

*Trans. Faraday Soc., 49, 711-16 (1953)*

## REVIEWS OF BOOKS

nischen Chemie, 8. Auflage.  
on. Teil B—Lieferung 2. Schluss des Elements  
n und Jod. Pp. 368.  
n. Teil B—Lieferung 3. Schluss der Verbindungen  
Teil A—Lieferung 5. Die Legierungen  
Rhodium, Palladium. Pp. 186.)

in Germany are to be congratulated on facilitating essential work of reference. "Gmelin" must be regarded as a model of research workers in any field of inorganic chemistry and accurate presentation of information of their compounds, and must be regarded as a model of the production of further volumes on elements not so well known, many such elements not being covered by the exhaustive reference work on inorganic chemistry. Supplementing sections which have already appeared in the element and its compounds, but do not include the physical properties of the element and its compounds, recently produced parts of this text-book reflect the latest measurements in all branches of inorganic chemistry of discriminating treatment of physico-chemical data, condensed account of the use of antimony electrode in the determination of hydrogen-ion concentration. The section on alloys brings into a single publication a large amount of information, much of which is of fundamental interest. Fully provided for by the section under recent references and detailed information concerning the elements made under different trade names. The section on temperature are presented in the direct and accurate manner of "Gmelin", and materially assist its effective use by research workers. A commendable feature of all the volumes is the inclusion of information published up to the middle of 1952. We are congratulated heartily on producing this series, maintaining the very high standard of printing and publishing of the published volumes.

A. J. E. W.

Vol. XIV. (The Physical Society, London, 1952)

gress Reports contains eleven articles which cover spectroscopy, nuclear physics, physics of the lower atmosphere. They are all by specialists, to some extent for specialist readers, but clarity to be intelligible to those who wish to keep abreast of developments in a particular field.

to the reviewer, contains a fascinating account of the work of Lamb and Retherford on the anomalous Zeeman effect. Any chemist the most useful article will probably be that by W. C. Price, of recent advances in ultra-violet spectroscopy.

the high standard set by its predecessors and

M. B.

## THE QUANTUM BEHAVIOUR OF COMPRESSED GASES

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The pressure-volume relationships of hydrogen and deuterium have been studied at 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 the 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 paper<sup>1</sup> this effect was calculated approximately for a Lennard-Jones and Devonshire<sup>2</sup> (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  $\epsilon^*$  are characteristic molecular parameters and  $r$  is the distance between the centres of the interacting molecules.

It was concluded<sup>1</sup> that the pressure of the gas is higher than it would be if the molecules behaved classically, by an amount

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

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  $\sigma$  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<sup>-3</sup> would be 470 atm deduced from the classical LJD theory<sup>†</sup> and 830 atm from the quantum theory.

In this paper we describe some pressure-density measurements to determine which of the two theories better describes the behaviour of H<sub>2</sub> and D<sub>2</sub> 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 Schultze<sup>4</sup> was considered most convenient. An apparatus of this type had previously been used in this laboratory.<sup>5</sup> 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 compressor<sup>6</sup> C, and on the other to a gas burette D in each case through a high pressure

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

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 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 burette had been calibrated previously<sup>5</sup> 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.

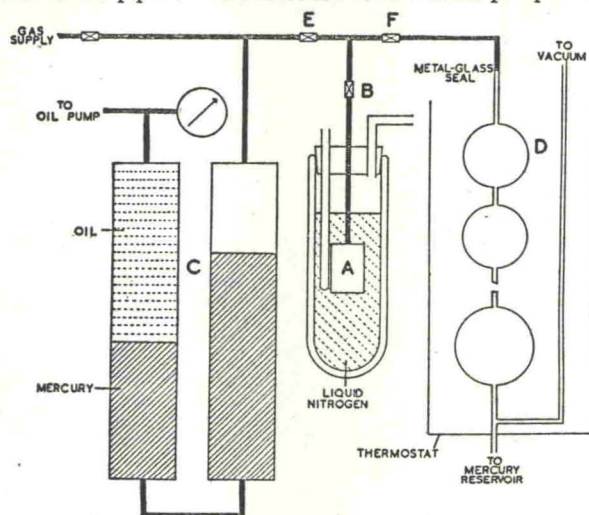


FIG. 1.—Schematic diagram of apparatus.

