L.—*A Theoretical Derivation of the Principle of Induced Alternate Polarities.*

By ARTHUR LAPWORTH.

THE great advances towards a definite theory of valency which have recently been made by Thomson (Silliman Lectures, 1903; *Phil. Mag.*, 1921, [vi], **41**, 510), Lewis (*J. Amer. Chem. Soc.*, 1916, **38**, 763), and Langmuir (*ibid.*, 1919, **41**, 868, etc.) have been followed by the appearance of numerous papers applying electrical conceptions to the reactions of carbon compounds. Of these may be specially mentioned the papers of Fry (*Z. physikal. Chem.*, 1911, **76**, 385, 398, 591; and numerous communications to the *J. Amer. Chem. Soc.*), of Robinson (T., 1916, **109**, 1030, 1038; 1917, **111**, 959, etc. Also, *Mem. Manchester Phil. Soc.*, 1920, **64**, ii, 17), and of Conant (*J. Amer. Chem. Soc.*, 1921, **43**, 1703). The suggestions of Prins (*Chem. Weekblad*, 1918, **15**, 571) and of Vorländer (*Ber.*, 1919, **52**, [*B*], 263) appear to be based on conceptions of strains which are not very clearly electrical in origin.

Recently the present author pointed out that a general law is apparent in the reactions of carbonyl compounds, and deduced from it a wider generalisation which he termed the " principle of induced alternate polarities " (*Mem. Manchester Phil. Soc.*, 1920, **64**, ii, 1). The principle had reference to the apparent electro-polar characters of the atoms in a chain at the moment of chemical reaction and was deduced without having recourse to any hypo-thesis of the mechanism of reaction. (Compare *Ann. Reports*, 1919, **16**, 87—89, where a summary of views expressed up to that time by Prins, Vorländer, and Lapworth is given; also Lapworth, *Mem. Manchester Phil. Soc.*, 1920, **64**, iii, 1.)

In his paper to the Manchester Society (*loc. cit.*, pp. 3 *et seq.*) the author pointed out that his views agreed more closely with those of Robinson, whose influence in modifying his attitude towards such questions was gratefully acknowledged, than with those of Fry, to whose figures his own sometimes bore a close and natural resemblance. He differed from Robinson, however, in some important respects, and, in particular, he did not regard it as necessary, or usually even desirable, to assume the occurrence of reactions within closed circuits, but preferred, as a rule, to postulate what may be termed, " reactivity induced from a distance," much as polarity may be induced in an uncharged body by the proximity of a charged one.

No one who carefully studies these apparently divergent views can fail to be struck with the fact that at many points they tend

to shade into one another or can fail to suspect that they might all be referred to a single fundamental principle or combination of principles, and in the present paper it is hoped to indicate where these may be looked for and how they may be brought into line with modern electronic theories such as those of Lewis, Langmuir, and Thomson (1903 and 1921). As some of the fundamental points connected with the discussion and the general mode of reasoning were indicated by the author more than twenty years ago, he now ventures to refer in the first instance to the communications in which this was done.

It was suggested (T., 1901, **79**, 1265, *et seq.* Compare also P., 1901, **17**, 93, *et seq.*) that the laws of change in carbon compounds are the (mathematically) necessary results of the operations of the laws of valency applied to the migration of the point or condition of free valency arising from a dissociation akin to ionisation.* It was noted, however, that what may now be termed a " simplifying factor " must also be operating and this was stated in the following form : " *The state of dissociation which leads to isomeric change exists, in general, only once in the molecule at any instant.*" These considerations led at once to the " $\alpha\gamma$-rule " for a chain of atoms such as carbon, and indicated that the alternate atoms in such a chain might be expected to exhibit similar powers of acting as the seats of ionic reactivity ; or, to use a phraseology now familiar in such connexions, the alternate atoms might be expected to show similar " polarities."

Consideration of a great variety of data such as those to which the author directed attention in his paper on the " Latent Polarities of Atoms, etc." (*loc. cit.*), has made it evident that induced alternate polarities frequently become manifest which cannot be explained by the " migration " of a " whole " free valency ; but by extending similar conceptions to include the migration of " partial " valencies with polar characters, it appears possible to construct a general explanation which is also remarkably consistent with the modern electronic views.

Modified Lines of Development of the " $\alpha\gamma$-Rule."

