THE MAGNETOCHEMICAL THEORY[1]

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The electrochemical theory, which at several epochs has so largely dominated the science of chemistry, must now be abandoned, or reduced to a quite subordinate rôle. While this theory is still useful in the interpretation of electrolytes and of numerous other substances in which there is a large degree of electrical polarization, it is now recognized to be incompetent to explain the cardinal phenomena of chemistry. The formation of chemical bonds by the coupling of two electrons, and in general the pairing of electrons which is of so nearly universal occurrence in atoms and molecules is by no means to be predicted from the electrochemical hypothesis.

The rarity and the peculiar properties of substances with odd molecules (molecules containing an uneven number of electrons), the existence of an even number of electrons in all stable inner shells, and the great predominence of atomic nuclei containing an even number of electrons[2] all show how far-reaching is the tendency of electrons to occur in pairs.

This phenomenon of the pairing of electrons has been overlooked in the development by physicists of the quantum theory of atomic structure, and it has remained as one of the few outstanding differences between the physicist's and the chemist's views of the atom. But in the last year or two many of the investigations of the physicists have pointed with equal certainty to the phenomenon of pairing, and to marked differences between atoms with even and odd numbers of electrons.

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[1] A revision of a paper presented at the dedication of the Sterling Chemistry Laboratory, Yale University, New Haven, Conn.

[2] See Harkins, J. Am. Chem. Soc., **42**, 1956 (1920).

First may be mentioned the ionization potential, which is the work required to eject an electron from a molecule. From the electrochemical theory it might be expected that the removal of an electron would be about as easy from an atom of argon with a positive nuclear charge of 18 and 18 electrons, as from the atom of potassium with a positive nuclear charge of 19 and 19 electrons. But we find that it takes but four volts to ionize a potassium atom while it requires fifteen volts to ionize the argon atom. An even greater disparity is found between helium with a positive nuclear charge of 2, and 2 electrons, and lithium with a positive nuclear charge of 3, and 3 electrons. The ionizing potential of lithium is five volts, that of helium is twenty-five volts. If we plot the ionizing potentials of the several elements against their atomic numbers we obtain zigzag lines[3] which show the striking difference between atoms with an odd number of electrons and those with an even number. In general the ionizing potentials are higher by several volts for the latter than for the former. This would correspond to a heat of ionization per gram atom greater by 50,000 to 100,000 calories for the even atoms than for the odd atoms, and this difference may indicate roughly the energy which would be set free when two odd electrons are coupled together to form a typical electron pair.

An equally striking difference between atoms with odd and even numbers is shown by recent developments in spectroscopy, which show very clearly that a doublet of spectral lines such as the *D* lines of sodium is characteristic of atoms with an odd number of electrons. On the other hand, the corresponding triplet of spectral lines occurs only with the even atoms. Thus the normal calcium spectrum contains a number of these triplets, but if the vapor is subjected to so violent a discharge as to eject one of the electrons from the calcium atom, leaving an odd number, a doublet spectrum entirely analogous to that of sodium is obtained. In the case of silicon it has been possible to remove the electrons one by one, thus obtaining spectra alternating between the triplet and the doublet type, as the

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[3] See Saunders, Science, **59**, 47 (1924).

atom is left successively with an even or an odd number of electrons.

Also from spectroscopic data we find a third striking confirmation of the theory of electron pairs, through the deductions of Sommerfeld upon the magnetic moment of different atoms. This abstruse method has not as yet been given the wide application of which it is capable, but enough has been done to indicate very strongly that if an atom or a molecule is a magnet its magnetic moment is equal to, or a multiple of, a unit magnet, which may be called the Bohr magneton. It appears further that every atom with an odd number of electrons has a magnetic moment, while the great majority of even atoms possesses no magnetic moment. Thus as we proceed through the series of elements arranged according to their atomic number, we may expect to find a regular alternation between magnetic and non-magnetic atoms.

