

THE MAGNETIC SUSCEPTIBILITY OF GASES

I. PRESSURE DEPENDENCE

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ABSTRACT

A method is described for measuring the magnetic susceptibility of gases which has certain advantages over those used by previous observers. With such an apparatus, it is found that the volume susceptibility of CO_2 , N_2 and H_2 is proportional to the pressure. Deviations from proportionality of the type observed by Glaser are found in the above gases upon introducing water vapor as an impurity in amounts probably less than a few hundredths of a percent.

IN ATTEMPTING to interpret the results of magnetic observations on matter, it is difficult to determine what effects are due to the molecules themselves, and what due to their interaction with each other. Because of this, results obtained with gases may be interpreted with most confidence, since in this case, isolated molecules without interaction are most nearly approximated. The fundamental quantity to be observed is K , the volume susceptibility, which measures the average induced moment per cc. Classical mechanics and quantum theory agree in predicting

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

or

$$K = c p. \quad (2)$$

a is a positive constant which is zero if there is no permanent magnetic moment in the molecule, and b is a negative¹ constant which measures the distribution of electric charge in the molecule. The experiments described below were undertaken to check Eq. (2). In a future communication I hope to take up the absolute values of the constants a and b , and their interpretation for various gases.

The proportionality between the volume susceptibility and the pressure must be established before any interpretation of the constants a and b can be undertaken as it is equivalent to the statement that the molecules in a gas do behave as isolated units with only thermal interactions to establish thermodynamic equilibrium. The first attempt to verify Eq. (2) experimentally was made by Glaser^{2,3,4} who found that it held only for O_2 and atomic

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¹ b may, for polyatomic molecules, be positive, though no such case has actually been observed or even suggested. See, for instance, J. H. Van Vleck, *Phys. Rev.* **31**, 597 (1928).

² A. Glaser, *Ann. d. Physik* **75**, 459 (1924).

³ A. Glaser, *Ann. d. Physik* **78**, 641 (1925-6).

⁴ A. Glaser, *Ann. d. Physik* **1**, 814 (1929).

diamagnetic gases, but that for CO_2 , CO , N_2 and H_2 certain characteristic deviations occurred. Subsequently, Lehrer,⁵ Hammar,⁶ and Vaidyanathan^{7,8} repeated this work, and found no anomalies of the type reported by Glaser. Hammar in a further paper⁹ suggested that the effect observed by Glaser might be due to the absorption of water vapor on the test body by means of which measurements are carried out, as he once found the effect, but made it disappear again by renewing the P_2O_5 in his cleaning train. Further Buchner¹⁰ showed that small temperature differences, if present, in the various parts of Glaser's measuring apparatus, might account for the observed phenomenon. Thereupon, Glaser in a brilliant series of papers^{11,12,13} succeeded in showing that by introducing small amounts (1%) of O_2 in CO_2 , he could produce a mixture which satisfied Eq. (2), but that with greater concentrations of O_2 anomalies reappeared; that in all probability adsorbed water vapor on his test body could not produce the effects observed; and that thermal disturbances were not present in his apparatus in a sufficient degree to influence his observations. From these results he deduces, and this is the weak point in his arguments, that other observers *had* O_2 as an impurity in their gases in just sufficient amounts (1% for CO_2) to hide the anomaly.

According to these papers, the relevant factors are small impurities of O_2 and H_2O . For the sake of completeness, let us add molecular orientation, which was first considered by Glaser himself, and two further ones whose influence has been tacitly neglected: excited states and ions. Molecular orientation in fields of the order of magnitude of those at present in use is not understandable¹⁴ on the basis of our present conception of the laws governing the behavior of molecules in a magnetic field, and may therefore be dismissed until the other possibilities are definitely disposed of. The presence of any radiation in the apparatus other than black-body radiation corresponding to the temperature of the gas under observation would destroy thermodynamic equilibrium and invalidate Eq. (2). As a matter of fact, excess of incoming radiation would produce an effect of the type observed by Glaser, though as nearly as one can calculate, it should be much smaller. Exact computations are impossible, as the electrical constitution of excited states is unknown. Actual observation on N_2 under various conditions of illumination ranging from almost complete darkness to very intense illumination of the gas between the pole pieces of the magnet gave no effect of the order of magnitude of that observed by Glaser. Further, the presence of 2 mg of radium within a few cm of the test body (see diagram of the apparatus in Fig. 1) gave no

⁵ E. Lehrer, *Ann. d. Physik* **81**, 229 (1926).

