Diamagnetic Susceptibilities of Shared Electrons

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By regarding the two shared electrons of a covalent bond as forming a doubly charged negative ion, and the molecule as consisting of positive and negative ions, one may, in some cases, assign diamagnetic susceptibilities to the constituent parts of the molecule. The values thus found are in good agreement with the experimental results.

1. INTRODUCTION

TO study the structures of covalent compounds by means of their diamagnetism, the author has assumed that the electrons shared by two atoms move in certain orbits under the influence of their centers of force and form an electron group in such a way as to render the atoms sharing these electrons positively charged.

Since, in this paper, the number of shared electrons we study is limited to two, the electron groups thus formed may be represented by a single symbol $\ominus$, and, for convenience, we consider $\ominus$ as an ion with two negative charges.

It is obvious that the assumption stated above gives the covalent idea an extraordinary meaning and we can thus explain the structures of molecules of covalent compounds in the same way as we have done in the case of electrovalent compounds.

Using the above assumption and utilizing the ionic diamagnetic susceptibilities of some kinds of ions obtained by Angus's modification of Slater's method[1] the author has derived the ionic diamagnetic susceptibility of $\ominus$ and calculated the molecular diamagnetic susceptibilities of a large number of compounds. The values thus found are in complete accord with experimental results. And we have, in this way, enlarged the scope of the magnetochemical investigations.

It is noted that the old structural formula for representing the constitution of a molecule together with the assumption stated above leads us to the neutralization of ions in the molecule.

The susceptibilities used are all given relative to the usual standard $\chi_{H_2O} = -7.2$ (throughout

[1] W. R. Angus, Proc. Roy. Soc. A136, 569 (1932).

this paper the susceptibilities have been multiplied by 10^7).

2. DERIVATION OF DIAMAGNETIC SUSCEPTIBILITY OF $\ominus$ ION

The diamagnetic susceptibility of the $\ominus$ ion has been derived from the molecular diamagnetic susceptibility of water on the assumption that water is a covalent compound; for, according to my assumption made at the beginning of the introduction, this molecule is formed by the neutralization of $2H^{+1} + 2\ominus + O^{+2}$ and, from the experimental value of the molecular diamagnetic susceptibility of water -129.6, we have

$$2\chi_{H^{+1}} + 2\chi_\theta + \chi_{O^{+2}} = -129.6.$$

Assuming the susceptibility of H^{+1} to be zero and using Angus's value $\chi_{O^{+2}} = -32.1$,[1] we find

$$\chi_\theta = -48.8. \qquad (1)$$

Of course, this is not the only way to obtain this value. The rigorous verifications (direct or indirect) of this value given in various sections not only justify our assumption concerning the structure of water but also lead us to believing that the $\ominus$ ion occurring in whatever molecules possesses the same diamagnetic susceptibilities.

3. STRUCTURES AND DIAMAGNETIC SUSCEPTIBILITIES OF METHANE SERIES

It is generally accepted that the compounds of methane series are covalent compounds. And, according to my structural theory, the first three members of this series may be represented by Fig. 1, (a), (b), and (c), respectively.

Since the proton H^{+1} and its shared ion $\ominus$ may be considered as forming a group i.e., $(\ominus H^{+1})^{-1}$, Fig. 1 may be replaced by Fig. 2 where the

$$H^{+1}$$
$$\ominus$$
$$H^{+1} \ominus C^{+4} \ominus H^{+1}$$
$$\ominus$$
$$H^{+1}$$

(a)

$$H^{+1} \quad H^{+1}$$
$$\ominus \qquad \ominus$$
$$H^{+1} \ominus C^{+4} \ominus C^{+4} \ominus H^{+1}$$
$$\ominus \qquad \ominus$$
$$H^{+1} \quad H^{+1}$$

