Page 486, equation 44, the term (U + $\Delta x$RT) should be enclosed in parentheses.

Page 498 and page 666, the terms of the right-hand member of equation 85 should read *alternately plus and minus.*

Page 498, last line, page 654, first line, and page 667, second line, for *decrease* read *increase.*

Page 499, equation 86, the letter $t$ has been omitted just in front of the last bracket sign.

In the 8th line of footnote 23 omit the negative sign before the last term of the equation.

Page 501, in equation 95 and the second line following it, for $T$ read $T_F$.

Page 663, equation (111), for V read $v$.

Page 667, equation (126), for $\Delta C_{P_0}-$ read $\Delta C_{P_0}\Delta t_F+$. Equation (129) change the sign in front of each term containing $\alpha$.

Page 670, line 20, for *to* read *by*.

Edward W. Washbu

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# THE ELECTRON CONCEPTION OF VALENCE.

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Introduction: 1. Limitations of the Problem. 2. Fundamental Hypothesis. 3. Carbon Compounds Containing Single Bonds. 4. Carbon Compounds Containing a Double Bond. 5. Carbon Compounds Containing a Triple Bond. 6. Relative Asymmetry. 7. Nitrogen Compounds Containing a Single Bond. 8. Nitrogen Compounds Containing a Double Bond. 9. Compounds Containing a Double Bond between Unlike Atoms. 10. Partial Valence. 11. Complex Inorganic Salts. 12. Summary.

## Introduction.

In a paper published in 1909,[1] the hypothesis of Sir J. J. Thomson, according to which the linkages between atoms in a compound are caused by the transfer of corpuscles,[2] was applied to a number of facts drawn chiefly from organic chemistry. An attempt will be made in this paper to develop the subject somewhat farther. The same fundamental hypothesis, in the sense of a "supposition which it is expected will be useful" will be used. The deductions which will be made from this fundamental hypothesis are not put forward as the only explanation of the phenomena in question but as a possible explanation simpler in some ways in correlating facts than some of the explanations in current use, and in a few cases offering explanations for facts which have not been explained heretofore. The isomerism in compounds containing a double bond may serve to illustrate the former and the physical properties of the saturated dibasic acids the latter.

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[1] *School of Mines Quarterly*, **30**, 179.

[2] "The Corpuscular Theory of Matter," pp. 138–9 (1907).

## 1. Limitations of the Problem.

The valence of an element may be defined as a number which shows how many unit atoms or groups (with the hydrogen atom as unit standard) may be held in combination by an atom of that element. These valence numbers are purely the result of experimental investigations, but have been correlated to a great extent by the Periodic Law from which may now be taken the maximum valence of an element. The problem to be taken up here is limited by a clear conception of valence and the hypothesis to be used later. It may be stated, however, that stability relations of compounds, isomeric and otherwise, can enter only qualitatively in the discussion of valence since quantitative results can be arrived at by the use of the free energy relationships alone.

A valence theory, to be acceptable, must include or be able to account for all compounds known. The fact that the compounds predicted or suggested by the theory are not known would also be less disadvantageous for the theory than if compounds were known for which the theory was not able to account. This non-existence of compounds predicted by a theory may be due to the very limited range of conditions under which most of the substances known at present have been prepared.

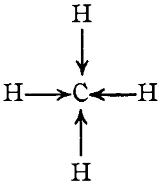
The subject of valence will not be taken up historically. Some or many of the ideas to be treated have been given before, but the work of those who have treated of this or of closely related subjects as for instance Abegg, and W. A. Noyes, will not be taken up in detail. It may be stated, however, that the scope of the subject matter and its treatment is different from that which has been given by others.

## 2. Fundamental Hypothesis.

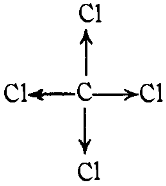
The hypothesis of Sir J. J. Thomson which will be elaborated here may be stated most concisely in his own words. "For each valency bond established between two atoms the transference of one (negatively charged) corpuscle from the one atom to the other has taken place, the atom receiving the corpuscle acquiring a unit charge of negative electricity, the other by the loss of a corpuscle acquiring a unit charge of positive. This electrical process may be represented by the producing of a unit tube of electric force between the two atoms, the tube starting from the positive and ending on the negative atom. . . . There is, however, one important difference between the lines representing the bonds and the tubes of electric force. The lines used by the chemist are not supposed to have direction. . . . On the electrical theory, however, the tubes of electric force are regarded as having direction starting from the positive and ending on the negative atom. . . . " This hypothesis supplements the structural formulas employed at present by giving the bonds direction. For convenience the lines which heretofore represented the bonds may be replaced by arrows, the direction of the arrows indicating the direction of the transfer of the corpuscles. Two atoms united in this way possess opposite electric charges. In regard to the direction of the valence when two atoms combine it seems fair to assume that this direction is ordinarily determined by the relative positions of the elements in the Periodic System. Namely, in the horizontal rows the elements of higher atomic weights are normally negative to the elements of smaller atomic weights. In the same vertical series, the main and subgroups must be considered separately, but on the whole the relations are fairly obvious here as well. This refers to the direction of the valences normally, but in certain cases the reverse direction may exist for a less stable form of a substance having the same composition. Thus, two forms of iodine chloride exist, which may be formulated $I \longrightarrow Cl$ and $I \longleftarrow Cl$, the presumption being that the former represents the stable form. Difficulty may also exist in assigning directed valences to compounds containing a number of linked carbon atoms, since the carbon atom appears to be able to take up a corpuscle or lose one with equal readiness. The inertness of carbon compounds in general also makes it more difficult to draw conclusions as to their structure and relative stabilities.