⁶ G. W. Hammar, *Proc. Nat. Acad. Sci.* **12**, 594 (1926).

⁷ V. I. Vaidyanathan, *Ind. Journal Phys.* **1**, 183 (1926).

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

⁹ G. W. Hammar, *Proc. Nat. Acad. Sci.* **12**, 597 (1926).

¹⁰ H. Buchner, *Ann. d. Physik* **1**, 40 (1929).

¹¹ A. Glaser, *Ann. d. Physik* **2**, 233 (1929).

¹² A. Glaser, *Ann. d. Physik* **3**, 1119 (1929).

¹³ A. Glaser, *Ann. d. Physik* **4**, 82 (1930).

¹⁴ F. Bitter, *Phys. Zeits.* **30**, 501 (1929).

change in the deflections of the order of magnitude of those to be expected if the Glaser effect is to be explained on the basis of the anomalous behavior of ions which are, of course, always present unless very elaborate precautions are taken.

Experimentally, then, the problem reduces itself to the determination of the effect of small amounts of impurities. To settle this question definitely for all possible impurities in varying amounts in all the gases on which observations have been made would require a very long investigation. In the following, I have gone only part way. The results obtained experimentally are that,

(1) CO_2 , N_2 and H_2 in which certainly not more than traces of H_2O and O_2 are present obey Eq. (2).

(2) A mixture of CO_2 and about 11% O_2 when dried as efficiently as possible, obeys Eq. (2).

(3) CO_2 , N_2 and H_2 , when contaminated by small amounts of H_2O (probably less than a few hundredths of a percent) do not obey Eq. (2), but give deviations of the type observed by Glaser.

The proof of these statements is contained in the rest of this report. Assuming their correctness, the present state of our knowledge concerning the applicability of Eq. (2) is summed up on the following statements.

Both linearity and departure from linearity have been observed in pressure susceptibility curves on samples CO_2 , N_2 and H_2 considered pure by the observers. The one observer, Glaser, who consistently obtains departure from linearity finds that linearity can be produced in CO_2 by critical amounts of O_2 impurity. He assumes that a similar effect exists for N_2 and H_2 and assumes that the samples used by other observers are contaminated with just this critical amount of impurity. Presumably, this critical amount of impurity would vary from gas to gas. The above assumption is possibly applicable to some observations, but it is certainly very improbable that it applies to all. It is certainly not applicable to the observations reported in this paper, since spectroscopic evidence is given that the purifying train removed all observable traces of O_2 from N_2 . Further, since the purifying train removed O_2 from N_2 satisfactorily, it probably did so equally well for H_2 and CO_2 . Further, since a mixture consisting of CO_2 and 11% of O_2 showed linearity, it is impossible to contend that this linearity was due to a 1% O_2 contamination. This much of the evidence seems straightforward, and disposes of the assumption that linearity in all observations is due to a critical O_2 impurity. The interpretation of the remainder of the evidence, that the addition of water vapor to the above gases gives anomalous effects, is not so clear. It shows merely that Glaser's results may be due to water vapor. But it is also conceivable that other substances might have a similar effect, and it is quite possible though highly improbable, that Glaser's results are due to some still undetermined and unsuspected cause. Taking the evidence all in all, however the following conclusions seem most plausible: that dry gases and gas mixtures obey Eq. (2); and that Glaser's anomalies are due to the presence of water vapor in his measuring apparatus.