(b)

$$H^{+1} \quad H^{+1} \quad H^{+1}$$
$$\ominus \qquad \ominus \qquad \ominus$$
$$H^{+1} \ominus C^{+4} \ominus C^{+4} \ominus C^{+4} \ominus H^{+1}$$
$$\ominus \qquad \ominus \qquad \ominus$$
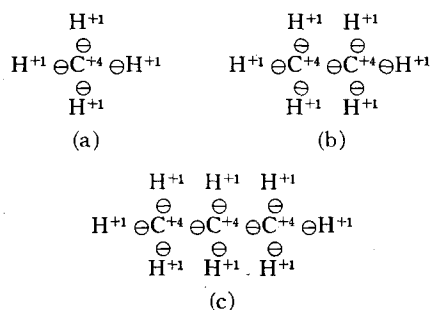$$H^{+1} \quad H^{+1} \quad H^{+1}$$

(c)

FIG. 1. (a), (b), and (c).

simple symbol G (call G-group) is used instead of $(\ominus H^{+1})^{-1}$.

Now, if we use the symbol $M_1{}^*$ to represent the structure (a) or (a'), and suppose that a proton is removed from it, the remaining part may be represented by $M_1{}^{-1}$, but when a G-group is supposed to be removed from (a') of Fig. 2, the remaining part is represented by $M_1{}^{+1}$. From these two symbols $M_1{}^{-1}$ and $M_1{}^{+1}$, the meaning of the general symbols $M_n{}^{-1}$ and $M_n{}^{+1}$ for a molecule M_n is obvious.

From Fig. 1, it is seen that when a proton in (a) is replaced by $M_1{}^{+1}$, the resulted molecule is (b) and, similarly, when a proton in (b) is replaced by $M_1{}^{+1}$, the resulted structure is (c). We have, in this way, obtained the structures of all molecules of methane series (the structures of isomerides are out of consideration).

We are now in a position to study the molecular diamagnetic susceptibilities of this series. Since $\chi_{H^{+1}}=0$, the loss of protons from any molecule does not affect its susceptibility and, according to my structural theory, the following relation holds:

$$\chi_{M_{n+1}} = \chi_{M_n{}^{-1}} + \chi_{M_1{}^{+1}}$$

or

$$\chi_{M_{n+1}} = \chi_{M_n} + \chi_{M_1{}^{+1}}, \qquad (2)$$

since $\chi_{M_n{}^{-1}} = \chi_{M_n}$. On the other hand, Pascal has shown experimentally that

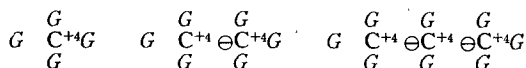$$\chi_{M_{n+1}} = \chi_{M_n} - 118.6.$$

$$G$$
$$G \quad C^{+4} \; G$$
$$G$$

$$G \quad G$$
$$G \quad C^{+4} \ominus C^{+4} G$$
$$G \quad G$$

$$G \quad G \quad G$$
$$G \quad C^{+4} \ominus C^{+4} \ominus C^{+4} G$$
$$G \quad G \quad G$$

FIG. 2. (a'), (b'), and (c').

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* Similarly, the symbols M_2, M_3, $\cdots$, M_n are used to represent, respectively, the structures of the second, third, $\cdots$, nth molecule of methane series.

Hence we have

$$\chi_{M_1{}^{+1}} = -118.6. \qquad (3)$$

Using this value as well as the value given in (1), we can calculate the molecular diamagnetic susceptibility of methane as follows:

$$\chi_{M_1} = \chi_{M_1{}^{+1}} + \chi_G = -(118.6+48.8) = -167.4,$$

on noticing that $\chi_G = \chi_\theta = -48.8$.

By means of this value, we can deduce from (2) the molecular diamagnetic susceptibilities of all molecules of methane series:

Calculated	Observed (Pascal)
$\chi_{M_1} = -\ 167.4$	
$\chi_{M_2} = -\ 286.0$	
$\chi_{M_3} = -\ 404.6$	
$\chi_{M_4} = -\ 523.2$	
$\chi_{M_5} = -\ 641.8$	(4)
$\chi_{M_6} = -\ 760.4$	-764.2
$\chi_{M_7} = -\ 879.0$	
$\chi_{M_8} = -\ 997.6$	-995.5
$\chi_{M_9} = -1116.2$	
$\chi_{M_{10}} = -1234.8$	-1245.0

The agreement between the calculated and the observed values is excellent, and we have, thus, verified both the values $\chi_{M_1{}^{+1}} = -118.6$ and $\chi_\theta = -48.8$ and the structures of methane series.

