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The Magnetic Susceptibility of Nitrogen Dioxide

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A method has been developed whereby sensitivities for volume susceptibilities as high as 3×10^{-15} can be obtained. The main improvement in the method over that of other observers is in the construction of lighter test bodies and the use of smaller fibers. The method is applied to the measurement of the susceptibility of NO_2. The results agree within the limit of experimental uncertainties with Van Vleck's theoretical value for the molecular susceptibility of NO_2 namely, $\chi(NO_2)=0.375\ \chi(O_2)$. The susceptibility of N_2O_4 comes in as a second order effect and the value $\chi(N_2O_4)=-30\times10^{-6}\pm20$ percent is in fair agreement with the value $\chi(N_2O_4)=-25.8\times10^{-6}$ obtained by T. Soné.

I. Introduction

In view of the large discrepancies in the results of various observers for the magnetic susceptibilities of many gases and of the growing theoretical interest in these experimental values, it seemed advisable to carry on a series of experiments designed to increase the dependability and accuracy of the measurements. With this view the writer has designed an apparatus for the measurement of low susceptibilities for gases such as hydrogen or helium, which are fairly inert and can be readily purified.

Nitrogen dioxide is of interest both theoretically and chemically; its susceptibility should be given by the formula derived by Van Vleck,[1] namely:

$$\chi(NO_2) = 4N\beta^2S(S+1)/3kT + N\alpha$$

where $N\alpha$ is a small residual term due to high-frequency elements, β is the usual Bohr magneton, and S is the spin quantum number of the molecule and is presumably equal to $\frac{1}{2}$ for NO_2. The susceptibility of O_2 is given by the same formula. However since the ground level for this molecule is a $^3\Sigma^{-1}$ state making $S=1$, it follows that $\chi(NO_2)/\chi(O_2)=0.375$. Experimentally Soné[2] finds this ratio to be about one sixth of this value. Verhoek and Daniels[3] have worked out the dissociation constant for nitrogen tetroxide, and it is of interest to see whether the use of their value for the dissociation constant would lead to a consistent correlation of the magnetic measurements.

II. Design of the Apparatus

The Faraday method, whereby an oblong shaped test body is suspended in a nonhomogeneous field surrounded by the gas under investigation, was used. The method has been improved upon and used for the measurement of

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[1] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, pp. 274.

[2] Také Sôné, Sci. Rep. Toh. Imp. Univ. **11**, 139 (1922).

[3] Verhoek and Daniels, J. Am. Chem. Soc. **53**, 1250 (1931).

the susceptibility of gases by Glaser,[4] Hammar,[5] and Bitter.[6] The tube used by the writer is similar to the one used by previous workers except that the important parts of the tube were given a conducting film of gold or platinum and grounded so that there could be no electrostatic effects (Fig. 1). It was then found that drifts of the test body and the change in total torque from day to day were, as far as could be observed, completely eliminated after the tube and moving parts were carefully grounded.

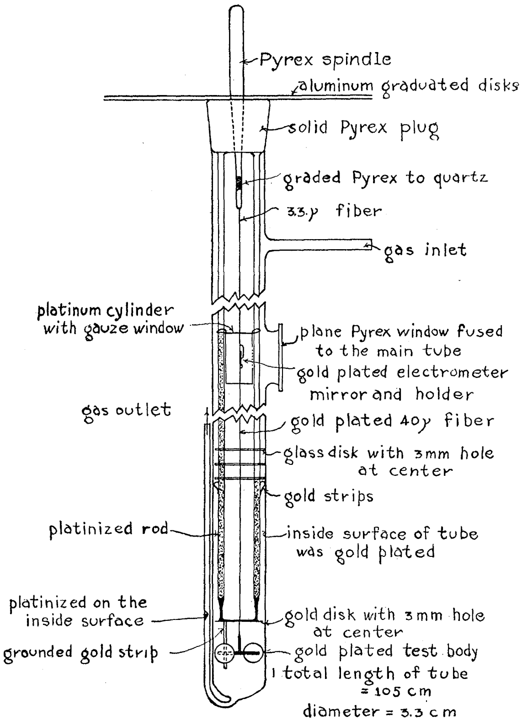

Fig. 1. Final tube.

