[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERISTY OF CALIFORNIA] DOUBLE AND TRIPLE BONDS, AND ELECTRON STRUCTURES IN UNSATURATED MOLECULES

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The conception of multiple bonds which will be presented here is based upon the Lewis¹ theory of molecular structure and valence, but departs from it in several essential respects. Among the more important differences is the assumption that while the group of eight² is usually maintained about each atomic kernel in any molecule, the valence bonds, whether "single" or "multiple," consist almost universally of but two electrons, mutually shared by two atoms.³

To show how this state might be realized, it will be recalled that the elements comprising the first period, lithium to fluorine, each possess 2 electrons which ordinarily do not act as valence electrons.⁴ They appear to form a sort of primary "shell," persisting through the entire period of elements and appearing also in hydride ion and in helium. In helium the group of two is very stable but in hydride ion it is much less so. In the other elements it may be intermediate between these two extremes, and it is possible that under circumstances which make it difficult for the group of eight to be completed about them, the inner electrons may themselves take part in the formation of octets. Adopting this hypothesis, the picture of the double bond which is now proposed is that of one atom in which the central electrons have been drawn into the outer octet, joined by two electrons to another atom in which the normal arrangement is preserved. In cases of triple bonding the inner two electrons are assumed to have been drawn into the outer shell in each of two adjacent atoms, there being again two electrons held in common. These linkings are illustrated and compared with the saturated bond in the accompanying formulas of ethane. ethylene and acetylene. The symbols here represent atomic nuclei, and all electrons outside are indicated by dots.

н н	нн	
•• ••	•• ••	•• ••
$\mathbf{H}:\cdot\mathbf{C}\cdot\colon\cdot\mathbf{C}\cdot\colon\mathbf{H}$	$: \cdot C \cdot : C :$	H:C:C:H
•• ••	•• ••	•• ••
н н	нн	
Ethane	Ethylene	Acetylene

¹ Lewis, This Journal, 38, 762 (1916). Langmuir, *ibid.*, 41, 868 (1919).

² Langmuir, *ibid.*, **42**, 274 (1920) emphasizes the importance of the octet of electrons.

 $^{\rm s}$ The two electron double bond is also assumed in the ''sextet'' theory of Rodebush and Latimer, ibid., 42, 1419 (1920).

 4 For example, taking the atomic number of carbon, 6, to represent the positive charge of the nucleus, there must be 6 electrons outside of the nucleus. Of these, 4 are the so-called valence electrons, leaving 2 which do not act as bonds in saturated compounds.

In the succeeding sections of this article the more general aspects of the above ideas will first be developed, following which specific applications will be made to the properties and reactions of various unsaturated substances.

General Considerations

Specification of Elements which can Form Multiple Bonds.—From a study of the properties of numerous substances, Lewis concludes that the ability to form non-polar multiple bonds is peculiar to the first period elements.⁵ The same conclusion follows readily from the present theory. Once a complete shell is formed about the inner two electrons the possibility of their participation in bond formation should be almost or quite excluded. This would lead to the requirement that one at least of any two doubly bonded atoms, and both atoms of a triple bond, must be of the first period.

Differentiation among the elements within the period, so far as bonding is concerned, is perhaps to be traced to the differing nuclear charges. Lithium, with its small charge, should more readily lose 1 electron, reverting to the group of 2, than gain 5, forming an unsaturated octet. The fluorine nucleus because of its large charge should easily gain and hold the one electron needed to complete both shells about it. The middle elements only will then show tendencies to form the unsaturated group.