It should be noticed that the mechanism by which H_2O influences the magnetic behavior of gases is by no means specified; it need not be adsorption in the test body, and in the light of Glaser's¹² work probably is not. It is, however, known that small amounts of H_2O do produce anomalous effects in gases. (For instance, ion mobilities¹⁵). This might suggest a clustering of gas molecules around H_2O molecules. Further the absence of any anomaly in argon and neon in Glaser's apparatus might be explained by assuming that these gases because of their chemical inertness do not cluster around H_2O molecules. However, such assumptions need experimental verification, and further discussion at present is useless. One more fact should, however, be observed, and that is that Glaser's arrangements for drying his gases are, as nearly as one can tell from his publications, extremely good, especially in his purifying train for H_2 , where the last unit is a liquid air trap containing charcoal! The only way in which any vapor could possibly contaminate this H_2 is if it were introduced in transferring the gas from the cleaning train to the apparatus (a step which is not described in his papers) or from the walls and ground joints of the apparatus itself.¹⁶ The latter is probably the only possibility, as in order to explain the fact that Glaser can repeat his results over and over again, a constant source of impurities would have to be assumed.

DESCRIPTION OF THE EXPERIMENTS

The method used in the measurements described below is essentially that employed by Glaser,² Hammar⁴ and Vaidyanathan.⁷ It consists in measuring the torque exerted by a gas on a solid body suspended in an inhomogeneous magnetic field. This solid body, called the test body, was constructed as shown in Fig. 1*a* and *b*. It is entirely of Pyrex glass with fused joints. At the bottom of a glass rod is a cylindrical vessel divided radially into four equal chambers. Two of these, *A*, had small holes in them to permit the surrounding gas to enter. The other two, *B*, could be sealed off. In this particular set of experiments, they were first exhausted, and sealed at *C'*. Then *C'* was dipped into liquid air, and they were sealed off at *C*. Above this test body was a small glass rod *D* so mounted that it could be either moved vertically or rotated horizontally around the stem of the test body. A small spring of tungsten wire was attached to hold it in place in any given position. If the test body with a vacuum in all four quadrants, is suspended between the pole-pieces of a magnet, it will be in equilibrium in some position which is adjustable by moving *D*. Actually *D* was moved and the suspension twisted until the test body would hang as nearly as possible with the dividing walls parallel and perpendicular to the line joining the pole pieces, both when the

¹⁵ H. Erikson, Phys. Rev. **34**, 635 (1929).

¹⁶ In one of his papers,¹² Glaser performed two experiments to show that water vapor does not enter his apparatus at this point. One consisted in showing that P_2O_5 was not attacked in a tube sealed to his system near the measuring apparatus; the other consisted in showing that a glass rod which changed its resistance when water vapor was adsorbed on its surface, did not do so in the course of a series of measurements. One can only say that these measurements are not quantitative and until one knows how little water vapor can be detected, no inference can be drawn.

magnet was on and off. If now, with the field on, a gas is admitted to the chambers *A*, the test body will evidently be deflected in such a way that *A* will approach the pole-pieces if the gas is paramagnetic, or recede from them if it is diamagnetic. The advantage of this test body over that used by Glaser is that it is made entirely of diamagnetic glass, and consequently, the

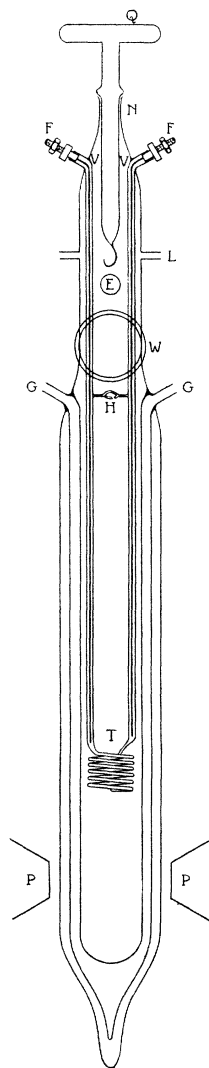


Fig. 2. Diagram of apparatus.

