The Present State of Valency Theory.

THE TILDEN LECTURE.

DELIVERED BEFORE THE CHEMICAL SOCIETY ON DECEMBER 14TH, 1939.

By L. E. SUTTON.

IN common with most other chemical theories, valency theory has progressed in leaps. These have mostly been caused by the application to chemistry of new physical concepts or theories. The discovery of the electron and of the nuclear atom, the development of Bohr's theory of atomic structure and most recently of the Heisenberg and Schrödinger systems of wave mechanics, have all initiated periods of special activity. The most recent of these began in the late 'twenties and is still going on, so it is appropriate at the end of a decade to review the progress which has been made.

In order to assess the present state of our understanding, it is first necessary to consider what would be expected of a complete and satisfactory valency theory. We may say that chemistry is concerned with the identification of substances and with the study of their interconversion. Its theory is all based upon the premise that there are atoms and molecules; and it is the part of valency theory to deal with the forces which bind atoms together to form molecules. This branch of chemical theory is therefore relevant to any enquiry into the properties of an individual molecule, or indeed to any enquiry into the properties of an assemblage of molecules, whether of one or of more kinds, so far as these are determined by the properties of the individuals. What are called the chemical properties of a substance relate to its tendency to change into something else, either alone or by reacting with other substances, under stated conditions of temperature, pressure, solvent, and illumination. Since they are properties of statistical assemblages and not of individual molecules alone, valency theory cannot give complete information about them. It should, however, play an important part in the assessment of the thermodynamic stability of one system relative to another by enabling us to compute the internal-energy change which almost always is an important part of the free-energy change and quite frequently is the dominating factor. Moreover, since it should provide values of the rotational and vibrational quanta for the molecules concerned, which are necessary in the calculation of the entropy change, it should also have an important bearing on the second term in the free-energy change. Valency theory in its widest sense should play a correspondingly important part in the treatment of the rate of reaction, for it should enable us to follow the changes which occur when two molecules approach very closely, as they do in the activation process.

The physical properties of a substance, which generally involve no permanent change of molecular species, may be of chemical interest either because they aid in its description or because they are related in some way to the stability; for example, we can use observed heats of formation to calculate the internal-energy change in a reaction and the observed rotational and vibrational levels in calculating the entropy change. In so far as they are functions of quantities which characterise individual molecules, as, for instance, the dielectric constant is of the electric dipole moment and the electrical deformability of the molecules, we should be able to calculate them with the aid of valency theory. The most important of the properties which can be measured are related to the following characteristics of molecules:

(1) The complexity, *i.e.*, whether it exists as the lowest possible unit, a small polymer, or a "giant molecule."

(2) The characteristic energies of electronic, vibrational, or rotational excitation, including the energy evolved when the molecule is formed from normal atoms.

(3) The interatomic distances, the spatial arrangement of the atoms, the moments of inertia, and the molecular volume.

(4) The force constants for vibrational movements in the molecule.

(5) The electrical and magnetic properties such as the permanent electric and magnetic dipole moments, the deformability by electric and magnetic fields, usually called

the polarisability and the diamagnetic susceptibility, and the anisotropy of these latter properties.

The scope of valency theory is therefore so great that it is quite impossible to make detailed comparisons of the ideal and actual performances in any but a small fraction of the whole field. I shall therefore compromise by indicating very briefly the general character of the advances, and then dealing more thoroughly with the progress in some topics which specially interest me.

First, we want to know if present theory can explain at all why there are forces which hold atoms together to form a molecule. It may be recalled that the Bohr theory indicated qualitatively that certain neutral atoms could lose electrons and others acquire them without a great expenditure of energy; if the resulting oppositely charged ions approach from infinity to within a few Ångstrom units of each other, more energy could be gained than was used up in the initial electron transfer. It was therefore possible to see how a stable, " electrovalently " bound ion pair could be formed : but no treatment of covalency, or bonding by the sharing of two electrons, which was even qualitatively satisfactory could be given. Early attempts to treat the structure of molecules were all based on a picture of ionic valencies deformed to a greater or lesser extent, as was for example Debye's early treatment of the configuration of the water and the ammonia molecules (" Polar Molecules," New York, 1929, p. 68). Present theory allows the energies of forming individual ions to be calculated with a considerable degree of precision (*e.g.*, Hartree and Black, *Proc. Roy. Soc.*, 1933, *A*, **139**, 311; Hartree and Hartree, *ibid.*, 1935, *A*, **150**, 9), and the energy gain when the ions approach closely can also be treated fairly well, so the qualitative picture has now become a quantitative one. A much greater triumph, however, is the successful treatment of covalency. For simple molecules such as H_2^-, H_2, He_2^+, it is now possible to calculate the potential energy as a function of internuclear distance and to show that it has the minimum required to explain the existence of a stable bond (Pauling and Wilson, " Introduction to Wave Mechanics," New York, 1935, Chap. XII; Penney, " The Quantum Theory of Valency," London, 1935; Dushman, " Elements of Quantum Mechanics," New York, 1938). One can calculate not only the maximum possible gain of energy, *i.e.*, the heat of formation of the molecule, and the equilibrium length of the bond, but also the force constant of stretching or compressing it, since this is given by the curvature d^2V/dr^2 of the V–r curve. For such simple molecules the calculated values are very accurate,* but for the generality of molecules, or for the bonds in molecules containing three or more atoms, no precise, quantitative *a priori* treatment can be given. Nevertheless, the qualitative pictures of the nature of covalency, of the conditions which affect the stability of a bond, and of the distinction in character between links formed by one, two, three, or more electrons, are most helpful.