### 3. Carbon Compounds Containing Single Bonds.

In taking up the compounds of carbon containing single bonds, the introduction of directive valence will not be of much value since the chemistry of these compounds is worked out fairly completely and satisfactorily without it. It may be of interest, however, to call attention to some points. As examples, it may first be mentioned that, as J. J. Thomson points out,[1] methane and tetrachloromethane might be represented by the formulas:

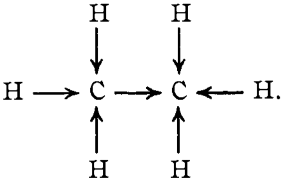


$$\begin{array}{ccc} & H & \\ & \downarrow & \\ H \longrightarrow & C & \longleftarrow H \\ & \uparrow & \\ & H & \end{array}$$



$$\begin{array}{ccc} & Cl & \\ & \uparrow & \\ Cl \longleftarrow & C & \longrightarrow Cl \\ & \downarrow & \\ & Cl & \end{array}$$

The carbon atom in methane has gained four corpuscles, while that in tetrachloromethane has lost four. Ethane is represented by the formula



$$\begin{array}{cccc} & H & H & \\ & \downarrow & \downarrow & \\ H \longrightarrow & C \longrightarrow & C & \longleftarrow H. \\ & \uparrow & \uparrow & \\ & H & H & \end{array}$$

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[1] *Loc. cit.*, p. 131.

In ethane, therefore, one of the carbon atoms will have a charge of four units of negative electricity and the other of two units, or comparing the carbon atoms of the two methyl groups, one will be negatively charged, the other positively. With ethane there is no evidence as to whether such a condition exists, but it may apply in the case of hexaphenyl ethane. Thus if Gomberg's triphenyl methyl is assumed to be hexaphenyl ethane, then the two triphenylmethyl groups composing it would be charged differently, and it is an interesting fact that solutions of the substance conduct the electric current[1] and that Gomberg early in his investigations explained this by assuming the existence of the "pseudoions" $(C_6H_5)_3C^+$ and $(C_6H_5)_3C^-$.

In the solid state, then, hexaphenylethane, colorless, would be present; in solution, the colored ions exist, and are more reactive than the unionized organic compound, as is generally the case. The same is true of the triphenylmethyl halides. The application of this view to the substances related to triphenylmethyl recently described by Schlenk[2] is obvious.

The saturated dicarboxylic acids may also be taken up briefly. In malonic acid the arrangement of the groups may be represented by $(CO_2H) \longleftarrow CH_2 \longrightarrow (CO_2H)$, the molecule being symmetrical. In succinic acid, the arrangement would be $(CO_2HCH_2) \longrightarrow (CH_2CO_2H)$,—unsymmetrical; in glutaric acid, $(CO_2HCH_2) \longleftarrow CH_2 \longrightarrow (CH_2CO_2H)$,—symmetrical; in adipic acid, $(CO_2HCH_2CH_2) \longrightarrow (CH_2CH_2CO_2H)$, or unsymmetrical; in pimelic acid, symmetrical again, and so on. These acids would therefore fall into two groups—those with an even number of carbon atoms having unsymmetrical directive valences, and those with an odd number of carbon atoms having symmetrical directive valences, and the acids of each group would be strictly homologous only with the acids of the same group. The fact that the saturated dibasic acids differ in properties depending upon whether an even or an odd number of carbon atoms is present is a well-known one and is spoken of in all text-books of organic chemistry. Thus the acids containing an even number of carbon atoms have higher melting points and smaller solubility than the acids with an odd number of carbon atoms immediately preceding and succeeding them, but show regularities when compared with the next acids with an even number of carbon atoms. These relations are accounted for when directive valences are considered. It is probable that similar relations apply to the saturated monobasic acids, but the direction of the valences cannot be shown as yet with sufficient certainty in their cases.

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[1] *Ber.*, 35, 2397; Walden, *Z. physik. Chem.*, 43, 451.

[2] *Ann.*, 372, 1.

## 4. Carbon Compounds Containing a Double Bond.

In taking up compounds of carbon containing a double bond, it is not possible to make any simple assumption regarding the direction of the valence when two groups combine, as was done with the singly bonded substances. It is necessary to consider all the possible cases and from a study of the reactions decide which formula may be assigned to a given compound.

The compounds containing a double bond may in general be divided into two classes: (1) compounds in which the two halves of the molecule are similar; and (2) compounds in which the two halves of the molecule are dissimilar. To the first class belong the substances of the general types $CR_2:CR_2$ and $CRR':CRR'$. Introducing the conception of directive valence, it is evident that there are possibilities of the existence of two isomers in each case; that is, the two valences (or corpuscles) may proceed from one carbon atom to the other, or one may proceed in one direction and one in the other;[1] or formulated as follows: $CR_2 \rightleftarrows CR_2$ and $CR_2 \rightrightarrows CR_2$; $CRR' \rightleftarrows CRR'$ and $CRR' \rightrightarrows CRR'$. If two isomers exist in any case, one would be expected to be more stable than the other; if only one substance of the general type exists, then it may be that the other is too unstable to be formed permanently, going over into the stable form, and it would be a question then, to determin by means of the chemical reactions of the substance, to which of the two types its reactions show it to conform best.

Of substances derived from the type $CR_2:CR_2$ none is known to exist in two forms.

Thörner and Zincke[2] observed the formation of a hydrocarbon melting at 243–4°, on heating α-benzopinacolin with soda lime at a temperature of 350–80°. They thought, from its composition, that it might be identical with tetraphenylethylene, even though it showed a higher melting point. On account of these observations of Thörner and Zincke it seemed worth while to test the possible existence of more than one form of tetraphenylethylene. But in no case have the results confirmed this supposition.