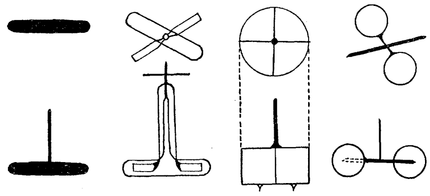

Fig. 2. Types of test bodies.

The main improvements in the method which the writer has introduced have come through the development of better test bodies and the use of smaller fibers. Four types of test bodies have been used by the writer. Fig. 2.

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[4] A. Glaser, Ann. d. Physik **75**, 459 (1924).

[5] G. W. Hammar, Nat. Acad. Sci., Proc. **12**, 597 (1926).

[6] F. Bitter, Phys. Rev. **36**, 1648 (1930).

The first type is a solid ellipsoid of the type used by Hammar[5] and by Glaser.[4] The one of this form used by the writer weighs 1.8 g. The second one is a hollow quartz ellipsoid weighing less than 1 g. It has the additional advantage that the quartz compensators reduce the total torque caused by the quartz to nearly zero. The ellipsoid is evacuated and sealed off, whereas the compensators are open to the gas. These compensators not only compensate for the torque caused by the field on the material of the test body itself but also reduce the effect of temperature disturbances. The third type of test body is similar to the one designed by Bitter,[6] except that fused quartz replaced glass. It has the apparent advantage of better symmetry; but its great disadvantage is that it weighs about 7 g. The compensation resulting from symmetry is apparent rather than actual, because, even if the test body were of perfect construction, there would be total compensation for only one position in the field, and if the test body be moved even a small distance from this position, the total torque would be increased to values as great as those obtained by the use of the other types of test bodies. The test body at the right of the figure is the type finally used. It consists of two evacuated spherical bulbs attached together and compensated by a small quartz rod. The one now in use weighs less than 100 mg and has a coat of evaporated gold on the surface. By allowing the test body to rotate until the surface comes in contact with a grounded gold wire, any accumulated electrostatic charges can be removed. With this type of test body it is possible to use much smaller fibers than with the other types and it has the further advantages that the magnetic field does not have to be held so constant, and changes in temperature are not so troublesome. The following table gives approximately the sensitivity of the four different types of test bodies which were used. The volume susceptibility of hydrogen for comparison is about 2×10^{-10}.

TABLE I. *Sensitivities of test bodies.*

Type:	I	II	III	IV
Sensitivity:	4×10^{-12}	1×10^{-13}	1×10^{-12}	3×10^{-15}

The compensators of the fourth-type test body were of such diameter and length that the total torque on the test body was nearly zero when in the position indicated by Fig. 3. The angle θ was made so that one could find a position of only slightly stable equilibrium; usually θ turned out to be about 75°. The nearer θ approached the angle giving unstable equilibrium, the longer would be the period of vibration and thus the higher the sensitivity, limited only for a given test body by the accuracy of the torsion head. Fig. 4 shows a typical curve of the relation of the torque to the angle α of the test

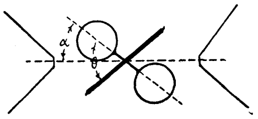

Fig. 3. Position of test body in the field.

body in the magnetic field. If A and B are angles of minimum and maximum torque, the difference of the torque at A and B depends upon the angle θ, and the value of the slope of the curve in Fig. 4 indicates the degree of stability, negative slopes meaning unstable equilibrium. Thus A and B are positions of neutral equilibrium and therefore high sensitivity; A on the curve would be a better angle than B because the total torque is less and therefore the fluctuations due to changes in field strength and temperature are smaller.

