The Contributions of Wave Mechanics to Chemistry.

The Tilden Lecture, delivered at Burlington House, on October 18th, 1951, and in Glasgow on January 18th, 1952.

By C. A. Coulson.

When the august Mendeleef was giving his Faraday Lecture before the Chemical Society in 1889, he said :

> " While science is pursuing a steady onward movement, it is convenient from time to time to cast a glance back on the route already traversed, and especially to consider new conceptions which aim at discovering the general meaning of the stock of facts accumulated from day to day in our laboratories."

He could hardly have said anything more appropriate to my intention here tonight. We know that Chemistry has been continuing its steady onward movement; and we know that wave mechanics has played a not insignificant rôle in that progress. It is a new conception and not without meaning in the interpretation of chemistry.

We may see this quite simply if we allow ourselves a moment's history. It was almost exactly a hundred years ago, in the year 1852, that Frankland talked about the " combining power of the attracting element " in chemical combination, and of its " being satisfied by the same number of these atoms," thereby paving the way for the idea of a definite valency for each atom. It was in 1860, only two years after Kekulé and Couper had conceived the idea of some sort of graphical mapping of a molecule, that Odling, and five years later Crum Brown, first drew lines to represent these valencies and began to picture for us the appearance and geometry of an atomic arrangement within a molecule. Halving the time interval we remember that it was only 50 years ago that the electron was discovered at Cambridge, and that this discovery opened up the possibility of a more detailed study of atoms and their resultant molecules. And now we once more halve the time interval. It was just over 25 years ago that wave mechanics was introduced to an already expectant world, partly prepared by new ideas about wave and particle properties in physics. When I went to Cambridge as an undergraduate, a year later, Heitler and London had just made their first, and most signal, incursion into chemistry by showing how we can explain the formation of a covalent bond, as in molecular hydrogen.

Wave mechanics seemed very strange in those early days. How well I recall my own astonishment when I learnt about it, in my first term at the university, from R. H. Fowler, who managed to communicate to me something of his own most evident excitement about it. Yet this strangeness is now passing, and we can look back on these twenty-five years, and can see how wave mechanics has done more than anything else to give us a real understanding of some parts of our subject.

That is what I want to do tonight; I want to stand back, without fuss or flourish, and try to assess the contribution of wave mechanics to Chemistry. I shall have very little that is brand new to offer : all that I can hope—or wish—is to leave with you an impression, a feeling, of the significance of what is still, to many, a rather esoteric and unsavoury study.

A Misconception.—But first, a misconception. Wave mechanics is not the answer to every chemical problem, though there are those who speak as if it were. When Schrödinger introduced his first paper in the *Annalen der Physik*, he said : " I believe the new method penetrates deeply to the true nature of the quantum rules," and he expressed the hope that it might be fruitfully generalised. So indeed it was. And before long it had become clear that *all* chemical problems could be expressed as the solution to a certain appropriate differential wave equation. But the equation cannot be rigorously solved—not even for atomic helium. And it took Coolidge and James three years of hard work to get an adequate approximate *ab initio* solution for molecular hydrogen. To solve the benzene problem in a similar way we set out with a differential equation involving about 120 independent variables. Dirac could say, in that famous Bakerian lecture of 1929 : " The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known." Yet the true contribution of wave mechanics is not here, as I have to remind myself when I am being urged to start immense schemes for the numerical evaluation of molecular integrals.

But if it is not here, where is it ? The answer is simple. Wave mechanics has shown us what is going on, and at the deepest possible level. We shall find, as we select a few examples, that it has taken the concepts of the experimental chemist—the imaginative perception that came to those who had lived in their laboratories and allowed their minds to dwell creatively upon the facts that they had found—and it has shown how they all fit together; how, if you wish, they have all one single rationale; and how this hidden relationship to each other can be brought out.

That's a pretty strong claim to make; but I make it. And, if you will let me, I will try to substantiate it. This I will do, by choosing three or four items to illustrate my argument. To some extent they are arbitrary; I apologise for any personal colouring that some of them may have. Let these do duty, then, for all the other examples. I shall not have time to explain them fully, nor to justify what I say; but that will not matter, since it is rather the scope, the insight, the relatedness of wave mechanics to what we may call classical chemistry, which I want to illustrate.