What is true of the purely theoretical calculation of heats of formation, bond length, and force constant is true also of most of the other characteristics enumerated above. For very simple cases, usually the hydrogen molecule, it is possible to calculate them quite accurately, but in general, although we can see how the calculations could be made in principle, they are actually impossible because of the mathematical difficulties. It is true also of the calculation of heats of activation. Only such simple reactions as $H_2 + D \rightarrow HD + H$ can be treated with any claim to precision (Eyring and Polanyi, *Z. physikal. Chem.*, 1931, *B*, **12**, 279), but the qualitative picture thus obtained is again most valuable (Discussion on Reaction Kinetics, *Trans. Faraday Soc.*, 1938, **34**).

The improved understanding of the nature of covalency has made possible qualitative, but very illuminating, treatments of covalency angles. The tetrahedral arrangement of the carbon valencies, the pyramidal arrangement for nitrogen, the flat one for boron, the non-linear one for water, the linear one for mercury, as well as the octahedral configuration for many six co-ordinated complexes, have all been explained in a convincing way (Pauling, " The Nature of the Chemical Bond," Cornell, 1939, Chap. III). Still more

---

* For the hydrogen molecule James and Coolidge (*J. Chem. Physics*, 1933, **1**, 825) obtained a theoretical dissociation energy of 102·6 kg.-cals./g.-mol.; the experimental value is 102·9 kg.-cals./g.-mol. The theoretical internuclear distance, 0·739 A., is exactly equal to the observed value.

striking, however, has been the success of a prediction that certain four co-ordinated complexes of transitional elements would prove to have the valencies directed along the diagonals of a square. It is now known with varying degrees of certainty that this can and does happen in nickelous, palladous, and platinous complexes of the type $[MX_4]$, as well as in cupric, argentic, and auric complexes—largely as a result of the work by members of this Society (see numerous references by Pauling, *op. cit.*; also Emeléus and Anderson, " Modern Aspects of Inorganic Chemistry," London, 1938, Chap. IV).

It is also possible to assert confidently that the effective covalency maximum for hydrogen is one, while that for elements in the first short period is four, because any other bonds would be exceedingly weak. It is not possible to give a theoretical limit so certainly for later elements : those in the second short period might be able to form up to nine bonds, but in the discussion of covalency angles it was shown that an atom could form six strong octahedral bonds by using one *s*, three *p*, and two *d* orbitals; * and it is possible that if the other three *d* orbitals are brought in, only relatively weak extra bonds would be formed, so that the apparent limitation to six in elements of the second short period and the first long period may be explainable. Steric considerations probably play a part too.

The most important general contribution which wave mechanics has made to chemistry is the conception of " resonance " (see Pauling and Wilson, *op. cit.*, Chaps. XI—XIII; Penney, *op. cit.*; Dushman, *op. cit.*, Chaps. X, XII, XIV; Pauling, *op. cit.*; Sidgwick, J., 1936, 533; 1937, 694), which lies behind most of the results cited above. It is one of extremely wide application, for we can say that the stabilities of certain atoms, of covalent links, and even of whole molecules are dependent on the phenomenon. A simple but reasonably accurate statement of the principle is that *if a system can be given two or more electronic structures which have equal, or roughly equal, energy contents and equal numbers of unpaired electron spins, and in which the nuclei are in not very different positions, then the actual electronic configuration will differ from that of any of these single structures, and will be a hybrid derived from them.* It will most closely resemble the single structure of lowest energy content.