It must, however, be pointed out that circumstances may arise such that two electrons may fail to pair with one another, so that each retains the properties of an odd electron. In the first long period of the elements we first meet the atoms of variable atomic kernel and here we find evidence of incomplete pairing. If we consider the following bi-positive ions, arranged in the order of atomic numbers, namely, Ti^{++}, V^{++}, Cr^{++}, Mn^{++}, Fe^{++}, Co^{++}, Ni^{++}, Cu^{++}, Zn^{++}, we can discover no evidence whatever of an alternation of properties. Whether we consider the stability of the ions or any other of their physical or chemical characteristics, we find a gradual and non-periodic change in properties from one end of the series to the other. Accordingly we might expect in this series of elements a failure of that alternation in magnetism which presumably holds for all of the elements below titanium, namely, the alternation between unit magnetic moment for odd atoms and zero magnetic moment for even atoms. This proves to be the case, and although it perhaps can hardly be claimed as yet that absolute proof can be given, we may accept with considerable confidence the conclusions of several investigators in this field to the effect that the magnetic moments in the above series of ions are 2 for

Ti^{++}, 3 for V^{++}, 4 for Cr^{++}, 5 for Mn^{++}, and then values decreasing, perhaps with equal regularity, down to Zn^{++} with zero magnetic moment. A similar phenomenon undoubtedly occurs in the middle part of each of the other long periods during the transition from one type of stable kernel to another type of stable kernel. Finally we shall find molecules which, although possessing an even number of electrons, show both in chemical and in magnetic properties evidence of odd or unpaired electrons. The most notable example is that of molecular oxygen which we shall discuss later.

These few exceptions to the rule of pairs only serve to emphasize the vast number of chemical molecules in which this rule holds, and since the electrochemical theory is unable to explain this phenomenon we must seek some other broad generalization to account for the pairing of electrons, which we must regard as the most fundamental manifestation of what has loosely been known as chemical affinity. The nature of this generalization has already been suggested in our consideration of the magnetic properties of substances.

If we assume with the physicists that every electron in a molecule is in orbital motion (without, however, committing ourselves to any general assumption that these orbits are centered or focussed about atomic centers) each such orbit, since it is an electric circuit, must be regarded as a small magnet. Indeed the assumption of such elementary magnets is in any case required in order to account for the magnetic properties of substances. Now two such magnets may be conceived as attracting one another,—although the laws of such attraction will presumably not be those of classical electromagnetics, but rather derived from quantum theory in such manner that the magnetic moment of an atom containing two like orbits will either be twice that of either moment alone, or will be zero. The latter case, corresponding to a mutual neutralization of the two magnets, may be regarded as giving a typical electron pair.

If therefore we are to speak of the electrons as the agents that bind together the atoms in molecules, we do not use the word "electron" in its narrowest sense, but we apply this term to the electronic orbit or elementary magnet as a whole. Thus when we state that the basic fact of chemistry is the pairing of electrons it would be more explicit to state that two isolated electronic orbits or magnets tend to couple with one another so as to eliminate their magnetic moments. The phenomenon is the same in principle whether the two elementary magnets belong to a single atom or to separate atoms. In the latter case the pair which is formed is the joint property of two atoms and is known as the chemical bond.

An interesting analogy to an atom containing a number of elementary magnets is furnished by a mechanical system containing a number of gyrostats. If such a system contains a single gyrostat in rapid motion, it responds in a very uncanny manner to any attempt to turn the axis of rotation. But if we have two equal gyrostats, set in a rigid frame, moving with equal speed in opposite directions and with the axes parallel and very close to one another, the system displays no gyrostatic effect as a whole. Such a model shows some similarity to the helium atom with its pair of coupled electronic orbits. If in the model one gyrostat is removed or simply stopped the system resembles the singly charged helium atom, which is an odd atom, and if both gyrostats are removed or stopped the system resembles the doubly ionized helium atom or alpha particle which is again even. I cannot help feeling that there is something more than a mere superficial resemblance between the alternation of properties in a model containing even and odd numbers of gyrostats and an atom containing even and odd numbers of electrons. It may be remarked that if in our model with two gyrostats these gyrostats are both set in motion in the same direction we have a double gyrostatic effect corresponding to the case of an atom or molecule with an even number of electrons but with a magnetic moment which is not zero but 2. This presumably represents the state of affairs in the oxygen molecule.

Now if we adopt the view that the electrons within an atom are essentially magnets we see that a study of the magnetic properties of substances is of the utmost importance to the chemist.