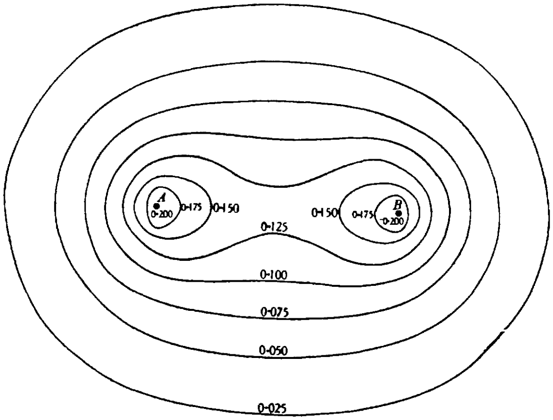


FIG. 1. *Contours of constant charge density for molecular* H_2. *This closely resembles the superposition of separate densities due to isolated* H *atoms except that a certain amount of charge has been attracted from the outer parts of the molecule into the region between the nuclei, where a " plateau " of charge exists at the mid-point.*

The Simple Chemical Bond.—Let me begin, as Frankland, Odling, Couper, and Crum Brown began 100 years ago, with a simple chemical bond. They drew it as a straight line; what do we now believe about it ? When Schrödinger introduced his wave mechanics it was recognised that a chemical bond was essentially electronic in origin, and that a normal single bond could be associated with just two electrons. In this we may trace the influence of J. J. Thomson and G. N. Lewis. But how these two electrons moved was a problem quite insoluble within the framework of Bohr's semi-classical quantum theory. It is almost unbelievable to contrast this state of relative ignorance with the detailed picture which is provided by the modern theoretical chemist. In the first place the search for any kind of orbit, in which the path of the electron could be followed from point to point, has been abandoned as conflicting with the Heisenberg uncertainty principle. In its stead we have the picture of a cloud of negative electronic charge; this cloud whose density is simply related to the wave function, spreads out over the bond, embracing both nuclei. We might say that the description of a bond is essentially the description of the pattern of the charge-cloud. There are two electrons, and only two, because the Pauli exclusion principle forbids any two electrons' having the same space-pattern unless they have opposed spins. As there are only two values for the spin variable, this restricts the normal chemical bond to two electrons.

Fig. 1 shows the density pattern for the simplest of all bonds, that of molecular hydrogen. It is astonishing to realise how much information is packed within such a diagram. Thus there is axial symmetry (which is the origin of the almost free rotation around a single bond); there is an approximate size for the molecule, since we can draw a contour, approximately an ellipsoid of revolution, inside which 95% of the total charge cloud will be found; and lastly the charge-cloud itself closely resembles the superposition of appropriate charge-clouds for the individual atoms of the bond except that a quite small, but definite, tendency exists for charge to concentrate in the region between the " nuclei " (*AB* in the Figure) at the expense of charge on the far sides of the nuclei. A simple physical reason exists for this : it is because when an electron is between the nuclei it is being attracted to both, with a gain in potential energy which is sufficient to pull electrons away from the outer regions It is true, as both theory and accurate *X*-ray analysis have shown, that the additional charge concentrated between the nuclei is usually only in the region of one-tenth to one-quarter of an electron. But this is enough to provide quite a substantial part of the bond energy; and further, because of this tendency for the charge-cloud to be localised between the nuclei, this phenomenon shows us why in a polyatomic molecule, where two electrons in a similar pattern may be used to describe each of the bonds, the bond properties associated with a bond (*e.g.*, the dipole moment, bond energy, force constant) are largely independent of the molecular environment of the bond in question. We have grown so used to the idea of bond properties, and we find them so useful in identification and classification, that we tend to forget how their existence follows from this account of the shape, size, and localisation of the charge-clouds that I have been describing.

All this insight follows from the wave-mechanical concept of a charge-cloud pattern. As we have seen, these patterns are found from the solutions of the appropriate wave equation. Such solutions are exceedingly difficult to get precisely, and, indeed, in the very last resort, we cannot entirely separate the charge-cloud for one bond from that for another bond. But, subject to certain reasonable limitations, Hund in Germany, Mulliken in America, and Lennard-Jones in Britain have shown that they can be found approximately in terms of suitable patterns (or orbitals, as they are now christened) for the isolated atoms.

