the relationship between them being

$$(1 + 12y^* + 25.2y^{*2} + 12y^{*3} + y^{*4})(1 + y^*)^{-1}(1 - y^*)^{-6} - 2v^{*2} = 0. \quad (4)$$

Thus, in conformity with the general considerations of de Boer^{11,12} our reduced quantal equation of state is of the type

$$p^* = f(T^*, v^*, \Lambda^*),$$

where f is a universal function.

For the general plot of p^* against v^* in fig. 4, we have selected the reduced temperature $T^* = 2.14$ corresponding to our experimental temperature $T = 78.9^\circ \text{K}$.

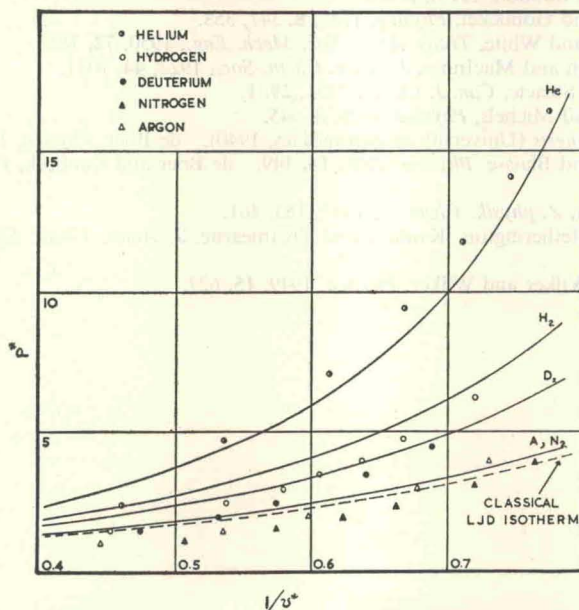


FIG. 4.—Reduced isotherms for $T^* = 2.14$. The full curves are the quantal isotherms.

TABLE 3.—MOLECULAR CONSTANTS

	ϵ^*/k ($^\circ\text{K}$)	D ($\text{cm} \times 10^{-8}$)	Λ^*
He	10.2	2.56	2.64
H ₂	37.0	2.92	1.73
D ₂	37.0	2.92	1.22
N ₂	96.6	3.72	0.225
A	120.3	3.41	0.187

for H₂ and D₂. The intermolecular force parameters and the values of Λ^* have been taken from the tables of de Boer.^{11,12} They are listed in table 3. The experimental data for He, N₂ and A were given by short extrapolations on the temperature scale from the measurements of Buchmann¹³ on He; Bartlett, Hetherington, Kvalnes and Tremearne¹⁴ on N₂; Michels, Wijker and Wijker¹⁵ on A.

Fig. 4 shows that the isotherm given by the classical theory is a fairly good representation of the behaviour of the heavy gases N_2 and A, and that the predicted differences between the quantal isotherms are in good agreement with the experimental differences between the light gases.

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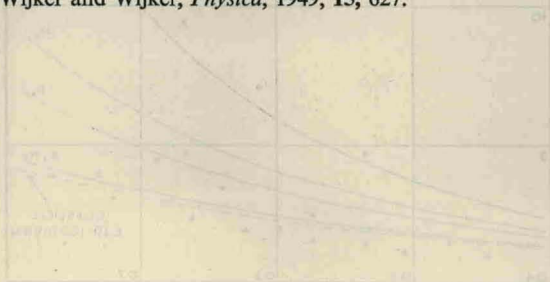


Fig. 4.—Reduced isotherms for $V/V_0 = 20$. The full curves are the classical isotherms.

TABLE 5. MOLECULAR WEIGHTS

Gas	Molecular weight	Gas	Molecular weight
A	130.1	Q	11.41
B	100.0	R	11.41
C	75.0	S	11.41
D	50.0	T	11.41
E	25.0	U	11.41
F	10.0	V	11.41
G	5.0	W	11.41
H	2.5	X	11.41
I	1.25	Y	11.41
J	0.625	Z	11.41

for H and D. The intermolecular force parameters and the values of μ have been taken from the tables of de Boer¹¹. They are listed in table 5. The experimental data for He, N_2 and A were given by their contributors on the basis of the measurements of the isotherms on the isothermometer of Hetherington, Kvalnes and Treamearne¹⁴ and Wijker and Wijker¹⁵.