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THE NATURE OF THE CHEMICAL BOND. II. THE ONE-ELECTRON BOND AND THE THREE-ELECTRON BOND

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The work of Heitler and London and its recent extensions[1] have shown that the Lewis electron-pair bond between two atoms involves essentially a pair of electrons and two eigenfunctions,[2] one for each atom. It will be shown in the following paragraphs that under certain conditions bonds can be formed between two atoms involving one electron or three electrons, in each case one eigenfunction for each atom being concerned. The conditions under which the one-electron bond and the three-electron bond can be formed will be stated, and their properties will be discussed. These bonds have not the importance of the electron-pair bond, for they occur in only a few compounds, which, however, are of especial interest on account of their unusual and previously puzzling properties.

The One-electron Bond.—The resonance phenomenon of the quantum mechanics, which provides the energy of the shared-electron chemical bond, occurs even between two unlike atoms when an electron-pair bond is formed, on account of the identity of the two electrons. But if only one electron is available, resonance is not expected in general. The application[3] of the first-order perturbation theory of the quantum mechanics to a system of two nuclei and one electron, although not leading to accurate numerical results, is illuminating. It is found that with two nuclei of different charges there occur in most cases only repulsive states, so that $Li + H^+$ or $Li^+ + H$ would not form a stable molecule LiH^+. Only when the unperturbed system is degenerate or nearly degenerate, as in H_2^+ where the two nuclei have the same charge, does there exist a resonance energy leading to molecule formation. The criterion for the stabilization of a single-electron bond by resonance energy is the following: *A stable one-electron bond can be formed only when there are two conceivable electronic states of the system with essentially the same energy, the states differing in that for one there is an unpaired electron attached to one atom, and for the other the same unpaired electron is attached to the second atom.*

By "essentially the same energy" it is meant that the energies of the states of the unperturbed system differ by an amount less than the possible

[1] Linus Pauling, THIS JOURNAL, 53, 1367 (1931).

[2] Throughout this paper the word eigenfunction will be used to denote a single-electron eigenfunction, such as one of the four tetrahedral bond eigenfunctions of a carbon atom.

[3] Linus Pauling, *Chem. Rev.*, 5, 173 (1928).

resonance energy. (In H_2^+ the resonance energy in the normal state is about 60,000 cal. per mole.) The criterion is of course satisfied in H_2^+, where the two nuclei are identical, and in H_3^+. We may write for these molecule-ions the electronic formulas

$$H \cdot H^+ \text{ and } H \cdot H \cdot H^+$$

This discussion may be given the following somewhat more precise form. Let us consider various functions of the coördinates of the electrons relative to those of the nuclei, which, as usual in molecular problems, are assumed to retain fixed positions.

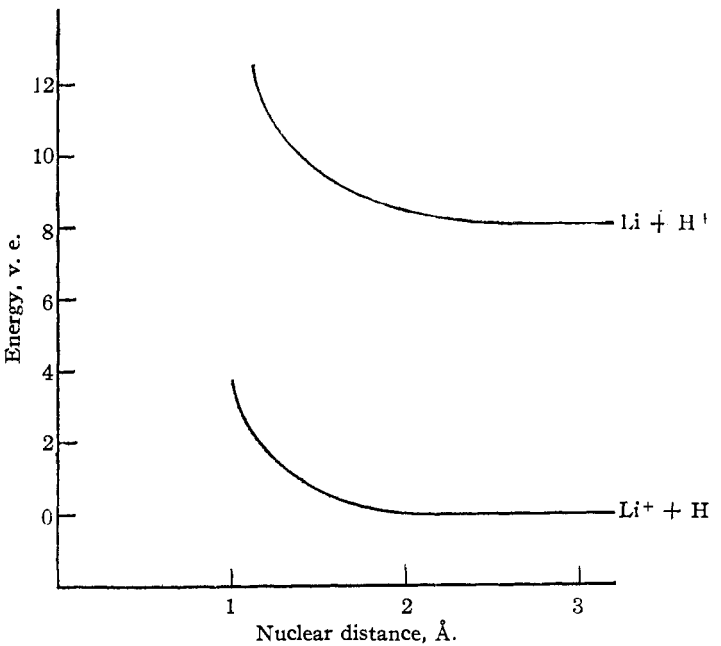


Fig. 1.—Potential curves for $Li^+ + H$ and $Li + H^+$ as functions of the nuclear separation.