It is assumed in the development that each atom in its organic chemical combination can be associated with a given (maximal) number of bonds or valency lines; that, whilst any atom may not have more than this maximal number associated with it, it may have less; and, lastly, that the total number of these bonds

* The idea of the " wandering " of a free bond arising from the process of ionisation had previously been utilised by Wislicenus in his work on " Tautomerie " (Ahrens-Sammlung), by Knorr, and by Brühl, with the object of explaining tautomerism (compare T., 1904, **85**, 48, footnote).

or valency lines (whole+fractional) in any part of a molecule remains constant unless there is definite reason to postulate that some have passed to or from another part of the molecule or to or from the surroundings.

This last proviso will appear inconsistent with the partial valency formulæ used by Thiele, and with the great majority of others now quite usually seen in works on organic chemistry ; but these are conventional, mathematically faulty, and incapable, without modification, of furnishing an explanation of the " principle of induced alternate polarities."

A glance at the Figures, I and II, will make clear the differences between the usual notation and that used by the present author. Certain missing partial valencies are denoted by the sign, $\times$, where in the usual notation these would appear as real partial valencies ; they will hereafter be referred to as " virtual." Attachment of a distinguishing sign, such as $\times$, to some of the free partial valency lines in many of the formulæ now in common use, would serve equally well.

A " virtual valency " may be defined by the statement that the sum of the " real " and " virtual " bonds and valencies attached to any atom in its organic chemical combinations is equal to the usual " maximal " valency of the atom as above defined. It is not to be confused with a " residual " or " latent " valency, which is an excess, or rather, an unshared quantity, of what, with a " virtual " valency, is in defect.

Now the conditions laid down at the beginning of this section permit of a great variety of modes in which valencies may be readjusted after a disturbance, some of these modes being dependent on the original disturbance and others not. In order to limit the modes in such a way as to exclude forms which the organic chemist, out of his experience, would consider purely fanciful, it is necessary to introduce such a " simplifying factor " as the author enunciated in 1901. (Compare italics on p. 417 of present paper.) The author now prefers to state it in the following extended form :

When any disturbance takes place in the number of shared or free valencies which are associated with an atom in its normal state of combination, then a constraint is usually set up and the atom strives to regain its normal condition. This may lead to a redistribution of valencies elsewhere ; but in the consequent changes due to the propagation of the strain along any part of the molecule the strains at all points in that part taken together cannot exceed the original constraint in that part. (The chances of a second disturbance arising independently at another point in the same molecule are small unless the first is so prolonged as to assume a static character, and in the following pages the results of a single initial disturbance only are considered.)

The first part of this assumption is obviously an attempt to apply, so far as it seems possible to do so, the " Principle of Least Action " which has been variously enunciated by Maupertius, Le Chatelier, and others.   A first approximation for the calculation of the values of the constraint and strains is indicated a little later on.

The most general relations to which the author desires to direct attention in the first instance can be deduced most readily from a consideration of possible " consequent " changes in part of a molecule, such, for example, as the part, $A_1 \ldots A_4$, in the central formula in either of the Figs. I or II.   These central formulæ are supposed to represent the molecules in their normal, or " resting " conditions. A_0, A_1, etc., are the symbols of atoms and A_0 is supposed to be joined directly to A_1, but is figured with all bonds, atoms, etc., otherwise associated with it in such a way as to make it possible to defer for the present any discussion of what it is precisely that is happening in that part of the molecule, as that is a large question independent of the immediate issue.   The $+$ and $-$ signs which are attached to the atoms in the central formulæ are in anticipation of the conclusions arrived at in later portions of the present paper and, as in the author's earlier paper (*Mem. Manchester Phil. Soc.*, *loc. cit.*), denote the " relative latent polarities " of the atoms; the atom, A_0, is the " key-atom " and, as formerly, is indicated by attaching a dot to its polar sign.

The molecule, represented in each case by the central formula, is assumed to suffer a " constraint," the primary effect of which on the part of the molecule below (A_0, etc.) is solely to alter the magnitude of the bond which attaches A_1 to the atom A_0.   It is required to determine what secondary or " consequent " readjustments in the bonds and valencies attached to the atoms in the chain, $A_1 \ldots A_4$, may take place without departing from the conditions laid down at the beginning of this section.

A full bond is for generality assumed to be divisible into three equal parts.