This is the view which was suggested by Mr. A. L. Parson,[4] who was the first to point out the remarkable parallelism between chemical and magnetic unsaturation. Since his paper was published a great deal of new experimental material has become available, especially through the work of Pascal, all of which shows that the resemblance between magnetic and other chemical properties is so striking that it cannot be attributed to any fortuitous coincidence, but demonstrates rather a great similarity if not a complete identity between the forces of magnetism and the basic forces of chemistry. Before developing this idea, however, we must review briefly Langevin's important theory of paramagnetism and diamagnetism.

THEORIES OF MAGNETISM

While every molecule must be regarded as containing within it a number of electrons, each of which is an elementary magnet, these magnets may be so adjoined one to another that the molecule as a whole has no magnetic moment, and this apparently is the case in the great majority of chemical molecules. If, however, the molecule as a whole has one or more units of magnetic moment, it may be called a *paramagnetic* or simply a magnetic molecule. If such a molecule is placed in a magnetic field, it will tend to orient itself like a compass needle in such manner to diminish the net magnetic field in its neighborhood. If this molecule is a part of a solid structure there may be forces of restitution which oppose the turning motion necessary for such orientation. Even in a gas, where the molecules are free from such forces of restitution, the thermal motion tends to prevent any particular orientation of the molecules. Since the thermal agitation which makes for randomness is greater the higher the temperature, we should expect that a more intense magnetic field would be required to produce a given degree of orientation of the molecular magnets the higher the temperature. This proves in fact to be the case, and the explanation which we have given is a qualitative statement of Langevin's theory of paramagnetism.

[4] Smithsonian Inst. Publ. 65, No. 11.

The phenomenon of *ferromagnetism*, characteristic of a few metals and alloys, although of the greatest practical importance, is of no great consequence for our present discussion. It is apparently only an exaggeration of paramagnetism due to the fact that the magnetic molecules are near enough to one another, or are so favorably situated, that when one molecule is oriented by an external magnetic field it in turn tends to orient neighboring molecules, and this cumulative process greatly augments the affect of a given external field.

In *diamagnetism* we deal with a minute effect which has proved very difficult to measure with high accuracy, but the measurements when once obtained are of the greatest significance to chemists. When we are dealing with typical paramagnetism the orienting of the magnetic molecules, when placed between the pole pieces of a magnet, produces a large and easily measured diminution of the net magnetic field. But in the absence of this gross effect of paramagnetism we may detect a small effect of the opposite sign, which is called diamagnetism. When a diamagnetic substance is introduced between the pole pieces of a magnet there is a small increase in the net magnetic field.

Langevin in accounting for diamagnetism assumes that unless a molecule is a magnet as a whole, and thus capable of turning in a magnetic field, no orientation at all is possible. In other words, the planes of the electronic orbits, which are the elementary magnets within the molecule, are held so rigidly in position that they cannot turn in a magnetic field. When such an orbit in a fixed plane is placed in a magnetic field it follows from the mathematical theory of electricity that the velocity of the electron in the orbit will be either increased or diminished by the external field in such a direction as always to increase the net magnetic field, this being the same phenomenon which is observed in the Zeeman effect. At ordinary temperatures the orbital motion of electrons is not supposed to be influenced by thermal agitation, and it is therefore to be predicted that diamagnetism will be found independent of the temperature, and such a conclusion is approximately substantiated by experiments. This is essentially Langevin's theory of dimagnetism.

The theories of Langevin have required some modification in order to bring them into accord with modern quantum theory, but the basic ideas remain the same. It would appear that Langevin's theory which supposes two distinct phenomena, the summation of whose effects may be used to account for the observed mechanical properties of substances, would be sufficiently flexible to satisfy the results of experiment, but we shall see that this is probably not the case, and that at least one additional phenomenon must be assumed before we can explain the magnetic behavior of substances.