Some of the methods tried to bring about the transformation of tetraphenylethylene consisted in heating the alcoholic solution of the substance with both alkali and acids, and with rapid and slow cooling of the solution for the subsequent crystallization and also cystallizing in the dark as well as in the direct sunlight. In place of acids or alkali, iodine was used in a similar way, but tetraphenylethylene was again obtained having the original melting point. Next tetraphenylethylene was heated

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[1] In those cases where one valence proceeds in one direction and one in the other it is assumed that the corpuscles which are transferred are localized on the atoms, as otherwise the carbon atoms would become electrically neutral, but no assumption is made as to their relative positions except for the one case where four unlike atoms or groups are combined, when the phenomena of optical activity demonstrate that the four directions of valences do not lie in one plane. This localization is tacitly assumed in all cases.

[2] *Ber.*, 11, 1396 (1878).

above its melting point and then suddenly chilled and it was also distilled and the distillate suddenly cooled, but no change was observed.

Tetraphenylethylene was also prepared by different methods, such as heating dichlorodiphenylmethane with diphenylmethane in a sealed tube for two days at 300°. Tetraphenylethylene was obtained in this way, but with much greater difficulty than where the two halogens are on different carbon atoms, as in case of mono-homo-diphenyl methane which yielded tetraphenylethylene very easily and is the method generally employed for its preparation. Tetraphenylethylene was also obtained in small amounts by heating benzophenone and diphenylmethane in the presence of phosphorus pentoxide. In both of the above methods, however, the melting point of the tetraphenylethylene was 220°. As a conclusion from these experiments it seems highly improbable that there exists an isomeric tetraphenylethylene.

The direction of the valences in the compounds of this group might be determined by following some of the addition reactions of closely related compounds. Since the molecule is perfectly symmetrical, it makes no difference in the resulting compound, in which way another substance, HI for instance, is added. If, however, as a typical example, propylene $CH_3.CH: CH_2$ is taken, there would be three possibilities: $MeCH \rightleftarrows CH_2$ and $MeCH \rightrightarrows CH_2$ or $MeCH \leftleftarrows CH_2$. On treating with HI, if either of the last two represents the structural formula, the I would all go to one carbon atom, and the H to the other, only one substance being formed; while if the first represents the structure, a mixture of two substances should be formed, the H and I being divided between the two carbon atoms. The reactions in this case might be represented as follows:

$$\underset{H \longrightarrow I}{MeCH \rightleftarrows CH_2} = MeCH_2 \longrightarrow CH_2I \text{ and } \overset{I \longleftarrow H}{MeCH \rightleftarrows CH_2} = MeCHI \longleftarrow CH_3.$$

The extent to which each of the products would be formed would depend upon the influence of the methyl group as compared with the hydrogen or the double bond, and upon the difference in polarity between the hydrogen and iodine; the smaller the difference the more nearly equal would be the amounts of the two products formed.

The following results were obtained by A. Michael:[1]

Propylene + HI formed principally $(CH_3)_2CHI$ together with a little $C_2H_5CH_2I$.

Propylene + ClBr yielded 5 parts $CH_3.CHBr.CH_2Cl$ to 7 parts $CH_3.CHCl.CH_2Br$.

Propylene + ClI yielded 1 part $CH_3.CHI.CH_2Cl$ to 4 parts $CH_2.CHCl.CH_2I$.

Propylene + HOCl formed principally $CH_3.CHOH.CH_2Cl$ and perhaps a little $CH_3.CHCl.CH_2OH$.

These examples have been quoted in order to throw some light, if possible, upon the direction of the valences in unsaturated compounds

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[1] *J. prakt. Chem.*, 60, 286–384, 409–86 (1899).

existing in one form, and they indicate that this form has the structure $CR_2 \rightleftarrows CR_2$. Propylene does not belong to this type of compound; but it seems fair to carry over the conclusions arrived at with propylene to the symmetrical compounds and to assign this structure to the substance, if only one form exists, and if two forms exist, to assign it to the more stable of the two.

Of substances derived from the type $CRR'{:}\,CRR'$ a large number of isomers are known, of which maleic and fumaric acids may serve as examples. The two forms of this type using the directive valences are $CRR' \rightleftarrows CRR'$ and $CRR' \rightrightarrows CRR'$ of which the former represents the more stable, the latter the less stable form. These two groups of substances belong to the fumaroid and maleinoid types, the fumaroid being the more stable, showing the higher melting point, less solubility and volatility, smaller heats of combustion, less color (if any is shown by either isomer), and, in the case of acids, smaller ionization constants than the maleinoid, all these properties being only different expressions for the difference in stability between the two forms. It will hardly be necessary to enter into a detailed description of the different substances included in this class. The possibilities of addition would be worked out in each case by the method indicated with propylene.

With the substances containing a double bond in which the two halves of the molecule are dissimilar, there are a greater number of possibilities, namely, $CR_2{:}\,CRR'$; $CR_2{:}\,CR'_2$; $CR_2{:}\,CR'R''$; $CRR'{:}\,CR'R''$; $CRR'{:}\,CR''R'''$. In each of these cases, using directive valences, there would be three isomers possible, one valence acting in each direction, both valences acting in one direction, and both in the opposite direction. The three possible isomers corresponding to these are not known for any one substance with certainty. The reason for this may be found in the fact that if the two halves of the molecule are made up of groups differing very much in properties, of the two isomers in which both valences act in the same direction, one will exhibit very much greater stability than the other, making it extremely difficult, if not impossible, to isolate the less stable form.

With regard to the cinnamic acids, it appears advisable at present to delay the application of directive valences until the properties of the isomers have been studied sufficiently in the solid and liquid states as well as in solution to allow of more definit characterization of each form than is possible at present.

The reaction described by Michael and Bunge,[1] according to which both the fumaroid and maleinoid crotonic acids add chlorine either in sunlight or the dark to form the same maleinoid dichloride can readily be accounted for with directive valences.

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[1] *Ber.*, 41, 2907 (1908).