Let Ψ_A and Ψ_B be functions which minimize the variational integral $E = \int \Psi^* H \Psi d\tau$ when the nuclei of the two atoms A and B (or two groups of atoms) are far apart, Ψ_A corresponding to the configuration A· B and Ψ_B to the configuration A ·B. Other electrons in the atoms or groups are of course also included in the eigenfunctions. The coördinates of each electron are taken relative to axes fixed by the nucleus to which the electron is attached. Thus if we neglect the K electrons in Li, the functions of interest for the system $Li^+ + H^+ + E^-$ would be a 2s eigenfunction for Li as Ψ_A, corresponding to $Li\cdot + H^+$, and a 1s eigenfunction for H as Ψ_B, corresponding to $Li^+ + \cdot H$. The values of the variational integral for Ψ_A and Ψ_B

$$E_A = \int \Psi_A^* H \Psi_A d\tau$$

and

$$E_B = \int \Psi_B^* H \Psi_B d\tau$$

are then to be calculated as functions of the distance between the two nuclei. If E_A and E_B differ considerably for all values of this distance D, then resonance will not occur; if they approach one another closely resonance is expected. Then a new function formed

from Ψ_A and Ψ_B, corresponding to the structure A·B, will give a curve lying lower than either E_A or E_B. Three cases are shown in Figs. 1, 2 and 3. In Fig. 1, E_A and E_B are separated by about 8 v. e. throughout their course, so that resonance is not expected, and E_A and E_B themselves represent two repulsive states of the system.[4] In Fig. 2, E_A and E_B coincide, because of the identity of the two nuclei involved, so that resonance is of importance at all internuclear distances. In Fig. 3 the functions Ψ_A and Ψ_B correspond to $A\cdot^- + B^+$ and $A + \cdot B$, respectively. E_A and E_B are widely separated for large internuclear distances, but because of the Coulomb attraction of the ions $A\cdot^-$ and B^+, E_B rapidly approaches E_A as D decreases. Resonance then occurs only at small internuclear distances. The normal state would have the structure A·B, which goes over to A·B as the nuclei are separated.

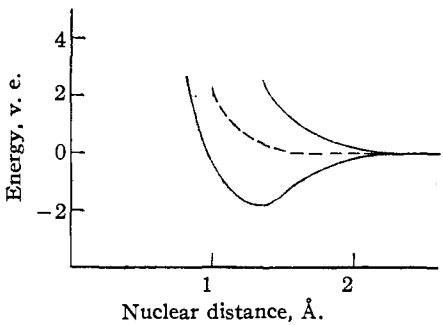


Fig. 2.—Potential curve for $H + H^+$ or $H^+ + H$ (dashed line) and for $H\cdot H^+$ (lower full line). The upper full line corresponds to the nuclear-antisymmetric repulsive state.

The boron hydrides offer an interesting problem. With boron trivalent, we should expect compounds such as BF_3, BH_3, etc. Actually the halides all do have the formula BX_3, and show no tendency to associate, while the simplest hydride, B_2H_6, has not begun to dissociate into $2BH_3$ at a temperature at which it begins to lose hydrogen. If BH_3 were given an electronic formula with an electron-pair bond between boron and each hydrogen, $H:\overset{H}{\underset{\cdot\cdot}{B}}:H$ the only electrons left to form a bond between the two boron atoms in B_2H_6 would be the K electrons, which are so tightly bound that there is no possibility that they take part in bond formation. Sidgwick suggested[5] that there are one-electron bonds in B_2H_6 and the higher hydrides, B_4H_{10}, etc. with the formulas

$$\begin{matrix} & H & H & \\ H: & \ddot{B} & : \ddot{B} & :H \\ & \dot{H} & \dot{H} & \end{matrix} \qquad \begin{matrix} & H & H & H & H & \\ H: & \ddot{B} & : \ddot{B} & : \ddot{B} & : \ddot{B} & :H \\ & \dot{H} & \dot{H} & \dot{H} & \dot{H} & \end{matrix}$$

pointing out that these structures agree with the unusual properties of the compounds, which are decomposed by water, give off hydrogen easily, and are immensely powerful reducing agents. In view of the quantum mechanical discussion of the one-electron bond, this suggestion is to be accepted. We write as the two structures to be discussed for B_2H_6

$$\begin{matrix} & H & H & \\ H: & \ddot{B} & : \ddot{B} & :H \\ & & \dot{H} & \end{matrix} + \cdot H \qquad \text{and} \qquad \begin{matrix} & H & H & \\ & \ddot{B} & : \ddot{B} & :H^- \\ & & \dot{H} & \end{matrix} + H^+$$

[4] The effect of polarization has been neglected. This is usually permissible, since polarization energies rarely amount to more than one or two volt-electrons.

[5] N. V. Sidgwick, "Electronic Theory of Valency," London, 1929, p. 103.