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 Goudekot<sup>7</sup> 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 Goudekot<sup>7</sup> and of Johnson and White<sup>8</sup> 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.<sup>9</sup> 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% D<sub>2</sub>O by a method similar to that used by Schiff and Steacie.<sup>10</sup> 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 D<sub>2</sub>

introduced. The reaction vessel was then cooled to a temperature of deep freezing and the reaction allowed to proceed. The vessel was then removed. After a short wait the pressure rose to 100 atm in about

pressure (atm)	T = 64°
350	
500	
790	
1000	
1250	

† measurements at

pressure (atm)	T = 64°
150	
200	
300	
350	
400	
500	
700	
900	

PRESSURE (ATM)

1000

500

0.002

FIG. 2.—Theoretical and experimental

gas through a liquid nitrogen trap. The reaction vessel was cooled while the reaction proceeded. A sample of hydrogen

the pipette was adjusted to the desired pressure, sealed by closing the needle valve B, the system and opened to the gas burette lines. After this had been done the mercury and the gas enclosed in the pipette were maintained at constant temperature in an oil bath connected to a mercury manometer. From volume and number of moles of gas initially enclosed in the pipette at the high pressure calculated. The correction was applied in these measurements to the cryostat temperature.

containing liquid nitrogen and fitted with a connecting line to the pipette. Temperature was measured in a pocket immersed in the liquid nitrogen. A line to a vacuum pump was also provided.

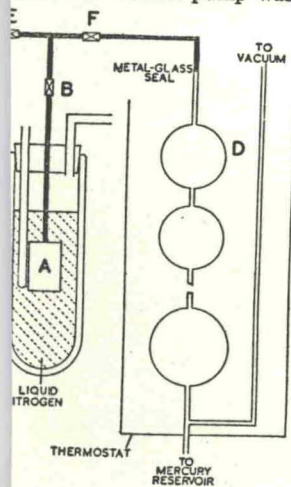


Diagram of apparatus.

and so obtain temperatures below the normal boiling point of the gas. The proportion of the enclosed gas was approximately 10% of the total. Care was taken to ensure that the gas was at the same temperature as the cryostat. Care was taken to ensure that the gas was at the same temperature as the cryostat. Care was taken to ensure that the gas was at the same temperature as the cryostat.

reaction of this volume which was immersed in the cryostat. These volume measurements of the compressibility of Michels and Goudek 7 and of Johnson 8

erg standard test gauges of the Bourdon type were used for the purpose of the investigation. The pressure was measured by the method of Hainsworth 9 at a pressure of 100-150 atm through a liquid nitrogen trap at 110° C and then through a steel trap into a pressure transducer.

by a method similar to that used by Schiff and Steacie 10 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<sub>2</sub>O instead of D<sub>2</sub>O.

ceeded. The reactor was closed and returned to the Dry Ice bath for about 20 minutes to "deep freezing" of the D<sub>2</sub>O. After this period it was opened and 100 g of calcium was 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 rose to 100 atm in about half a minute. The deuterium was then passed at about 40

TABLE 1.—ISOTHERMS OF HYDROGEN

T = 64.5° K		T = 78.9° K	
pressure (atm)	density (mole cm <sup>-3</sup> )	pressure (atm)	density (mole cm <sup>-3</sup> )
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<sub>2</sub>O with calcium.