Laws of Force.—The laws of force which hold at short distances between positively charged particles, between negative electrons, and between positive and negative particles, are of great importance in any theory of atomic or molecular structure. Unfortunately very little is known concerning these laws. From experiments⁶ on scattering of α particles it is indicated that the inverse-square law of repulsion of positive particles holds to within 10⁻¹¹ cm. of the nuclei of certain metallic atoms. The inverse-square law of repulsion is usually assumed to hold for electrons also. The paired electrons of the Lewis tetrahedral atom, however, require the assumption that electrons in the shells of atoms attract each other when close together. The little independent evidence which exists on this point is negative in character. Fewer double charges are obtained,⁷ for example, when the molecules of air or particles of shellac or sulfur are ionized by various agents than might be expected if the electrons which are expelled exist in closely associated pairs. In spite of this, the attractive

⁵ The author's thanks are due to Professor Lewis for permission to include this generalization, which has not been published. Its significance hinges largely on the idea of the non-polar bond. Thus molecules containing only such bonds have small external fields, form low melting, readily volatile substances, etc., ideas which are elaborated in the several papers already referred to. Here it will only be said that there are few, if any, exceptions to the rule above.

^e Chadwick, Phil. Mag., 40, 734 (1920).

⁷ Millikan and Fletcher, *ibid.*, **21**, **7**53 (1911). Kelly, *Phys. Rev.*, **16**, 260 (1920).

force idea presents many appealing features, and it may be necessary later to accept it. At the present time, however, it appears desirable to do without this assumption if possible.

Turning to the case of a positive and a negative particle, Lewis⁸ points out that Coulomb's law must fail at short distances, and suggests that the force changes periodically in a certain region from attraction to repulsion. In Fig. 1⁹ which depicts one such possibility, the force, f, between particles is plotted against the distance, r, separating them. The inverse-square law is not approached until r is relatively large. The points A, B and C represent equilibrium positions to which electrons displaced by small amounts would tend to return. That a number of such positions¹⁰ are present in or about all atoms cannot be doubted. For purposes of illustration and with no intent to assign definite causes or laws, Fig. 1 will be

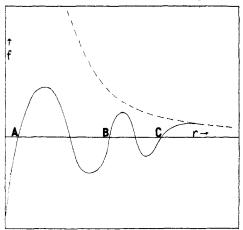


Fig. 1.—Deviations from Coulomb's Law.

assumed to represent this condition in a rough qualitative way, and will be used to correlate the facts discussed under the following topics.

Formation of "Extended Octets."—In saturated molecules, the inner 2 electrons of a carbon atom may be imagined to be located, for example, at A in Fig. 1, while the shell of 8 has the radius B. The formation of a multiple bond requires the exertion of powerful disruptive forces upon the electron shells (as in the splitting off of

chlorine atoms with their tightly held electrons). Under such influences, 2 of the 10 electrons are lost entirely by the atom, and the inner 2, together with the remaining 6 of the original octet, are assumed to be drawn out to form a new shell of larger size at C. The increased size assumed and the absence of the center electrons has suggested the designation of this group as the "extended octet."

Reactivity and Stability.—The new grouping is well suited to represent the characteristics of unsaturated bodies. These in general cannot be classed as highly reactive, which is attested by the fact that in the typical cases they are thermodynamically unstable. They should therefore decompose into other substances if they were reactive. The presence of the

⁸ Lewis, Science, N. S., 46, 297 (1917).

⁹ From a paper by Dushman, Gen. Elec. Rev., 20, 407 (1917).

¹⁰ Corresponding in the static atom to the different orbits of Bohr's model.

octet structure may account in part for this lack of great activity. The possibility of returning to the regular grouping, and the weakened constraints on the electrons (indicated by the smaller slope of the curve in Fig. 1 near the outer equilibrium positions) render them more reactive than similar saturated bodies.

The change with temperature in the stability of such a substance as acetylene is interesting. At ordinary temperatures the amplitudes of the electrons in Position C in Fig. 1 will be small. As the temperature is increased, however, they gain sufficient energy to carry them past the minimum in the curve to the left of C. Their transfer to the inner positions is then spontaneous, and a reaction occurs, the products of which are carbon (with the normal octet) and hydrogen. As the temperature is still further increased, the thermal energy of the electrons becomes so great that they can no longer remain in the inner positions, and the formation of the extended octet is favored. Acetylene therefore becomes stable with respect to hydrogen and carbon.

