

THE MAGNETIC SUSCEPTIBILITY OF GASES
II. TEMPERATURE DEPENDENCE

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ABSTRACT

The susceptibilities of CO₂, N₂ and H₂ are measured at room temperature and at liquid air temperature using O₂ as a standard. The results are:

	Molecular susceptibility $\times 10^6$	
	298°K	88°K
CO ₂	-24.2	—
N ₂	-14.8	-14.2
H ₂	-5.8	-3.3

The relative values at room temperature are in fair agreement with most previous observations, but the absolute values are more diamagnetic than any previously recorded. The low temperature observation on N₂ can be interpreted as meaning that if a permanent moment is present, it is less than 1/25 of a Bohr magneton. The large change observed in H₂ is entirely unexpected, and the observations should be repeated.

IN A previous communication,¹ hereafter referred to as Part I, the proportionality between volume susceptibility of gases and pressure was established, thus clearing the way for an examination and interpretation of the temperature dependence. On the assumption that there is no diamagnetic orientation and that the molecular susceptibility of polyatomic gases is unaffected by temperature changes through such mechanisms as, for instance, slight differences in nuclear separations in various thermally excited states, the expression for the volume susceptibility may be written

$$K = \left(\frac{a}{T} + b \right) \frac{p}{T} \quad (1)$$

p and T stand for pressure and absolute temperature; a is a positive constant which measures the permanent moment of the molecule; b is a negative constant which measures the diamagnetism. The work described below is concerned chiefly with the gases O₂, H₂, and N₂. For O₂ b may be taken equal to zero, and in this form Eq. (1) has been tested² over a considerable range of temperatures and pressures and found to hold. For H₂ and N₂ it has heretofore been assumed that $a=0$, and it is the chief purpose of this paper to check this assumption, and to discuss the absolute values of the constant b .

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¹ F. Bitter, Phys. Rev. **35**, 1572 (1930).

² K. Onnes and E. Oosterhuis, Konink. Akad. Wetensch, Amsterdam, Proc. **15**, 1404 (1913). Communication No. 134d from Phys. Lab. Leiden.

THE APPARATUS

The apparatus used in the following measurements is essentially the same as that described in Part I. A liquid air trap was introduced between the gasometer containing pump oil and the quartz furnace containing copper filings in order to prevent any vapors from reaching the furnace. Further, in order to reduce the volume of the purifying train, two of the three drying tubes were removed, leaving one tube containing P_2O_5 and the long spiral immersed in liquid air to accomplish the drying of the gases. The functioning of the train was checked spectroscopically as described in Part I.

Preliminary trials at low temperatures showed that the measuring apparatus described in Part I was not satisfactory. Even after the Dewar had been filled with liquid air and left standing for hours, the test body would not come to rest. This was due to slight convection currents, which were greatly reduced by enclosing the test body in a chamber of slightly different design as shown in Fig. 1. The resistance thermometer was eliminated

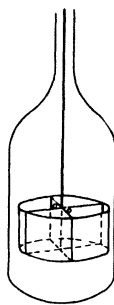


Fig. 1. Diagram of apparatus.

entirely. The container was immersed in liquid air up to the constricted portion. This was done by means of a Dewar flask which fitted between the pole-pieces of the magnet. In this way the test body was almost completely surrounded by walls at liquid air temperature, and heat was brought into the measuring chamber only along the long thin stem of the test-body. Further trials showed that this arrangement was satisfactory. The temperature was read on a pentane thermometer immersed in the liquid air bath. Its accuracy was first checked against the boiling point of pure O_2 .

THEORY OF MEASUREMENTS

Previous work had established the proportionality between, first, pressure and deflection of the test body; and second, pressure and volume susceptibility. From this, proportionality between deflection and susceptibility could be inferred for all measurements carried out at any given temperature. Thus if δO_2 and δH_2 represent the deflections produced by O_2 and H_2 at a pressure of say 1 cm, we may write

$$(K_{H_2})_{T,p} = \left(\frac{\delta H_2}{\delta O_2} \right)_T (K_{O_2})_{T,p} \quad (2)$$

In the following, oxygen was used as a standard, it being assumed³ that its volume susceptibility, K_{O_2} at 20°C and 76 cm pressure was 0.14×10^{-6} , and that its volume susceptibility at any other temperature T could be found by multiplying the above figure by $(293/T)^2$.