MAGNETIC AND CHEMICAL UNSATURATION

The magnetic susceptibility is the quantity which best measures the magnetic properties of substances. Its sign is positive for paramagnetic, negative for diamagnetic substances. Pascal has shown that the magnetic susceptibility of various compounds may often be regarded as additive, so that by assigning values for the susceptibility per gram atom, or the atomic susceptibility, to a number of elements the susceptibility per gram molecule of a large number of compounds may be obtained by their summation. Thus he obtains, for example, the atomic susceptibilities of chlorine, bromine and iodine given in the following table:

	χ_α	Z	χ_α/Z
Cl	−210	17	−12.3
Br	−319	35	−9.1
I	−465	53	−8.8

The first column gives the atomic susceptibility ($\chi_\alpha \times 10^7$), the second the atomic number, which is the number of the electronic orbits in the atom, and the third column gives the quotient, which represents the susceptibility produced on the average by each electronic orbit. If the orbits were all alike we should expect this quotient to be a constant, which is obviously not the case. Indeed we should expect from the Bohr theory that the outer orbits of bromine and iodine would contribute more to the susceptibility than the orbits of chlorine, but the results show that just the reverse is true. It is evident from these figures, and from those for other elements, that we still have far to go before we can obtain any quantitative theory of atomic susceptibilities. A similar remark applies to the additivity of atomic susceptibilities. Thus for the calculation of the magnetic properties of organic substances Pascal assigns the following atomic susceptibilities ($\times 10^7$): hydrogen, -30.5; carbon, -62.5; oxygen, -48. By mere summation from these figures it is possible to calculate satisfactorily the molecular susceptibilities of a large number of saturated hydrocarbons, of alcohols and of ethers. But there are some serious discrepancies which become very pronounced when we consider the so-called unsaturated compounds. Thus Pascal was forced to introduce a correction of $+57$ for the double bond carbon to carbon, and $+66$ for the double bond carbon to oxygen. In other words, the unsaturated substances are much less diamagnetic than would be calculated by the rule of additivity.

In re-examining Pascal's data in an attempt to assign values of the susceptibility, not to the several atoms, but rather to the electron pairs which they contain, I have made a number of calculations which are not yet concluded, but which show that there is a good deal of arbitrariness in the choice of the particular susceptibilities which Pascal assumes. There are other sets of values which agree fully as well with his measurements as his own values, but if we adopt such a set we still find that a corresponding correction in the same direction has to be made for the unsaturated compounds. We are therefore dealing with something real which must be explained.

There are other exceptions to the rule of additivity. Indeed this rule is to be regarded only as a first approximation, and more exceptions and corrections to it will be found the more numerous and more accurate our experimental determinations become. But this is the very reason for urging the accumulation of accurate magnetic data, for these departures from additivity already furnish the best quantitative expression for the degree of unsaturation of organic substances that has so far been obtained.

I shall not repeat here the arguments which are given in my monograph on "Valence"[5] to show how close is the parallelism, between chemical and magnetic unsaturation in organic molecules, nor how the process of magnetic conjugation goes hand in hand with chemical conjugation (using the latter term in its most general sense to indicate any change in the structure of molecules which diminishes residual affinity). But rather I shall point out that these variations in susceptibility of organic molecules significant as they are, are really very small when compared with the variations which we meet when we consider the whole field of chemistry.

Let us consider first nitrogen and its oxides. Until recently the measurements of the susceptibility of these substances was so inaccurate that it was not even possible to verify the prediction that only the two odd molecules, NO and NO_2, would be found paramagnetic. However, the very recent work of Soné[6] furnishes the necessary accurate data. His results are given in the accompanying table in which the figures show the molecular susceptibilities (taken for the gases at 20°C.).

	SUBSTANCE						
	N_2	N_2O	N_2O_3 (liquid)	N_2O_4 (liquid)	N_2O_5 (solid)	NO_2	NO
Molecular suceptibility (× 10^7)	−76	−190	−160	−260	−32	+2,070	+14,700

I do not know whether the value for NO_2 is given for the equilibrium mixture of NO_2 and N_2O_4 or has been calculated to pure NO_2, but in any case the figures show how sharp a line may be drawn between the five even molecules, which are diamagnetic, and the two odd molecules, both of which are strongly paramagnetic. When we realize that the essential difference between two molecules of NO_2 and one molecule of N_2O_4 is that the two odd electrons or electronic orbits of the former have been clamped together to provide the chemical bond in the latter, we have

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[5] Am. Chem. Soc. Monograph Series, 1923.

[6] Soné, Sci. Repts. Tohuku Imp. Univ., **11**, 139 (1922).

as striking an illustration of the significance of pair formation as could be desired.