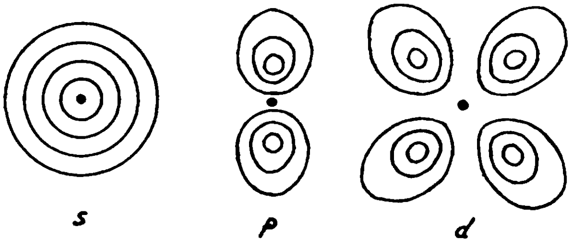


FIG. 2. *Charge-clouds of electrons in certain atomic orbitals. The s-type patterns being spherically symmetrical, may be bonded in any direction equally; the p-type, being directed, form strong bonds only along their preferred direction.*

Here we get more light thrown on some famous debates of older days. Between 40 and 50 years ago chemists were much concerned about the problem of whether the affinity of an atom should be thought of as acting centrally in all directions (as would be involved without question in the early ionic notions of Berzelius), or in certain specified directions (as is implied in the models of a tetrahedral carbon atom due to van't Hoff and le Bel). The uncertainty is now very easily removed. Both points of view are right—according to the circumstances—and we can usually tell which description to apply in any given situation. The answer depends on the shape of the atomic orbital out of which the molecular pattern is to be formed. Fig. 2 shows a few of the familiar atomic charge clouds. Some of them are evidently spherically symmetrical, others have a strong directional character. It is not surprising that when an atom, such as H or Li, makes use of one of the *s*-type oribtals to form a bond, the affinity lies equally in all directions; but when, as in O or S, an atom uses two of the *p*-type orbitals, its affinity is located in certain specified directions associated with the axes of the two available *p*-orbitals.

I have purposely used rather old-fashioned language (or perhaps old-fashioned thought-forms) in the above account, because I was anxious to contrast the new account of directional forces in chemical combination with older, pre-wave-mechanical ones. Listen to this, from Werner, about 40 years ago : " The fact that an atom is able to combine with a definite maximum number of atoms is . . . interpreted as meaning that the affinity of an atom only comes into action through a definite number of units of valency, which are considered as independent forces. According to this conception the unit of valency consists of a fraction of the affinity of the atom appearing as an independent force." How much easier, today, to say that these independent forces are the unpaired electrons of the atom, with charge-clouds directed in space with certain mutual relationships (*i.e.*, valency angles) but each permitting the use in conjunction with a suitable charge-cloud from a neighbour atom, in the formation of a molecular pattern of localised electron-pair bonds. But let us continue with Werner : " Some experimenters assume that these independent forces (or units of valency) act only from different positions on the surface of an atom, and that multivalent atoms therefore have their units of valency separated and assigned to definite points on their surfaces . . . the amount of affinity saturated by the linking up of two atoms is distributed on a definite circular segment on the surface of the atom." It was not until the advent of wave-mechanics that we could finally reject this hooks-on-the-surface-of-a-billiard-ball account of chemical bonding.

Another way of relating the directional character of an atomic orbital to its bonding power is to notice that whereas an orbital of *s*-type must overlap any adjacent charge-cloud equally in all directions, an orbital of *p*-type will overlap most efficiently only along its axis of symmetry. What I am describing is the now famous criterion of maximum overlapping, due originally to Pauling and Slater; this is surely one of the most important single principles in the whole of theoretical chemistry, and almost deserves to rank with the Pauli exclusion principle in its profound influence on chemical theory.

Consider, to illustrate the significance of all this, the case of H_2S. Once we recognise that all the electrons in the S atom are fully paired and therefore unavailable for bonding, with the exception of two whose patterns are similar to the *p*-orbitals of Fig. 2 (strictly 3*p* atomic orbitals), and that these two orbitals are associated with directions at right angles to each other, as in Fig. 3, then we can see immediately why the HSH angle in H_2S is so close to 90°, with a value of about 92°. It is true that several other refinements would need to be incorporated in this account before it could be said to provide a rigorous demonstration. But what I went to stress is the natural, immediate, almost inevitable character of this and other similar valency angles, once we have grasped quite elementary wave-mechanical ideas.