TABLE 2.—ISOTHERMS OF DEUTERIUM

T = 64.5° K		T = 78.9° K	
pressure (atm)	density (mole cm <sup>-3</sup> )	pressure (atm)	density (mole cm <sup>-3</sup> )
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

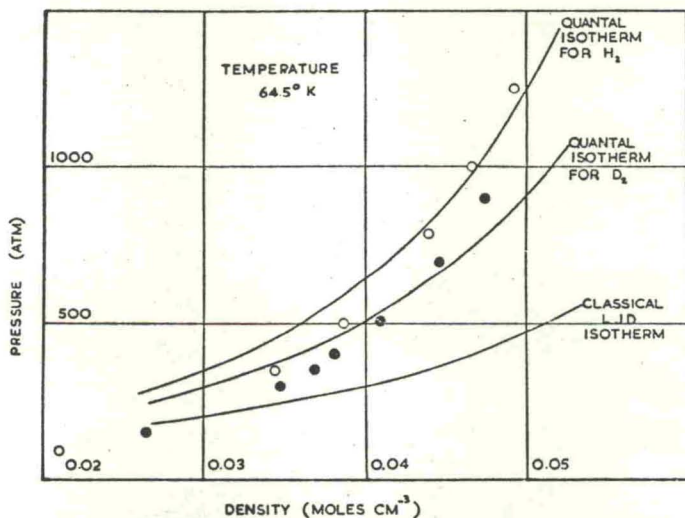


FIG. 2.—Theoretical and experimental isotherms at 64.5° K. The open circles are the experimental points for H<sub>2</sub>, the filled circles are for D<sub>2</sub>.

atm through a liquid nitrogen trap into the gas compressor. It is, perhaps, noteworthy that Schiff and Steacie 10 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<sub>2</sub>O instead of D<sub>2</sub>O.

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.

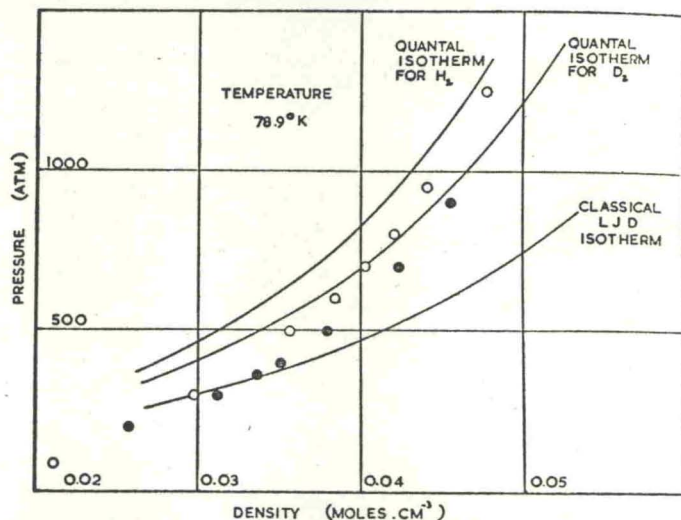


FIG. 3.—Theoretical and experimental isotherms at 78.9° K. The open circles are experimental points for H<sub>2</sub>, the filled circles are for D<sub>2</sub>.

#### DISCUSSION

In the figures, our results are compared with the classical LJD and quantal isotherms for H<sub>2</sub> and D<sub>2</sub> 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 H<sub>2</sub> or D<sub>2</sub> 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 Michels from a quantal analysis of the second virial coefficients of H<sub>2</sub> and D<sub>2</sub>. The assumption of the identity of the fields between H<sub>2</sub> and D<sub>2</sub> molecules is justified by the similarity in behaviour of these gases<sup>7</sup> when the temperature is high enough to render the quantum effects unimportant. We have interpolated in the table of Wentorf, Buehler, Hirschfelder and Curtiss<sup>3</sup> 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 H<sub>2</sub> and D<sub>2</sub> 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 H<sub>2</sub> and D<sub>2</sub> 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:

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

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

H.  
 $\epsilon^* = h^2 D(m\epsilon^*)^{-1/2}$  which  
 is the reduced equation

$$\Delta p^* = T^* \left[ v^* \right]$$

where  $y^*$  is a function of  
 $(1 + 12y^* + 25 \cdot 2y^{*2})$   
 in conformity with  
 the quantal equation of state

where  $f$  is a universal function.  
 For the general plot  
 temperature  $T^* = 2.14 \epsilon^*$