The application to benzene and some of its derivatives is obvious, but will not be enlarged upon here.[1]

*Note added November 12.*—Stobbe and Wilson[2] prepared three forms of the para- and of the meta-nitrobenzaldeoxybenzoin and showed that they are true isomeric chemical compounds. The existence of the three forms can be accounted for with directive valences as described, but the structure to be assigned to each form is as yet uncertain.

## 5. Carbon Compounds Containing a Triple Bond.

With regard to carbon compounds containing a triple bond, there are evidently many possibilities in the way of drawing formulas involving directive valences, most of which are entirely unnecessary, if not actually incapable of realization, at the present time, since very few, if any, isomeric compounds of this kind are known. It may be shown, however, that the stable form of triple-bonded compounds is in all probability best represented by the structure $\mathrm{RC} \underset{\longleftarrow}{\rightrightarrows} \mathrm{CR'}$. Taking acetylene dicarboxylic acid, perhaps the simplest example which could be chosen, treatment with 10 per cent. hydrobromic acid at ordinary temperatures for five days yielded bromofumaric acid, the conditions being such that bromomaleic acid would not be transformed into bromofumaric acid.[3] The same was found in the case when hydrochloric acid was used. The reaction here is

$$\mathrm{(CO_2H)C} \underset{\longleftarrow}{\rightrightarrows} \mathrm{C(CO_2H)} + \mathrm{HBr} = \mathrm{(CO_2H)BrC} \rightleftarrows \mathrm{CH(CO_2H)}.$$

Bromine and acetylenedicarboxylic acid yielded 30 per cent. dibromomaleic acid and 70 per cent. dibromofumaric acid. Considering the structure of acetylenedicarboxylic acid,

$$\mathrm{(CO_2H)C} \underset{\longleftarrow}{\rightrightarrows} \mathrm{C(CO_2H)},$$

and the reagent bromine, it is evident that there is the same chance or tendency of addition to each of the three bonds, or that one-third of the compound would be transformed into

$$\mathrm{(CO_2H)BrC} \rightrightarrows \mathrm{CBr(CO_2H)}$$

and two-thirds into $\mathrm{(CO_2H)BrC} \rightleftarrows \mathrm{CBr(CO_2H)}$.

## 6. Relative Asymmetry.

The introduction of directive valence into organic formulas does not affect the view of the tetrahedral form of the carbon atom in so far as this applies to single bonds. This view only requires that the four valences do not act in one plane.[4] The case is different, however, for the double-

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[1] This has been done in the preliminary paper, pp. 187–8.

[2] *Ann.*, 374, 237 (1910).

[3] Michael, *J. prakt. Chem.*, [2] 46, 210 (1892).

[4] It may be pointed out that the existence of the third active malic acid (Crassulaceen-malic acid) may be explained by the direction of the valence between the central carbon atoms (for the properties of this acid cf. Werner, *Lehrbuch der Stereochemie*, p. 114).

bond isomerism. Without going into the advantages and disadvantages of the theory of "geometrical isomerism," it may be pointed out that directive valences afford an explanation for the existence of isomers which does not involve the spatial relations between the groups at all but refers the isomerism to the double linkage between the atoms.

The subject of relative asymmetry which appears to involve both the tetrahedral model and geometrical isomerism remains to be considered.

Without entering into the details of the question, it may be stated that if "pseudoasymmetry" be extended to those cyclic compounds for which the explanation of relative asymmetry has been used, the experimental facts will permit of explanation without involving the position of the groups on one side or the other of the ring.[1] This has been pointed out by A. W. Stewart in his book on "Stereochemistry"[2] in which he states that "relative asymmetry" is only a special case of "pseudoasymmetry."

## 7. Nitrogen Compounds Containing a Single Bond.

The study of the compounds of nitrogen in which directive valence (or transfer of corpuscles) takes the place of the usual method of linkage between the atoms may be pursued in the same way as with the compounds of carbon. The nitrogen atom has the power of taking up three corpuscles, as shown by ammonia, or of losing five. The latter cannot be seen directly since the compounds of nitrogen with the univalent elements capable of taking up corpuscles (namely, the halogens) are unstable under ordinary conditions, but is evident from the compounds of nitrogen with oxygen. The difference between the two extreme states of nitrogen would be eight units of valence, or the nitrogen in ammonia differs from the nitrogen in nitric acid by eight corpuscles. The difference in the direction of the valence (or the loss or gain of corpuscles) can be followed much more readily with the nitrogen than with the carbon compounds, since a more evident difference in the properties of the compounds results, making it fairly easy to follow a given nitrogen atom containing a certain charge through a series of compounds and their derivatives. Nitrogen in addition to being able to take up three corpuscles is able to take up a fourth, if at the same time one is also given up, ammonium compounds being formed.[3] With the compounds of nitrogen, just as with carbon, if an element or group is joined by means of a single bond, this bond may be assumed to have a definit direction depending upon whether the element or group is electronegative (capable of taking up a corpuscle) or electropositive (capable of giving up a corpuscle) toward the nitrogen. A possible exception to this may be quoted from an article by Meisen-

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[1] For the development of "pseudoasymmetry" cf. Werner, *Loc. cit.*, pp. 29 and 129.

[2] P. 142.

[3] Cf. Sir William Ramsay, *J. Chem. Soc.*, 93, 785 (1908).

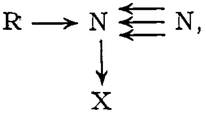
heimer,[1] in which he considered it probable that in methylethylphenylhydroxyl ammonium hydroxide, the two hydroxyl groups are united to the nitrogen by unequal valences.