The lowest possible energy state of the actual system, *i.e.*, the " ground " state, will be lower than that of the lowest single component structure. In particular cases, such as the hydrogen molecule which will presently be discussed, it can be seen that this stabilisation of the ground-state structure relative to the simple single structures is directly due to the changed electron distribution—in the ground state the electrons are shifted in such a way that the attractive forces in the system are increased and the repulsive ones decreased. It may be presumed that this is generally true; so if we accept the new electron distribution as a direct consequence of the application of wave mechanics, the effects upon the energy follow necessarily from electrostatics. The source of the so-called resonance energy—which is the name given to the difference between that of the actual state and a weighted mean of those of the component structures—then seems less mysterious. In *excited* hybrid structures there are corresponding destabilisations.

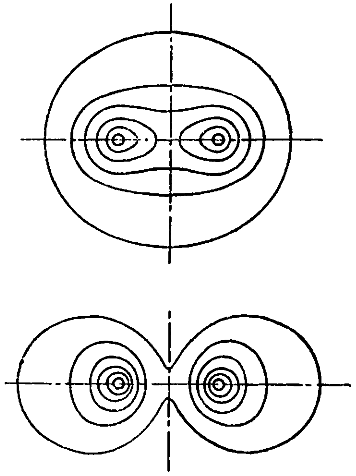
This view may be illustrated by the particular case of the hydrogen molecule (Penney, *op. cit.*). If we imagine that two normal hydrogen atoms are brought close to each other and that they retain the spherically symmetrical electron distribution which they each had when they were an infinite distance apart, then it will be found that they repel, because the repulsions between the electrons, and more especially those between the nuclei, overweigh the attractions of the nuclei for the electrons which do not belong to them. If we apply wave mechanics to find the actual electron distributions,† we see that there are two possibilities, shown by the electron-density diagrams in the figure. In the first of these the electrons are removed from the space at the ends to the space between the nuclei, with the result that the repulsions between nuclei are decreased by the improved screening, and the nuclei are attracted to the dense central electron cloud, so the system

---

* Pauling, *J. Amer. Chem. Soc.*, 1931, **53**, 1367. An " orbital " is the wave-mechanical equivalent of the Bohr orbit.

† Resonance arises because we can draw alternative structures : (*a*) with electron 1 on nucleus A, and electron 2 on nucleus B; (*b*) with electron 2 on nucleus A, and 1 on B. They have equal energies.

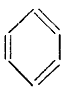
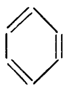
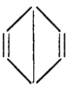
is stabilised. In the other, the reverse happens and the system is destabilised. The first is the ground state; the latter is the first excited state.

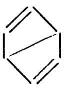


The electron-density contour diagrams for the ground and the first excited state of the hydrogen molecule.

Besides this kind of resonance, which arises from the possibility of writing two structures which differ only by the exchange of two electrons (hence the term " exchange energy "), we may have resonance with others, called ionic structures, in which either one of the nuclei has *both* electrons. If the energies of what we may call the purely covalent and the ionic structures are not very different, and if they have the same number of unpaired electrons, as they usually do, it is a theoretical necessity that there should be resonance between them. This is discussed in more detail later.

When we come to consider a large molecule, we can treat the covalent bond as a unit and not consider the resonance within it in detail, so that if we can write several different Lewis–Langmuir structures which satisfy the fundamental conditions already given, we may expect that there will be resonance between them. This way of treating large molecules is convenient because it enables us to use a representation with which we are familiar in discussing new phenomena. Such molecular resonance is sometimes called " mesomerism " (Ingold, J., 1933, 1120). The classic example of it is benzene, for which we can write two Kekulé structures and three Dewar structures :



The resonance thus made possible can account for the stability which characterises this ring system. These ideas were adumbrated by organic chemists, who reasoned inductively from chemical properties [Robinson, Two Lectures on an " Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions," Inst. of Chem., 1932; Ingold, *Chem. Revs.*, 1934, **15**, 225]. Wave mechanics enables us to deduce them from general principles which originally were arrived at in attempts to explain a great diversity of physical data; so a synthesis of ideas has come about similar to that which came from the inductive Lewis theory of atomic structure and the deductive Bohr theory.

Resonance should affect not only the energy but all the physical properties of a molecule, and the chemical properties too. Whereas the heat of formation from the atoms must be greater than that of any component structure, such properties as bond length, valency angle, force constant, and electric dipole moment * should be intermediate between the extreme values found in these component structures. For instance, in benzene it is found that the molecule has all its bonds of an equal length, 1·39 A., intermediate between that of a pure single bond, 1·54 A., and that of a pure double bond, 1·34 A. So, too, nitrous oxide which can be given the two oppositely polar structures

$$\overset{-}{N}{=}\overset{+}{N}{=}O \text{ and } N{\equiv}\overset{+}{N}{-}\overset{-}{O}$$

actually has an electric dipole moment of very nearly zero. If, therefore, we wish to predict the properties of a molecule, it is essential that we should know what component structures are important and what their individual properties are.