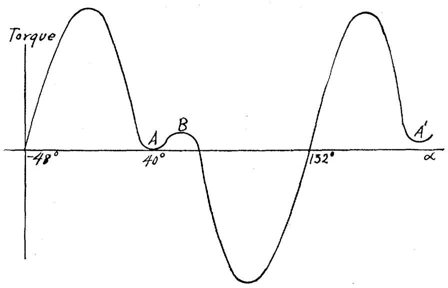

Fig. 4. Torque as a function of the angle α.

If A and B are too close together, it becomes difficult to keep the test body between these positions when the field is initially being applied; that is, while the field is rising from 0 to its final constant value. With a period of about one minute, sensitivities have been reached for which volume susceptibilities of 3×10^{-15} were observable.

The torque on a twisted fiber varies directly as the angle through which the fiber is twisted, inversely as the length, and inversely as the fourth power of the diameter. Thus for the highest sensitivities it is desirable to have a fiber of such diameter that the error in reading the torsion head will be less than that of the scale of the optical lever used to tell the position of the test body in the field. For a 3μ fiber with a 100 mg test body the torque is more than 2 revolutions of the fiber per atmosphere of hydrogen, and over 1500 revolutions per atmosphere of oxygen. The strength of this fiber is not sufficient for the heavier test bodies but is many times the strength necessary for the light test bodies.

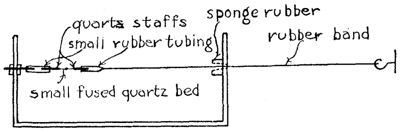

Fig. 5. Fiber drawing apparatus.

Fibers of any diameter as low as 1μ can be readily drawn where it is not required that each end of the fiber be attached to a large staff of quartz. However, since shellac or other organic compounds could not be used in this experiment for connecting the fiber to the torsion head because of the action of NO_2, it was necessary to devise an apparatus capable of drawing a fiber of a given diameter and length from two quartz staffs without breaking the fiber. The fiber drawing apparatus consisted merely of a stretched rubber band holding a quartz staff which would fly into a sponge rubber socket when released. (Fig. 5) At present fibers as small as 0.6μ in diameter and 50 cm long have been successfully made with this apparatus. The variation in the diameter along the entire length is less than 0.1μ, except for about 1 cm at each end. It has been found possible to draw the quartz staffs down very sharply to a 3μ to 5μ fiber. The absence of gradual tapering means that there is a definite point of contact between the staff and fiber upon which a microscope can be focused for centering purposes. The fiber is then centered very simply by heating the quartz staff in a horizontal position until its sags, due to its own weight, to the correct position. Fibers can be centered in this manner to within a radius of 5μ.

Because mercury is attacked by NO_2, a special pressure measuring device, due to Professor Daniels,[3] was used whereby the pressures of $NO_2+N_2O_4$ were measured by balancing the pressure of $NO_2+N_2O_4$ on the one side of a glass diaphragm against that of air on the other side. The pressure of air was then measured using an ordinary manometer.

TABLE II. *Taken at 20.05°C.*

Pressure of $NO_2+N_2O_4$ in cm of Hg	Torque on the fiber in revolutions	Pressure of $NO_2+N_2O_4$ in cm of Hg	Torque on the fiber in revolutions
1.94	60.752	35.58	153.558
2.99	66.000	37.69	156.727
4.18	71.995	39.55	159.998
5.28	76.087	41.66	163.079
6.28	80.991	43.51	166.254
7.49	85.925	45.89	169.988
8.67	90.080	48.20	173.728
9.89	94.182	50.00	175.675
10.92	97.082	51.52	178.165
12.64	102.429	52.64	179.648
14.42	107.522	54.23	182.272
17.03	114.623	55.91	184.382
18.43	118.358	51.09	177.673
19.87	121.720	46.72	171.678
21.21	124.827	41.53	163.694
22.68	127.988	36.55	154.603
23.94	130.814	32.25	147.338
25.36	133.585	27.89	139.090
26.91	136.580	23.52	129.947
28.10	139.135	19.28	120.088
28.72	140.170	15.56	110.64
30.55	144.195	11.76	100.05
34.01	150.414	7.85	86.791
32.25	147.659	4.54	74.148