The even molecules in this group of substances are themselves not of the saturated type. Let us therefore go to the other extreme and consider the most saturated substances which chemistry affords, namely, the rare gases. We have already seen that there is no strict correlation between the susceptibility of a molecule and the number of electron orbits or elementary magnets which it contains, and we have intimated that this lack of correlation may be due to differences in degree of saturation. If therefore we compare chlorine (atomic no. 17), which we have seen to have an atomic susceptibility -210×10^{-7} in its compounds, with its next neighbor argon (atomic no. 18) we should expect the susceptibility of the latter to be somewhat greater, partly because it has one more electron, and especially because argon is an extremely saturated molecule. We are, however, hardly prepared for the enormous difference which has been experimentally obtained. From the work of Tänzler[7] we find the atomic susceptibility of argon to be -2128×10^{-7}, a value which is over ten times as great as that which Pascal assigns to chlorine. There are so many false values given in the literature of magnetism, many of which are wrong even in sign, that I had been inclined to attribute this large value for argon to experimental error. But the work of Tänzler has been corroborated by that of Soné[8] who finds the diamagnetism of argon to be so large as to cause a marked discrepancy between the susceptibility of atmospheric nitrogen and of pure nitrogen, and he calculates a value for argon which is of the same order of magnitude as that which we have just given.

The value obtained by Tänzler for helium is even more striking. For this atom, which contains but two electrons, the susceptibility is found to be -393×10^{-7}. Of all electron pairs this one in the helium atom apparently comes the nearest to satisfying the conditions assumed in Langevin's theory, namely, that the plane of each electron orbit remains fixed while the external

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[7] Tänzler, Ann. Phys., **24**, 931 (1907).

[8] Soné, Phil. Mag., **39**, 305 (1920).

magnetic field is applied. If therefore we are to assume that Langevin's theory is correct in so far as it goes, we are led to suppose that every electron pair in any substance contributes to the atomic susceptibility at least -400×10^{-7} unless this effect is either inhibited or is overshadowed by some other effect which in some way is connected with the degree of unsaturation within the atom or the molecule.

This is a point which we shall further discuss presently. In the meantime let us give one more illustration to show how great is the variation of magnetic susceptibility even in a group of substances having approximately the same number of electronic orbits per molecule. The four substances listed in the accompanying table all have molecular numbers (sum of atomic numbers) of either 16 or 18. The first column gives the formula of the gas, the second the number of electrons in the molecule, and the third the molecular susceptibility at 20°C. The value for oxygen is one obtained by Soné; the values for the two hydrocarbons are calculated by the method of Pascal and are presumably nearly correct. We see at once from the table that the difference between the susceptibility of a saturated and an unsaturated organic compound is really very small compared to the total variation in susceptibility. The case of oxygen, which is a typical paramagnetic substance, is so interesting as to warrant some further discussion.

	ELECTRON NUMBER	MOLECULAR SUSCEPTIBILITY $\times 10^7$
A	18	−2,128
C_2H_6	18	−308
C_2H_4	16	−190
O_2	16	+33,400

(Since the preceding paragraphs were written a paper by Wills and Hector ([7a]) has appeared in which the susceptibility of helium is found to be only one twenty-seventh as great as that obtained by Tänzler. This throws doubt also upon the latter's value for argon. It is evident that such discrepancies must be

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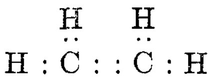
[7a] Phys. Rev., **23**, 209 (1924).

cleared away before we can make any quantitative deductions from magnetic data. In a later section of this paper some of the statements based on Tänzler's data may have to be modified.)

THE CASE OF OXYGEN

If we consider the three substances, ethylene, formaldehyde and oxygen, with the conventional formulae $H_2C = CH_2$, $H_2C = O$, and $O = O$, we see that they form a continuous series, and we might expect to be able to predict the magnetic properties of oxygen from those of the first two substances. However, a careful determination of the magnetic properties of ethylene and formaldehyde will probably show that they have small negative susceptibilities, while the susceptibility of oxygen is large and positive. This difference must correspond to a radical difference in molecular structure. In my paper of 1916 the possibilities of tautomerism in molecules containing a double bond were discussed. In one tautomer the double bond consists of two pairs of electrons shared between two atoms. In another tautomer the bond is broken in a polar manner, so that one of the electron pairs becomes the sole property of one of the atoms. This is the tautomeric form which Lowry has recently considered as responsible for many of the reactions of unsaturated compounds. But it is the third type of tautomerism which I suggested that interests us here. In this tautomer one of the bonds is broken in such a way as to be equally divided between the two atoms, so that each atom possesses an odd electron.