In hydrazine, using directive valences, the two nitrogen atoms should have different properties ($H_2 \rightrightarrows \underset{(\alpha)}{N} \longrightarrow \underset{(\beta)}{N} \leftleftarrows H_2$), the α atom possessing one negative charge, the β atom three negative charges. If a compound containing two molecules of hydrochloric acid and one of hydrazine is formed in which both nitrogen atoms are pentavalent, then the β nitrogen atom having gained four corpuscles and lost one is comparable to the nitrogen atom in ammonium salts and the α nitrogen atom having gained three corpuscles and lost two is comparable to the nitrogen atom in amine oxides or amine dihalides. The properties of hydrazine dihydrochloride bear out this comparison. Of the two hydrochloric acid molecules which may be added, one is given off readily, and hydrazine itself behaves more like a substance capable of forming a mono-acid base than a di-acid base. Substituting the hydrogen atoms of hydrazine by different groups, in general only one compound would be stable even if an isomer should be formed under exceptional circumstances (for instance $RHN \longrightarrow NHR'$ and $RHN \longleftarrow NHR'$). If the entering groups do not differ from each other too greatly, it would be possible to isolate such unstable isomers in some cases. This appears to have been done by Willgerodt[2] by the reaction between dinitrochlorobenzene and phenylhydrazine or α- or β-naphthylhydrazine, and perhaps in other cases.

## 8. Nitrogen Compounds Containing a Double Bond.

The compounds of nitrogen containing a double bond would include the azo and diazo derivatives. It will not be necessary to go into detail with the azo compounds, since so few isomers belonging to this class are known.[3]

Among the diazo compounds it will be necessary to include the diazonium compounds, which will be spoken of first. These are derived from ammonium salts in which the three hydrogen atoms are replaced by one nitrogen atom which shows similar properties. The formula of the diazonium salts may therefore be represented by



$$\begin{array}{l} R \longrightarrow N \overset{\longleftarrow}{\underset{\longleftarrow}{\longleftarrow}} N, \\ \phantom{R \longrightarrow {}} \downarrow \\ \phantom{R \longrightarrow {}} X \end{array}$$

one nitrogen being the ammonia nitrogen combined with RX, the other being the nitrous acid nitrogen. For the syn and anti diazo compounds

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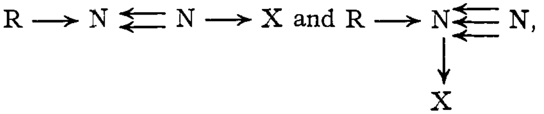
[1] *Ber.*, 41, 3966 (1908).

[2] *J. prakt. Chem.*, [2] 37, 449 (1888); 43, 177 (1891).

[3] The only certain cases of isomerism here appear to be with *p*-azophenol, Willstätter and Benz, *Ber.*, 39, 3492 (1906); 40, 1578 (1907) and with azobenzene, Gortner and Gortner, THIS JOURNAL, 32, 1294 (1910).

there are evidently the two formulas containing the groupings $.N \leftleftarrows N.$ and $.N \leftrightarrows N.$ possible. In the formation of diazo compounds from a primary amine and nitrous acid, the first product formed is always the syn compound making it extremely probable that these are derived from the grouping $R.N \leftleftarrows N.X$ or $R \longrightarrow N \leftleftarrows N \longrightarrow O \longleftarrow H$, the ammonia and nitrous acid nitrogens retaining their charges. Syn compounds can very readily be converted into anti compounds, most simply by the action of alkali in solution, but anti compounds cannot be converted directly again into syn, showing that the anti form is the more stable. This is also brought out by comparing some of the physical properties[1] of the two series. The anti diazo compounds may then be assigned the structure $R \longrightarrow N \rightleftarrows N \longrightarrow O \longleftarrow H$ analogous to the stable forms of the ethylene isomers in which the two valences also act in opposite directions. The chemical reactions which show the syn compounds to be more reactive than the anti are their greater explosiveness and the fact that they can be more easily reduced and oxidized. In coupling, the syn compounds also show their great reactivity as compared with the anti.

The relation between syn diazo compounds and diazonium compounds is a very close one. They are readily transformed into each other, alkalies favoring the formation of the diazo derivatives, acids of the diazonium, while in solution both exist in equilibrium testifying to the readiness with which they are transformed into each other. All this is readily understood when directive valences are used, the structure of the two classes being represented by



$$R \longrightarrow N \leftleftarrows N \longrightarrow X \text{ and } \begin{array}{l} R \longrightarrow N \Lleftarrow N, \\ \qquad\quad\; \downarrow \\ \qquad\quad\; X \end{array}$$

the X group or element (electronegative toward nitrogen as the direction of the valence shows) shifting its bond from the one nitrogen to the other.

The replacement of the diazo group by other groups on the benzene (or naphthalene) nucleus is a well-known and characteristic property of these compounds. The more unstable syn derivatives decompose in this way fairly readily, the ease, of course, depending to some extent upon the substance used, while with the anti derivatives these reactions do not occur, or are very slow in their progress. The greater reactivity of the syn compounds would perhaps account for this, but it seems possible in this case to look for a deeper underlying cause. The great variety of groups which combine with the benzene nucleus when the nitrogen is eliminated, including hydroxyl, alkoxyl, halogen, cyanogen,

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[1] The syn compounds are more soluble and show a lower melting point than the anti.

