

THE MAGNETIC SUSCEPTIBILITIES OF SEVERAL ORGANIC GASES

BY FRANCIS BITTER

ABSTRACT

A method for measuring the magnetic susceptibilities of gases similar in principle to that used by Wills and Hector but simpler in operation was developed. The following results given in molecular susceptibility $\times 10^6$ were obtained: methane (CH_4), -12.2 ; ethane (C_2H_6), -27.3 ; propane (C_3H_8), -40.5 ; butane (C_4H_{10}), -57.4 ; isobutane (C_4H_{10}), -56.3 ; ethylene (C_2H_4), -12.0 ; acetylene (C_2H_2) -12.5 ; using as standards H_2 , -3.94 and N_2 , -11.8 . These values are in error by less than 4 percent relative to each other. It is shown that the results cannot be reconciled with the assumption that the susceptibility of one of these molecules is equal to the sum of the susceptibilities of the atoms of which it is made up. The hypothesis is suggested that the susceptibilities of these substances are determined by the binding electrons, and it is shown that this assumption leads to a satisfactory interpretation of the observations if the two CH_2 groups of ethylene are supposed held together by electrostatic forces, and the two CH groups of acetylene by a bond similar to the ordinary C-C bond, such as in the $\text{C}_n\text{H}_{2n+2}$ molecules. It is shown that among the previous measurements of the susceptibility of H_2 and N_2 those made by Wills and Hector are probably the most nearly correct.

DETERMINATIONS of the magnetic susceptibilities of gases were made by a method which is a modification of that developed by Wills and Hector.¹ In principle the latter depended on making a solution of a paramagnetic salt in a diamagnetic liquid such that its volume susceptibility is equal to that of an unknown gas. In operation this method proved rather tedious, and since susceptibilities in terms of other gases were sufficient, it was decided to compare these directly to each other, without making use of an intermediate substance.

METHOD AND APPARATUS

It is assumed that the volume susceptibility of a mixture of gases obeys the additive law. More precisely, if the total pressure of a mixture of n gases at the temperature T is P , and the partial pressures of the constituents are $p_1, p_2, p_3, \dots, p_n$, and their respective volume susceptibilities are $k_1, k_2, k_3, \dots, k_n$, then the volume susceptibility K , of the mixture is given by

$$K = (1/P) \sum_{k=1}^n p_k k_k. \quad (1)$$

This equation was tested by Lehrer² and found to hold. There seems to be no reason for doubting its validity as long as no chemical reaction takes place within the mixture, and the measurements are made at normal temperatures and pressures.

¹ A. P. Wills and L. G. Hector, Phys. Rev. **23**, 209 (1924).

² E. Lehrer, Ann. d. Physik **81**, 229, (1926).

In measuring susceptibilities by the method described below use is made of the mechanical force which an inhomogeneous field exerts on atoms or molecules. In the case of gases this manifests itself in a slight pressure difference maintained between regions in and out of the field, and although such small differences are not capable of direct *measurement*, it was found possible to *detect* even smaller ones, and a balance method based on such detection was developed.

In the diagram in Fig. 1, K is a wooden frame surrounding the pole-pieces M of the magnet, and rigidly connected to it. To this frame is attached the microscope F and the manometer containing the constriction E , so that the horizontal branches can be well centered between the pole-pieces and kept there. In the manometer is a liquid containing colloidal particles whose motion can be observed with the microscope. Above one branch is a mixture of two gases, and above the other a third gas. To determine whether the mixture is more or less diamagnetic than the third gas, the gas-water inter-

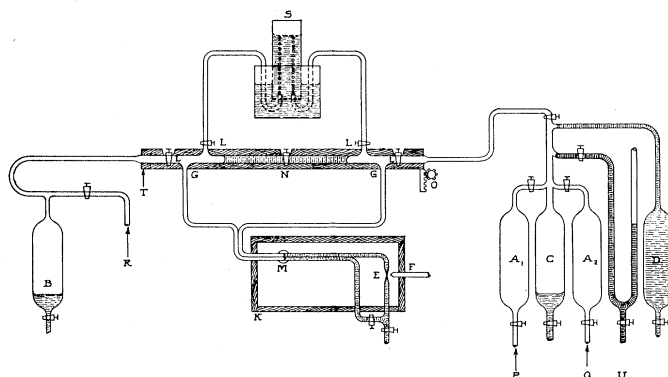


Fig. 1. Diagram of apparatus.