This leads us to ask about valency angles in carbon. A new feature appears : hybridization. But even this is natural and simple enough if we approach it in the right way, and links on to some of the older view-points. Since the ground state of an isolated carbon atom is described

FIG. 3. *Valence angle in* H_2S. *Each* S–H *bond may be regarded as formed by combination of a hydrogen* 1s *atomic orbital with a sulphur* 3p *orbital. The available* 3p *orbitals are directed at* 90° *as shown on the left. On the right are shown the resulting bond patterns* (*this is rather schematic, since the detailed shape is not yet known with confidence*).

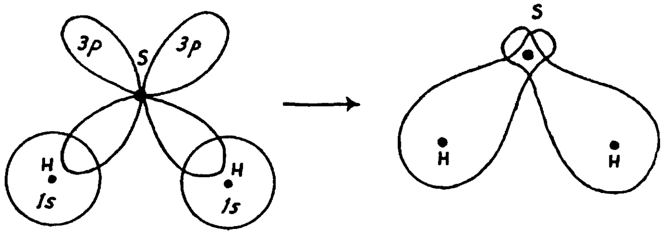
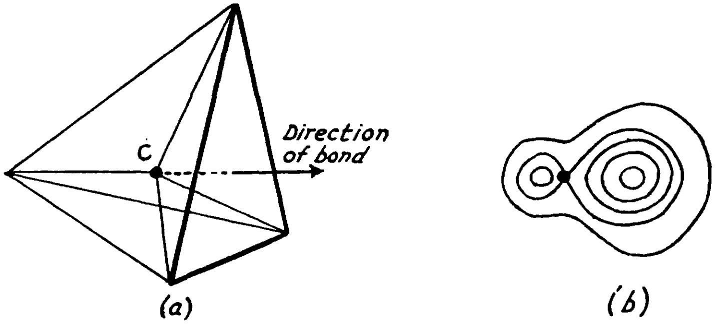


FIG. 4. (a) *Hypothetical division of the charge-cloud of a carbon atom in state* sp^3 *into pyramidal regions* (*only one of which is shown fully, to avoid confusion*), *each of which may then be used to form a bond.* (b) *Wave-mechanical version in which the combination of an* s *and a* p *atomic orbital to form a hybrid orbital,* $s + \lambda p$, *leads to a charge-cloud heavily concentrated in one region, similar to* (a).



by the atomic configuration $(2s)^2(2p)^2$, it would be expected to be bivalent. This can be increased to quadrivalency by promoting one of the 2*s* electrons to a vacant 2*p* oribtal, to give a configuration $(2s)(2p)^3$. It is interesting to notice that the total charge-cloud associated with these four electrons is spherically symmetrical. The most natural and obvious way of dividing this cloud into parts suitable for building four bonds to adjacent atoms is to divide the spherical charge (Fig. 4*a*) into regions and to suppose that the charge within one region can be used to form a bond in the direction defined by that region. One symmetrical mode of division provides four regions all equivalent but tetrahedrally oriented with respect to each other. Now what is important for our present purposes is that this procedure is effectively the same as saying that instead of trying to use the original *s*, *p* orbitals, we use mixtures, or hybrids, of them. A linear combination of a 2*s* and a 2*p* orbital does in fact give a new orbital whose charge-cloud lies almost wholly on one side of the atomic nucleus, and which closely resembles (Fig. 4*b*) one of the separate regions of charge suggested in Fig. 4*a*. In such ways as this we begin to see how hybridization appears almost unevitably. Of course there is much more to be said about it than this, but at least the way is clear for us to approach the question of valency angles and bonding in many types of molecular complex. As we all know, a very large degree of order and systematization has resulted from wave-mechanical considerations essentially equivalent to those outlined above. We can see, for example, that if a central atom is to form six bonds to its ligands, these are very unlikely to be coplanar, but are much more likely to be octahedral; for six coplanar bonds would leave unused a good deal of the charge-cloud (see Fig. 4*a*). We can also see why, if we take different proportions of *s* and *p* in the case of carbon, we shall effectively be dividing up the atomic charge-cloud unequally. So some of our bonds will be stronger than others. In addition the overlapping power of the hybrid will be changed. We should therefore expect a small variation in the covalent radius r_c as the degree of mixing varies. This (Fig. 5) is exactly what is found, the covalent radius changing by several hundredths of an Ångström unit according to the degree of hybridization. This is the origin of many of the small changes in, for example, the length of the C–H bond in aliphatic, olefinic, aromatic, and acetylenic molecules. Carbon is a relatively simple atom to deal with in this way. But Pauling has shown how, in more complex situations such as those that occur in the transition metals and their alloys, the same ideas may be used. Once again I would like to stress the naturalness of this description.