It is noticed that all these values are a little lower than those calculated by Pascal. This is due to the fact that the first value $\chi_{M_1} = -167.4$ is a little lower than that calculated by Pascal:

$$\chi_{M_1} = 4\chi_H + \chi_C = -(4 \times 29.3 + 60) = -177.2.$$

We shall see later that the calculated values given in (4) will be more agreeable with the experimental results than those calculated by Pascal.

4. STRUCTURES OF ALKYL SULPHIDES
$(C_nH_{2n+1})_2S$

In my structural theory, the molecules of alkyl sulphides,

$$CH_3SCH_3, \quad C_2H_5SC_2H_5, \quad C_3H_7SC_3H_7, \quad \cdots,$$
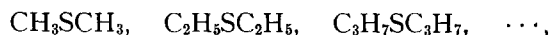
should be formed by the neutralizations, respectively, of

$$2M_1{}^{-1}+S^{+2}, \quad 2M_2{}^{-1}+S^{+2}, \quad 2M_3{}^{-1}+S^{+2}, \quad \cdots,$$
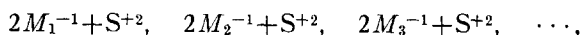
Using the first three values of (4) and Angus's value[1] $\chi_{S^{+2}} = -109.9$, we can calculate the

TABLE I.

Name	Formula	Neutralization of ions	$-\chi_m$	$-\chi_{(NO_2)}^{+1}$
Tetranitromethane	$C(NO_2)_4$	$M_1^{-4*}+4(NO_2)^{+1}$	436.8	67.4
Nitroethane	$C_2H_5NO_2$	$M_2^{-1}+(NO_2)^{+1}$	354.2	68.2
Orthonitrotoluene	$CH_3 \cdot C_6H_4 \cdot NO_2$	$B^{-2}{}_{1,2}+M_1^{+1}+(NO_2)^{+1}$	729.6	63.0
Nitrobenzene	$C_6H_5 \cdot NO_2$	$B^{-1}+(NO_2)^{+1}$	615.4	67.4
1:3-Dinitrobenzene	$C_6H_4 \cdot (NO_2)_2$	$B^{-2}{}_{1,3}+2(NO_2)^{+1}$	669.0	60.5
1:3:5-Trinitrobenzene	$C_6H_3 \cdot (NO_2)_3$	$B^{-3}{}_{1,3,5}+3(NO_2)^{+1}$	750.7	67.6

* The methane molecule after losing its four protons.

molecular diamagnetic susceptibilities of these molecules:

$$\begin{array}{ccc} & & \text{Observed} \\ \text{Calculated} & & \text{(Pascal)} \end{array}$$

$$\chi_1 = -(2\times167.4+109.9) = -444.7 \qquad -449.3$$
$$\chi_2 = -(2\times286.0+109.9) = -681.9 \qquad -678.7$$
$$\chi_3 = -(2\times404.6+109.9) = -919.1 \qquad -917.8$$

The agreement between the calculated and the observed values is surprisingly good. We have thus, on the one hand, verified the values -167.4, -286.0, -404.6 and the structures of alkyl sulphides on the other. It should be noted that we have, in this way, verified indirectly the values (1) and (3) from which the calculated values (4) have been obtained.

5. DERIVATION OF MAGNETIC SUSCEPTIBILITY OF NITRO-GROUP (NO₂)

The aim of the derivation is to show that the calculated values given in (4) are extremely consistent with the molecular diamagnetic susceptibility of benzene -548, the mean value obtained from the values observed by different workers.

Before doing so, let us give a short account of the structure of benzene. If we assume its structure to be represented by Fig. 3** and use the symbol B to designate it, then when a proton
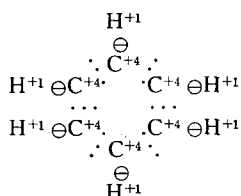

FIG. 3.