The first of these consists of a B_2H_5 group and an H atom, the second of a $B_2H_5^-$ ion and a proton. If the values of E for these two structures differ by only one or two volt-electrons for small internuclear distances, our criterion for the formation of a one-electron bond is satisfied. The energy of formation of $B_2H_5 + H$ from $B_2H_5 + E^- + H^+$ is 13.53 v. e., and the interaction energy of B_2H_5 and H is small. The electron affinity of B_2H_5 may be estimated as 3 v. e. and the Coulomb attraction of $B_2H_5^-$ and H^+ may well contribute 10 or 11 v. e. to the energy of the second configuration, as shown in Fig. 3, so that it is not at all improbable that the two curves approach each other in the region of interest. We accordingly conclude, in default of another structure, that the one-electron bond is to be accepted for the boron hydrides, whose existence provides the strongest evidence that the condition for the formation of this bond is satisfied.

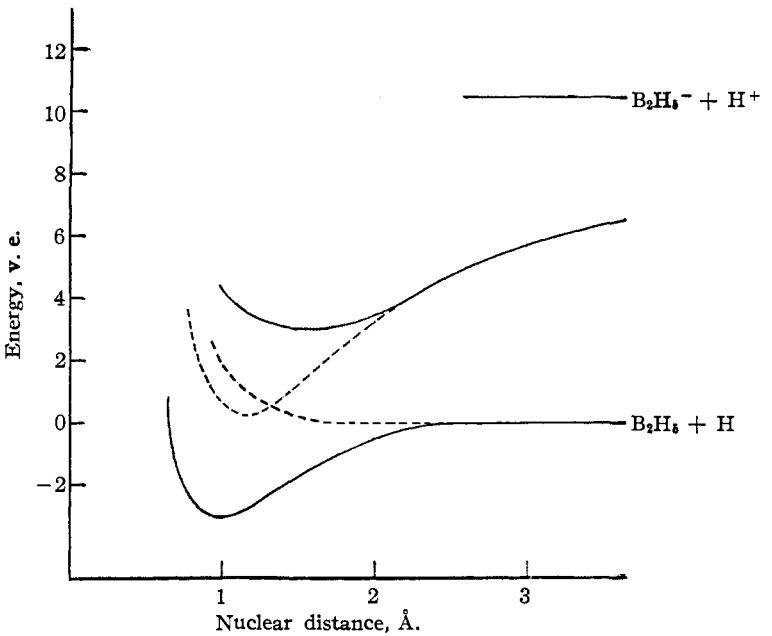


Fig. 3.—Potential curves for B_2H_6. The two dashed lines are potential curves for the structures $B_2H_5 + H$ and $B_2H_5^- + H^+$, the lower full line that for the normal B_2H_6 molecule and the upper one that for an excited state of the molecule.

The electronic formulas written above are not to be interpreted as indicating that two of the six hydrogen atoms in B_2H_6 are singled out for the one-electron bonds. Instead the various configurations with different pairs of hydrogen atoms attached in this way are all included in the final structure, since they correspond to the same energy, and this additional degeneracy provides further resonance energy, increasing the stability of the molecule.

Sidgwick decided from consideration of the compounds containing them that one-electron bonds are stable only when one of the atoms so linked is hydrogen. From the foregoing theoretical considerations this is to be rejected. It would be surprising if Li_2^+, Na_2^+, etc., were not stable, with dissociation energies about two-thirds as great as those of Li_2, Na_2, etc., and it is possible that other compounds involving one-electron bonds between two unlike atoms will be discovered.[6]

The Three-electron Bond.—The approximate solution of the wave equation for a system composed of a pair of electrons attached to one nucleus and a single electron attached to another nucleus has shown that the resonance forces corresponding to interchange of the three electrons are in the main repulsive. Thus normal He and H have no tendency whatever to molecule formation.[7] But if the two nuclei are identical or nearly so, an additional degeneracy is introduced, for the two configurations A: $\cdot$B and A$\cdot$:B, in one of which atom A contains an electron pair and B an unpaired electron, and in the other A contains an unpaired electron and B an electron pair, then have nearly the same energy. The interactions of the two atoms will then cause the eigenfunction for the normal state of the system to be the stable nuclear-symmetric combination of the eigenfunctions corresponding to these two configurations; and the accompanying resonance energy will lead to the formation of a stable molecule containing a three-electron bond.

A three-electron bond, involving one eigenfunction for each of two atoms and three electrons, can be formed in case the two configurations A: $\cdot$B *and* A$\cdot$: B *correspond to essentially the same energy.* As in the case of the one-electron bond, "essentially the same energy" means that the energies of the two unperturbed configurations differ by an amount less than the possible resonance energy.

