THE ROLE OF MAGNETISM IN VALENCE

BY E. H. WILLIAMS

ABSTRACT

A brief statement concerning the electrochemical and magnetochemical theories is made, together with a description of some of the phenomena for which the electrochemical theory does not give a satisfactory explanation. It is pointed out that one of the tests in favor of the magnetochemical theory would be the changing of a paramagnetic substance to a diamagnetic substance when the valence is modified so as to change the molecule from one of odd molecular number to one of even molecular number. To test this point measurements were made of the magnetic susceptibilities of a number of carefully prepared compounds of variable valence such as CuO and Cu_2O. The results show that the compounds of Cu, Bi, Pb and Sn of odd molecular number are paramagnetic while those of even molecular number are diamagnetic. On the other hand MnO (odd) and Mn_2O_3 (even) are both paramagnetic, the former slightly more so. CoO (odd) is strongly ferro-magnetic while Co_2O_3 (even) is paramagnetic. AgO and Ag_2O are both diamagnetic suggesting that possibly AgO is of the form Ag_2O_2 (even).

THE electrochemical theory has, for many years, been the predominating theory in the science of chemistry. It explains very beautifully the type of chemical phenomena met with in electrolytes, especially those of inorganic compounds. There are, however, other fundamental phenomena in chemistry and physics for which the electrochemical theory, in its present form at least, does not give a satisfactory explanation. For example, the symmetrical grouping of electrons which is of so common occurrence in molecules, the fact that the majority of chemical compounds, especially the organic compounds, are diamagnetic and the formation of chemical bonds by the coupling of electrons are phenomena that are difficult to explain by the electrochemical theory alone.

In order to account for some of the phenomena for which the electrochemical theory does not give a satisfactory explanation, various magnetochemical theories have been proposed from time to time, but thus far very little experimental evidence has been brought forth either to prove or to disprove these theories. Among those who have advocated some form of magnetochemical theory may be mentioned A. L. Parson,[1] G. N. Lewis,[2] J. Dorfmann,[3] B. H. Wilsdon,[4] and E. C. Stoner.[5]

[1] A. L. Parson, Smithsonian Misc. Coll. **65**, 11 (1916).
[2] G. N. Lewis, Am. Chem. Soc. Mon. Ser. (1923); Chem. Rev. **1**, 231 (1924).
[3] J. Dorfmann, Zeits. f. Physik **23**, 286 (1924).
[4] B. H. Wilsdon, Phil. Mag. **49**, 354, 900, 1145 (1925).
[5] E. C. Stoner, Phil. Mag. **49**, 1289 (1925).

If one examines the chemical compounds that may be obtained he is surprised at the frequency with which even molecules occur and the scarcity of odd molecules. (By odd molecules is meant molecules having an odd number of electrons.) Furthermore one is struck by the marked differences in the physical phenomena exhibited by odd and even atoms and molecules. First may be mentioned ionization potential or the work required to eject an electron from an atom. With very few exceptions elements with odd atomic number have a lower ionizing potential than those with even atomic number. The relations between ionization potentials and atomic numbers have been very clearly summed up by F. A. Saunders[6] who shows that in general, the ionizing potentials are higher by several volts for atoms with an even number of electrons than for those with an odd number.

Spectroscopy also shows striking differences between atoms and molecules with odd and even numbers. For example, doublets of spectral lines, such as the D lines of sodium, are characteristic of atoms with odd numbers of electrons such as those appearing in column I of the periodic table. Those elements appearing in column II give spectral lines that are either singlets or triplets while those odd numbered elements appearing in column III give doublets and quadruplets. Again, when new atoms are created by the removal of one or more electrons from an atom the spectral properties of these temporary atoms depend on whether the new atom has an odd or an even number of electrons left. Thus the spectral properties of Al^{++}, Mg^{+} and Na are similar, each having eleven electrons. Likewise the spectral properties of Al^{+} and Mg, each with twelve electrons, resemble each other. From the above and other physical phenomena we are led to conclude that whether the atom or molecule contains an odd or an even number of electrons determines in large measure many of the phenomena connected with it.