It appears that this type of rupture of the double bond occurs to a large extent in the oxygen molecule, so that the predominant form of molecules in oxygen is quite different from that in ethylene, as can be represented in the two formulae,  $\mathrm{H} : \overset{\mathrm{H}}{\ddot{\mathrm{C}}} : : \overset{\mathrm{H}}{\ddot{\mathrm{C}}} : \mathrm{H}$ and $: \underset{\cdot}{\ddot{\mathrm{O}}} : \underset{\cdot}{\ddot{\mathrm{O}}} :$. We may thus regard the paramagnetic properties of oxygen as due to the existence in its molecule of two odd atoms.

Now if this is the correct explanation of the magnetic properties of oxygen it implies the existence of great differences between the chemical properties of oxygen and of a substance like ethylene. A molecule containing an odd electron is characterized by very high reactivity, and no case is known of a reaction between two odd molecules that requires any measurable time for the completion of the reaction. We must therefore inquire whether this is also a property of molecular oxygen.

When this question is first asked we might be inclined to answer it in the negative, for we know that most processes of oxidation are very slow, but a little further consideration leads us to reverse this decision. It has been shown for a large number of oxidations in the neighborhood of room temperature, and it is usually presumed to hold true for all, that the first step consists in the formation of a peroxide, and that this peroxide is then converted into a normal oxide by a process which may be very slow. The latter process does not concern us, and we must simply inquire as to the rate of formation of the peroxide. Here we have, I think, sufficient evidence to state that if the peroxide is slow in forming it is always because of some inertness in the other reacting substance and not in the oxygen. And this idea is corroborated by the fact that whenever an odd molecule forms a peroxide with molecular oxygen the reaction is instantaneous. Of the large number of organic odd molecules which have been obtained since Gomberg first discovered triphenylmethyl, nearly all combine with oxygen at ordinary temperatures to form peroxides, and in all cases the reaction, as far as we can ascertain, is instantaneous. An even severer test is furnished by a reaction occurring at very low temperatures. Nitric oxide (although having an odd molecule), is colorless even in the liquid state at the temperature of liquid air. If a little oxygen is introduced into a vessel containing the colorless nitric oxide the latter becomes instantly colored, probably through the addition of one NO to one of the atoms of oxygen to form NO_3, or by the addition of one NO molecule to each of the odd atoms of O_2 to form a substance with the formula N_2O_4, but presumably differing from ordinary N_2O_4 in being a true peroxide.

On the other hand, the molecule of ethylene appears always to need some activation before it can take part in an addition reaction.[9] Even in the presence of an odd molecule like triphenylmethyl, with which oxygen forms a peroxide instantaneously, the corresponding addition of ethylene can hardly be made to go at all, although the resulting compound would certainly be quite stable. Chemical evidence therefore supports the magnetic evidence that the assumed double bond in oxygen is broken in a symmetrical manner so as to leave to each atom an odd electron. This must be true of the majority, although perhaps not of all of the oxygen molecules. Some anomalies in the temperature coefficient of the magnetic susceptibility may indicate that there is an equilibrium between two tautomeric forms, the magnetic and the non-magnetic, and that this equilibrium changes with changing temperature.

The enormous difference in magnetic properties between the oxygen molecule and other molecules to which we attribute double bonds seems to support the idea that the change from a non-magnetic to a magnetic molecule is not a gradual process, but that the molecule must possess at least one unit of magnetic moment or no magnetic moment at all.

A NEW VIEW OF DIAMAGNETISM

Let us now for the sake of simplifying our problem exclude from our consideration the paramagnetic molecule, which in Langevin's theory is able to orient itself as a whole in a magnetic field, and restrict our attention to the diamagnetic molecule. Let us further accept Langevin's theory that the velocity in the electron orbits changes in a magnetic field in such a way as to increase the net field. Moreover, I shall assume that this effect is a comparatively large one as evidenced by the high negative susceptibility of helium and argon, and therefore that the negative susceptibility of most substances, owing to this phenomenon alone, would be much larger than that which is experimentally found, were it not for another phenomenon which is not considered in Langevin's theory.