face of both arms is brought between the pole-pieces as indicated in the diagram, and a uniform field H applied. This exerts no force on the liquid of the manometer because of symmetry. But the changes in pressure of the gases when the field is applied will disturb the equilibrium of the system, and from the direction of the deflection of the colloidal particles it can be determined which suffers the greater decrease in pressure, and hence which has the greater susceptibility.

In order to bring the liquid to rest in the above position the following arrangement was adopted. Consider the stop-cocks L closed and the stop-cock N open. Then the arms of the manometer are connected to each other by means of the liquid column surrounding N . The tube containing this liquid is mounted on a board with a hinge at T and a gear at O so that its inclination can be varied, and the liquid column be made to slide to the left or right, thus creating a slight pressure difference between the two arms of the manometer sufficient to bring the liquid to rest. In order to make this part N separately movable, all connections to the stationary parts of the

apparatus were made by means of long fairly flexible glass tubes, about 3 mm in diameter. In order to fill in gases for measurements the liquid in the manometer was raised to the points *G*, *N* closed, and *L* opened, and gases flushed through from the containers *B* and *C* into the reservoir *S*. The dimensions of the apparatus were such that after allowing four or five gallons to flow through the apparatus in the course of about an hour, all traces of air were removed. The gases were then sucked down to *M* by lowering the liquid in the manometer, the system brought to rest by closing *L*, opening *N*, and levelling with *O*, and an observation made. Two methods to check the assumption of a uniform field over *M* were employed. Air was admitted to both sides of the manometer, and it was found that over a considerable region within *M* the manometer suffered no deflections upon application of the field. Suppose that nevertheless the fields over the two arms were not equal $H_1 = H + \delta H$, $H_2 = H$. Then we have approximately:

$$\delta p_{air} = \delta p_1 - \delta p_2 = \frac{1}{2} K_{air} \cdot 2H\delta H$$

If Δp is the smallest pressure change which can produce an observable deflection, and the largest inhomogeneity present, δH , is such that it will produce, using air, a change in pressure δp_{air} , we have:

$$\Delta p > \delta p_{air} = K_{air} H \delta H.$$

But since the volume susceptibilities of all the gases used were much smaller than the volume susceptibility of air, the change in pressure, δp_x , due to an inhomogeneity δH would be correspondingly smaller, and we have:

$$\Delta p > \delta p_{air} > \delta p_x = K_x H \delta H$$

and the inhomogeneities in the field are not sufficient to affect the results.

In Fig. I, A_1 , A_2 and *B* represent the storage tanks for the three pure gases *P*, *Q*, and *R*. The gases *P* and *Q* were admitted to the chamber *C* in amounts determined by readings on the mercury manometer *U*. This mixture was then thoroughly stirred by passing it back and forth between the chambers *C* and *D*.

Attempts were first made to handle and measure the gases at pressures of about 20 atmospheres, but this proved to involve practical difficulties, mainly in connection with developing suitable valves to replace the stop-cocks, and it was found that sufficient sensitivity could be obtained by other means, thus making it possible to keep the apparatus simple and easy to construct and handle.

In order to get conveniently strong fields without resorting to excessive currents, pole-pieces with a small diameter were selected. This was 1 cm and their distance apart 3 or 4 mm. Fields of over 20,000 gauss proved unnecessary, and a current of 15 or 20 amperes through the coils of the large Weiss electromagnet used was ample. The constriction *E* was chosen very small. Some having inside diameters of 0.05 mm were tried and proved quite feasible. Because of the difficulty of bringing the small particles to rest in

these very small ones, constrictions having inside diameters of about 0.1 mm were actually used. These were drawn so that the constricted portion was as short as possible, thus offering a minimum of resistance to the flow of the liquid in them. Also the walls were made thin so that small particles could readily be seen through them. The particles were obtained by grinding gum mastic into a powder which was stirred into the liquid of the manometer.