III. RESULTS

To find the susceptibility of NO_2 it is necessary to know the dissociation constant for $N_2O_4 \rightleftarrows NO_2$ at various temperatures. The dissociation constant $k(N_2O_4)$ is given by:

$$k(N_2O_4) = p^2(NO_2)/p(N_2O_4)$$

where $p(NO_2)$ and $p(N_2O_4)$ represent the partial pressures of NO_2 and N_2O_4. Verhoek and Daniels[3] have measured this constant to about 2 percent for the temperatures 25°C, 35°C, and 45°C. The value of $k(N_2O_4)$ can therefore be found for any other temperature from van't Hoff's equation:

$$\log \frac{k_1}{k_2} = \frac{\Delta H}{2.303R} \frac{T_2 - T_1}{T_2 T_1}$$

where ΔH is the heat of dissociation. From these equations, and a knowledge of the total pressure of the gas, the amount of NO_2 present can be readily calculated. As the susceptibility of NO_2 is about 50 times that of N_2O_4, if we plot the torque on the torsion head against the partial pressure of NO_2 we should get nearly a straight line, inasmuch as the torque due to any gas is proportional to the pressure of that gas. Fig. 6 shows a typical curve of the

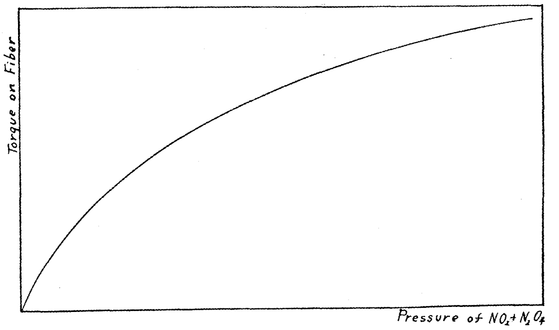

Fig. 6.

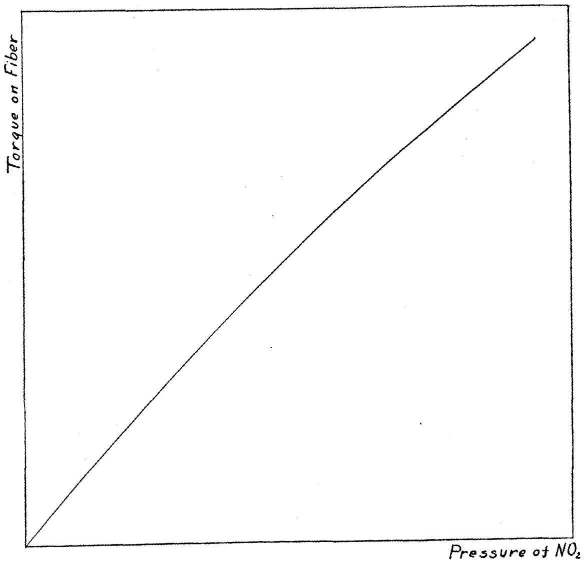

Fig. 7.

observed torques plotted as ordinates and the pressures of $NO_2+N_2O_4$ as abscissas. Fig. 7 shows a typical curve of the observed torques plotted against the partial pressures of NO_2. The slight curvature is due to the fact that the susceptibility of N_2O_4 is not zero. The curve of Fig. 8 was obtained from the data of Table III, first, by deriving from knowledge of the value of the dissociation constant, a curve of type in Fig. 7 for the susceptibility of N_2O_4 by assuming that $\chi(N_2O_4) = -2.5$ percent $\chi(NO_2)$. Fig. 8 gives the value $\chi(NO_2) = 0.390\chi(O_2)$ and is in good agreement with the theoretical value of 0.390 $\chi(O_2)$ calculated by Van Vleck,[1] which may be in error by as much as 3 percent or 4 percent because of the small neglected terms. Another factor which