If we are to accept the Bohr atom with its revolving electrons we must assume that each revolving electron constitutes a magnet just as any circular current does. According to this theory every molecule must be regarded as containing within it a number of electrons, each of which is an elementary magnet. As has been shown by Parson and others, these magnets may be so related to each other that the molecule as a whole has little or no magnetic moment which apparently is the case in the great majority of chemical molecules. In a few substances, however, the molecule may have one or more unneutralized

[6] F. A. Saunders, Science **59**, 47 (1924).

elementary magnets. Such substances exhibit paramagnetic properties and when placed in a magnetic field the molecule tends to orient itself in such manner as to diminish the net magnetic field in its neighborhood.

The lack of accurate magnetic data makes it difficult to predict the behavior or grouping of electrons from the point of view of magnetism. One may assume that any arrangement of the electrons that is symmetrical will produce diamagnetic conditions whereas unsymmetrical arrangements will produce paramagnetism. Also one may assume that if there is an even number of electrons in the atom they will group themselves in pairs in such manner as to neutralize each other and thus produce diamagnetism whereas if the atom contains an odd number of electrons there will necessarily be one that cannot be paired and this will produce external effects if not neutralized by an electron in some other atom.

It is in this connection that the possibility of magnetism being one of the factors in valence comes in. That the odd electron has something to do with valence is undoubtedly true. Whether the forces are electric or magnetic, or both, is the question that has to be answered. Any solution must necessarily take into account the fact that the electric forces due to the charges must be several thousand times greater than the magnetic forces due to the revolving electrons if we can apply the laws of electromagnetics. The fact that the electrochemical theory which has been held in the past fails to explain some of the important phenomena of chemistry and physics suggests the problem of studying in more detail the electromagnetic theory. The present investigation was undertaken in order to get additional data bearing on this phenomenon and to determine, if possible, the role of magnetic forces in valence.

One method of joining of two electronic orbits is suggested in Figs. 1 and 2. A revolving electron is equivalent to a magnet with polarity as shown in Fig. 1. Two such electromagnets approaching each other, as in Fig. 2, will be drawn together with a magnetic force which depends on some inverse function of the distance apart. There is nothing to prevent the electronic orbits overlapping each other and thus making the distance between effective poles very small. If the atom contains an even number of electrons one might expect, according to the magnetochemical theory, that they would all pair off and thus form a diamagnetic substance. However, one does not have to look far to find substances of even atomic number that are not diamagnetic. Two of the most magnetic substances known, namely, iron and nickel, are of even atomic number as is oxygen which is also quite strongly magnetic. However, it must be remembered that oxygen is exceptional in its behavior in many other instances[7] and that iron and nickel may be produced in the non-magnetic state according to recent results by L. R. Ingersoll and S. S. DeVinney.[8]

In making a magnetic test between the electrochemical and the magnetochemical theories of valence, it is necessary to experiment on substances of odd atomic number in order to obtain positive evidence. Take for example the oxides of copper, CuO and Cu_2O. The atomic number of copper being 29 and that of oxygen 8, it is seen that CuO has a molecular number 37 which is odd. The copper atom may be

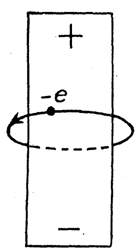

Fig. 1.

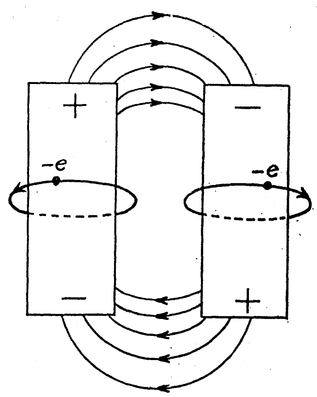

Fig. 2.

thought of as having 14 pairs and one odd electron and the oxygen atom 4 pairs while the compound CuO has 18 pairs and one odd electron. CuO then, should be paramagnetic which is found to be the case. If now, one more atom of copper with its 14 pairs and one odd electron be added to the CuO molecule one should expect one of two things to happen. Either the odd electron of the added copper atom would manifest its magnetism by making the substance Cu_2O more magnetic or the odd electron of the CuO would combine with the odd electron of the added copper atom forming another pair and thus neutralizing the magnetic effect of both. If the latter case were true the substance Cu_2O should be diamagnetic and the magnetic force could easily be thought of as the valence bond or at least as contributing to it. Experiments show that Cu_2O is diamagnetic.

[7] G. N. Lewis, J. Amer. Chem. Soc. **46,** 2027 (1924).
[8] L. R. Ingersoll and S. S. DeVinney, Phys. Rev. **26,** 86 (1925).