Another way of looking at the problem is to neglect the mutual repulsion of the electrons. Then the eigenfunction for one electron in the field of two essentially identical nuclei is either the nuclear-symmetric one, which gives rise to the stable one-electron bond, or the nuclear-antisymmetric one, which corresponds to a repulsive potential function. Two electrons with opposed spins can be introduced into the nuclear-symmetric eigenfunction, producing an electron-pair bond with about double the energy of a one-electron bond (neglecting the mutual repulsion of the electrons). This eigenfunction is then completely occupied, according to Pauli's principle, and a third electron must be introduced into the nuclear-antisymmetric eigenfunction, whose repulsive potential neutralizes the attraction of one of the nuclear-symmetric electrons, producing a three-electron

[6] The lavish use made of one-electron bonds by some English authors is without justification.

[7] G. Gentile, *Z. Physik*, **63**, 795 (1930).

bond with about the same energy as a one-electron bond. With four electrons, two are necessarily nuclear-symmetric and two nuclear-antisymmetric, so that there is no tendency to form a strong bond.

The Helium Molecule and Molecule-ion.—The simplest example of a molecule containing a three-electron bond is the helium molecule-ion, in which a 1s eigenfunction for each of two identical atoms is involved. The two unperturbed states of equal energy are $He: \cdot He^+$ and $He\cdot^+ : He$. The formation of this molecule might be represented by the equation

$$He\ 1s^2\ ^1S + He^+\ 1s\ ^2S \longrightarrow He_2^+ (1s + 1s)^3\ ^2\Sigma$$

Three dots in a horizontal line placed between the two atomic symbols may be used to designate a three-electron bond: $He \cdots He^+$.

Evidence has been advanced[8] that the neutral helium molecule which gives rise to the helium bands is formed from one normal and one excited helium atom. Excitation of one atom leaves an unpaired 1s electron which can then interact with the pair of 1s electrons of the other atom to form a three-electron bond. The outer electron will not contribute very much to the bond forces, and will occupy any one of a large number of approximately hydrogen-like states, giving rise to a roughly hydrogen-like spectrum. The small influence of the outer electron is shown by the variation of the equilibrium internuclear distance within only the narrow limits 1.05–1.13 Å. for all of the more than 25 known states of the helium molecule.

Oxides of Nitrogen.—Nitric oxide and nitrogen dioxide are very unusual substances in that they are stable odd molecules with no steric excuse such as triphenylmethyl has. Thus if we give NO the double-bonded structure $:\dot{N}::\ddot{O}:$, we would expect two such molecules to combine to N_2O_2 by pairing their unshared electrons with an energy of reaction of about 3 v. e. But the substance does not show this behavior. G. N. Lewis wrote[9] of nitric oxide, "Of all the substances which have odd molecules it exhibits the least degree of unsaturation. It is colorless, and at ordinary temperatures does not associate into double molecules, although this process seems to occur at low temperatures. By some method which is not yet understood, the odd electron is obviously much more firmly held in the molecule, and the molecule itself is more nearly saturated, than in the case of any other odd molecule."

I believe that the explanation of these facts is provided by the three-

[8] W. Weizel, *Z. Physik*, **59**, 320 (1929). Weizel and F. Hund [*ibid.*, **63**, 719 (1930)] have discussed the possible electronic states of the helium molecule. Neither one, however, explains why He $1s^2$ + He^+ 1s form a stable molecule-ion, nor gives the necessary condition for the formation of a three-electron bond. In earlier papers they assumed that both atoms had to be excited in order to form a stable molecule [W. Weizel, *ibid.*, **51**, 328 (1928); F. Hund, *ibid.*, **51**, 759 (1928)].

[9] G. N. Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., Inc., New York, 1923, p. 128.

electron bond. Nitrogen and oxygen have nearly the same effective nuclear charges, so that we might expect the two states $:\dot{N}::\ddot{O}:$ and $:\ddot{N}::\dot{O}:$ to have nearly the same energy, in which case resonance between them would lead to a more stable combined state involving a double bond and a three-electron bond $:N\dddot{:}:O:$. This, the normal state of NO, would lie about 1.5 v. e. below the energy level expected for $:\dot{N}::\ddot{O}:$, and so would not tend to polymerize.