Arrangement of Electrons.—For the sake of simplicity the arrangement of electrons in all octets has been assumed to be essentially cubic. In all probability the actual structures are often intermediate between cubes and tetrahedra, and may closely approach the latter, on account of the attraction exerted by the nuclei on the electrons of the bonds. A grouping by twos (which is in no sense pairing due to attraction) may also result if there is a maximum in the repulsion-distance curve of electrons, as assumed by Mr. Huggins of this Laboratory. In any event the tetrahedral direction of the four bonds in saturated compounds is no doubt maintained. It is this direction of bonds, rather than any atomic configuration, which has been valuable in organic chemistry.

For the sake of convenience in representation, no attempt is made in general in the formulas of this paper to indicate distortions from the cubic arrangement or the enlarged size of extended octets.

Free Rotation.—The differences between single or triple bonds and the double bonds of this theory should not be overlooked. The structures about the former two are entirely symmetrical. In the latter this symmetry is absent. Due to the different sizes of the connected octets, the electrons in double bonds are probably spread apart farther than usual in the normal bond. The abnormal stresses which result between the electrons of the bond and those of each of the adjoining structures (perhaps even involving the inner electrons of the normal octet) might easily be such as to oppose free rotation of the atomic shells with respect to each other. Indeed, when analyzed in this light there is little difference between the 2-electron bond of this theory and the 4-electron bond with the tetrahedral arrangement. Especially when it is recalled to what extent

the prevention of rotation is due to specific effects,¹¹ it appears that differences of the double from the single bond are of degree only, and the ideas above provide sufficient basis for the interpretation of the facts.

Type Reactions.—The substances which may add directly to unsaturated bodies are confined to two fairly definite groups, the one consisting of bodies like the halogens and halogen hydrides, the other embracing substances which are themselves unsaturated. The molecules of the first type may be regarded as potentially ionized, or ready to separate with an unequal division of electrons between two atoms. When a bromine molecule, for example, collides with a molecule of acetylene the rearrangement indicated below may be assumed to occur. The reaction may be

described as the telescoping of one of the bromine¹² atoms with one of the extended octets, the breaking of the loose bond of bromine to bromine, and the attachment of the second bromine atom to the other carbon octet, sharing two of its electrons. By a repetition of this process another molecule of bromine might be added. The condensation of molecules in which there are multiple bonds is similar to the first stage above. As illustrated in the next section, it consists simply in the telescoping of two extended octets, the regular double bond arrangement being formed. The saturated carbon octet does not usually show this property of telescoping with one of the extended octets, probably because the former is always protected by surrounding atoms.

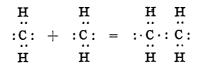
Structures and Properties of Typical Substances

Chain Hydrocarbons.—The simplest hydrocarbon which should exist according to the present theory is methylene. It is, however, a high temperature form, and the failure of the numerous attempts to prepare it is evidence that it is too reactive to exist at ordinary temperatures. Its condensation to ethylene offers the simplest example of the second type of reaction of the preceding section and for this reason is shown below.

Ethylene and acetylene have already been used as type substances. It remains only to point out that when all of the electrons in the outer

¹¹ As evidenced by the differing temperatures at which different unstable forms go over to their stable isomers. In those syntheses where only a single form is produced, it even seems that the rate of transformation of the unstable to the stable form is high even at ordinary temperatures.

 12 Symbol letters for elements after the first period represent the entire atomic kernel.



shell are not acting directly as bonds, the attached hydrogen nuclei (positive electrons) no doubt have some freedom of motion from one position to another. This is illustrated in the formulas below, which are also used to introduce a method of representation which will prove convenient later.



Fig. 2.-Formulas of ethane, ethylene and acetylene.

By this plan the projections of the electron cubes are indicated by squares. Figs. 2 and 3 show ethane, ethylene and acetylene, with possible tautomeric forms of the last two. In some of these, certain of the hydrogen nuclei are assumed to be held jointly by 4 electrons.

A substituted ethylene could, by the present theory, exist in two isomeric forms. Thus propylene might have either of the two formulas of Fig. 4.



Fig. 3.-Modified formulas of ethylene and acetylene.