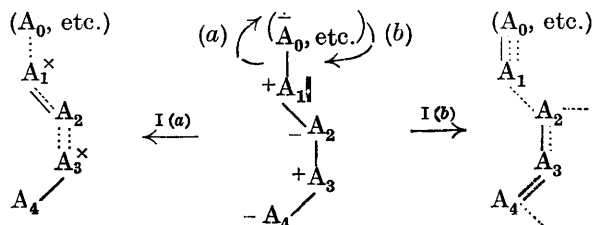The curved arrows indicate the directions of movement of the partial valencies to or from the bond, $A_0 A_1$.

FIG. I.

Case I (Fig. I).   Where the constraint is such that the bond between A_0 and A_1 is (Ia) decreased or (IIb) increased by (two) partial valencies, respectively (Ia) passing to, or (Ib) proceeding from, the system (A_0, etc.) or the exterior, and hence the total of the bonds and valencies attached to the atoms in the chain, $A_1 \ldots A_4$, suffers a corresponding decrease or increase, respectively.
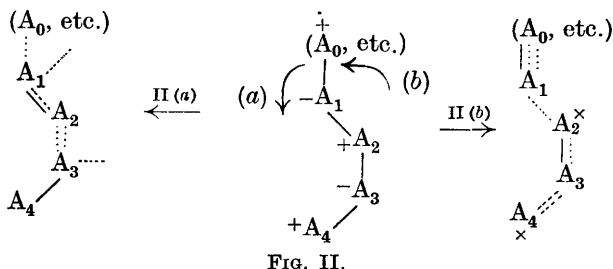
FIG. II.

Case II (Fig. II).   Where the constraint is such that the bond between A_0 and A_1 is (IIa) decreased or (IIb) increased by (two) partial valencies, respectively (IIa) passing to, or (IIb) proceeding from, the chain, $A_1 \ldots A_4$, itself ; and hence the total of the bonds and valencies attached to the atoms in the chain $A_1 \ldots A_4$ undergoes no change.

It will be clear that there are theoretically four distinct modes * in which the change in the bond, $A_0 A_1$, may be effected.   In deciding what are the probable forms that the part of the molecule below (A_0, etc.) may assume, as a consequence of the occurrence of each of the four modes, the postulates above laid down have been applied, together with the " simplifying factor."   In using the latter it has been assumed, as a first approximation, that the magnitude of the constraint is proportional to the change in the magnitude of the bond, $A_0 A_1$, and that the strain at each atom is proportional to the change in the number of " free " real valencies or of " virtual " valencies which are attached to it,† the strain being reckoned as positive in all instances.

The relation postulated between " constraint " and " strain " provides, for example, some reasonable premise for understanding why it is not permissible to assume that the atom A_1 in Fig. I(a) can be restored after the constraint, towards its original valency

* Cases where new rings are formed are not considered here, though as recent work on intra-annular tautomerism indicates, they may arise far more frequently than has hitherto been suspected.

† In reality the strain associated with a new real free valency varies with the element, and probably in the order $C>N>O$.   For a new virtual valency the order is inverted, and probably $O>N>C>H$.

by borrowing one or two partial valencies from, say, the bond between A_2 and A_3; for such a process would lead to such structures as

$(A_0$, etc.) $(A_0$, etc.)

$\times A_1$ A_1

$A_2^\times$ or $A_2^{\times \times}$

$A_3^\times$ $A_3^{\times \times}$

A_4 A_4
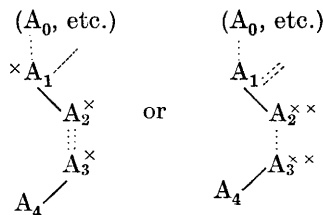
respectively, in the former of which the strain (calculated on the basis that one full free bond or one new full " virtual " valency corresponds with unit strain) is $4 \times \frac{1}{3}$ and in the latter is $6 \times \frac{1}{3}$, whilst the original constraint at A_1 was only $2 \times \frac{1}{3}$.   The constraint in the part (A_0, etc.) is not considered.

Now with the foregoing provisions it can be shown, best algebraically, that the only possible modifications of the system, $A_1 \ldots A_4$, are as follow :

Case I(a).   They are such as have only " virtual " valencies, and these on the " odd " atoms only [unless any of the " even " atoms originally (central formula) had real " free " (latent) valencies, in which case these may diminish].