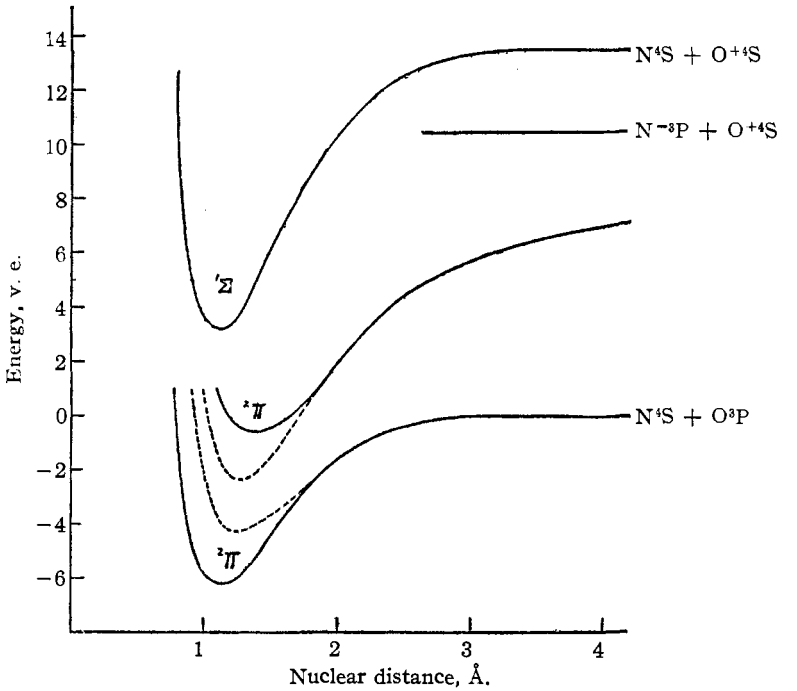


Fig. 4.—Potential curves for nitric oxide. The two dashed lines are potential curves for the structures $:\dot{N}::\ddot{O}:$ and $:\ddot{N}::\dot{O}:$, the lowest full line that for the normal molecule $:N\dddot{:}:O:$, the next for the excited $^2\Pi$ state, and the uppermost that for the normal ion $:N:::O:^+$.

This argument may be repeated in greater detail. Each atom in the molecule contains four L eigenfunctions, σ_b, $\pi+$, $\pi-$, and σ_0, of which the last is not important for bond formation. A normal nitrogen and a normal oxygen atom can combine to form a double-bonded Π^2 molecule.

$$N\ 2s^22p2p2p\ ^4S + O\ 2s^22p^22p2p\ ^3P \longrightarrow NO\ (2\sigma_0^22\pi)(2\sigma_0^22\pi^2)\{2\sigma_b2\pi + 2\sigma_b2\pi\}\ ^2\Pi$$

or

$$:\dot{N}\cdot + \cdot\ddot{O}: \longrightarrow :\dot{N}::\ddot{O}:$$

An assumed potential function for this state is drawn in Fig. 4. The dissociation energy is taken to be about 4.5 v. e., rather than the usual

value of about 6 v. e. for double bonds with carbon, for the reason that the small bond energy is not enough to change the s–p quantization with the formation of more suitable bond eigenfunctions, the bond instead being formed by p-eigenfunctions for each atom. A similar double-bonded $^2\Pi$ state can also be formed from nitrogen and oxygen ions

$$N^- 2s^2 2p^2 2p 2p\ ^3P + O^+ 2s^2 2p 2p 2p\ ^4S \longrightarrow NO\ (2\sigma_0^2 2\pi^2)(2\sigma_0^2 2\pi)\{2\sigma_b 2\pi + 2\sigma_b 2\pi\}\ ^2\Pi$$

$$:\dot{\ddot{N}}\cdot^- + \cdot\dot{\ddot{O}}:^+ \ldots :\ddot{N}::\dot{O}:$$

A potential function for this state is also shown in Fig. 4. In drawing this the electron affinity of nitrogen was taken to be 3 v. e., and a Morse curve for small values of r was combined smoothly with a Coulomb curve for large values in such a way that the Coulomb interaction of the two ions contributed 8.5 v. e. to the energy of formation of the molecule. (I have found this rather arbitrary procedure satisfactory for ionic states of other molecules.) It is seen that these two $^2\Pi$ states approach to within 2 v. e. of one another, so that resonance is to be expected, on account of the rather large overlapping of the 2π eigenfunctions of the two atoms. Assuming the resonance energy to be of the order of magnitude of 2–3 v. e., the normal state $:N\vdots\vdots O:$, obtained by combining these two $^2\Pi$ states, has the potential function shown. The eigenfunction orthogonal to that of the normal state, also a combination of the two $^2\Pi$ states, leads to a potential function lying above the upper original one; it is the excited $^2\Pi$ state of NO, 5.6 v. e. above the normal state, and with the large equilibrium internuclear distance of 1.42 Å.