There is another way of looking at this question of stereochemical forces, which is worth mentioning, even though it does not lead to the same quantitative discussion as hybridization. Let us consider carbon again, and suppose that we have an isolated atom with its four valency electrons in the configuration sp^3. These four electrons are described by an atomic wave function ψ which is a function of the four sets of co-ordinates $x_1, y_1, z_1, x_2 \ldots z_4$. We could write it $\psi(x_1 \ldots z_4)$. The probability interpretation of the wave function—which is an alternative to the charge-cloud interpretation, and leads to the same final answers—asserts that the probability of the four electrons' being at the points $x_1 \ldots z_4$ is given by $\psi^2(x_1 \ldots z_4)$. We may now ask: what are the values of $x_1 \ldots z_4$ which will make this probability greatest? For we could say that these were the most likely relative positions in which to find our four electrons simultaneously. It is not hard to show that the answer is that the most likely simultaneous positions are those of four points tetrahedrally arranged around the nucleus. It is easy to conclude from this that since we are going to use each one of the electrons to form a bond, a tendency will exist for these bonds to be tetrahedral around the central atom. We must not press this type of argument too far, even though, as Linnett, Artman, and Van Artsdalen have shown, it predicts an angle slightly less than tetrahedral in NH_3, where two lone-pair electrons replace one of our previous bonding ones. What this argument does is to give us insight into the way in which the Pauli exclusion principle, by trying to separate electrons with parallel spins, automatically " prepares " the atom for appropriate bond formation. We begin to " feel " why valency angles are what they are.

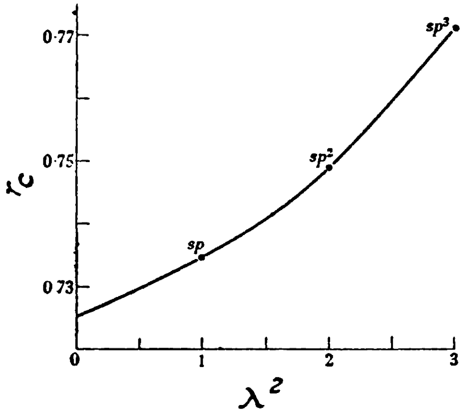


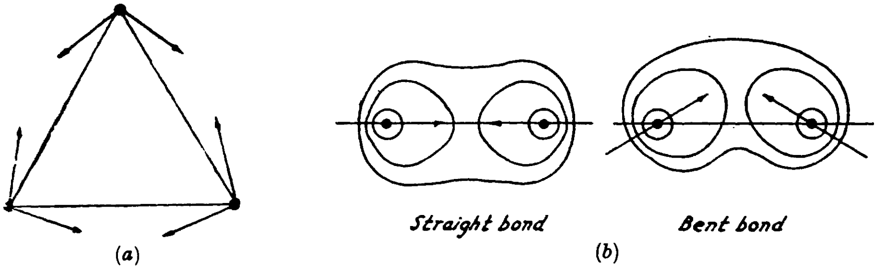
FIG. 5. *Variation of covalent radius* r_c *of carbon with degree of hybridization.* λ *denotes the parameter which governs the relative amounts of* s *and* p *in the hybrid orbital* s + λp. *The values* $\lambda^2 = 1, 2,$ *and* 3 *are appropriate for acetylenic, aromatic, and aliphatic carbon.*