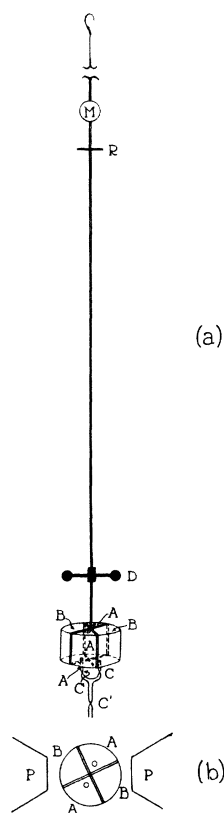


Fig. 1a. and 1b. Diagram of test body.

magnetic forces acting on it are practically independent of the temperature. The advantage over Hammer's test body lies in its symmetry, so that the magnetic forces acting on it do not have to be compensated by a large twist of the supporting fiber. In this way, the zero position (position of rest in a vacuum) is made practically independent of the field strength and of

The diagram illustrates a complex glass apparatus for studying the reaction of hydrogen with phosphorus pentoxide. Key components include:

- Gas Inlet:** Hydrogen (H_2) enters the system at stopcock C.
- Drying Tube:** The gas passes through a horizontal tube labeled D.
- Pressure Gauge:** A circular gauge labeled F is connected to the main line at stopcock E.
- Absorption Tubes:** The gas then passes through a series of three horizontal tubes containing different substances: $CaCl_2$, P_2O_5 , and glass wool with P_2O_5 .
- Manometer:** A U-tube manometer labeled H is used to monitor the pressure of the gas.
- Condenser:** A coiled tube labeled L is used to condense any vapors.
- Trap:** A U-tube trap labeled M is used to catch any remaining liquid.
- Exit:** The gas can be directed "to apparatus" or "to discharge tube" or "to M^cLeod pumps".
- Other Components:** Stopcocks A, B, C, E, G, and J are used to control the flow of gas. A gas source B is also shown.

Fig. 3. Diagram of cleaning train.

body was in place, came just below R , Fig. 1*a*, so that if in lowering the system into its container the fiber should break, the test body would be caught by H instead of dropping to the bottom of the container.

For the preliminary experiments the purifying train was very simple, consisting of a small quartz furnace, containing copper wire, a tube containing CaCl_2 and finally a liquid air trap. With this apparatus, the effect of light and γ -rays was investigated, and found to have no influence on the shape of the pressure susceptibility curves, as mentioned above. The gases used were taken from steel cylinders under pressure. The first measurements were made on CO_2 and the curves in Fig. 4 obtained. The liquid air trap was, of course, not in operation. The system was so slow in coming to rest that before proceeding with the measurements, a small damping coil of copper wire was attached to the rod D , Fig. 1a. This greatly improved the accuracy with which readings could be made. The next measurements were made with N_2 , and the curves in Fig. 5 repeated several times, alternately

with and without liquid air. These experiments indicated that the critical factor was purification and that probably the water vapor given off by the CaCl_2^{17} (which has a partial pressure of about 0.3 mm) was responsible for the departures of the observations from linearity, since the introduction

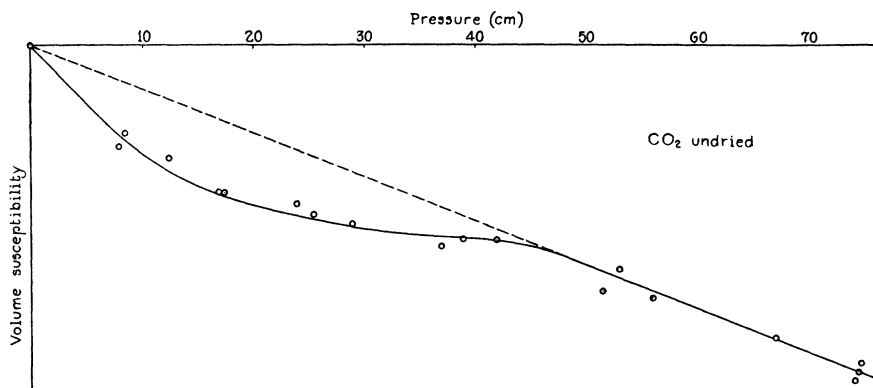


Fig. 4. Pressure susceptibility curve of undried CO_2 .