Case I(b).   They are such as have only new real " free " valencies, and these on the " even " atoms only.

Case II(a).   They are such as have only real " free " valencies, and these on the " odd " atoms only.

Case II(b).   They are such as have only " virtual " valencies, and these on the " even " atoms only [unless any of the " odd " atoms originally (central formula) had real " free " (latent) valencies, in which case these may diminish].

The central formulæ in Figs. I and II are denoted without any free valencies on the atoms, $A_1 \ldots A_4$, and additional figures would be required to cover the considerable variety of possibilities. The complications which are indicated within the square brackets in the immediately preceding paragraphs may work out in a variety of ways according as the atoms with latent valencies are readily deprived of their valencies or not.   As will be shown later, there is reason to believe that oxygen and nitrogen, the elements of most frequent occurrence in carbon compounds with latent valencies, adhere very firmly to their valencies; and even with the halogens there appears to be no reason to suppose their free valencies ever lead to the complications in question.   Where these complications come into operation, then of course the " $\alpha\beta$-rule " and not the " $\alpha\gamma$-rule " will obtain (compare T., 1898, **73**, 457).

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The formulæ to left and right in Figs. I and II may therefore be regarded as general expressions for the results of some possible changes in a chain, $A_1 \ldots A_4$, in which the atoms in the " resting " states of the molecule (central figures) have no " free " (latent) bonds or valencies, or, at least, none which is brought into operation as the result of the constraint ; they are the " activated " forms (Robinson, *Mem. Manchester Phil. Soc.*, 1921, **64**, ii, 17).   The principles indicated in the figures must apply whatever be the precise physical interpretation attached to the chemist's bond or valency line, providing that it has the properties assumed in deducing the relations with which the figures correspond.   The necessary simplifications of the figures for the case where a bond is assumed to be divisible into two parts only will readily be made out, as also will modifications thereof, such as, for instance, those in which the strain is not propagated from its original point or is propagated without the distribution (between two atoms) which, for the sake of generality, is suggested in the figures.   Extensions to cases where double bonds are present or to those in which the constraint is sufficient to lead to complete disruption of the bond between two atoms will be self-evident.

Interpretations Based on Modern Electronic Views of Valency.

The author, in compiling all previous papers, had in mind the older view that bonds and valencies denoted something of the nature of tubes of force, and it is possible to make out a good case for such a conception even at the present time when chemical combination is coming to be generally accepted as associated with a sharing of electrons by the atoms.   It is, however, necessary to bear certain points clearly in mind.   For instance : if the laws of valency assumed at the beginning of the preceding section hold quite strictly for the tubes of force, then it has to be assumed that in each atom, considered in its organic combinations, there is a constant number of tubes of force shared by its nucleus and its electrons, and these are included in the symbol for the atom.

Thus, if in Figs. I and II each whole or partial bond or valency line is assumed to stand for a certain number of Faraday tubes which are joining electrons in one atom to the nucleus of its neighbour, then the new " real " free partial valency lines in the formulæ to left and right would represent Faraday tubes proceeding outwards to the surroundings, and the " virtual " valencies would denote tubes proceeding outwards from nuclei.   The former would be associated with negative fields and the latter with positive ones.   It is thus not difficult to perceive that the arrangement of

+ and — signs in the central formulæ are just those which would be suggested by a study of the reactions of the compounds, and we have a theory which is apparently a generalised form of that proposed by Conant (*loc. cit.*) to explain some reactions of carbonyl compounds.

There is, however, another way of interpreting such figures, to which the author's attention was first directed by Professor J. B. Cohen in a private communication (October 9th, 1921), the relevant part of which may be quoted :

" Why do you split up your bond into three partial valencies rather than two ? If you took two it would fit in with the Lewis-Langmuir atom and your partial valency might represent one electron."

The present author would not wholly abandon the conception of a partial valency line as denoting tubes of force, especially for interpreting the extreme manifestations of the induced polarity phenomena, such as, for example, its effect on the order of acidity of the cresols, which is not easy to understand on the " electron-migration " view alone. But the results displayed in the preceding section must apply either to Faraday tubes or to electrons, or to both, providing only that they obey the laws of valency as defined and limited in that section.