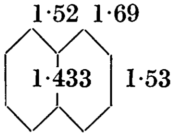
Although it is generally impossible to answer both of these questions from theory alone, yet it is possible in some relatively simple cases to answer the first one. By using

---

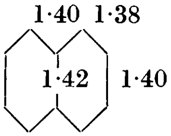
* In so far as the paramagnetic dipole moment of a molecule depends upon the unpaired electron spin, it cannot have an intermediate value because of the restriction on resonance between structures with different numbers of electron spins.

experimental data to answer the second one, it is then possible to predict the properties of the molecule under discussion. The conjugated carbon systems or polyenes, and the carbon free radicals, have in effect been so treated (see Pauling and Wilson, *op. cit.*, Chap. XIII; Penney, *op. cit.*; Pauling, *op. cit.*, Chap. IV; Lennard-Jones, *Proc. Roy. Soc.*, 1937, *A*, **158**, 280; Lennard-Jones and Turkevich, *ibid.*, p. 297; Penney, *ibid.*, p. 306; Coulson, *ibid.*, 1938, *A*, **164**, 383; Wheland, *ibid.*, p. 397; Penney and Kinch, *ibid.*, p. 409).

Two approximate methods have been employed. The " electron-pair " or " localised bond " method is based directly on the idea expounded above of building up the actual structure from simple component ones, and when their contributions have been computed the resonance energy may be related to the heats of formation of single, double, and triple carbon–carbon bonds, which can be measured experimentally. An order or multiplicity can be calculated for each bond in the molecule—it is generally non-integral and is, for instance, 1·62 in benzene—and then from curves relating bond energy or bond lengths to bond order, constructed from data for integral bonds, the individual bond energies and lengths may be read off by interpolation. The " molecular orbital " method takes a complex orbital, like that of each electron in the hydrogen molecule, as the constructional unit from which to build the still more complex orbitals of the mobile electrons in the compounds under discussion. These electrons are those which are shifted around to form the different structures in the other treatment. Their energy, as a group, is thereby related to the energy of the unit orbit which in turn is expressible as a function of the energies of single, double, and triple carbon bonds. In more elaborate treatments the stretching force constants of these bonds are introduced too, and both the energies and lengths of the bonds may then be computed. The two methods usually agree quite well with each other and with the experimental results, as may be shown by the figures for naphthalene. The bond orders calculated by the electron-pair method are shown in (I), and the distances (in A.) in (II).



(I; Bond orders.)



(II; Bond lengths, A.)

The calculated heat of formation on the Sidgwick–Bowen basic values is 1888 kg.-cals./g.-mol., while the observed one is 1884. The molecular orbital method gives exactly the same values for the bond-lengths and 1881 for the heat of formation. The individual lengths have not been determined experimentally, but the mean value is 1·41 A.

When the conjugated system is heterogeneous, the theoretical methods become less exact and usually fail to give any quantitative information. In the most general case, then, we can predict neither the relative importance of possible component structures nor their properties.

Any further progress must be made empirically. We may try to predict what the chemical and physical properties of a molecule would be if it had a single Lewis–Langmuir structure, and if they prove to be different we may conditionally ascribe this to resonance. By examining a large number of examples we may hope to see regularities which will enable us to make rules about the occurrence of resonance and especially as to what constitutes a " reasonable " structure, *i.e.*, one which participates to an important extent in a given compound. It is most important that we should succeed in this task, for the great danger of the idea of " resonance " is that, because it is so general and so adaptable, it can be made to explain almost any peculiarity of any particular compound if licence to postulate suitable component structures be granted. If many such *ad hoc* treatments were made without reference to general rules, the resulting anarchy might bring the whole idea into disrepute. It is obvious that, not only should as many classes of compound as possible be examined, but also the properties considered should be as varied as experimental limitations allow.

Before discussing the results of attempts to formulate general rules, it may be as well to indicate what are the marks of respectability which are held to characterise a non-resonating system, for obviously on the soundness of these standards depends the validity of all our subsequent arguments. Some of them were arrived at empirically, before the idea of resonance had flowered; others were reached with the aid of the new theory; but all are based on the idea that Nature strives to be simple.