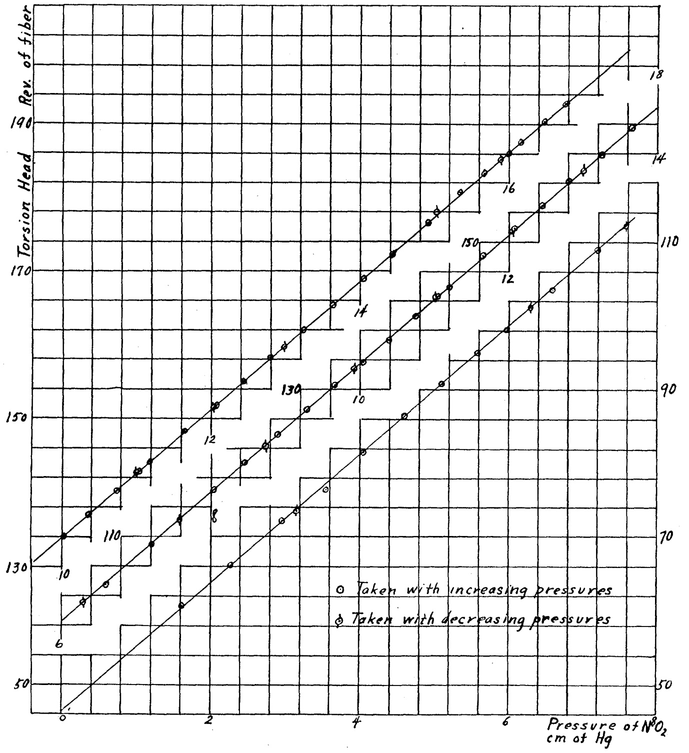

Fig. 8.

TABLE III. *Taken at 20.02°C.*

Pressure of Oxygen in cm of Hg	Torque on fiber in revolutions
1.63	84.34
3.75	130.66
6.73	198.70
9.62	263.51
12.25	320.50
15.08	383.63
18.30	454.65

might further account for the difference between this value and the theoretical value is the uncertainty in the value of $k(N_2O_4)$. The value $\chi(N_2O_4) = -30$ 10^{-6} agrees within the limit of error with Soné's value of -25.8×10^{-6}. Fig. 8 and three other curves at different temperatures give the values listed in Table IV. It is to be noted that the agreement with the theoretical value is better for the higher temperatures, which are nearer the temperatures for which $k(N_2O_4)$ was determined. Through the entire work the susceptibility of O_2 was used as a standard. Table III.

TABLE IV.

Temperature	$\chi(NO_2)/(\chi N_2O_4)$	$-\chi(N_2O_4)/\chi(NO_2)$	$\chi(N_2O_4) \times 10^6$	$(\chi(O_2) = 3330 \times 10^{-6})$
22.60°C.	0.370	2%	−25.0	
20.54	0.382	2.5%	−31.3	
20.05	0.390	2.5%	−31.3	
19.17	0.400	2.8%	−35.0	

The volume susceptibility of NO_2 computed from the above relative values is $k(NO_2) = 579 \times 10^{-10}$. Sensitivities for k of about 10^{-12} were used, therefore the small deviations from the curves of the observed points could not be attributed to the lack of sensitivity.

An error of 0.1°C in the measurement of temperature would change the value of the dissociation constant by an amount sufficient to account for most of the deviations. However, with a thyratron tube arrangement for control, observed room temperatures was maintained constant to within 0.1°C; in addition the temperature of the tube was read to 0.01°C, on a 0.001°C thermometer, and corrections applied for each point on the curve.

IV. CONCLUSION

The results for NO_2 are entirely satisfactory and in accord with the theoretical value of Van Vleck.[1] They remove the previous very bad agreement between theory and the only existing experimental results by Soné. The results for N_2O_4, determined from the small curvature of the curves, should be correct to within 20 percent. Further work is being undertaken to determine the susceptibility of hydrogen and some other common gases.

The writer wishes to express his appreciation to Professor Mendenhall for his guidance throughout the duration of the work, to Mr. Foerst, the mechanician, for his cooperation in the construction of the apparatus, and to Mr. Verhoek and Professor Daniels for the preparation of the liquid $NO_2 + N_2O_4$.