** The structure was obtained from Thomson's formula for benzene and, in this paper, the three-electron groups existing between the carbon atoms do not enter into consideration.

H^{+1} is removed from B, the structure of the remaining part may be represented by B^{-1}. On the other hand, when a G-group is supposed to be removed from it, the remaining structure is represented by B^{+1}. But when more than one proton or G-group is removed from B, a more complicated symbol for representing the structure of the remaining part is needed. Let us suppose 3 protons or 3 G-groups in the position 1, 3, 5 to be removed from B, the symbol for representing the remaining structure, in the first case, is $B^{-3}{}_{1,3,5}$ and, in the second, $B^{+3}{}_{1,3,5}$. The meaning of the other symbols such as $B^{-2}{}_{1,2}$, $B^{-3}{}_{1,2,4}$, etc., is evident. Knowing this, one will meet no difficulty in studying the neutralizations of ions in the molecules of benzene derivatives. Since the mean value of the molecular diamagnetic susceptibility of benzene is $\chi_B = -548$ and since the loss of protons from B does not affect its diamagnetic susceptibility, we have $\chi_{B^{-n}} = -548$, where n denoting the number of protons lost.

To derive the magnetic susceptibility of the group (NO₂), let us consider the structures of molecules contained in the first column of Table I. If we assume the group to be singly positively charged, i.e., $(NO_2)^{+1}$ (here the question whether the atoms in the group are in covalent combination or in electrovalent combination is out of consideration), the neutralizations of the ions in these molecules should be such as shown in the third column. The fourth column gives the molecular diamagnetic susceptibilities observed by Pascal; while in the last column are contained the derived values of $\chi_{(NO_2)}^{+1}$. The derivations are easily carried out and need no illustrations.

The close agreement among the derived values indicates that the calculated values given in (4) are consistent with the observed value $\chi_B = -548$. The results also show that our assumption that the group (NO₂) is singly positively charged is

TABLE II.

Name	Formula	Neutralization of ions	Calculated	Experimental
Phenol	C_6H_5OH	$B^{+1}+(OH)^{-1}$	611.7	610.0
Resorcinol	$C_6H_4(OH)_2$	$B^{+2}{}_{1,3}+2(OH)^{-1}$	675.4	672.0
Phloroglucinol	$C_6H_3(OH)_3$	$B^{+3}{}_{1,3,5}+3(OH)^{-1}$	739.1	733.4
Anisole	$C_6H_5 \cdot O \cdot CH_3$	$B^{+1}+(O^{-2}M_1{}^{+1})^{-1}$	719.5	726.0
Phenetole	$C_6H_5O \cdot C_2H_5$	$B^{+1}+(O^{-2}M_2{}^{+1})^{-1}$	838.1	844.8
Guaiacol	$C_6H_4(OH)(OCH_3)$	$B^{+2}+(O^{-2}M_1{}^{+1})^{-1}+(OH)^{-1}$	783.2	791.0
Paranitrophenol	$C_6H_4(OH)(NO_2)$	$B^{+2}{}_{1,4}+(\ominus NO_2)^{-1}+(OH)^{-1}$	677.4	670.0
2:4-Dinitrophenol	$C_6H_3(OH)(NO_2)_2$	$B^{-3}{}_{1,2,4}+2(\ominus NO_2)^{-1}+(OH)^{-1}$	743.1	731.5

justifiable. From these derived values, we find the mean value:

$$\chi_{(NO_2)^{+1}} = -65.7. \qquad (5)$$

This value will be used in the next section.

6. MOLECULES CONTAINING NEGATIVELY CHARGED OXYGEN ATOMS VERIFICATION OF ANGUS'S VALUE $\chi_{O^{-2}} = -112.5$

We have seen that the oxygen atom in a water molecule is positively charged. We are now going to prove that the oxygen atoms in some kinds of molecules such as those contained in the first column of Table II are negatively charged. The procedure is to assume the oxygen atoms*** in these molecules to be doubly negatively charged i.e., O^{-2} and, then, to give O^{-2} a susceptibility -112.5 obtained theoretically by Angus[1] in evaluating the molecular diamagnetic susceptibilities of these molecules. The old structural formulas give us the neutralizations of ions as shown in the third column. The forth and the last column contain the calculated and the experimental (Pascal) values of the molecular diamagnetic susceptibilities.