It is supposed that the heat of formation of a molecule can be expressed as the sum of constant values characteristic of each link; and furthermore, that the heat of formation of a pure covalent link A–B * is the mean of those for A–A and B–B (Pauling, *op. cit.*, Chaps. II and IV; Pauling, *J. Amer. Chem. Soc.*, 1932, **54**, 3570; Pauling and Yost, *Proc. Nat. Acad. Sci.*, 1932, **18**, 414; Sidgwick, "The Covalent Link in Chemistry," Cornell, 1933, Chap. IV). It is possible to check these standards, for since resonance should cause the energies to be greater than normal, experimental values should never be less than those so predicted. This is in fact substantially true.

Interatomic distances are supposed similarly to be equal to the sums of constants—radii—characteristic of each atom. In pure ionic bonds these depend somewhat upon the nature of the environment, but in pure covalencies they are independent (Pauling, *op. cit.*, Chap. V; Sidgwick, *op. cit.*, Chap. III). Actual bonds may be either longer or shorter than the sum of the radii, according to the structures concerned in the resonance. Resonance in a molecule as a whole is detected by its effect on the lengths of individual bonds. Force constants and interatomic distances are hardly to be considered as entirely independent data for our present purposes, since some empirical relation, such as that expressed by Badger's rule,† appears to exist between them.

It is known that no such simple addition of characteristic vectors is adequate for the correlation of electric dipole moment data, because the electric deformations produced by each dipole in other parts of the molecule are often relatively large (Sutton and Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 482), but some allowance for these effects can be made. In order to overcome this difficulty we may either attempt to compare the moment of the compound under examination with that of a similar one in which resonance should not occur (Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668; *Trans. Faraday Soc.*, 1934, **30**, 789), or we can attempt to calculate the interactions (Groves and Sugden, J., 1937, 1992). Where compared, the two methods agree qualitatively. Sometimes, when the effect of possible resonance on the dipole moment is large, as in the previously mentioned case of nitrous oxide, a useful qualitative answer can be obtained without making any correction for interaction.

It has been assumed, with inadequate justification, that the dipole moments of a purely covalent link or of unshared electrons on an atom are small, and it is consequently supposed that the greater parts of the observed bond moments are due to resonance with ionic structures.

Other properties, such as electric deformability or molecular refractivity, diamagnetic susceptibility, and the molecular volume or the parachor show a fair degree of additive character: but since it is less easy to predict how the normal values of these properties will be modified by resonance than it is for the foregoing ones, they have on the whole proved less useful for attacking resonance problems.

When these criteria of normality are applied to the data, the following generalisations emerge:

(1) Resonance of some kind, additional to that implied by a normal covalency, occurs in an isolated bond when it is formed between two unlike atoms.

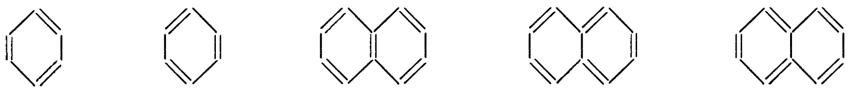
(2) Resonance occurs in a molecule as a whole when it is possible to draw for it alternative structures which have the same number of bonds of normal length, and which do

---

* The mean used should be the geometric one, but the arithmetic one is more convenient to apply and is usually sufficiently accurate.

† That $k_0(r_e - d_{ij})^3 = 1{\cdot}86 \times 10^5$, where k_0 is the force constant in dynes/cm., r_e is the equilibrium length (in A.) of the bond, and d_{ij} is a constant characteristic of all diatomic molecules made up of one element in the i^{th} row and one in the j^{th} row of the Periodic System (Badger, *J. Chem. Physics*, 1934, **2**, 128).

not involve the complete transference of electrons from one atom to another. The Kekulé structures for benzene, or the related ones for naphthalene, are typical.



(3a) There will be resonance if we can draw structures which have one covalent bond less than normal, but which require no transference of electrons from one atom to another. Examples are provided by butadiene and diphenyl:

Butadiene.

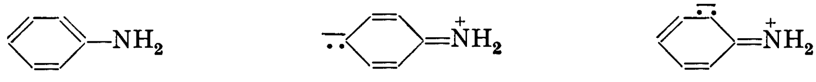
Diphenyl.

The bond shown by a broken line, the "long" bond, has the qualitative character of a covalency but is exceedingly weak because the distance between the nuclei is much greater than that at which the potential energy is a minimum. It is a purely formal bond, and the structures containing it are less stable than the "ordinary" ones by almost the whole of the dissociation of a C–C bond, so they are frequently called the first excited structures. They can cause additional resonance in cyclic polymers such as benzene or naphthalene. Individually they may play only a small part, but they may be quite important as a class if sufficiently numerous; so they are more important in diphenyl than in butadiene, and again in naphthalene than in benzene.