But the physical properties of such isomers could hardly differ sensibly, and no chemical method could distinguish between them. However, in a chain of 4 or more carbon atoms with one double bond, the "position" of the latter is not necessarily uniquely determined. The molecule represented in Fig. 5 might break on oxidation at either side of the extended carbon atom, and the second of the two added halogen atoms might in the



Fig. 4.—Formulas of propylene.

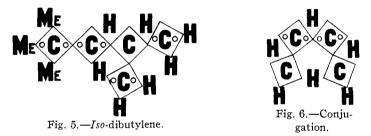
same way go to either of the adjacent normal octets. In general, due to the dissymmetry of the molecule, reactions will be "directed" so that they occur mainly in one way. Sometimes, however, these directive influences will be weak and the molecule will not react exclusively in either way. This behavior is experimentally found in the case of *iso*-dibutylene, and the

single formula of Fig. 5 takes the place of two of the ordinary ones, represented in tautomeric equilibrium below.

$$(CH_3)_3C-CH_2-C$$
 CH_2
 CH_2
 CH_3
 $CH_3)_3.C-CH=C$
 CH_3
 CH_3

It is not desired to imply that actual shifting of a double bond between tautomeric or isomeric forms will never be found, for a mechanism involving little disturbance of the molecule as a whole is possible by the present theory. This may consist simply in the passage of the inner electrons from one atom to another, either directly or by replacement of the 2 bonding electrons, allowing the latter to enter the inner position in the adjacent atom. It seems that such shifts might readily occur in either way, particularly at high temperatures or during reactions with other molecules.

A conjugated system may be represented by 2 extended octets at the ends of a 4-carbon atom chain. It is likely also that the end atoms are



often close together and joined by a loose "hydrogen bond,"¹³ as in the formula of Fig. 6. When addition occurs it may then be at the two end carbon atoms, the first addition product being,

$$\begin{array}{cccc} H & H & H & H \\ \vdots \cdot C \cdot \vdots \cdot C \cdot \vdots \cdot C \cdot \vdots & C \\ \vdots Br \vdots & H & H & \vdots Br \end{array}$$

Under the influence of the attraction of the bromine atom attached to the remaining extended octet at the end of the chain, the two inner electrons may be assumed to be drawn from the central atom to this one, giving

H	H	\mathbf{H}	H
••	••	••	••
$: \cdot C \cdot :$	$\cdot C \cdot :$	С	:• C • :
••	••	••	••
:Br :	н	\mathbf{H}	:Br :

The next addition will now be on the center atoms.

¹³ Rodebush and Latimer, Ref. 3, and Huggins have assumed such bonds. The attraction of 1 hydrogen nucleus by 4 electrons, as discussed in this paper, is a somewhat similar idea.

Benzene.—The formation of benzene from acetylene, which is suggestive in connection with the structure of the former, probably consists in the telescoping of 3 molecules of acetylene to form a ring. Either of the structures in Fig. 7 might result from such a reaction, and both appear to be well suited to represent the properties of the substance. Both structures are very symmetrical and compact, and the constraints which apparently would be present should make the molecule unusually rigid and inert, though it must still be unstable on account of the extended octets which are present. Both formulas represent the carbon atoms as being

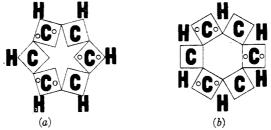


Fig. 7.-Benzene formulas.

in a single plane, and the two *ortho* positions are identical with each other in both. The structure in Fig. 7(b) presents obvious possibilities of reduction to hexamethylene, and of condensed ring formation. Neither reduction nor condensation to naphthalene appears to be as directly possible with rings of the first type, though not necessarily excluded.

The three extended octets are still the more reactive points of the above structures, and when one of the hydrogen atoms of the molecule repre-

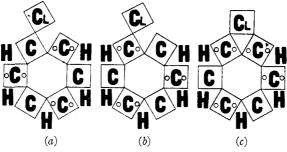


FIG. 8.—Rearrangements in chlorobenzene.