sulphur, sulphonic acid, aromatic hydrocarbon residues, etc., shows that the reaction is not limited to any one group or class. The common phenomenon in all these reactions is the elimination of nitrogen and the cause of the reaction may justly therefore be found in the tendency of the nitrogen to be set free. The difference in the nitrogen in the syn and anti diazo compounds may be represented by $\longrightarrow \mathrm{N} \begin{smallmatrix}\longleftarrow\\ \longleftarrow\end{smallmatrix} \mathrm{N} \longrightarrow$ and $\longrightarrow \mathrm{N} \begin{smallmatrix}\longleftarrow\\ \longrightarrow\end{smallmatrix} \mathrm{N} \longrightarrow$ and upon being set free, if the trivalent nitrogen still persists, the syn would be represented by $\mathrm{N} \begin{smallmatrix}\longleftarrow\\ \longleftarrow\\ \longleftarrow\end{smallmatrix} \mathrm{N}$ and the anti by $\mathrm{N} \begin{smallmatrix}\longleftarrow\\ \longleftarrow\\ \longrightarrow\end{smallmatrix} \mathrm{N}$. If the trivalent property becomes transformed into some other, then there appears to be no reason why one form should give off the nitrogen any more readily than the other. The reaction is then referred back to the tendency of the nitrogen in the diazo compounds to form the nitrogen molecule $\mathrm{N} \begin{smallmatrix}\longleftarrow\\ \longleftarrow\\ \longleftarrow\end{smallmatrix} \mathrm{N}$. This leads to the conclusion that in the nitrogen molecule, the two atoms are charged differently, one positively, the other negatively. The same fact is indicated by the formation of nitrogen when ammonium nitrite is heated, and the reverse action.[1]

## 9. Compounds Containing a Double Bond between Unlike Atoms.

So far isomerism caused by two atoms of an element combined in different ways, which was explained as being due to the difference in the direction of the valence, has been considered chiefly. The same principles should be applicable to combinations of different elements and the possibilities of isomerism due to the double bond in these cases should follow analogous rules. Following the reasoning used in the example already discussed, it is possible to limit the cases of possible isomerism somewhat in considering combinations of two dissimilar elements. When two dissimilar elements unite by a single bond, the direction in which the corpuscle is moved in order to establish this linkage is, in general, perfectly definit, the opposite direction occurring only under exceptional conditions. If a second linkage (or a double bond) is established between the two atoms, the direction in which the second corpuscle moves will either be the same or opposite to that of the first corpuscle, giving rise to two isomeric compounds of the same structure differing only in the direction of one valence. These two isomers would differ in stability, and the more stable one may for the present be assigned the structure in which both valences possess the same direction, since this appears to be the most reasonable view in the union of two dissimilar atoms. This subject may

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[1] This deduction holds only for the nitrogen molecule, but the conclusion that an atom may possess a different charge depending upon the conditions is not new. Cf. W. A. Noyes, *J. Am. Chem. Soc.*, **32**, 1070. " . . . . This is in accord with the hypothesis first proposed by the writer in 1901 (*Ibid.*, **23**, 463) that atoms of the same element may in different cases assume either positive or negative charges. Essentially the same fundamental idea has been proposed quite independently by Abegg and, from a wholly different point of view, by J. J. Thomson."

be exemplified by the carbonyl group. Following the reasoning given, the structure $:C \rightrightarrows O$ would be the stable one; if an isomer occur, the grouping $:C \rightleftarrows O$ would be assigned to it, whereas the grouping $:C \leftleftarrows O$ would be so unstable as to render the compounds in which it might be expected to exist, too unstable to be isolated. These stable isomers differ in structure then from the stable isomers in which two carbon or nitrogen atoms are united by a double bond, the direction of the two valences being opposite to each other in the latter, in the same direction in the former.

A large number of isomeric compounds containing a double bond between two unlike atoms are known. To begin with the simplest case of all, benzophenone is known to exist in two modifications, one stable, the other labile and going over into the stable form with great ease. Of these modifications, the stable one, melting at 48.5°, may be assigned the structure $(C_6H_5)_2C \rightrightarrows O$ and the labile one, melting at 25°, the structure $(C_6H_5)_2C \rightleftarrows O$.[1] Other ketones which exist in two modifications are known. Among these may be mentioned *p*-tolylphenylketone, stable variety melting at 59–60°, labile variety melting at 55°, and fluorenone. Perhaps the two forms of *o*-quinone and of diphenoquinone belong to this group.

A group of substances derived from the ketones, or in general from compounds containing the carbonyl group, occur in isomeric forms which may be explained in the same way as with the simple ketones. The classes showing this isomerism are the oximes, hydrazones, semicarbazones, chloroimides, etc. It seems hardly necessary to enter into any details with regard to the structures of these classes of compounds, since the method of treatment is the same as that already used, and the stability and other relations would be taken up similarly. A few lines may, however, be devoted to the oximes. On treating an aromatic aldehyde with hydroxylamine directly the "anti" aldoxime is formed first and can be converted into the "syn" form by suitable treatment. From this, the anti form would be assigned the structure $RH : C \rightrightarrows N \longrightarrow O \longleftarrow H$ and the syn form the structure $RH : C \rightleftarrows N \longrightarrow O \longleftarrow H$. The different properties of the two forms of the aldoxime would then be due to the difference in linking between the carbon and nitrogen atoms in the two cases. Similar reasoning applies to the ketoximes, the structure to be assigned to the two forms which differ in the union between the carbon and nitrogen atoms and the reactions of these forms differing according to the influence of that union. In the Beckmann rearrangement, the group which would exchange positions with the hydroxyl depends upon the nature of that group as compared with the nature of the nitrogen atom.

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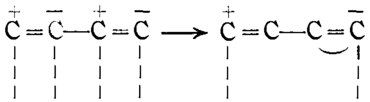
[1] Schaum, *Chem.-Ztg.*, 47, 417 (1910) states that the two modifications differ chemically.

Thus the isomerism which has been explained heretofore by geometrical isomerism in all these classes may be referred to the direction of the two valences in the double bond without considering the spatial position of the groups. All double-bond isomerism may be attributed to the same cause.