(3b) There will be resonance if there are structures with the normal number of covalent bonds, but a single transference of charge. Examples are numerous, *e.g.*:

Carbon dioxide. $O{=}C{=}O$ $\overset{+}{O}{\equiv}C{-}\overset{-}{O}$ $\overset{-}{O}{-}C{\equiv}\overset{+}{O}$

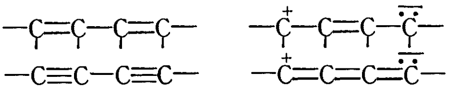
Aniline.



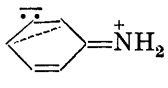
(4) There may be resonance if there are structures with two bonds less than normal but no transference of charge, one bond less and one transferred charge, or two transferred charges. The second type is quite common; it may occur in polyenes, conjugated unsaturated ketones, and other compounds in addition to that permitted under rule (3a). Such a structure, too, provides the only way in which the effects of conjugation may appear at the *m*-position of a benzene ring.

Butadiene.

Diacetylene.



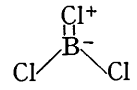
Aniline.

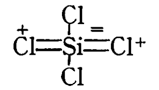


It is probable that no general rule can be made about the relative importance of the number of transferred charges, and the number of missing bonds in determining the importance of a particular structure: it seems likely to vary from case to case.

These rules appear to be reasonably adequate for organic compounds, but it is less certain that they are for inorganic ones. New types of structure become possible when an atom has an incomplete octet, or can expand its valency group, or can use orbitals in the penultimate group for covalency formation as can the atoms of the transitional

(III.)



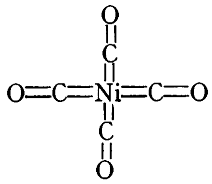


(IV.)

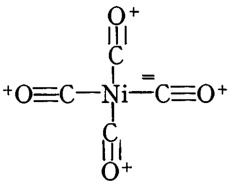
elements. Such structures as (III) for boron trichloride and (IV) for silicon tetrachloride have more bonds than the usual ones but also more transferred electrons or formal charges.

Sometimes the number of bonds may be unaltered and the number of formal charges less, as in the structure (V) for nickel carbonyl compared with (VI); or again, the number of

(V.)



$$\mathrm{O{=}C{=}\overset{\overset{\displaystyle O}{\|}\atop C\atop \|}{\underset{\|\atop C\atop \|\atop O}{Ni}}{=}C{=}O}$$

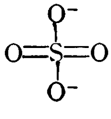


$$\mathrm{{}^{+}O{\equiv}C{-}\overset{O^{+}\atop |||\atop C\atop |}{\underset{|\atop C\atop |||\atop O^{+}}{Ni}}\overset{=}{-}C{\equiv}O^{+}}$$

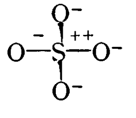
(VI.)

bonds may be greater and the number of formal charges less, as in the structure (VII) for the sulphate ion compared with (VIII).

(VII.)



$$\mathrm{O{=}\overset{O^{-}\atop |}{\underset{|\atop O^{-}}{S}}{=}O}$$

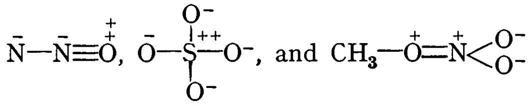


$$\mathrm{\overset{-}{O}{-}\overset{O^{-}\atop |\,{+}{+}}{\underset{|\atop O^{-}}{S}}{-}O^{-}}$$

(VIII.)

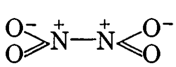
Since the rules previously given are essentially empirical, the justification for extending and revising them to cover such instances must come from experimental data. At present, however, it appears difficult to interpret these in a reasonably simple and convincing manner; and although there is some support for the unusual structures given above, the question is far from settled.

In the rules given there is an implication that structures with several transferred electrons are relatively unimportant. In an effort to generalise, it has been suggested as a quite rigid rule that structures with like formal charges on adjacent atoms, or several on one atom, are not "reasonable" (Pauling, *op. cit.*, Chap. VI; Pauling and Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 13). This explains some experimental facts, such as the apparent unimportance of the following structures in nitrous oxide, the sulphate ion, and