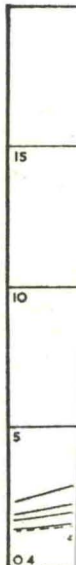
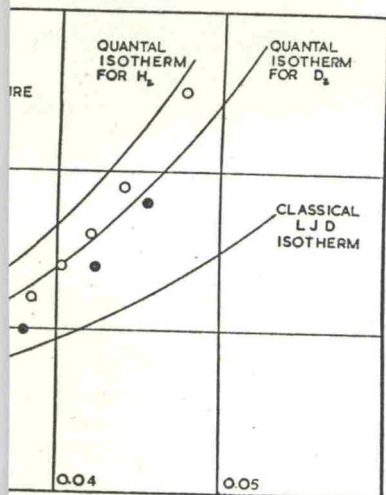


FIG. 4.—Reduced isotherms.

He  
 H<sub>2</sub>  
 D<sub>2</sub>  
 N<sub>2</sub>  
 A

H<sub>2</sub> and D<sub>2</sub>. The  
 data were taken from the  
 experimental data for  
 the temperature scale  
 of Hetherington, Kvalne  
 and A.

are given in tables 1 and 2 in the form of pressure-density curves, as shown schematically in fig. 2 and 3.



(MOLES .CM<sup>3</sup>)  
 Isotherms at 78.9° K. The open circles are for H<sub>2</sub>, the filled circles are for D<sub>2</sub>.

DISCUSSION

Compared with the classical LJD and quantum statistics at 78.9° K. The theoretical curves for the potential energy between a pair of molecules are given by eqn. (1) with  $\epsilon^* = 50.75 \times 10^{-16}$  ergs, and the virial coefficients of H<sub>2</sub> and D<sub>2</sub>. The difference between H<sub>2</sub> and D<sub>2</sub> molecules is just noticeable at 78.9° K when the temperature is high enough. We have interpolated in the table of Curtiss<sup>3</sup> to find the classical LJD pressures of eqn. (2) to obtain the quantal isotherms. At the experimental points lie closer to the quantal isotherms, particularly at the higher densities. This fact alone, however, is not sufficient to justify the use of the quantal inflation of the pressure. It may be inaccurate at these reduced pressures. A significant fact, therefore, is that the difference between the experimental and the classical predictions at high density is roughly that predicted by quantum statistics. Classically there would, of course, be no difference.

The same comparison can be met by plotting the experimental data together with the results for other similar gases. It is then possible to compare the experimental data for light gases and the predictions of quantum statistics. For this, we introduce the quantities:

$$p^* = pv_0/N\epsilon^* = pD^3/\epsilon^*,$$

$$v^* = v/v_0 = v/ND^3,$$

$$T^* = kT/\epsilon^*,$$

where  $v_0$  and  $D$  are the van der Waals and Curtiss.<sup>3</sup> It is also convenient to express the results in terms of the dimensionless parameters

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

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

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

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

It is in conformity with the general considerations of de Boer<sup>11,12</sup> our reduced equation of state is of the type

$$p^* = f(T^*, v^*, A^*),$$

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  $T = 78.9^\circ \text{K}$

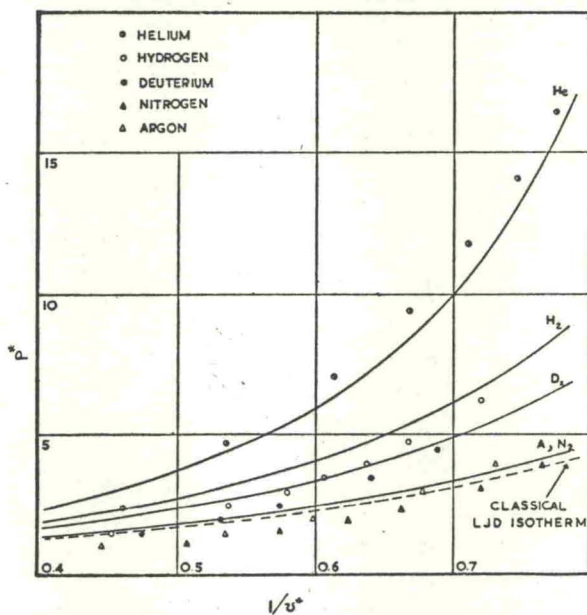


Fig. 4.—Reduced isotherms for  $T^* = 2.14$ . The full curves are the quantal isotherms.