of a liquid air trap gave readings along a straight line. Consequently, the cleaning train was rebuilt with a view to carefully checking the effect of impurities. The system built is shown in Fig. 3. The tank containing the gas to be measured is connected to the system at *A*. *B* is a gasometer containing

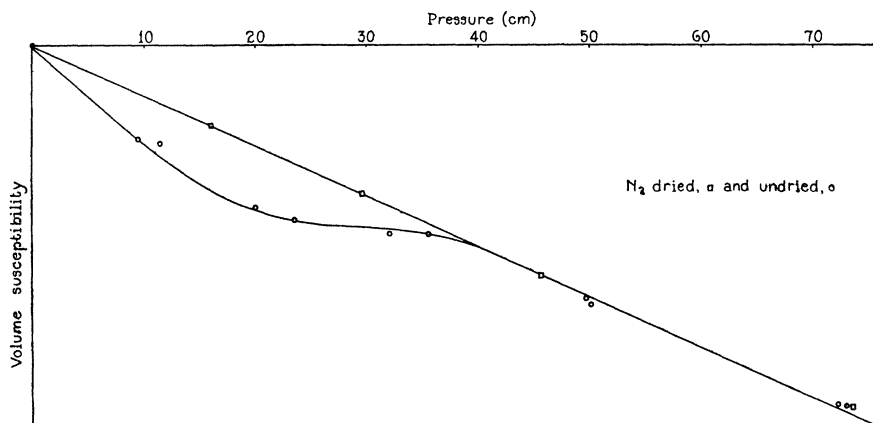


Fig. 5. Pressure susceptibility curves. \square and \circ N_2 .

pump oil, and was a great convenience in admitting the gases. *D* is a quartz tube 60 cm long and 2.5 cm in diameter filled with copper wire. At either end the tube was fused to short pieces of smaller tubing and these sealed with

¹⁷ This CaCl_2 was in the system while adjustments were being made, and had already taken up a good deal of water. The partial pressure of 0.3 mm is given in A. Goetz, *Physik und Technik des Hochvakuums*, p. 114, Second Edition.

sealing wax to the two way stopcocks *C* and *E*. The tube *D* was first covered with asbestos, then wound with chromel resistance wire in such a way that the near end from the point of view of gas entering the system could be kept red hot, while the far end did not glow at all. *F* is a bulb containing O_2 for measurements on gases mixed with O_2 . From this point, there were two approaches to the measuring apparatus. One went through a wash bottle *H* containing an 85% mixture of H_2SO_4 and H_2O whose specific gravity was 1.775. Such a mixture has according to the Landolt Bernstein Tables a vapor pressure of 0.15 mm. This path could be isolated from the system by means of the stopcocks *G* and *J*, and these were not opened until the first measurements with dry gases were finished. The other path went through three drying tubes, each about 1 meter long and 2–3 cm in diameter. The first contained $CaCl_2$, the second P_2O_5 , and the third P_2O_5 spread on glass wool. At this point the two paths joined again and were connected through a large stopcock to the pumps, a McLeod gauge, a mercury manometer, and to the apparatus through a glass spiral containing approximately 2 meters of glass tubing which could be immersed in liquid air. Immediately before the measuring apparatus a small discharge tube with a quartz window was fused to the system, so that a photograph of the spectrum of every gas could be taken immediately after a measurement. The procedure in filling a gas was to pump out the whole apparatus from *E* on, except for the measurements with dry gases, in which the wash-bottle *H* was not evacuated. In about 10 minutes the pressure could be reduced to 10^{-3} mm. The oil in the gasometer was sucked up to the stopcock *B*, which was then closed. The gas to be measured was then blown through the apparatus from *A* and out at *E*. Then the furnace *D* was heated and H_2 flushed over the copper to activate it. Then more gas was flushed through from *A* to remove the H_2 . Then *E* was closed and *B* opened until the gasometer was full, when the stopcock *A* was closed. Then by opening *E*, gas could be let into the measuring apparatus from the gasometer. In this way the system could be filled without applying a vacuum to the reducing valve on the gas tank. Before beginning measurements the apparatus was filled and evacuated two or three times. The magnet was operated by a bank of storage batteries, giving 21 amperes and the current kept constant to about 0.01%. The coils were immersed in transformer oil which was cooled with water circulation, so that with the above current, the magnet was at a temperature only a few degrees above room temperature.