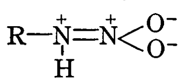
$$\mathrm{\overset{-}{N}{-}\overset{-}{N}{\equiv}\overset{+\atop +}{O},\ \overset{-}{O}{-}\overset{O^{-}\atop |\,{+}{+}}{\underset{|\atop O^{-}}{S}}{-}O^{-},\ and\ CH_3{-}\overset{+}{O}{=}\overset{+}{N}{<}{O^{-}\atop O^{-}}}$$

methyl nitrate respectively, as judged by bond lengths; but it is not in agreement with the fact that nitrogen tetroxide has a symmetrical structure O_2N-NO_2, which must be derived from (IX) and the other permutations, or that ethylnitramine has a resonance energy of about 20 kg.-cals./g.-mol., which presumably arises from resonance with the structure (X), in addition to that between the two structures (XI) and (XII) which was included in the calculation of the "normal" heat of formation. It seems probable that this rule is useful as a rough guide, but that it is not strictly true in the form given because, in actual fact, complete electron transferences do not occur in such single Lewis–Langmuir structures. The electric dipole moment of the N⟶O bond is about 4 D. (unpublished measurements by Hunter and Leonard), which indicates that the transference is only half complete. Similarly, the moment of the O→O bond appears to be only about 3 D. (Lewis and Smyth, *J. Amer. Chem. Soc.*, 1939, **61**, 3063). Another determining factor may be the nature



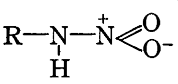
$$\mathrm{{O^{-}\atop O}{\geqslant}\overset{+}{N}{-}\overset{+}{N}{\leqslant}{O^{-}\atop O}}$$

(IX.)



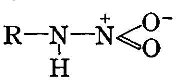
$$\mathrm{R{-}\underset{H}{\overset{+}{N}}{=}\overset{+}{N}{<}{O^{-}\atop O^{-}}}$$

(X.)



$$\mathrm{R{-}\underset{H}{N}{-}\overset{+}{N}{\leqslant}{O\atop O^{-}}}$$

(XI.)



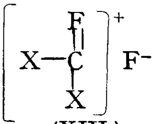
$$\mathrm{R{-}\underset{H}{N}{-}\overset{+}{N}{\leqslant}{O^{-}\atop O}}$$

(XII.)

of the atom in which a given formal charge is placed; thus, a structure in which fluorine is made positive is relatively improbable, whereas one in which oxygen is made negative is probable.

If a bond of a molecule is completely ionised, it frequently becomes possible to rearrange the valencies in one or other of the ions so formed in a way which would not be possible if the key bond were to remain covalent, and the question arises whether it is permissible to consider that such further structures, which would be allowed by rule (3b), are actually in resonance with others wherein the bond is covalent.

It has been suggested (Brockway, *J. Physical Chem.*, 1937, **41**, 185), for example, that in a fluoroparaffin with more than one fluorine atom on any carbon atom there is resonance between the normal covalent structure and ionic ones of the type (XIII). This obviously cannot happen if there is only one fluorine atom on carbon, and therefore it is possible to explain the very much greater stability to hydrolysis and the contraction of the C–F bonds observed for the first group of compounds compared with the second. If this were correct, the apparent heat of formation, calculated from thermal data, of the C–F bond in the first group would be greater than it is in the second: but in actual fact this is not so. In β-fluoroethyl alcohol it is 117, in ββ-difluoroethyl alcohol 122, and in carbon tetrafluoride 110 kg.-cals./g.-mol., so there is no systematic difference.



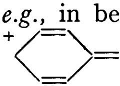
$\left[X{-}\overset{\overset{F}{\|}}{\underset{\underset{X}{|}}{C}}\right]^{+}F^{-}$

(XIII.)

A similar explanation has been offered (Pauling, Springall, and Palmer, *J. Amer. Chem. Soc.*, 1939, **61**, 927) for the remarkable fact that the methyl–carbon bond in methylacetylene is 0·08 A. shorter than a normal single carbon–carbon bond (1·54 A.). Structures $H^+\overset{-}{C}H_2{=}C{=}CH$ and $H^-CH_2{=}C{=}\overset{+}{C}H$, made possible by ionising a C–H bond, would allow the C–C bond to acquire some double-bond character and so make it contract. This suggestion, however, is not in harmony with the evidence of heats of hydrogenation (Conn, Kistiakowsky, and Smith, *ibid.*, p. 1868) which are given below (in kg.-cals./g.-mol.) :

$C_2H_2 + H_2$	+ 42·24		$C_2H_4 + H_2$	+ 32·82	
		2·65			2·71
$CH_3{\cdot}C{\equiv}CH + H_2$	+ 39·59		$CH_3{\cdot}CH{=}CH_2 + H_2$	+ 30·11	
		1·96			2·16
$CH_3{\cdot}C{\equiv}C{\cdot}CH_3 + H_2$	+ 37·63		$CH_3{\cdot}CH{=}CH{\cdot}CH_3 + H_2$	+ 27·95	