To arrive at the calculated values, one should take notice of the following points:

(1) No attention has been directed to the question of isomerides.

(2) Since $\chi_B = -548$, we have

$$\begin{aligned}
\chi_{B^{+1}} &= \chi_B - \chi_G = -(548-48.8) = -499.2, \\
\chi_{B^{+2}} &= \chi_B - 2\chi_G = -(548-2\times48.8) = -450.4, \qquad (6) \\
\chi_{B^{+3}} &= \chi_B - 3\chi_G = -(548-3\times48.8) = -401.6.
\end{aligned}$$

(3) When $M_1{}^{+1}$ or $M_2{}^{+1}$ combines with O^{-2}, their diamagnetic susceptibilities are respectively (see sections 8 and 9)

$$\chi M_1{}^{+1} = -107.8$$

and

$$\chi M_2{}^{+1} = -(107.8+118.6) = -226.4.$$

*** Except those contained in the nitro-group (NO_2).

(4) $(\ominus NO_2)^{-1}$ represents the combination of $\ominus$ and $(NO_2)^{+1}$, and its susceptibility is therefore

$$\chi(\ominus NO_2)^{-1} = -(48.8+65.7) = -114.5.$$

The agreement between the calculated and the experimental values is extremely close. We have thus confirmed our assumption that the oxygen atoms in these molecules are doubly negatively charged. Finally, it should be noted that Angus's value $\chi_{O^{-2}} = -112.5$ can be verified here only by assuming the value $\chi_\theta = -48.8$ to be true.

7. DERIVATION OF MAGNETIC SUSCEPTIBILITY OF CARBONYL GROUP (CO) AND STRUCTURES OF AMIDES

The susceptibility of the group (CO) can be derived from the molecular diamagnetic susceptibilities of ketones and aldehydes contained in the first column of Table III on the assumption that the group is doubly positively charged, i.e., $(CO)^{+2}$ (here the question whether the atoms in the group are in covalent combination or in electrovalent combination is out of consideration). It will be seen that the derivation is based on the value given in (1) and the calculated values given in (4). The neutralizations of ions in ketones and aldehydes should be such as indicated in the third column of Table III. The fourth column gives the molecular diamagnetic susceptibilities observed by Pascal and the last column, the derived values of $\chi_{(CO)^{+2}}$. The method of arriving at the derived values may be illustrated by acetone. Since the neutralization of this molecule is $M_1{}^{-1}+(CO)^{+2}+M_1{}^{-1}$, using the first value of (4) we find

$$\chi_{(CO)^{+2}} = -(337-2\times167.4) = -2.2.$$

The other derived values may be found in a similar way remembering that $\chi M_n{}^{-1} = \chi M_n$.

The constancy of the derived values shows that the value (1) is consistent with the cal-

TABLE III.

Name	Formula	Neutralization of ions	$-\chi_m$	$-\chi_{(CO)^{+2}}$
Acetone	$CH_3 \cdot CO \cdot CH_3$	$M_1^{-1} + (CO)^{+2} + M_1^{-1}$	337.0	2.2
Methylethylketone	$CH_3 \cdot CO \cdot C_2H_5$	$M_1^{-1} + (CO)^{+2} + M_2^{-1}$	456.0	2.6
Methylpropylketone	$CH_3 \cdot CO \cdot C_3H_7$	$M_1^{-1} + (CO)^{+2} + M_3^{-1}$	575.0	3.0
Methylbutylketone	$CH_3 \cdot CO \cdot C_4H_9$	$M_1^{-1} + (CO)^{+2} + M_4^{-1}$	691.2	0.6
Methylhexylketone	$CH_3 \cdot CO \cdot C_6H_{13}$	$M_1^{-1} + (CO)^{+2} + M_6^{-1}$	933.0	5.2
Acetaldehyde	$CH_3 \cdot CHO$	$M_1^{-1} + (CO)^{+2} + G$	220.8	4.6
Propionaldehyde	$C_2H_5 \cdot CHO$	$M_2^{-1} + (CO)^{+2} + G$	339.8	5.0
Butyraldehyde	$C_3H_7 \cdot CHO$	$M_3^{-1} + (CO)^{+2} + G$	457.9	4.5
Heptaldehyde	$C_6H_{13} \cdot CHO$	$M_6^{-1} + (CO)^{+2} + G$	815.0	5.8