Since in the case of elements with even atomic number there are no odd electrons, one may ask whence comes the valence bond? Evidently, as Parson has shown in another connection, two pairs may be joined together to form a stable non-magnetic configuration.

As stated above it is the tendency for electrons to occur in symmetrical groups or in pairs and for this reason it is difficult to obtain many substances of odd molecular number. To make the test that the author is trying to make an element of odd atomic number must be obtained in two compounds; one where the element has a valence of two and the other where the valence is one or three. The author is indebted to B. S. Hopkins of the Chemistry Department of this University under whose direction most of the substances thus far used have been prepared. Care has been taken to eliminate ferromagnetic substances and where there has been any question as to purity a second or even a third sample has been prepared.

The method used was the same as that used by the author in previous magnetic investigations on rare earth oxides, namely, the Curie balance method. The balance was calibrated from time to time but throughout the investigation it has remained practically constant. The amount of the sample used in each test varied from about 40 mg in the case of MnO to 180 mg when some of the diamagnetic substances were being tested.

TABLE I

Magnetic Susceptibilities

Substance		$\chi \times 10^6$ dyne cm per gm.
CuO	(odd)	+1.35
Cu_2O	(even)	− .34
$CuCl_2$	(odd)	+8.77
$CuCl$	(even)	− .41
$CuBr_2$	(odd)	+2.71
$CuBr$	(even)	− .34
BiO_2	(odd)	+1.55
Bi_2O_3	(even)	− .26
PbO	(even)	− .19
PbO_2	(even)	− .20
SnO	(even)	− .14
SnO_2	(even)	− .14

Results have been grouped under two tables. Each value is the mean of a large number of determinations with fields varying from 2000 to 4500 lines per sq. cm and for two or more samples for any given material. In Table I are placed those substances which can be said to be in agreement with the magnetochemical theory in that the odd molecule is paramagnetic and the even molecule is diamagnetic thus indicating that the odd electrons have been paired to help form the valence bond. Many other illustrations similar to the oxides of lead and tin where both molecules are even could be given. In Table II are placed those substances the magnetic measurements for which do not give good evidence in favor of the magnetochemical theory. Lewis, in the article referred to above, quotes the results of Soné for nitrogen and its oxides which are in agreement with the results shown in Table I.

Results given in Table II require special consideration. Manganese, atomic number 25, is very close to the ferromagnetic group, iron, cobalt and nickel, atomic numbers 26, 27 and 28. Two different samples of the oxides of manganese were prepared by different chemists

TABLE II

Magnetic susceptibilities

Substance		$\chi \times 10^6$ dyne cm per gm.
MnO	(odd)	+66.3
Mn_2O_3	(even)	+63.1
CoO	(odd) (H = 1190 c.g.s. units)	+630.0
Co_2O_3	(even)	+27.5
AgO	(odd)	− .14
Ag_2O	(even)	− .58

and both gave approximately the same results both in magnitude and in having a lower value for the even than for the odd molecule. One advocating the magnetochemical theory might argue that inasmuch as the even molecule has smaller magnetic susceptibility there is evidence of some pairing of electrons when the manganese atom with its odd electron is added to MnO.

Oxides of one of the ferromagnetic elements, cobalt, were used. These showed interesting properties in that the compound CoO (odd) was not only highly magnetic but showed very decided ferromagnetic properties, the susceptibility varying from about 940×10^{-6} dyne cm per gm for a field of about 15 gauss, the lowest field at which the apparatus could be used, down to 265×10^{-6} dyne cm per gm for a field of 4245 gauss. The magnetic susceptibility of Co_2O_3, on the other hand, was practically constant and was very small compared with CoO.

The compounds of silver were peculiar in that both the odd and the even molecule gave diamagnetic susceptibilities. This suggests the possibility that the AgO (odd) was of the form Ag_2O_2 (even). Further work is to be done in the near future on this substance as well as on other substances of this type.[9]

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[9] Since submitting this work to the PHYSICAL REVIEW, papers in the same field by S. S. Shaffer and N. W. Taylor (J. Am. Chem. Soc. **48,** 843 (1926)) and by N. W. Taylor (Ibid., **48,** 854 (1926)) have appeared. These experimenters, working with different substances and using a different method, arrived at conclusions essentially the same as the author's.