Nevertheless it at once becomes apparent on applying Professor Cohen's suggestion to the interpretation of partial valency formulæ such as have been used latterly, for example, by Robinson and by the present author (*Mem. Manchester Phil. Soc.*, 1920, **64**, ii, 1, 17, and other places indicated in the latter paper), that a remarkably consistent application of modern electronic theory to carbon compounds has already been developed and was only awaiting such a suggestion before taking definite form.

Thus, by limiting the subdivisions of the single bond to two parts (electrons), denoting appropriate valencies as " virtual " * (that is, as indicating missing electrons), and replacing Robinson's looped latent valency signs for nitrogen and oxygen by ordinary free valencies (unshared co-valency electrons), interpretations of reactivity and chemical change appear which are the most striking agreement with modern electronic views. But it would also seem to follow that these views must admit, and Thomson's already appear to do so, of a certain amount of elasticity in the conception of " duplets " as the minimum number of electrons required for, at least, sub-stable atomic attachments. The broad rules of reactivity and substitution in the aliphatic and aromatic series, the

* For example, all those free valencies attached to atoms with + signs in the author's paper.

basic properties of heterocyclic compounds such as pyridine, pyrrole, and glyoxaline, and other problems of equal general interest receive explanations of a satisfying kind in terms of electronic properties of the atoms of the elements.

The transformations required to follow the points to which attention was directed in the last paragraph are so simple as to be, in most cases, almost self-evident to any who are familiar with these modern views, and they will not be dealt with in detail here. In the present communication, discussion of this aspect of the general question will be confined to a consideration of the function of the " key-atom " in inducing alternate polarities, and the interpretation of the results in the preceding sections on the assumption that a partial valency shall denote one electron.

It will be evident, in the first instance, that an atom with a " virtual " partial valency is one which has been deprived of one electron ; that an atom, which in the " activated " form of the molecule has a new " real " free partial valency, is one which has one more unshared electron than it has in the resting state of the molecule.   An atom of the former kind will tend to be associated with a positive field and will be able to unite directly with atoms of the latter kind, which will tend, also, to be associated with negative fields, usually more intense than the positive fields of the other type (compare Briggs, T., 1908, **93**, 1564 ; 1917, **111**, 253 ; 1919, **115**, 278).   The propagation of the " constraint," then, as a rule (see Figs. I and II) consists simply in the movement of electrons in an atom [say A_2, Fig. I(a)] from one shared position to another. Carbon atoms in their normal organic chemical combinations have, of course, eight electrons in their outer shells, all shared ; if, in the activated forms of the molecule one is denoted as having a " virtual " partial valency, then it has only seven electrons in its shell ; if denoted with a real free partial valency, then it has eight electrons in its shell, but one of these electrons is unshared.

Such a conception, however, seems certainly to require that atoms may be held together, momentarily at least, by one electron only in common.   Although the three chief exponents of the modern electronic theories appear to agree that a single shared electron is an unstable form of union, it is not definitely excluded, and Thomson seems to admit the possibility in several places (*Phil. Mag.*, 1921, [vi], **41**, 521), for PCl_5, and p. 538, where he says " the two cells would be united only by a single electron which *might quite likely* be insufficient to hold them together " (the italics are the present writer's).

Now assuming that the " negative key-atom," A_0 in Fig. I, is operating merely in virtue of a tendency to a variation in the

number of electrons which it shares with the atom A_1, then we may surmise that

(a) A_0 should be an atom with a variable co-valency.

(b) A_0, if it can function as in Fig. I(a), should be an atom which readily *falls* in co-valency.

(c) A_0, if it can function as in Fig. I(b), should be an atom which readily *rises* in co-valency.

(d) A_0 should in any case be an atom which, when it varies in co-valency, adheres strongly to its electrons—and, in particular, more strongly than carbon adheres to its electrons.

Now the atoms of oxygen and nitrogen certainly have the properties (a), (b), and (c), and all to a well-marked degree, when these elements occur in their so-called " bivalent " and " ter-valent " states respectively (compare Langmuir, *J. Amer. Chem. Soc.*, 1919, **41**, 927). The halogens exhibit similar properties, but, it may fairly be said, to a less marked degree (fluorine is not here considered). The author has already pointed out that " bivalent " oxygen and " tervalent " nitrogen are by far the most effective (negative) " key-atoms " and that (" univalent ") chlorine appears to exert, although to a much less marked extent, a somewhat similar " polarising " influence (*Mem. Manchester Phil. Soc.*, 1920, **64**, ii, 5). Moreover, the order of the affinity of the three elements, oxygen, nitrogen, and carbon, for the electrons in their outer shells (" octets "), is no doubt the order of the proximity of the electrically neutral atoms to the stable arrangement in the neon and this indicates the descending order : $O > N > C$ (compare Briggs, *Phil. Mag.*, 1921, [vi], **42**, 449, 450).