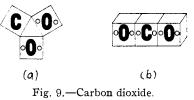
sented in Fig. 7(b), for example, is substituted, the new group will usually be attached to one of them. Following the attachment a subsequent change may or may not occur according to the nature of the substituent. If the latter is a halogen or a singly bonded group, a shift of electrons similar to those assumed in the discussion of conjugation may follow, in this case extending throughout the molecule. As represented in Fig. 8(a) and (b),

the structure first formed goes over to one in which the reactive octets are ortho-para to the new group. If, however, it is an extended octet which originally becomes attached to an extended octet of the ring, then apparently the shift of electrons does not occur. The remaining two reactive octets will then be in the meta position to the substituted group, and the second addition will be on one of them. The factors determining whether or not the shift postulated above will occur, are perhaps the electro positive or negative character of the group substituted and the size of the octet. The groups strongly attracting electrons will cause the shift, if at the same time an existing distortion of the electron arrangement, due to linkage of octets which are dissimilar in size, is relieved. One or the other or both of these factors are probably operating in the case of the halogens, hydroxyl, or any normal carbon octet. With such groups as -CHO, -COOH, -CN, etc., the connecting octet is itself extended according to the present idea, and of approximately the same size as the reactive octets of the ring, so a symmetrical and unstrained connection can be made between the two. The fact that the groups -SO₃H and -CF₃ direct to the meta positions may possibly be regarded as evidence of the importance of the size effect, since in each of these cases the connecting octets are probably considerably larger than the normal carbon octet, though neither is extended in the sense used here.

The preceding considerations apply equally well to either of the two proposed formulas. The following applies chiefly to the one chosen for illustration in Fig. 8. If the latter is assumed, substituted atoms or groups must be attached in the plane of the ring, and probably "cover" rather completely the position originally occupied by the displaced hydrogen atom. In some instances it would seem that the new atom might become attached to two points of the ring, by a telescoping process like that discussed in the ordinary reactions. Fig. 8(c) shows such an attachment of a chlorine atom. Consequences which might be expected to follow this linkage are the increased difficulty of removing a halogen atom from the benzene ring, and second, after three extended octets had been converted by this process to ordinary ones, the reactivity of the molecule with regard to substitution should be largely destroyed. Both of these conclusions may possibly be of service in interpretation of actual phenomena.

Oxides of Carbon.—In assigning a structure to carbon dioxide, consideration of its properties in relation to those of substances of analogous composition is particularly important. The formula which seems most satisfactory in this respect is shown in Fig. 9(a). Bearing in mind that elements after the first period cannot in general have the extended grouping, it is clear that a similar representation is possible for carbon disulfide but not for silicon dioxide or silicon disulfide, a distinction which is supported by the actual character of the substances. This experimental

distinction militates strongly against such formulas as that in Fig. 9(b) for carbon dioxide, for if this type of bonding is possible in carbon dioxide or carbon disulfide it is difficult to see why it should not be in silicon dioxide or disulfide. It is therefore assumed in all later applications that 1 atom seldom shares more than 2 electrons with any other 1 atom.



The treatment of ions, or other substances which exist only in polar solvents or polar crystals, constitutes an interesting field in itself which cannot be included here. The possibilities of solvation when in solution, and of complete separation of all the atoms of the solids into charged units of the crystal lattice, may make definite formulation difficult or meaningless in such cases. To show that some of the provisional requirements may be met, however, the reaction of carbon dioxide with oxide ion (and a few later examples) are given. The formula in Fig. 10 for carbonate ion, for



Fig. 10.—Reaction of CO_2 with oxide ion.

instance, gives a "saturated" structure without addition of further oxide ion, hence orthocarbonate ion will not ordinarily form. The unity of the carbon dioxide group is preserved in this tormula, which gives it advantages analogous to those of the Berzelian type for oxygen acids and salts. The breaking of the polar bonds of the ion when it enters a crystal, resulting in the formation of 3 symmetrically placed oxide ions about a central charged carbon atom would satisfy the usual ideas of crystal structure, and so on.

Carbon monoxide is given the formula (: \mathbf{C} : \mathbf{O}) . Its reaction with hy-

drogen, yielding formaldehyde, may be written

Other characteristic reactions are those which occur under suitable stimuli with hydrogen chloride, chlorine and ammonia. Since only one molecule of

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each of the latter substances ordinarily adds to the carbon monoxide molecule, the resulting compound in each instance is supposed to be of the type indicated in Fig. 11, where the halogen atom has telescoped with both of the extended octets of the carbon monoxide.