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[9] See for example Stewart and Edlund, J. Am. Chem. Soc., **45**, 1014 (1023).

We must now attempt to discover the nature of this phenomenon. Langevin postulated an electron orbit, the plane of which is incapable of turning when an electric field is applied. This postulate we shall now abandon, and we shall regard the immobile condition assumed by Langevin only as a limit which is approached when the elementary magnets within the atom are in conditions of the greatest stability. Thus we shall consider the elementary magnets, or orbits, as held in definite positions by constraints which may vary greatly in strength. When we speak of a tightly held electron we shall imply that a given turning force will produce only a small actual turning of the orbit, while a loosely held electron implies a considerable turning movement when the same force is applied.

It is evident that any turning of the elementery magnets caused by an electric field will be such as to diminish that field, and thus will produce an effect in the direction of paramagnetism. In so far therefore as any turning is possible it will give rise to a less negative value of the susceptibility than would be calculated from Langevin's theory.

This simple theory seems to me to give a remarkable insight into the nature of magnetic and chemical unsaturation. Any condition of strain within the molecule removes the electron pairs from positions of the greatest stability into positions where they are more loosely held, a process which at the same time increases the chemical reactivity and diminishes the diamagnetism.

Perhaps the pair of electrons which is the most rigidly held is the one in the helium atom. In argon we have, in addition to the corresponding pair of electrons, two groups of eight, each of which may best be regarded as a regular tetrahedron with a pair of electrons at each corner. Such a group of eight is evidently an extremely stable structure from a magnetic as well as from a chemical standpoint, although the diamagnetism of argon per electron pair is less than that of helium. If, however, we build up a structure exactly like that of argon but with a different nucleus, so that the atom as a whole has a charge, a system of far less stability and far greater mobility is obtained. Thus potassium ion and chloride ion have the same structure as argon, but solid potassium chloride, which is built up of such ions, has a diamagnetism per atom less than one-tenth of that of argon.

Whenever a pair of electrons is shared between two atoms to form a chemical bond, the constraints are greatly loosened, and this is true even in the tightest bonds such as those between carbon and carbon and between carbon and hydrogen. This is shown by the fact that we have already cited, that the diamagnetism of ethane is only about one-seventh per electron pair as great as that of argon. When one of the bonded atoms is that of an electronegative element, which tends to obtain complete possession of the bonding pair, this effect is enhanced, and becomes especially great when two electronegative atoms are bonded together. Such compounds always exhibit a condition of pronounced unsaturation.

In general we may assume that in its most stable state a pair of electrons is almost completely self-satisfied in a magnetic sense, so that there is no appreciable magnetic field except in the immediate neighborhood of the pair. But as the constraints become weaker and the pair is opened up the residual magnetic field becomes larger and influences other atoms at considerable distance. It is this stray magnetic field which in my opinion is meant by chemists when they speak of residual affinity.

When two atoms in the same or in different molecules both possess strong residual fields they may approach and orient themselves in such a manner as to neutralize this field and produce a condition of greater saturation. This I believe is what in the most general sense is called conjugation.

We have seen that the formation of single bonds is alone sufficient to produce a condition of unsaturation through the loosening of electronic constraints. Still more is this the case when two electron pairs are held jointly by the same two atoms in a double bond, and this is clearly brought out in the work of Pascal. But in those cases where this unsaturation can be partly eliminated by a process of conjugation, as in the benzene ring, or in the carboxyl radical, then the diamagnetic susceptibility is correspondingly enhanced.

If we consider a molecule with a double bond as one in which the elementary magnets that constitute the bond are largely freed from the constraints which interfere with their turning, and if we consider that in some molecules conditions are especially favorable to such freedom of turning, we might imagine two of these magnets so far distorted from their normal position that they would be able to snap into a new position in which their magnetic moments would no longer neutralize but augment one another. This I believe to be the state of affairs in the molecule of oxygen, and it is of much interest to investigate further the magnetic properties of doubly bonded molecules to find other cases in which a similar phenomenon occurs.