With this equipment the experiments were resumed. The first gas examined was CO_2 . The results of three runs are shown in Fig. 6. The gas went through the drying tubes at the rate of about 2 liters an hour. The spiral *L* was at room temperature. Although the points are somewhat scattered about the line drawn in the figure, there can be little doubt that they lie along a straight line. All measurements on CO_2 were complicated by the fact that in spite of the damping, the test body would continue to swing over a range of a few tenths of a millimeter for some time, usually about 1/2 hour, sometimes longer, and these swings were not perfectly regular. The

effect was especially large at atmospheric pressure. Apparently the swinging would die down and then suddenly start up again. This effect was observed only with CO_2 , not with a vacuum, or air, or O_2 or N_2 or H_2 in the apparatus. The observed points on Fig. 6 at atmospheric pressure are indicated by a line, as no single definite deflection could be obtained. Further, the zero

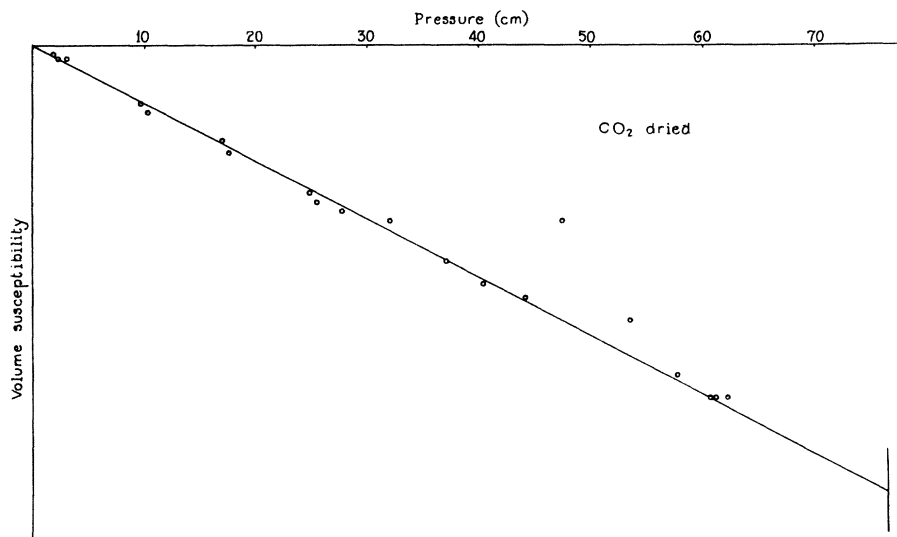


Fig. 6. Pressure susceptibility curve of dried CO_2 .

position of the apparatus did change between runs, as observed by Glaser in his papers. The cause of this zero-shift has not been determined. I am of the opinion that it is due to the changes in adsorbed layers on the test body, and hope eventually to build an apparatus that can be baked out to

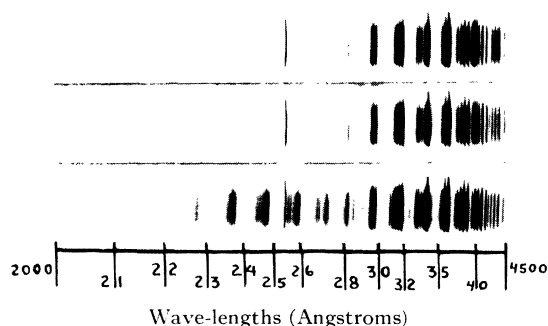


Fig. 7. N_2 band spectrum in varying degrees of purity.

test this point. The next measurements were made on N_2 with and without a liquid air trap, and three runs gave points lying on a straight line at least as closely as the points in Fig. 5. The spectroscopic photographs for N_2 proved to be the only useful ones. With CO_2 and H_2 , small impurities of O_2 and H_2O did not show. The spectrograph used was a small one made by Hilger with a quartz prism for use in the ultraviolet. In Fig. 7, are repro-

ductions of sample photographs. All three photographs were given the same exposure, 30 secs, with the same current and were taken with a gas pressure of about 3 cm in the discharge tube.