The potential function for normal NO^+, with a structure like that of the nitrogen molecule

$$N\ 2s^2 2p 2p 2p\ ^4S + O^+ 2s^2 2p 2p 2p\ ^4S \longrightarrow NO^+(2\sigma_0^2)(2\sigma_0^2)\{2\sigma_b 2\pi 2\pi + 2\sigma_b 2\pi 2\pi\}\ ^1\Sigma$$

$$:\dot{N}\cdot + \cdot\dot{\ddot{O}}:^+ \longrightarrow :N:::O:^+$$

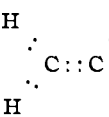
is also shown in Fig. 4. The unusually large dissociation energy for a triple bond, 10.3 v. e., is to be attributed to the effect of polarization of the nitrogen atom by the oxygen ion.

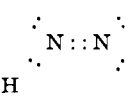
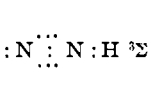
There are two electronic configurations which might be written[10] for NO_2

[10] This structure rather than a ring structure is supported by two pieces of evidence relative to nitro compounds and the nitrite ion. It was kindly pointed out to me by Dr. H. A. Stuart of Koenigsberg that p-dinitrobenzene has no electric moment, in contrast to p-diaminobenzene. The moment of the latter compound does not vanish because the three bonds formed by the amino nitrogen are directed toward tetrahedron corners, causing the moment of the amino group to be non-collinear with the nitrogen–carbon bond; in consequence the two amino moment vectors are not opposed. (The observed moment is the root mean square of the instantaneous resultant moment, which varies as the amino groups rotate about the single bonds, vanishing only when the two moment vectors are opposed.) With a ring structure, $R:\ddot{N}:\ddot{O}:$ with $:\ddot{O}:$ below, the nitro group would

$:\ddot{O}:\dot{N}::\ddot{O}:$ and $:\dot{O}:\ddot{N}::\ddot{O}:$. As in the case of NO, these should have nearly the same energy, and so should interact to give a structure with a three-electron bond, $:\ddot{O}:\overset{\cdot\cdot}{N}::\ddot{O}:$ (The oxygen atoms are not non-equivalent, for the double bond changes places regularly with the single and three-electron bond.) This stabilizes the odd electron, as in NO, and in consequence NO_2 shows only a small tendency to polymerize to N_2O_4 or to combine with NO to N_2O_3.

The Oxygen Molecule.—There are two reasonable alternative structures for the normal oxygen molecule, the double-bonded $^1\Sigma$ structure $:\ddot{O}::\ddot{O}:$ and the $^3\Sigma$ structure $:\ddot{O}:\overset{\cdot\cdot}{O}:$ involving one electron-pair bond and two three-electron bonds. Both are formed from normal atoms. It is difficult to decide from *a priori* arguments which is the more stable. With s–p quantization retained, the double bond, formed with p-eigenfunctions, is expected to be weaker than a carbon–carbon double bond, and to have a bond energy of 4–4.5 v. e.; but no sound estimate of the dissociation energy for the second structure can be made. It is actually found that the normal state is a $^3\Sigma$ state, with a $^1\Sigma$ state lying 1.64 v. e. higher. Hence the normal oxygen molecule contains one electron-pair bond and two three-electron bonds. Despite the triplet state (two unpaired electrons), the molecule is not highly unsaturated, because of the stabilizing influence of the three-electron bonds; on the other hand, no electronic activation of the molecule is necessary before polymerization or other chemical reaction.

Ethylene must have the double-bonded $^1\Sigma$ structure  for there are not enough unshared electrons available for the O_2-like $^3\Sigma$ structure. It is known to be diamagnetic.

N_2H_2 should have two low-lying states,  $^1\Sigma$ and  $^3\Sigma$

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behave similarly, in disagreement with experiment. But with the structure the atoms are coplanar, and the moment vector and the R–N bond are collinear, causing the moments of two para nitro groups to cancel each other.

The structure $:\ddot{O}:\dot{N}::\ddot{O}:^-$ for the nitrate ion (with the double and single bonds changing places) leads to an angle of 125°16′ between the two N–O bond directions. which might be increased somewhat through repulsion of the two oxygen atoms. This is supported by the value 130° found recently through the x-ray investigation of the crystal structure of sodium nitrite. (G. E. Ziegler, paper given at the meeting of the American Physical Society, Washington, D. C., May 1, 1931.)

The fact that aromatic azo compounds are all diamagnetic shows that their normal state is the $^1\Sigma$ state. The difference between O_2 and RN_2R is probably connected with the greater bond energy of the latter, and the resultant changing of s–p quantization for the nitrogen atoms.