The microscope used had a magnification of $150\times$. The diameter of the manometer tube between the pole-pieces was in the neighborhood of 3 mm. The smallest observable displacement of the meniscus between the pole-pieces can now be calculated. If we assume³ 1 mm to be the smallest observable displacement in the eye-piece of the microscope, this represents $1/150$ mm actual displacement in the constriction, and this in turn is produced by a displacement x of the meniscus given by:

$$x = (0.1)^2 / (150 \times 3^2) = 7.4 \times 10^{-6} \text{ mm.}$$

In order to produce these deflections with the small pressures available it was necessary to use liquids with a small viscosity, and further, in order to avoid the trouble of having continually to clean the tubes of the manometer, a liquid which wet the surface readily in spite of slight impurities on the walls was desirable. Several were tried, and methyl alcohol finally used. The smallest pressure differences that were observed with this apparatus were of the order of 10^{-3} dynes/cm².

MEASUREMENTS AND MATERIALS

Hydrogen and nitrogen were used as standards. Since the susceptibility of all gases measured was greater than that of nitrogen, the procedure was to dilute the unknown gas with hydrogen and to determine for what concentration the volume susceptibility of the mixture was equal to that of nitrogen. In determining the following results the values used for the susceptibility of hydrogen and nitrogen are those given by Wills and Hector⁴ which are:

$$\chi(\text{N}_2) = -11.8 \times 10^{-6}; \quad \chi(\text{H}_2) = -3.94 \times 10^{-6} \quad (2)$$

All the gaseous members of the methane series were measured, as well as one gas, ethylene, with a double bond, and one gas, acetylene, with a triple bond. The values are given in Table I.

TABLE I. *Molecular susceptibilities of various gases.*

Gas		$\chi \times 10^6$	Gas		$\chi \times 10^6$
Methane	CH ₄	-12.2	Isobutane	C ₄ H ₁₀	-56.3
Ethane	C ₂ H ₆	-27.3	Ethylene	C ₂ H ₄	-12.0
Propane	C ₃ H ₈	-40.5	Acetylene	C ₂ H ₂	-12.5
Butane	C ₄ H ₁₀	-57.4			

³ 1 mm is about the smallest apparent deflection that could be observed because the particles were never actually at rest.

⁴ L. G. Hector, Phys. Rev. **24**, 418 (1924), and reference 1.

In Fig. 2 are plotted along (A) the above results for the methane series. The points for hexane, octane, and decane, indicated by solid triangles, were measured by Pascal⁵ on substances in the liquid state. Pascal used water as his standard, and assumed -7.5×10^{-7} to be the proper value for its specific susceptibility. The value at present accepted is -7.2×10^{-7} , and this was used in the work of Wills and Hector¹ in their determinations of hydrogen and nitrogen. The values plotted are therefore Pascal's observations reduced in the ratio 7.2/7.5. The points for pentane, hexane, and heptane, indicated by solid circles, are observations by Vaidyanathan⁶ on substances in the vapor state.

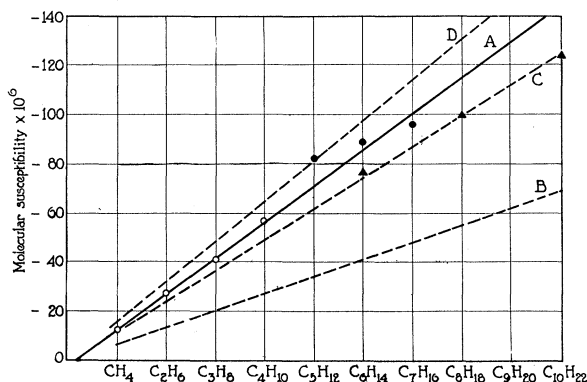


Fig. 2.. Molecular susceptibility as a function of molecular composition. The solid circles are measurements by Vaidyanathan on substances in the vapor state. The solid triangles are measurements by Pascal on substances in the liquid state. The points for methane, ethane, propane, and butane represent measurements in terms of H_2 and N_2 described in this paper. The points as plotted along line A are based on susceptibilities of H_2 and N_2 as measured by Wills and Hector. Using values for H_2 and N_2 found by other observers these measurements would lie along lines B, C, and D.