The first photograph was taken with N_2 passed over the hot copper, $CaCl_2$, P_2O_5 and the liquid air trap. In the second, the liquid air trap was removed. In the third, the liquid air trap was replaced but the furnace which heated the copper turned off. In the first picture, the NO bands are entirely absent. In the second, they begin to appear. This means that the water vapor which has passed all three drying tubes is sufficient, on dissociation, to produce a detectable amount of NO. The NO bands in the third photograph are due entirely to the O_2 present in the gas, as it comes from the tank, all water having been absorbed¹⁸ in the liquid air trap. A gas analysis showed that the N_2 in the tank contained only 0.6% of O_2 .

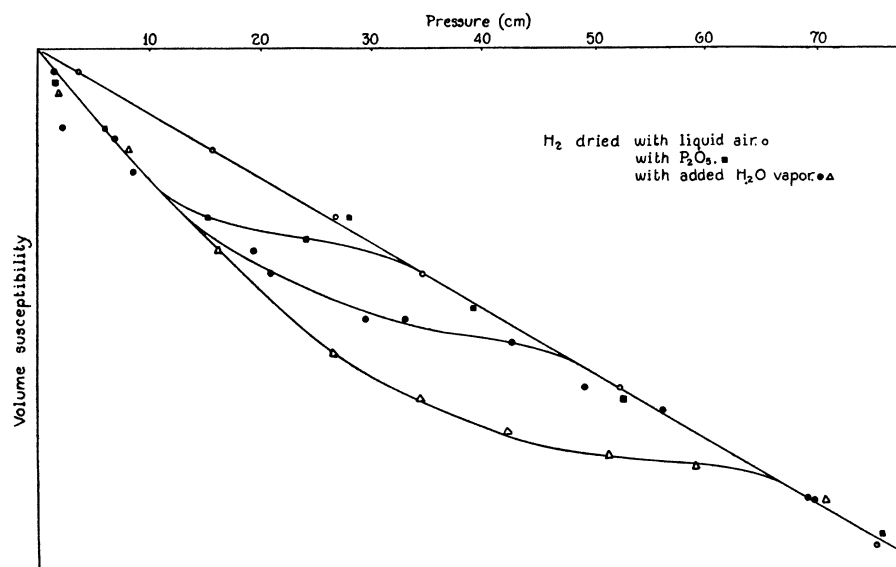


Fig. 8. Pressure susceptibility curves of H_2 with varying amounts of water vapor.

The next measurements were made on H_2 dried over P_2O_5 , but not with liquid air. This gave a very small Glaser effect. Upon the introduction of liquid air, however, a further run gave a perfectly straight line. The interpretation of this seems very straightforward; namely, that in spite of preliminary flushings over the copper in the furnace, this was not completely reduced, and that therefore, the H_2 entering the drying tubes contained more water vapor than any of the gases previously used; if this is so, it follows that a drying train, in all 3 meters in length, left sufficient amounts of water vapor in the gas to be detectable. It is also interesting to note that the one gas in

¹⁸ With longer exposure times the NO bands would appear even on photographs of N_2 as pure as I could make it. That this was due to the heating of the electrodes could be shown by taking two photographs of 30 secs duration each immediately after each other. The second showed NO bands, while the first did not. This sets a lower limit to the amount of water vapor detectable, but this is surely very small, as P_2O_5 has a vapor pressure of 10^{-4} mm and ice at liquid air temperatures 10^{-7} mm. See Goetz.¹⁷

which Hammar observed a Glaser effect was H_2 , which, for the reasons given above, probably contained more water vapor than either N_2 or CO_2 . The view that the H_2 leaving the furnace was very wet is further substantiated by the next measurements. The liquid air was removed and the gas admitted to the apparatus via the wash bottle *H*. The first runs gave very large Glaser effects, as in the lower curve in Fig. 8, but after considerable flushing, it was possible to repeat several times the curve in Fig. 8, which showed an intermediate Glaser effect. If the gases were saturated in the wash bottle, this corresponds to a water vapor pressure of .15 mm.