## 10. Partial Valence.

The fundamental hypothesis used in this paper to account for chemical combination requires that the atoms joined by the transfer of a corpuscle should possess electric charges, the atom which loses the corpuscles, a positive charge, the atom which gains the corpuscle, a negative. In general, therefore, the parts of a molecule should be charged differently, and should therefore be able to attract the parts of other molecules possessing opposite charges. This attraction evidently will be different in character and intensity from the attraction between two atoms combined chemically by the transfer of a corpuscle. In this connection it is of interest to quote from Thiele's original paper on partial valence in which the analogy between double bonds and molecular magnets is drawn, in which he does not, however, refer the forces to the action of electric charges:[1] "Man könnte sich einen solchen Ausgleich vielleicht so vorstellen, dass the Atome einer Doppelbindung entgegengesetzt positiv und negativ geladen seien, $\overset{+}{C} = \overset{-}{C}$. Bei benachbarten Doppelbindungen würden sich dann the inneren Ladungen ausgleichen:



$$\overset{+}{C}=\overset{-}{C}-\overset{+}{C}=\overset{-}{C} \longrightarrow \overset{+}{C}=C-C=\overset{-}{C}$$

Man erhielte dann eine Anordrung, ähnlich der, die benutzt wurde, im mit Hülfe der 'Molekularmagnete' die Constitution der Magnete zu erklären."

Evidently with the use of directive valence, the charges on the atoms are not distributed as simply as pictured in this analogy, but each atom or group combined with the carbon atoms involved will have its effect on these. It would also not be necessary for each of the carbon atoms involved to exert its attractive force. It may be pointed out that the partial valences need not be, and probably are not, the most important factors involved in causing a chemical reaction to take place, and that all that need be assumed is that they exert a directive influence on the entering groups or atoms when addition takes place to a double bond. This fact harmonizes the conclusions drawn so far in this section with those obtained in the sections where the direction of the valences in double bonds were considered. Explanations for individual reactions on the basis of this view, which accounts for partial valence as the attraction of the electrically charged parts of a molecule will not be given here.

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[1] *Ann.*, 306, 89–90 (1899).

Within recent years, partial valence has been used to explain a somewhat different phenomenon, namely, the formation of quinhydrones,[1] while "Nebenvalenzen" have been used to account for the existence of a number of isomeric compounds by Hantzsch.[2] With the view of partial valence, which may include the "Nebenvalenzen" as used by Hantzsch, developed here it would then appear that the electric attraction between certain atoms or groups of the same or different molecules is sufficiently strong to produce configurations stable enough to exist under ordinary conditions and to produce characteristic individual effects, such as in the first case mentioned, distinctive color. The laws governing these differences in intensity of the partial valences can only be found as a result of experimental investigation.

Electric attraction between electrically charged atoms has suggested a possible explanation for an entirely different class of phenomena, namely, that of the anomalies existing in aqueous solutions of highly ionized electrolytes. The following quotations are taken from a paper by A. A. Noyes.[3] "......This principle is that the ionization of salts, strong acids, and bases is a phenomena primarily determined not by specific chemical affinities, but by electrical forces arising from the charges on the ions.........."

"The molecular explanation of these facts and the more general conclusions drawn from them would seem to be that primarily the ions are united somewhat loosely in virtue of their electrical attraction to form molecules, the constituents of which still retain their electric charges and therefore to a great extent, their characteristic power of producing optical effects and such other effects as are not dependent on their existence as separate aggregates. Secondly, the ions may unite in a more intimate way to form ordinary uncharged molecules, whose constituents have completely lost their identity and original characteristics. These two kinds of molecules may be designated electrical molecules and chemical molecules, respectively, in correspondence with the character of the forces which are assumed to give rise to them......The facts, moreover, indicate that chemical molecules are formed from the ions in accordance with the principle of mass-action, but that electrical molecules are formed in accordance with an entirely distinct principle, whose theoretical basis is not understood."

It is evident that the two kinds of molecules referred to here are strictly comparable with the substances spoken of as formed by the transfer of corpuscles (chemical bonds) and those formed by electrical attraction or partial valence, with the addition that in aqueous solution phenomena

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[1] Willstätter, *Ber.*, 1908, and others.

[2] Hantzsch, *Ber.*, 1910, chiefly.

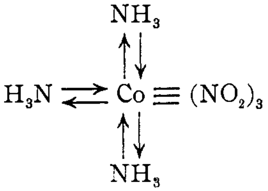
[3] THIS JOURNAL, **30**, 351–2 (1908).

are made apparent and predominate which do not appear to an appreciable extent with the organic compounds which were chiefly considered heretofore.

## 11. Complex Inorganic Salts.

The direction of the valence in the simple inorganic salts which ionize in aqueous solution can readily be determined. Some interesting conclusions have been pointed out for these in the section on Partial Valence. The complex inorganic salts cannot be treated in as simple a manner. It is not necessary, however, to develop the hypothesis for these here as this has already been done by Sir William Ramsay in his Presidential Address before the London Chemical Society in 1908.[1] The part of this address relating to the subject in question will be quoted and may serve to show how the assumptions made may be applied to the cobaltammine nitrites:.[2]

"Just as the nitrogen atom in $NH_4Cl$ takes one electron from the hydrogen of the HCl and gives one up to the chlorine, so it appears reasonable to suppose that in these cobaltammines each nitrogen atom of the three ammonia groups takes from the cobalt atom one electron, while it gives one at the same time. The formula of the triammino-nitrite would therefore be



$$\begin{array}{ccc} & NH_3 & \\ & \uparrow\downarrow & \\ H_3N \rightleftarrows & Co & \equiv (NO_2)_3 \\ & \uparrow\downarrow & \\ & NH_3 & \end{array}$$

If another molecule of ammonia be added, then the cobalt atom gives to the nitrogen of the ammonia an electron, but does not receive one in return. The nitrogen atom of that ammonia group is then "overloaded" for it has received four electrons in addition to its normal five,[3] making nine in all; now it appears that no element can be associated with more than eight in all. Hence that nitrogen atom must lose an electron. This it imparts to one of the $(NO_2)$ groups, which parts company with the cobalt atom, and, as a complex ammonium nitrite is now present, it is ionizable on solution in water. A glance at the proposed formula will explain the conception

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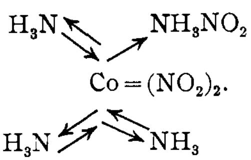
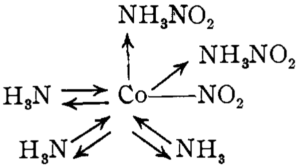
[1] "The Electron as an Element," *J. Chem. Soc.*, 93, 774.