Of the gases measured, the methane series was furnished by the Carbide and Carbon Chemical Corporation. The impurities in the propane, butane and isobutane were guaranteed to amount to less than 3 percent. The methane and ethane, however, had no guarantee, and it was stated that they contained considerable portions of each other as impurities. An analysis was therefore undertaken, and carried out in the laboratories of Dr. Lincoln T. Work of the Chemical Engineering Department of Columbia University. The results are given below, the percentage referring to volume.

Methane Sample				Ethane Sample			
CO ₂	0.0%	CO	0.0%	CO ₂	0.2%	CO	0.1%
C ₂ H ₄	0.1%	CH ₄	80.7%	C ₂ H ₄	2.3%	C ₂ H ₆	90.6%
C ₆ H ₆	0.3%	C ₂ H ₆	16.1%	C ₆ H ₆	0.5%	H ₂	5.7%
O ₂	0.2%	N ₂	2.6%	O ₂	0.3%	N ₂	0.3%

The first five gases in each case were tested for by absorption, and the amount of the last three present as impurities determined by explosion with a known amount of oxygen.

⁵ P. Pascal Ann. de Chim. et de Phys. [8] 25, 289 (1912)

⁶ V. I. Vaidyanathan, Phys. Rev. 30, 512 (1927).

The acetylene used was commercial Prest-o-lite acetylene, and to it was attributed by its maker a purity in the neighborhood of 99 percent. The ethylene was furnished by the Ohio Chemical and Manufacturing Co. and was guaranteed to contain less than 0.5 percent of impurities. The standards, hydrogen and nitrogen, were also furnished by the Ohio Chemical and Manufacturing Co., and were of guaranteed purity 99.9 percent and 99.2 percent respectively.

All gases before being admitted to the apparatus were rid of oxygen either by being bubbled through long containers of pyrogallol or by being passed over red hot copper filings, or both. Further, since it was found necessary to use liquids with considerable vapor pressures in the apparatus, all gases were first saturated with the vapors of any liquid with which they came into contact by being bubbled through long tubes containing glass chips and the liquid in question.

The following mixtures were found to have the same volume susceptibility as nitrogen, the percentage referring to volume. "Methane" and "Ethane" refer to the mixtures described above.

71.2% "Methane" + 28.8% Hydrogen	15.0% Isobutane + 85.0% Hydrogen
36.0% "Ethane" + 64.0% Hydrogen	98.0% Ethylene + 2.0% Hydrogen
21.5% Propane + 78.5% Hydrogen	91.6% Acetylene + 8.4% Hydrogen
14.7% Butane + 85.3% Hydrogen	

The results for the last five gases were calculated from these data. The first two had first to be corrected for the impurities by the aid of equation (1). In doing this, the following values of χ were used: for CO_2^7 , -18.7×10^{-6} ; for C_6H_6^8 , -83×10^{-6} .

As a check on the assumption of a uniform field a mixture of propane and hydrogen was balanced against ethylene. This gave:

$$21.7 \text{ percent Propane} + 78.3 \text{ percent Hydrogen}$$

With the value found above for ethylene, this leads to a value for propane of -40.9×10^{-6} , in good agreement with that previously found.

The experimental error in the observations themselves is in every case less than 1 percent. That is, values determined from successive observations never differed by more than 1 percent. The error in the results produced by the impurities may be calculated as follows:

The presence of m percent of an impurity having the susceptibility nK where K is the susceptibility of the gas under consideration will change its susceptibility to K' , where

$$K' = \frac{100-m}{100} K + \frac{m}{100} nK = 1 - \frac{m(1-n)}{100} K.$$

Therefore $m(1-n)$ is the percentage change in the susceptibility produced by the impurity. Since the impurities in the case of the saturated hydrocarbons are almost entirely adjacent members of the series for which n has a value less than 2, and m is less than 3, and since for ethylene and acetylene $0 < m < 1$, we may say with confidence that in every case the error

in the susceptibility produced by the impurities is less than 3 percent. Thus the total relative error in the results is less than 4 percent.