TABLE 3.—MOLECULAR CONSTANTS

	$\epsilon^*/k$ (°K)	$D$ (cm $\times 10^{-8}$ )	$A^*$
He	10.2	2.56	2.64
H <sub>2</sub>	37.0	2.92	1.73
D <sub>2</sub>	37.0	2.92	1.22
N <sub>2</sub>	96.6	3.72	0.225
A	120.3	3.41	0.187

for H<sub>2</sub> and D<sub>2</sub>. The intermolecular force parameters and the values of  $A^*$  have been taken from the tables of de Boer.<sup>11,12</sup> They are listed in table 3. The experimental data for He, N<sub>2</sub> and A were given by short extrapolations on the temperature scale from the measurements of Buchmann<sup>13</sup> on He; Bartlett, Hetherington, Kvalnes and Tremearne<sup>14</sup> on N<sub>2</sub>; Michels, Wijker and Wijker<sup>15</sup> 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.

We wish to express our thanks to Dr. J. F. Pearse for helpful discussions, to the design of the apparatus and to Mr. S. J. Lake for constructing much of it. Our thanks are also due to Prof. T. G. Hunter for making available the laboratory space in which the work was carried out.

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## THE VAPOUR PRESSURE AND ORTHOBARIC DENSITY OF NITROUS OXIDE

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The vapour pressure of nitrous oxide has been determined from 12° C to the critical point, and the orthobaric densities from 20° C to the critical point. The apparatus consisted of a calibrated, heavy-walled, hard-glass pressure tube containing the gas sample, confined over mercury, and thermostated with a vapour bath. Visual observation of the dew points, boiling points and critical points was thus possible. Pressures were determined with a free piston gauge to 0.01 atm, and temperatures to 0.01° C with mercury-in-glass thermometers. A cathetometer capable of reading to 0.001 cm was used to make the volume measurements.

The vapour pressures obtained are substantially lower than the I.C.T. values and are represented by the equation

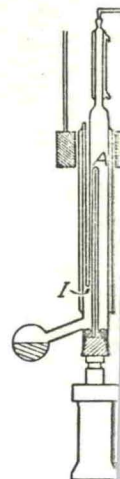
$$\log_{10} p \text{ (atm)} = 4.6258 - (858.63/T).$$

The results are compared with other determinations on the vapour pressure and orthobaric densities of  $N_2O$ .

In the course of measuring the vapour pressure and orthobaric densities of mixtures of  $CO_2$  and  $N_2O$ , these properties of pure  $N_2O$  were determined. The vapour pressures obtained were consistently lower than the I.C.T. values,<sup>1</sup> while the orthobaric densities showed only slight differences. The I.C.T. vapour

pressures at high temperatures from 15° C to the critical point were made by observations were made by them - 100° C to - 30° C. Systematic deviations from the I.C.T. values and support the present

APPARATUS.—(a) High pressure cell, the central feature of which is a pressure tube confined over mercury. (b)  $CO_2$ . Observations were made corresponding to the liquid air region at 20° and 28° C. This length of meniscus was correlated with the work of Michels, Blaisse and Michels, and a soft iron stirrer actuated



a steel compressor block. The pressure tube A was also filled with mercury. It was connected to a Bourdon gauge B with oil. H was a round-bottom flask of mercury in the jacket. The heads in the apparatus were made to revolve by a soft iron stirrer. The  $CO_2$  at the ice point was used. The pressure tube A was wrapped with aluminium foil. Ethyl alcohol and water were used in the jacket. The bottom, which was heated, was used for boiling a pure liquid. The pressure was constant, and can be easily adjusted. The temperatures from 34.6° C to - 100° C were required, being achieved by the use of a liquid nitrogen system to produce the low temperatures. The system to smooth the pressure was of the type used by Wadsworth.