

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

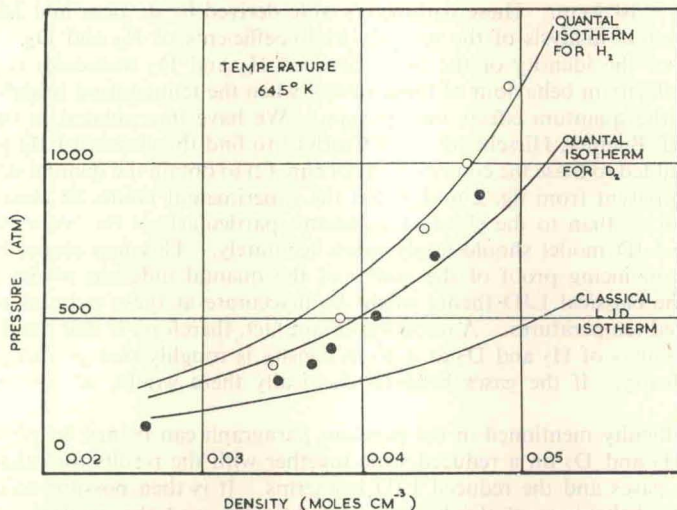


FIG. 2.—Theoretical and experimental isotherms at 64.5°K . The open circles are the experimental points for H_2 , the filled circles are for D_2 .

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.

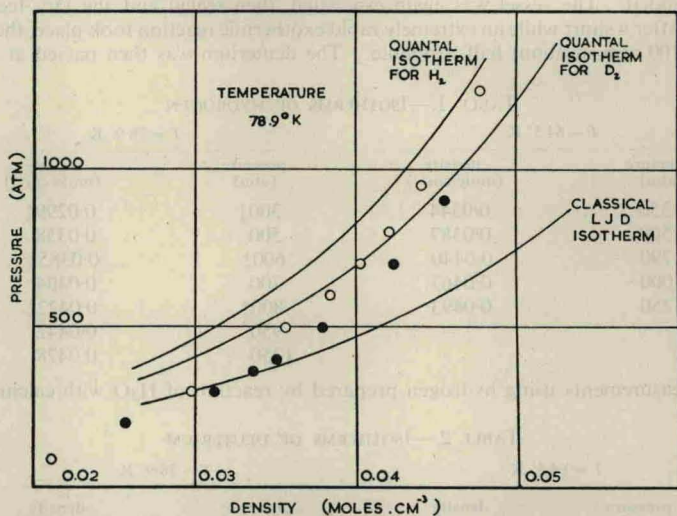


FIG. 3.—Theoretical and experimental isotherms at 78.9° K. The open circles are the experimental points for H₂, the filled circles are for D₂.

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