The Compounds of Nitric Oxide.—It might be expected that combination of NO with an alkyl radical would result in a double-bonded $^1\Sigma$ molecule, containing no unpaired electrons.

$$R. + :\dot{N}::O: = R:\ddot{N}::\ddot{O}:$$

This structure, however, does not account for the observed properties of the nitroso compounds, as mentioned by Lewis, from whom we continue to quote. "Professor Branch has pointed out to me that this behavior of nitric oxide is very closely related to the anomalous properties of the nitroso compounds. When NO combines with another free radical (odd molecule) such as an alkyl group, we should expect this union of two odd molecules to produce a fully saturated compound. But this is not the case. Not only does NO in the free state behave nearly like a saturated substance, but when combined with an odd molecule like methyl it does not appear to conjugate with the odd electron of the latter. So the resulting compound, although possessing an even number of electrons, has the properties of odd molecules. The nitroso compounds in general are highly colored and they almost invariably tend to form double molecules, as though each single molecule had an odd electron." In a discussion of the unusual magnetic behavior of complex ions containing nitric oxide, Professor Lewis suggested to me that a $^3\Sigma$ structure as in the O_2 molecule might be stable rather than the $^1\Sigma$ double-bonded structure. This is evidently the explanation of the properties of organic nitroso compounds; the similarity of the N and O atoms permits the formation of an electron-pair bond and two three-electron bonds, giving the O_2-like $^3\Sigma$ structure.

$$R. + :\dot{N}::O: = R:\dot{N}:\dot{O}:$$

Two such $^3\Sigma$ molecules could then combine without preliminary electronic excitation, perhaps to form the compound

$$\begin{matrix} R:\ddot{N}:\ddot{O}: \\ :\ddot{O}:\ddot{N}:R \end{matrix}$$

or (as suggested to me by Professor T. D. Stewart of the University of California on the basis of chemical evidence) a similar compound in which nitrogen atoms are bonded together.

Compounds of several different types might be formed by introduction of nitric oxide into complex ions. If the metal atom provides one of the electrons of the electron-pair bond, NO should assume the O_2-like $^3\Sigma$ structure. If both bond electrons come originally from NO (which then

behaves like NH_3, CO, etc. in complexes), a $^2\Pi$ structure as in NO itself would be retained, except that the interaction with the other atoms in the complex would probably destroy the orbital moment, so that this structure would more correctly then be given the symbol $^2\Sigma$. A third possibility is that the NO molecule not only contributes both bond electrons but also lose an additional electron to the complex, and so acquire a triple-bonded structure like that of the nitrogen molecule.

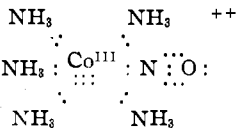
$$M + :N\overset{\cdot\cdot\cdot}{::}O: = \cdot M:N:::O:$$

Further variety is also possible through attachment of NO by the oxygen atom rather than the nitrogen atom.

In the preceding paper[1] it was mentioned that the known magnetic moments of nitroso complexes

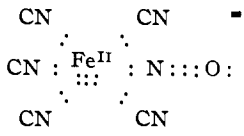
$Na_2[Fe(CN)_5NO]\cdot 2H_2O$	$\mu = 0.00$
$[Ru(NH_3)_4\cdot NO\cdot H_2O]Cl_3$	0.00
$[Ru(NH_3)_4\cdot NO\cdot Cl]Br_2$	0.00
$[Co(NH_3)_5NO]Cl_2$	2.81

offered a puzzling problem, which has now been solved. Let us discuss the cobalt complex first. Here there are six groups attached to the cobalt atom by electron-pair bonds, which make use of the six d^2sp^3 octahedral eigenfunctions of cobalt, leaving three $3d$ eigenfunctions available for additional unshared electrons. Now we expect either cobaltous or cobaltic cobalt with 7 or 6 additional electrons, respectively. There is room for only six $3d$ electrons, however; the seventh electron in a cobaltous complex would necessarily occupy a level such as $4d$ lying several volt-electrons higher, and would make the compound unstable. Accordingly this is a cobaltic compound, the cobalt atom having given up one electron to NO, which then assumes the O_2-like $^3\Sigma$ structure.

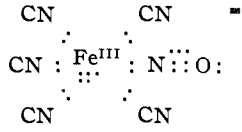


(Here NO plays a role similar to that of Cl or CN in complexes, and may appropriately be called electronegative.) This $^3\Sigma$ complex should have a magnetic moment of 2.83 Bohr magnetons, a value in excellent agreement with the observed 2.81.

