

THE QUANTUM BEHAVIOUR OF COMPRESSED GASES

BY H. G. DAVID AND S. D. HAMANN

C.S.I.R.O., Division of Industrial Chemistry, High Pressure Laboratory,
Sydney University, Australia

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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 H_2 and D_2 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

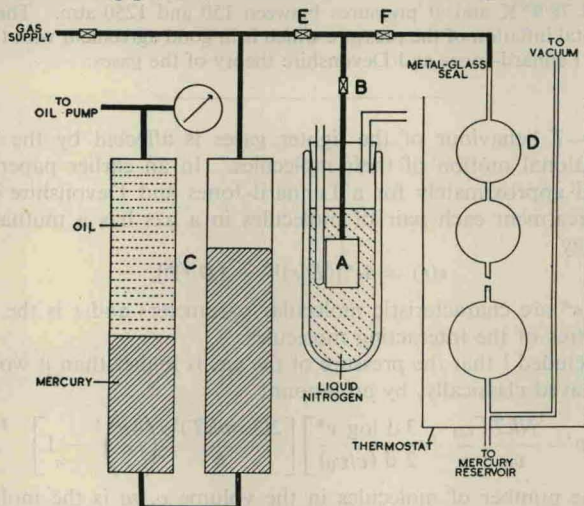


FIG. 1.—Schematic diagram of apparatus.

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