Hydrogen, which appears to exert a slight " polarising influence " of the opposite kind (" positive "), would have to come under Case II (Fig. II); but as it is difficult to see how the Rutherford hydrogen atom could share more than two electrons with another atom, it seems necessary to suppose that here only Case II(a) applies : that is to say, that hydrogen, acting as " key-atom," does so by a partial dissociation from its partner, to which it abandons one of the electrons it previously shared with it. This is at least entirely consistent with the crude conception of the formation of hydrion in which a combined hydrogen atom drops both electrons, or with the modified view (which the author prefers), namely, that the dropping of one electron by a combined hydrogen atom is the precedent to the ionisation of acids. In the same connexion may be recalled the experiments of Langmuir and others which have furnished proof of the separate existence of free, neutral hydrogen atoms; that is, of hydrogen atoms with but one electron each.

It will be evident that on an electron-distribution diagram, even

more simply than on a force-field diagram, a satisfactory explan-
ation of the " principle of induced alternate polarities " may be
worked out by combining the relations discussed in the previous
sections of the present paper with the Lewis-Langmuir-Thomson
theories of chemical combination. It is not difficult to perceive
many directions in which the conceptions suggest new lines of
advance in organic chemical theory, but it is impossible within the
scope of a short communication to enter into detail.

Before concluding this paper, it appears worth while to attempt
to summarise more obvious possible causes of the " constraint "
postulated in the earlier pages. Briefly these would appear to be :

(*a*) Absorption of thermal or radiant energy, leading in the
first instance to redistributions of atomic attachments, usually at
the atoms with variable co-valencies.

(*b*) Ion formation, by dissociation, at the " key-atoms."

(*c*) Ion formation by association, as, for instance, by the form-
ation of a complex ion by union of the molecule, at the " key-atom,"
with a simple ion.

(*d*) Non-ionic association with other uncharged molecules, which
occurrence, like (*b*) and (*c*), would be likely to upset the balance
of forces and lead to new distributions of the electrons or of the
tubes of force or, of course, of both.

(*e*) Tendency to certain molecular distributions of affinity.

As an instance of what is meant under the last heading may
be mentioned that inspection of a very large number of the most
acceptable formulæ based on the conjugation theory of Thiele
seems to indicate that there is a definite tendency in carbon chains
to something like an even distribution of valency; for example,
forms such as $=A_1-A_2=$ tend to arrange themselves as
$=A_1=A_2=$. Now the presence of an oxygen or a nitrogen
atom at the end of such a system would almost certainly facilitate
the occurrence of such a rearrangement owing to the readiness
with which these atoms vary in their co-valencies, and at the same
time the order of the polarities of the atoms in the system would be
determined by the greater tendency for the oxygen or nitrogen
atom to retain the maximal number of electrons in its outer shell.
In such a case, evidently, the constraint does not originate at the
" key-atom," but the result is the same as if it did originate there.
This conception, *mutatis mutandis*, is likely to apply for atoms
other than oxygen or nitrogen, and is one to which the author
attaches very great importance, especially, but not only, in its
application to static forms; it would appear to receive immediate
and striking application in connexion with molecules having alternate
single and double linkings and to *cyclo*aromatic compounds in

particular, especially as Thomson has already pointed out that the most suitable arrangement of the benzene molecule is that in which the pairs of atoms in the ring share electrons in threes, and not in twos and fours alternately (*Phil. Mag.*, 1921, [vi], **41**, 535).

In conclusion, the author desires to emphasise two points : (1) that whilst the interpretation of a partial valency as an electron can be reconciled in the most striking manner with present-day formulæ and reactions as pictured by organic chemists, it would be premature wholly to abandon the force-field view, which is clearly related to it and which in some cases seems better fitted to account for the facts ; (2) that, as illustrated in Figs. I and II, it is not the mere weakening or strengthening of a bond that determines the order of the induced polarities in a chain and consequently the modes in which the atoms in the chain react, but rather, whether or not the excess (or defect) in the bond is made up from (or passes to) the chain itself.

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