culated values (4) and this implies that the value (3) $\chi_{M_1^{+1}} = -118.6$ is accurate. From the derived values we find the mean value:

$$\chi_{(CO)^{+2}} = -3.7. \qquad (7)$$

This value will be used in the calculations of molecular diamagnetic susceptibilities of amides. For doing so, we shall, first of all, consider the structure of the group $(CONH_2)$. Since ammonia is generally accepted as a covalent compound, the neutralization of ions in NH_3 should be $N^{+3} + 3\ominus + 3H^{+1}$. Using Angus's value $\chi_{N^{+3}} = -20.9$,[1] we find for the molecular diamagnetic susceptibility of NH_3,

$$\chi_{NH_3} = \chi_{N^{+3}} + 3\chi_\theta + 3\chi_{H^{+1}}$$
$$= -(20.9 + 3 \times 48.8) = -167.3. \quad (8)$$

This is in good agreement with the experimental result -170.5 (Gray). If we now assume the group $(CONH_2)$ to be a combination of the ions $(CO)^{+2} + (N^{+3} + 3\ominus + 2H^{+1})^{-1}$ or simply $(CO)^{+2} + (NH_2)^{-1}$ and represent it by the symbol $(CONH_2)^{+1}$, then its diamagnetic susceptibility may be found from (7) and (8),

$$\chi_i = \chi_{(CO)^{+2}} + \chi_{(NH_2)^{-1}}$$
$$= -(3.7 + 167.3) = -171.0 \quad (9)$$

since $\chi_{(NH_2)^{-1}} = \chi_{NH_3}$.

This value will be used in the calculations of molecular diamagnetic susceptibilities of amides.

From the old structural formulas for the molecules contained in the second column of Table IV, we can immediately obtain the neutralizations of ions shown in the third column. Since the calculations of the molecular diamagnetic susceptibilities of all these molecules except dimethyloxamide are easily carried out, only the method for obtaining the susceptibility of this molecule is necessary to give here. When one of the two protons in the $(CONH_2)^{+1}$ group is replaced by M_1^{+1}, the diamagnetic susceptibility of the resulted group $(CONHCH_3)^{+1}$ should be

$$\chi_i = \chi_{(CONH_2)^{+1}} - \chi_{H^{+1}} + \chi_{M_1^{+1}}$$
$$= -(171 + 118.6) = -289.6$$

and from this follows immediately the molecular diamagnetic susceptibility of dimethyloxamide:

$$\chi_m = \chi_\theta + 2\chi_i = -(48.8 + 2 \times 289.6) = -628.0.$$

The excellent agreement between the calculated and the experimental (Pascal) values given in the fourth and the last column affords verification of the value (9) on the one hand and confirmation of the structures of amides on the other.

8. DERIVATION OF MAGNETIC SUSCEPTIBILITY OF (CH_2OH) GROUP

This can be done by considering the structures of the molecules shown in the second column of

TABLE IV.

Name	Formula	Neutralization of ions	$-\chi_m$ Calculated	$-\chi_m$ Experimental
Formamide	$H \cdot CONH_2$	$G + (CONH_2)^{+1}$	219.8	218.9
Acetamide	$CH_3 \cdot CONH_2$	$M_1^{-1} + (CONH_2)^{+1}$	338.4	340.8
Benzamide	$C_6H_5 \cdot CONH_2$	$B^{-1} + (CONH_2)^{+1}$	719.0	723.0
Oxamide	$CONH_2CONH_2$	$\ominus + 2(CONH_2)^{+1}$	390.8	389.8
Phthalamide	$C_6H_4(CONH_2)_2$	$B^{-2} + 2(CONH_2)^{+1}$	890.0	913.0
Dimethyloxamide	$COHCH_3 \cdot COHCH_3$	$\ominus + 2[(CO)^{+2}(NHCH_3)^{-1}]^{+1}$	628.0	630.7
Urea	$NH_2 \cdot CONH_2$	$(NH_2)^{-1} + (CONH_2)^{+1}$	338.3	336.0

TABLE V.