DISCUSSION OF RESULTS

The choice of the values (2) for the susceptibilities of hydrogen and nitrogen can be rendered plausible by the following consideration. Other values are to be found in the literature as follows:

	Molecular Susceptibility $\times 10^6$	
	H ₂	N ₂
Také Soné ⁷	-3.94	-7.4
Wills and Hector ¹	-3.94	-11.8
Glaser ⁸	-(3.94)	-7.4
Lehrer ²	-5.0	—
Vaidyanathan ⁹	—	-12.9

Glaser measured nitrogen in terms of hydrogen, and the value -7.4 for nitrogen is found by assuming -3.94 for hydrogen. Using Glaser's or Také Soné's values in computing my results for the methane series, it is found that they lie along the dotted line *B* in Fig. 2. This cannot be reconciled with the observations of Pascal and Vaidyanathan for the higher members of the series. Similarly using Lehrer's value -5.0 for hydrogen and the value -11.8 for nitrogen, the line *C* is obtained. And using Vaidyanathan's value -12.9 for nitrogen and -3.94 for hydrogen, the line *D* is obtained.

If it is assumed that the linear relation found for the first four members of this series extends to the higher members in the vapor state, then *A* is surely the best of the four lines in Fig. 2. This is taken as an indication that the values for nitrogen and hydrogen found by Wills and Hector are most nearly correct, and these are consequently used in the calculations.

The results plotted along *A* in Fig. 2 may be represented by the formula:

$$\chi(\text{C}_n\text{H}_{2n+2}) = (-14.5n + 2.0) \times 10^{-6}.$$

(In the further discussion the factor 10^{-6} will be omitted for simplicity). This expresses the fact that in chains of this sort the electronic distribution repeats itself periodically, and that at the ends of the chains certain irregularities manifest themselves and are taken into consideration through the term independent of n . Pascal assumed that the magnetic properties were determined by the atoms themselves and found from many measurements on relatively complex molecules containing carbon, hydrogen, and other atoms that the susceptibility of a compound could be written as the sum of the susceptibilities of the atoms of which it is made up. Carbon and hydrogen were found to have values such that

$$\begin{aligned} \chi(\text{C}_n\text{H}_{2n+2}) &= -6.0n - 2.9(2n+2) \\ &= -11.8n - 5.8. \end{aligned}$$

⁷ Také Soné, *Phil. Mag.* **39**, 305 (1920).

⁸ A. Glaser, *Ann. d. Physik* **75**, 459 (1924).

⁹ V. I. Vaidyanathan, *Phil. Mag.* **5**, 380 (1928).

This cannot be reconciled with the fact that for this series the constant term is shown to be positive. An obvious extension is to assume the susceptibility to be a function of the bonds as well as of the atoms. Thus, if $\chi(\text{C-C})$ represents the quantity to be attributed to a C-C bond, this would give

$$\begin{aligned}\chi(\text{C}_n\text{H}_{2n+2}) &= n\chi(\text{C}) + (n-1)\chi(\text{C-C}) + (2n+2)(\chi(\text{H}) + \chi(\text{C-H})). \\ &= n[\chi(\text{C}) + \chi(\text{C-C}) + 2(\chi(\text{H}) + \chi(\text{C-H}))] \\ &\quad + 2[\chi(\text{H}) + \chi(\text{C-H})] - \chi(\text{C-C}).\end{aligned}$$

This is then a possible explanation of the positive constant without having recourse to paramagnetism. A real test of such an assumption cannot be undertaken with the data at present available, and any conclusive interpretation of the results described in this paper must be deferred to some future date when more information is available concerning the susceptibilities of molecules containing relatively few atoms.