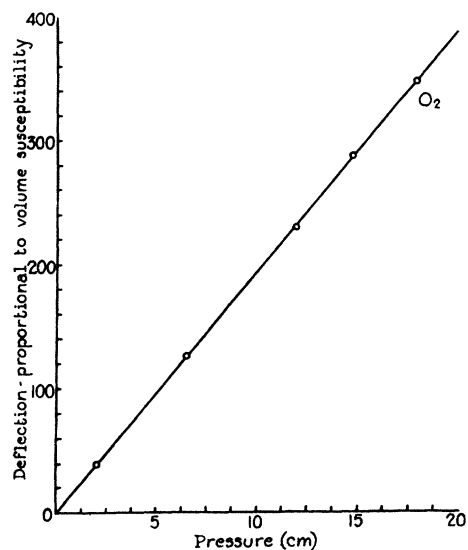


Fig. 2. Deflection, or volume susceptibility of O_2 in arbitrary units plotted as a function of the pressure, the observations being made at room temperature.

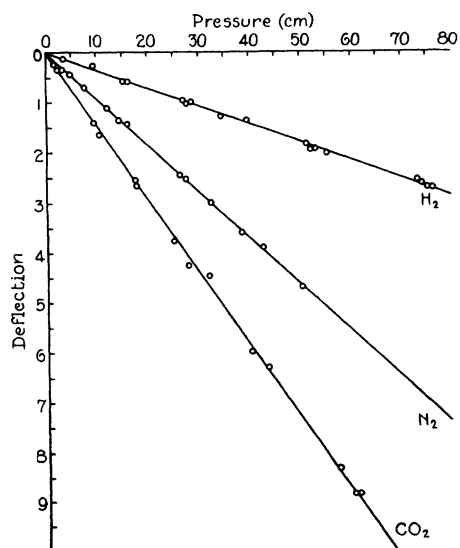


Fig. 3. Deflection or volume susceptibility of H_2 , N_2 , and CO_2 in the same units as those used in Fig. 2, plotted as a function of the pressure, the observations being made at room temperature.

³ J. H. Van Vleck, Phys. Rev. **31**, 608 (1928).

In making a measurement the procedure was therefore the following: first plot the pressure vs. deflection curves, as in Figs. 2, 3, 4 and 5. From these obtain the quantities (δ_{H_2}), and by substituting the numbers thus

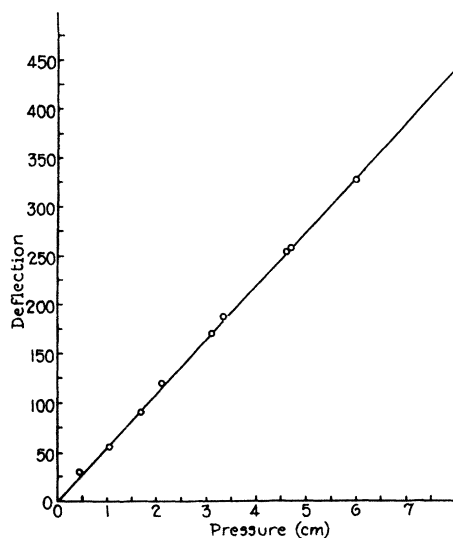


Fig. 4. Deflection, or volume susceptibility of O_2 in arbitrary units plotted as a function of the pressure, the observations being made at the temperature of liquid air.

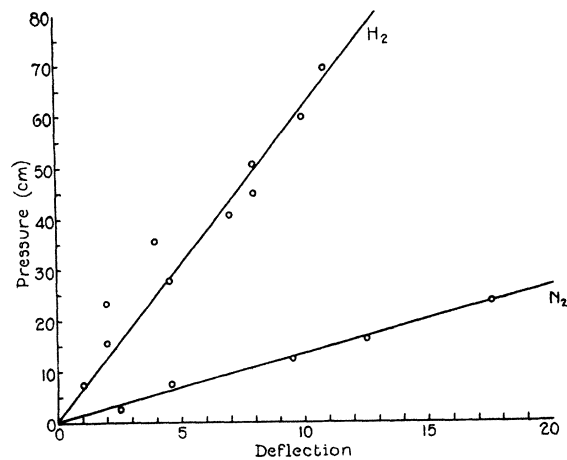


Fig. 5. Deflection, or volume susceptibility of H_2 and N_2 in the same units as those used in Fig. 4, plotted as a function of the pressure, the observations being made at the temperature of liquid air.

obtained into Eq. (2), the absolute values of the volume susceptibility at any temperature could be obtained.