[2] Pp. 785-7.

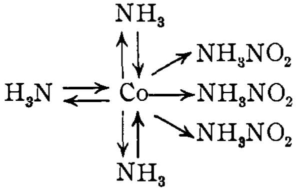
[3] The nitrogen atom is assumed by Ramsay to carry five corpuscles normally. In the deductions given here this assumption is not made in the same form, but practically the same assumption, based also upon experimental facts, is made with regard to the number of corpuscles which an atom is able to gain or lose.



The remaining formulas[1] may be written similarly, thus:



and



Why is the group $Co(NH_3)_3(NO_2)_3$ not ionizable? Let us first inquire: Why is cobalt nitrate ionizable? (Cobalt nitrite is unknown). Because the cobalt atom gives up an electron to each of the three $NO_3$ groups, remaining itself an ion. That is, the metal cobalt has three electrons associated with it; what we call "metallic cobalt" is a "tri-electride of cobalt." As "cobaltion," it has parted with its three electrons. But in the last of the compounds above, the cobalt has not three electrons at its disposal; it has already parted with them to the $NH_3NO_2$-groups. And we are led to conclude that in the non-ionizable compound the cobalt does not, as in its ordinary salts, part with three electrons, but that it receives them from the nitro groups."

This explanation of the cobaltammine nitrites evidently agrees with the views of structure developed here. The nomenclature differs slightly from that in general use. The formulation of other complex salts could doubtless be carried out in the same way, but will not be attempted here as it is only desired to show the possibilities of the conception of directive valences.

## 12. Summary.

An attempt has been made in this paper to apply the hypothesis of J. J. Thomson, according to which chemical bonds are formed by the transfer of a corpuscle from one atom to another, to a number of classes of compounds.[2]

The most interesting result obtained is that all cases of isomerism connected with the presence of a double bond, whether between like or unlike atoms, have been referred to the direction of the valences of the double bond, instead of to spatial configurations as heretofore.

The existence of certain isomers and the explanation of some hitherto

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[1] For the remaining cobaltammine nitrites.

[2] This is not the only hypothesis which may be used. The interesting deductions of J. Stark (*Jahrb. der Rad. Elekt.*, 5, 124 (1908)) based upon a different fundamental assumption may be cited, although he includes chiefly phenomena of a different kind.

unexplained reactions have also been referred to the directions of the valences.

The existence of "partial valence" is shown to follow from the electric charges of the atoms in a molecule.

Applications of the hypothesis to inorganic compounds have been taken from the work of A. A. Noyes and of Sir William Ramsay.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY. No. 183.]

# RESEARCHES ON QUINAZOLINES (TWENTY-SIXTH PAPER). THE SYNTHESIS OF SOME STILBAZOLES, HYDRAZONES AND SCHIFF BASES IN THE 4-QUINAZOLONE GROUP.[1]

BY MARSTON TAYLOR BOGERT, GEORGE DENTON BEAL AND CARL GUSTAVE AMEND.

Received September 24, 1910.

Various papers from this laboratory[2] have shown that in the 4-quinazolone group it is a relatively simple matter to prepare derivatives carrying a methyl group in position 2 and amino groups on either or both the benzene and miazine portions of the nucleus. Such substances constitute interesting material for the study of the action of these various groups with aldehydes.

For, it is well known that methyl groups on a nuclear carbon adjacent to the nitrogen of a heterocycle, as, for example, in the $\alpha$-picolines, the quinaldines, and the like, easily condense with aldehydes to compounds of the type R.CH : CH.R′, in which R represents the heterocycle and R′ the radical of the aldehyde used.[3] For compounds of this type where R′ is a simple or substituted benzene nucleus, the name "stilbazole" has been introduced,[4] on account of the structural similarity of such substances to the stilbenes.

The condensation of aldehydes with *Bz*-amino compounds, or anilines, to compounds of the R.N:CH.R′, or Schiff base type, is also an old story.

Bülow[5] and others[6] have shown that aldehydes condense to hydrazones with the *N*-amino groups of nitrogen heterocycles.

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[1] Read at San Francisco meeting of the Society, July 15, 1910.

[2] Bogert *et al.*, THIS JOURNAL, 32, 784 and 1297 (1910).

[3] Jacobsen and Reimer, *Ber.*, 16, 2006 (1883); Wallach and Wusten, *Ibid.*, 16, 2008 (1883); Döbner and Miller, *Ibid.*, 18, 1646 (1885); Ladenburg, *Ibid.*, 19, 439 (1886); Baurath, *Ibid.*, 20, 2719 (1887), and 21, 818 (1888); Bulach, *Ibid*, 20, 2047 (1887); Heyman and Königs, *Ibid.*, 21, 1424 and 2167 (1888); Eckhardt, *Ibid.*, 22, 279 (1889); Busch and Königs, *Ibid.*, 23, 2682 (1890); von Grabski, *Ibid.*, 35, 1956 (1902); Löw, *Ibid.*, 36, 1666 (1903); and others.

[4] Baurath, *Loc. cit.*

[5] *Ber.*, 40, 4749 (1907).

[6] Bogert and Gortner, THIS JOURNAL, 31, 947 (1909).