The values for the methylated acetylenes are not very different from that for acetylene itself. Moreover, the methyl–carbon bonds in the methylethylenes are of normal length (Pauling and Brockway, *ibid.*, 1937, **59**, 1223), so no special resonance need be postulated for them; yet the heats show that there is no more resonance energy in the methylacetylenes than there is in the methylethylenes, and that, presumably, is none at all. Once again, it is likely that there is no simple answer to our question. The structures suggested for the polyfluoro-compounds may be unsatisfactory because they make fluorine positive, while those for the methylacetylene may be unimportant because considerable energy is required to ionise a C–H bond.* There may, however, be cases where they play a part, *e.g.*, in benzyl chloride, where we might have a small contribution from the structure



$=CH_2]Cl^-$ which has no particularly improbable feature. Research aimed specifically at solving this general question would be very valuable.

One of the most necessary present tasks in this field of chemistry is a more complete correlation of the results from different kinds of experimental investigation. It will have been noticed that the immediate conclusions drawn from, let us say, bond length and heat data, do not always agree; and it is desirable that these discrepancies should be catalogued.

Sometimes, as in the instance of methylacetylene, the comparison shows up a difficulty which for the present must remain unsolved; sometimes it shows up an inconsistency which can more easily be corrected. For instance, it has been argued that the fact that the energy of a link A–B is generally greater than the mean of those of links A–A and B–B can be satisfactorily explained by postulating resonance between the pure covalent structure and one ionic structure, let us say A^+B^-, only. The excess energies can be related to constants x_A and x_B characteristic of the atoms, and, in view of the above postulate, these are termed the electronegativities of A and B. Now the bonds of many supposedly simple compounds, such as the inorganic halides, are shorter than the normal covalent length. This appears not to be a direct effect of polar character. It has been attributed to increase in bond order (Pauling, *op. cit.*, Chap. VIII; Brockway and Jenkins, *J. Amer. Chem. Soc.*, 1936, **58**, 2036); as we have already seen (p. 550), it may be possible that

---

* It is true that a C–H bond in methylacetylene appears to be partly ionised, judging by the chemical behaviour, but this is the ≡CH link and *not* one in the methyl group.

double-bonded structures resonate with the normal single-bonded one for silicon tetrachloride. Alternatively, the contractions may be due to changes in the hybrid character of the bonding orbitals which do not mean a change in bond order. The exact cause is not important for this discussion, for if it involves *any* resonance other than that between a simple covalency, defined as a mean of those in A–A and B–B, and an ionic structure, the excess energy of the bond cannot *all* be correlated with the ionic character. There is no doubt at all that bond energies can be calculated empirically from atomic constants, and the usefulness of this to chemical theory can hardly be over-emphasised, but it is an over-simplification to designate these constants as electronegativities. This represents only part of the truth, and how big a part we do not yet know.

There are many other problems and unanswered questions which might be raised. We might ask why fluorine appears from some evidence to form double bonds and become electrically positive, while other evidence indicates that this is the last thing it is likely to do ; we might ask what hydrogen bonds are ; we might ask why those bonds with oxygen which develop the higher valencies of phosphorus and sulphur are so very short : but these and many other questions are, comparatively speaking, questions of detail, while our concern is with principles. Admittedly, one major topic, the relation between resonance and chemical properties, has been mentioned only incidentally ; but a full discussion of this subject could not be included in a discourse of this kind.

We may summarise the empirical attack on the physical properties by saying that an attempt has been made to explain deviations from a set of reasonable, though somewhat arbitrary, standards of normality for bonds and molecules with the aid of a small number of postulates. These are (1) that abnormalities in a bond arise from changes in the hybrid character of the orbitals used for covalency formation, without change of bond order, or by resonance between a covalent structure and an ionic one, or by change in bond order; (2) that abnormalities in a molecule as a whole arise from resonance between different Lewis–Langmuir structures, and that they may be regarded as the sums of abnormalities in the individual bonds.

A considerable amount of success has been achieved, but it must be remembered that in applying this method of minimum hypotheses we are striving to make Nature appear simple, and that Nature may object. The recent discovery that the forces between non-bonded atoms are apparently much greater than had been believed (Conn, Kistiakowsky, and Smith, *loc. cit.*) is a warning to us to expect more surprises. It may be that we shall have to think more of the molecule as a whole rather than as a collection of bonds.

I hope that I have succeeded in indicating both the achievements and the difficulties which remain to be solved. For the present there are less interesting but more pressing matters to attend to ; but we must hope that some day these will be settled and that we shall be able to return peacefully to our proper interests.