RESULTS AT ROOM TEMPERATURE

As is evident from the above, these results may be divided into the following individual measurements: The ratio of the volume susceptibilities of a pair of gases; and the calibration, which involves the assumption of an absolute value for some standardizing substance. The division of the results into these two groups may conveniently be applied to the results of other observers, as most of their work has also been carried out in this fashion. Unless this is done, a faulty calibration would make all the measurements appear wrong, instead of showing up in the calibration as it ought. The results are shown in Table I.

TABLE I. Ratios and absolute values of the molecular susceptibilities of diamagnetic gases as found by various observers. (Vaidyanathan did not measure H_2 , but found an absolute value of -12.9×10^{-6} for N_2 , which multiplied by 0.39 gives (-5.0) which for the sake of comparison, is listed above. All the measurements were carried out at room temperature.)

	Hammar ⁴	Wills & Hector ⁵	Glaser ⁶	Lehrer ⁷	Vaidyanathan ⁸	Také Soné ⁹	Author
H_2/N_2	0.39	0.33	0.54	—	—	0.54	0.39
H_2/CO_2	.23	—	.22	.23	—	—	.24
N_2/CO_2	.59	—	.39	—	.63	—	.63
$H_2(\times 10^6)$		-3.94	—	-5.0	(-5.0)	-3.94	-5.8

In the first part of the table, the agreement for H_2/CO_2 is good, and the value may be taken with considerable confidence as 0.23 ± 0.01 . The next best is N_2/CO_2 where three of the four measurements point to 0.61 ± 0.02 as the correct value. The origin of the too low value for N_2 found by Glaser is not at all clear, and further work on this point should prove very interesting. Assuming that these two ratios are right, they give for H_2/N_2 $0.23/0.61 = 0.38$ in good agreement with the results of Hammar and myself (0.39). The agreement among the various absolute values for H_2 is very poor, and at present there seems to be no way of choosing the most nearly correct. I wish to add, however, that the use of the values for H_2 and N_2 found in this work would not invalidate the arguments advanced in an earlier paper¹⁰ on the susceptibility of organic gases, where the measurements of Wills and Hector on N_2 and H_2 were used as standards.

RESULTS AT LIQUID AIR TEMPERATURE

For N_2 the ratio of the molecular susceptibility at 298°K to that at 88°K was found to be 1.04, which means that, within the experimental error, the

⁴ G. W. Hammar. Thesis. California Institute of Technology. 1926.

⁵ A. P. Wills and L. G. Hector, Phys. Rev. **23**, 209 (1924). L. G. Hector, Phys. Rev. **24**, 418 (1924).

⁶ A. Glaser, Ann. d. Physik **75**, 459 (1924).

⁷ E. Lehrer, Ann. d. Physik **81**, 229 (1926).

⁸ V. I. Vaidyanathan, Phil. Mag. **5**, 380 (1928).

⁹ Také Soné, Phil. Mag. **39**, 305 (1920).

¹⁰ F. Bitter, Phys. Rev. **33**, 389 (1929).

susceptibility is expressible by an equation of the form $K = bp/T$. More accurately, it can be stated that if the N_2 molecule had a magnetic moment of $1/50$ of a Bohr magneton, this would just have sufficed to change the above ratio from 1.00 to 1.04, and that hence, if the N_2 molecule does actually have a permanent moment, this is surely less than, say $1/25$ of a Bohr magneton.

The result for H_2 is unexpected.

$$\frac{(\chi_{H_2})_{298^\circ K}}{(\chi_{H_2})_{83^\circ K}} = 1.82$$

This measurement involves considerable uncertainty, as is seen from the way the points are scattered about the line in Fig. 5. They represent data taken in two consecutive runs, and the difficulties in making accurate readings were due to unusually large random motions of the test body. It would have been highly advisable to repeat these observations, but this was impossible for lack of time. The above ratio is so large, however, that it is impossible to attribute it to any experimental error save that of O_2 contamination, which, in view of the precautions taken, seems out of the question. The result may therefore be stated by saying that at liquid air temperatures the molecular susceptibility of H_2 is only about half of its value at room temperature. Such an effect could be due to either an actual decrease in the size of the hydrogen molecule, or to an alignment of its axis parallel to the field in the ground state with no rotational energy. There seems to be no reason to expect either of these effects, even when the existence of a nuclear spin is taken into consideration. Future work on hydrogen should take into account possible differences between the para and ortho states.