Groups Containing Carbon, Hydrogen and Oxygen.—The structure of formaldehyde has just been indicated. Its own reactions, condensations,



Fig. 11.-Reaction of CO with HCl.

etc., are quite similar in type to those already discussed. Its higher homologs appear to require little comment, other than to point out the possibility that they are to be represented by formulas like one of those for acetaldehyde in Fig. 12. (Compare with acids below.)

Keto-enol tautomerism is an illustration of an equilibrium which requires no change in the basic structure of the reacting molecules, according to the present theory. The group which is present in a 1:3-



Fig. 12.—Acetaldehyde.

diketone, for example, may be represented as in the first formula in Fig. 13. Here the presence of the extended octets on each side of the central CH_2 group no doubt has a tendency to extend its carbon atom also, rendering the hydrogen nuclei rather labile, and facilitating the exchange pictured in the figure.

The carboxyl group is itself quite polar, and the properties ordinarily assigned as typical are those which it shows in polar solvents. In non-polar media and as vapors, acids usually exist as double molecules. Since the following remarks presuppose the carboxyl structure to be essentially unaffected by solvation or association, they are tentative in character and limited to a few only of the numerous suggestions which occur. Formic acid is represented in Fig. 14(a). Here the 2 hydrogen nuclei are located at opposite sides and slightly outside of the enclosure formed by the other 3 atoms. With the loss of one of the hydrogen ions the remaining one would then be drawn to a position in the center of the entire molecule from which it might be difficult to withdraw it, explaining the monobasicity of the acid. When some radical is attached to the carboxyl carbon, the

symmetry of the molecule is lost and the oxygen-oxygen bond is often broken by the attraction of the radical for one or the other of the oxygen atoms. The various possible stages of separation are shown in Fig. 14(b). The hydrogen ion is thought of as shifting from one loose point of attachment to another, being only a little more firmly held by the extended carbon octet than by the oxygen. These views are in accord with the idea of Lewis that organic acids in general, exist in the form of tautomers, one of which is highly dissociated and one of which is very weak.

Nitrogen.—Elementary nitrogen in the present scheme is (:N:N:). The symmetry of this arrangement is of a higher type than in any other unsaturated substance, which perhaps accounts in part for its low ex-

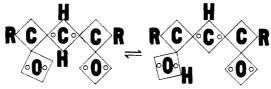


Fig. 13.-Keto-enol tautomerism.

ternal field and small reactivity with respect to polymerization or addition. The formula indicates that nitrogen could actually lose electrons to another element only with the greatest difficulty, but should be able to acquire them, forming nitride ion. In the latter respect it is, as a matter of fact, fairly reactive. The molecule should withstand high temperatures with little dissociation because the extended form is thus favored and because complete octets cannot be formed by the individual atoms. Nitrogen and carbon monoxide are isosteric, in Langmuir's¹⁴ terminology, with each other and with cyanide and acetylide ions.

To take up the individual types of the compounds of nitrogen would unduly extend this discussion and add little new in principle. Numerous

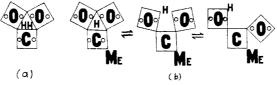


Fig. 14.—Formic and acetic acids.

structures which seem to permit satisfactory interpretation of the facts in this field are readily devised.

Oxygen.—The ethylenic character of oxygen appears from the formula (:•O•:O:). Less symmetrical, it should be more reactive than nitrogen. ¹⁴ Langmuir, THIS JOURNAL, **41**, 1543 (1919). Also its dissociation at very high temperatures should be more complete than in the case of nitrogen, for each atom may have an octet as in the equation

$$:\cdot \ddot{\mathbf{O}} \cdot : \ddot{\mathbf{O}} \cdot : = 2 : \mathbf{O}$$

In low temperature oxidations, particularly of the very electropositive metals, the formation of the peroxide group or ion, $:\cdot \overset{\circ}{O} \cdot : \cdot \overset{\circ}{O} \cdot :$, seems

a natural consequence of the oxygen structure.