The results obtained so far seemed fairly conclusive, except for CO_2 , where it might conceivably be contended that the straight line in Fig. 6 is due to just that amount of O_2 (1%) impurity which according to Glaser destroys the anomaly. The first argument against such a view is that the furnace certainly purified N_2 so that nothing like 1% of O_2 was left as an impurity, and that consequently, there is every reason to believe that it

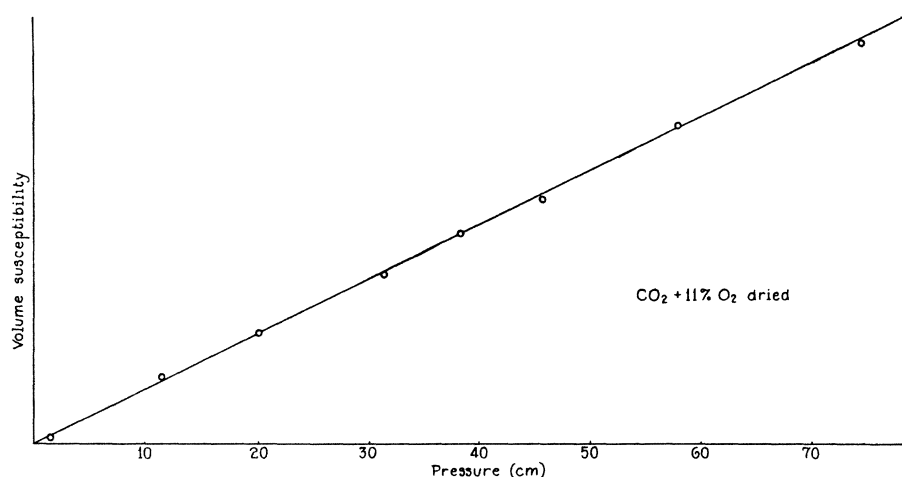


Fig. 9. Pressure susceptibility curve of the mixture 89% CO_2 + 11% O_2 .

did the same for CO_2 . The problem can, however, be attacked from another angle. According to Glaser,¹¹ the paramagnetic mixture of CO_2 plus about 11% O_2 should definitely show an anomaly at low pressures. This was tried with the gas dried in the train described above, and the observations indicated no such effect. The results are plotted in Fig. 9. The concentration of O_2 in this experiment was calculated on the basis of the relative deflections for the mixture and pure CO_2 . Deflection for CO_2 plus O_2 /Deflection for pure $\text{CO}_2 = +7.5/-9.0 = -.83$. According to Glaser, an anomaly should certainly be observed for O_2 concentrations corresponding to values of the above ratio between $-.9$ and 0 . This effectively disposes of the argument that normal behavior of CO_2 is due to a 1% O_2 impurity, since such normal behavior is found in a mixture which certainly contains much more than 1% of O_2 .

In conclusion, I wish to take this opportunity of expressing my appreciation of the very beautiful work done by Mr. William Clancy in blowing the glass parts of the apparatus previously described.

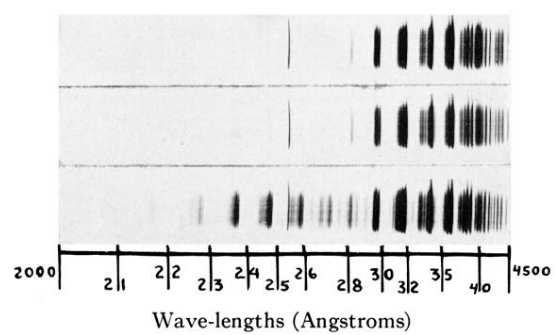


Fig. 7. N₂ band spectrum in varying degrees of purity.