A similar structure for the iron compound would involve quadrivalent iron, which is very improbable, either bivalent or trivalent iron being expected. If NO loses an electron to iron, assuming the triple-bonded $^1\Sigma$ structure, the resulting bivalent iron atom, with six d^2sp^3 bonds and six unshared $3d$ electrons, will also be in a $^1\Sigma$ state, making the compound as a whole diamagnetic.



Another conceivable $^1\Sigma$ state for the complex results from pairing the odd electron of trivalent iron with that of neutral NO.

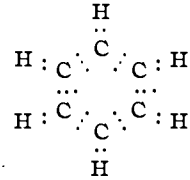


This is probably also involved to some extent in the normal state of this complex, which can then not be said to contain either bivalent or trivalent iron alone.

The ruthenium compounds are entirely analogous to the iron compound.

A profitable discussion of more of the numerous complexes containing NO can be given only after further experimental data, especially relative to magnetic moments, have been collected.

It may be mentioned that the three-electron bond developed above is *not* present in the benzene molecule, for which certain investigators have suggested the structure



We have seen that a three-electron bond is less stable than an electron-pair bond, so that this structure would provide a very unstable rather than a very stable benzene ring.

I am grateful to Professor G. N. Lewis for his valuable suggestion relative to the structure of the nitroso compounds and for his stimulating interest in the work as a whole.

Summary

It is shown that a stable shared-electron bond involving one eigenfunction for each of two atoms can be formed under certain circumstances with either one, two, or three electrons. An electron-pair bond can be formed by two arbitrary atoms. A one-electron bond and a three-electron bond, however, can be formed only when a certain criterion involving the nature of the atoms concerned is satisfied. Of these bonds the electron-pair bond is the most stable, with a dissociation energy of 2–4 v. e. The one-electron bond and the three-electron bond have a dissociation energy

roughly half as great, about 1–3 v. e. The hydrogen molecule-ion, $H{\cdot}H^+$, triatomic hydrogen ion, $H{\cdot}H{\cdot}H^+$, boron hydrides $H:\overset{H}{\underset{H}{B}}:\overset{H}{\underset{H}{B}}:H$, etc., lithium molecule-ion, $Li{\cdot}Li^+$, etc., contain one-electron bonds. The helium molecule and molecule-ion, $He\cdot\cdot\cdot He$ and $He\cdot\cdot\cdot He^+$, nitric oxide, $:N\overset{\cdot\cdot}{\cdot\cdot}:O:$, nitrogen dioxide, $:\overset{\cdot\cdot}{O}:N::O:$, and oxygen molecule, $:\overset{\cdot\cdot}{O}:\overset{\cdot\cdot}{O}:$, contain three-electron bonds. A discussion of nitroso compounds, in particular dealing with their magnetic moments, is also given.

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A STUDY OF SOLUTIONS OF ETHYL ALCOHOL IN BENZENE, IN WATER, AND IN BENZENE AND WATER

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The results of several investigations[1] have indicated that the molecular weight of ethyl alcohol in dilute aqueous solutions as determined by the freezing point method is normal. Curve A in Fig. 1, plotted from Pickering's data[1] shows the range in concentration through which the deviation from the theoretical freezing point lowering Curve (T_A), is not large.

Similar investigations[1a,2] of solutions of ethyl alcohol in benzene show that above extremely low concentrations of alcohol the observed freezing point lowering is much less than would be expected from the freezing point law. Curve (B) in Fig. 2, is plotted from Pickering's data, curve (B^1) is plotted from our data, while curve (T_B) is the theoretical freezing point lowering curve for solutions of alcohol in benzene. Peterson and Rodebush[3] have shown that for concentrations up to 2.262 g. of alcohol in 1000 g. of benzene the molecular weight of alcohol as calculated from freezing point data is normal. They state that above this concentration, however, the usual freezing point formulation does not apply.

It would seem from these investigations that ethyl alcohol exists in a different molecular form when dissolved in benzene than when dissolved in water. It has been suggested by some workers that evidence as to whether or not this is true should be obtained by the study of the distribution of alcohol between the two nearly immiscible solvents, water and benzene.

[1] (a) S. V. Pickering, *J. Chem. Soc.*, **63**, 998–1027 (1893); (b) R. Abegg, *Z. physik. Chem.*, **15**, 209–261 (1894); (c) F. M. Raoult, *Compt. rend.*, **124**, 885–890 (1897); (d) E. H. Loomis, *Z. physik. Chem.*, **32**, 578–606 (1900).

[2] F. Viala, *Bull. soc. chim.*, **15**, 5–11 (1914); N. Perrakis, *Compt. rend.*, **176**, 1137–1140 (1923).

[3] J. M. Peterson and W. H. Rodebush, *J. Phys. Chem.*, **32**, 709–718 (1928).