Boron Compounds.—The simplest well recognized gaseous hydrides of boron are of the formulas B_3H_3 , BH_3 and B_2H_6 , structures of which are shown in Fig. 15. The last two obviously offer difficulty in representation



Fig. 15.-Hydrides of boron.

by the ordinary theory. It is also interesting to note that B_2H_6 substitutes rather than adds halogen. It is therefore saturated in the sense that benzene is, *i. e.*, because the boron atoms are almost completely protected by the outer atoms.

There appear to be no volatile oxides of boron. Metaborate ion, BO_2^- , may be given a structure similar to that assigned to carbon dioxide. While the latter does not show as much ability to polymerize as might be expected from its formula, BO_2^- apparently does, resulting in such ions as $B_4O_7^-$, and with a reducing agent, $B_4O_6^-$. An interesting analogy is presented in the cases of BO_2^- , CO_2 and NO_2^+ . The last is present, potentially at least, in N_2O_4 . The tendency, like that of carbon dioxide, to add oxide ion should be opposed by the negative charge of the metaborate and assisted by the positive charge of the nitro group. The latter should then not exist in the presence of appreciable quantities of oxide or hydroxide ion, but be completely changed to nitrate ion, and the former should form with some difficulty the orthoborate ion, as is the case.

Brief mention will be made of the boron halides. Boron trifluoride, for example, will be written : $\mathbf{F} \cdot \mathbf{B} : \mathbf{F} \cdot \mathbf{F}$. From this formula it would be pre-

dicted that a suitable octet might telescope with the extended boron atom. This behavior is found with halide ions and with ammonia.

Summary

In this paper the suggestion is offered that multiple bonding involves

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the transfer of two electrons from the inner to the outer shell in one or both of two adjacent atomic kernels, the group of 8 being preserved about each, with 2 jointly held electrons constituting the bond. This hypothesis is sufficient to explain the restricted region of the periodic system in which elements characterized by multiple bond formation occur. To meet requirements imposed by the facts relating to stability, reactivity and free rotation, the electrons of unsaturated octets are assumed to be held in equilibrium positions at greater distances from the nucleus than in the ordinary case, the transfer from the extended position to the usual ones liberating energy. No attractive force between electrons is assumed, and the electron arrangement is taken as cubic, (though subject to distortion).

Upon this basis a mechanism is provided for addition and condensation reactions. Interesting viewpoints are afforded in the study of conjugation, the structure and substitution reactions of benzene, and tautomeric shifts of double bonds. Formulas are illustrated and discussed which represent (more satisfactorily in several cases than other current theories do) many of the properties of chain hydrocarbons, the oxides of carbon, the carbonyl and carboxyl groups, nitrogen, oxygen, and the hydrides and oxygen containing ions of boron.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ARKANSAS] THE SOLUBILITY OF POTASSIUM PERMANGANATE IN SOLU-TIONS OF POTASSIUM SULFATE AND OF SODIUM, SULFATE

By H. M. TRIMBLE Received June 27, 1921

Raymond B. Stringfield, in discussing the sodium manganate process for the manufacture of potassium permanganate,¹ points out certain solubility effects which are interesting from both the practical and the theoretical standpoint. In the course of the process potassium permanganate is separated by crystallization from a mother liquor which contains, in addition to permanganate, a small percentage of free alkali and varying quantities of the sulfates, chlorides and carbonates of sodium and potassium. Stringfield says, "Various mixtures of chlorides, carbonates and sulfates are observed to repress the solubility of permanganate greatly, a mother liquor of 3.0% being common, and 1.0% not uncommon, against a normal solubility of potassium permanganate in pure water of 6.0 to 7.0%." These facts suggested an investigation of the solubility of potassium permanganate in solutions of these salts. Sackur and Taegener² have determined the solubility in solutions of potassium carbonate, potassium chloride and potassium hydroxide at several temperatures. Their results

¹ Stringfield, Chem. Met. Eng., 22, 1027 (1920).

² Sackur and Taegener, Z. Elektrochem., 18, 723 (1912).