Name	Formula	Neutralization of ions	$-\chi_m$	$-\chi_{(CH_2OH)^{+1}}$
Methyl alcohol	$H \cdot CH_2OH$	$G + (CH_2OH)^{+1}$	218.9	170.1
Ethyl alcohol	CH_3CH_2OH	$M_1^{-1} + (CH_2OH)^{+1}$	342.7	175.3
n-Propyl alcohol	$C_2H_5CH_2OH$	$M_2^{-1} + (CH_2OH)^{+1}$	459.8	173.8
n-Octyl alcohol	$C_7H_{15}CH_2OH$	$M_7^{-1} + (CH_2OH)^{+1}$	1048.3	169.3
Glycol	$CH_2OH \cdot CH_2OH$	$\ominus + 2(CH_2OH)^{+1}$	386.9	169.1

Table V. In my structural theory the group should be a combination of the ions $C^{+4} + 2\ominus + 2H^{+1} + (O^{-2} + H^{+1})^{-1}$ and consequently may be represented by $(CH_2OH)^{+1}$ and the molecules may, therefore, be formed by the neutralizations of ions shown in the third column. The fourth column gives the molecular diamagnetic susceptibilities observed by Pascal, and the last column, the derived values of $\chi_{(CH_2OH)^{+1}}$.

The derivations are easily carried out and need no illustrations. The mean value of the derived values is

$$\chi_{(CH_2OH)^{+1}} = -171.5. \qquad (10)$$

The close agreement among the derived values shows that the value (1) and the calculated values (4) are consistent. We shall see that the value (10) is exact and can be used to explain some observed facts by assuming that the value $\chi_{O^{-2}} = -112.5$ is true.

We know that the molecular diamagnetic susceptibility of methyl alcohol can be calculated by the relation:

$$\chi_m = \chi_G + \chi_{(CH_2OH)^{+1}}$$
$$= -(48.8 + 171.5) = -220.3. \qquad (11)$$

But, if we consider the neutralization of ions in this molecule as $(CH_3)^{+1} + (OH)^{-1}$ or $M_1^{+1} + (OH)^{-1}$, we have

$$\chi_{M_1^{+1}} + \chi_{(OH)^{-1}} = -220.3$$

and

$$\chi_{M_1^{+1}} = -107.8 \qquad (12)$$

since $\chi_{(OH)^{-1}} = -112.5$. This shows that when M_1^{+1} combines with $(OH)^{-1}$, its diamagnetic susceptibility changes from -118.6 to 107.8, i.e., decreases by -10.8. This result is extremely remarkable and accords completely with experimental results which we shall describe in the next section.

Besides, we have seen in this derivation that if we write $C_nH_{2n+1} \cdot CH_2OH$ as the general formula for alcohols, then when the series is ascended from methyl alcohol, the increment of diamagnetic susceptibility for every member of this series may be considered the same, i.e., -118.6.

9. PARAMAGNETIC PROPERTY OF CARBON ION C^{+4}

In the preceding sections we have obtained the following results:

$$\chi_{M_1^{+1}} = -118.6, \quad \chi_{(CH_2OH)^{+1}} = -171.5.$$

Since these results can be considered as firmly established and the values $\chi_G = \chi_\theta = -48.8$ and $\chi_{O^{-2}} = -112.5$ have been well verified, we can from them derive the ionic susceptibility of the carbon ion C^{+4}. Thus from

$$\chi_{M_1^{+1}} = \chi_{C^{+4}} + 3\chi_G = -118.6$$

and

$$\chi_{(CH_2OH)^{+1}} = \chi_{C^{+4}} + 2\chi_G + \chi_{(OH)^{-1}} = -171.5$$

we find

$$\chi_{C_1^{+4}} = +27.8 \quad \text{and} \quad \chi_{C_2^{+4}} = +38.6, \qquad (13)$$

where C_1^{+4} and C_2^{+4} denote the carbon ion C^{+4} in M_1^{+1} and $(CH_2OH)^{+1}$, respectively. We are thus led to the natural conclusion that the carbon ions C^{+4} possess paramagnetic properties and their paramagnetic susceptibilities are different as they are in different types of molecules.