Before closing the discussion, however, it is worth inquiring what the application of the above hypothesis to ethylene and acetylene would give. It is assumed that $\chi(\text{H})$, $\chi(\text{C-H})$, and $\chi(\text{C})$ are unchanged, and the above results show that

$$\chi(\text{CH}_4) = \chi(\text{C}_2\text{H}_4) = \chi(\text{C}_2\text{H}_2)$$

or, after canceling the factor $\chi(\text{C})$ from both sides

$$\begin{aligned}4(\chi(\text{H}) + \chi(\text{C-H})) &= 4[\chi(\text{H}) + \chi(\text{C-H})] + [\chi(\text{C}) + \chi(\text{C}=\text{C})] \\ &= 2[\chi(\text{H}) + \chi(\text{C-H})] + [\chi(\text{C}) + \chi(\text{C}\equiv\text{C})]\end{aligned}$$

Assuming that paramagnetism does not enter, an assumption which can be regarded only as plausible, and to be judged by its consequences, this would give

$$\begin{aligned}\chi(\text{C}) &= \chi(\text{C}=\text{C}) = 0 \\ \chi(\text{C}\equiv\text{C}) &= 2[\chi(\text{H}) + \chi(\text{C-H})].\end{aligned}$$

Through elimination in the above equations the following values are obtained:

$$\begin{aligned}\chi(\text{C-C}) &= -8.25 \\ 2[\chi(\text{H}) + \chi(\text{C-H})] &= -6.25 \\ \chi(\text{C}\equiv\text{C}) &= -6.25.\end{aligned}$$

Evidently, a value different from zero for a bond means that in some way electron orbits are to be associated with it, and a zero value means that this is not the case. Bearing this in mind it is interesting to see that the electrons can be arranged in groups of two in a very simple way, as postulated by G. N. Lewis¹⁰ Heitler and London,¹¹ and others, for occupied

¹⁰ G. N. Lewis, Valency and Atomic Structure.

¹¹ W. Heitler and F. London, *Zeits. f. Physik* **44**, 455 (1927).

valences. In the carbon atom the two K electrons form in each case such a group, thus leaving four more to be considered.

With every C-H bond are associated the one electron from hydrogen and one of the L electrons of carbon. This leaves for the end carbon atoms of the saturated chains one electron each, and for the rest two each, and these are exactly sufficient for an arrangement of two for every C-C bond. In the case of ethylene two of the L electrons of each carbon atom are associated with their respective C-H bonds, leaving two to be accounted for in each atom. But $\chi(\text{C}=\text{C})=0$ indicates that these do not take part in the bond, and they may thus be considered as forming a closed group of two in their respective L_1 shells, as Heitler¹² assumed for the L_1 electrons of nitrogen in the N_2 molecule. In order that such a configuration should form a molecule it is necessary that the Coulomb forces themselves should give a potential energy curve with a minimum. Until more is known about the structure of the CH_2 group it is impossible to verify this. But that such is possible may be seen from a calculation¹³ of the Coulomb forces for the H_2 molecule which show this feature. In acetylene, the value of $\chi(\text{C}\equiv\text{C}) = -6.25$ of the same order as $\chi(\text{C}-\text{C}) = -8.25$ might be taken to indicate that the triple bond is similar to a single bond. This would leave the two L_1 electrons in a closed group of their own, one L_2 electron of each carbon atom associated with the corresponding hydrogen electron, and the remaining two associated with each other in the $\text{C}\equiv\text{C}$ bond. Exact agreement of the $\chi(\text{C}-\text{C})$ and $\chi(\text{C}\equiv\text{C})$ susceptibilities cannot be expected because of the disturbing effect of the L_2 electrons in the latter case, both on the C-C as well as the C-H bonds.

In conclusion I wish to express my indebtedness to Professor A. P. Wills for suggesting the method used in this research.

PHYSICS LABORATORIES,
COLUMBIA UNIVERSITY.
September 1, 1928.

¹² W. Heitler, *Zeits. f. Physik* **47**, 839 (1928).

¹³ W. Heitler and F. London, *Zeits. f. Physik* **44**, 462, (1927).