To interpret these facts, the author assumes that the two electrons contained in the K-shell of C^{+4} can exist in different excited states in which their resultant magnetic moment does not vanish, and the different paramagnetic susceptibilities of C^{+4} correspond respectively to these different excited states, and that in cases where the two electrons return to normal state the ion becomes diamagnetic; it is only in these cases that the formula for evaluating the ionic diamagnetic susceptibilities is applicable.

Now the question arises: if a carbon ion C^{+4} could exist in a series of excited states, what would be the corresponding paramagnetic susceptibilities? To solve this question completely, a paramagnetic theory for the positive ions of this sort is needed. It is sure that the values given in (13) are two of these corresponding paramagnetic susceptibilities. For the present, our important task is to investigate whether the results given in (13) can be in conformity with some other observed facts. We shall show that we have such cases.

Angus and Hill[2] in their systematic investigation on the diamagnetic susceptibilities of the (CH_2) group and isomerides showed that the diamagnetic increment for the conversion of an acid into its methyl ester was -107. This result may be considered completely the same as I have found at the end of the last section and can be fully explained as follows: When the proton in the group (COOH) is replaced by M_1^{+1}, the carbon ion C^{+4} in M_1^{+1} changes its excited state, in other words, jumps from a lower state defined by the paramagnetic susceptibility $+27.8$ to a higher state defined by the paramagnetic susceptibility $+38.6$, and the increase of paramagnetic susceptibility from $+27.8$ to $+38.6$ of C^{+4} in M_1^{+1} when touching to O^{-2} causes the decrease of diamagnetic susceptibility of M_1^{+1} from -118.6 to -107.8 as indicated at the end of the last section.

They also noted that for esters the value of χ_{CH_2} was the same irrespective of whether the series is ascended through R or R' in RCOOR'. This fact together with what we have described at the end of the last section suggest that when M_n^{+1} combines with O^{-2}, among the n positive

[2] Angus and Hill, Trans. Faraday Soc. **39**, 185 (1943).

carbon ions C^{+4} in M_n^{+1}, only the one which touches it directly changes its paramagnetic state from $+27.8$ to $+38.6$.

This is an important remark which can be used to explain the difficulty described by Angus and Hill.[2] Putting $n=0$ in the general formula $(CH_2)_n HOH$ for alcohols to obtain the final member of this series, the relation $\chi_m = n\chi_{CH_2} + b$ becomes $\chi_m = \chi_{HOH} = -95$. This value is considerably different from the value -129.6 for water.

It seems to me that this difficulty can be explained perfectly by the remark just mentioned. If we write $C_n H_{2n+1} \cdot OH$ as the general formula for alcohols, the neutralization of ions in each molecule of this series is $M_n^{+1} + (OH)^{-1}$, and among the n ions C^{+4} in M_n^{+1} only the one which touches the group $(OH)^{-1}$ directly possesses a paramagnetic susceptibility $+38.6$. This tells us that the relation $\chi_m = n\chi_{CH_2} + b$ should be replaced by

$$\chi_m = (n-1)\chi_{CH_2} - 107.8 + b. \qquad (14)$$

Putting $n=0$, we have

$$b = \chi_{HOH} + \chi_{CH_2} + 107.8. \qquad (15)$$

The value of b defined in this way would represent the molecular diamagnetic susceptibility of water and would be equal to -112.5 if water were an electrovalent compound. But, as we have seen water is necessarily a covalent compound, it is therefore, still unreasonable to expect the value b even obtained from (15) to be agreeable with the value -129.6 for water.