But of course there are occasions in which the geometrical construction of the molecule prevents us from doing what we should like; prevents us, for example, from using hybrids on two atoms A and B which overlap as much as would have been possible without the geometrical constraint provided by the rest of the molecule. A particular case is *cyclo*propane, where the equilateral triangular arrangement of the three carbon atoms compels the valence angles to be 60°. It is easy to show that no satisfactory pair of hybrids can be found in carbon to point at so small an angle. Instead, as Moffitt and the present writer showed several years ago, we have to strike some kind of compromise between the desire to satisfy the criterion of maximum overlapping by using pairs of orbitals directed as nearly towards each other as possible, and to use hybrids with a particularly strong directional character. In the event, it seems that we have to use hybrids which point, as shown in Fig. 6*a*, at an angle of about 22° away from the formal bond directions. As a result the bond is " bent," and has a charge-cloud somewhat schematically represented by Fig. 6*b*. The significance of this is quite obvious; since the hybrids do not overlap so strongly, the bonds will be weak. An alternative way of speaking is to say that the molecule is strained. But notice how closely Baeyer's early ideas have been translated into wave-mechanical language. We no longer speak of elastic threads being bent: but we speak of a charge-cloud lacking axial symmetry, and of wasted overlapping power. And what is more, we can calculate the strain.

One further point emerges very naturally from this discussion. Since the electrons on atoms A and B are such that their charge-clouds do not overlap to the maximum degree possible, it follows that they are more loosely coupled in establishing one of the carbon–carbon bonds. This, for reasons that will appear later, is an explanation of the familiar conjugating power of the *cyclo*propyl group, when placed next to a double bond, as in *cyclo*propylethylene.

π-Electron Chemistry.—The time has come to turn to a rather different application of wave mechanics—what we loosely call resonance in organic unsaturated and aromatic molecules. Listen first to these familiar words of Kekulé. They were written in 1865, during his tenure of the chair of Chemistry at Ghent : " I was sitting writing at my text-book, but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire, and dozed. Again the atoms were gambolling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of this kind, could now distinguish larger structures of manifold conformation; long rows, sometimes more closely fitted together; all twisting and turning in snake-like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I awoke; and this time also I spent the rest of the night in working out the consequences of the hypothesis." Now it is quite true that the vision of a snake seizing hold of its own tail was not new. As Professor Read has pointed out, it is " a symbol in ancient Egypt of eternity, a symbol in ancient Greece of the Platonic idea of the unity of matter, and a symbol among the alchemists of rejuvenation." It was also a symbol for the early Celtic Christian Church. What Kekulé had seen in this evening vision was, of course, the closed-ring structure of benzene. But what he saw, as it were " in a glass darkly," has been taken up by more modern wave mechanics. For that closed ring of carbon atoms implied the possibility that tiny electrical currents might flow around the ring : and those snakes of his that bit their tails were the prototype of what we now call delocalized molecular orbitals, charge-cloud patterns such as that in Fig. 7 which extend all round the ring, and suggest that an electron in such an orbital may be found at any one of the atoms of the ring Here, in fact, is the beginning of an explanation of the remarkable power which planar aromatic molecules possess, of transmitting electrical influences from one region of the molecule to another. It is true that only some of the valency electrons—the so-called π-electrons—are to be treated like this. But it is easy to see which they are, and to calculate approximate energies and charge distributions for them. And with this concept there comes automatically the proper description of the molecular shape, and the abandonment of the Ladenburg prism formula, and the other models of Claus and Armstrong and others.

FIG. 6. (a) *Arrows denote the directions in which the hybrids which are to be used in forming the* C–C *bonds of* cyclo*propane are pointing.* (b) *The difference between a " straight " and a " bent " bond.*



Several other things follow from all this very simply. For example there is the regular-hexagonal nature of the benzene ring, with all its sides equal. We all know what a puzzle this was to the older chemists, and how attempts were made to satisfy the chemists' feeling that all the C–C bonds must be equivalent, by supposing some sort of dynamic oscillation between what are now called Kekulé forms. All this has gone : and in its place we show from the nature of the molecular orbitals for the π-electrons that all the bonds should be equal in the ground state, though in some of the possible excited states this may no longer be true.

I cannot forbear, however, from recalling how, in one sense, Kekulé presaged a way of looking at these conjugated and aromatic molecules which was to be taken up and developed properly only when wave mechanics was available. I am thinking of the notion of resonance, developed in this connection particularly by Pauling. It is still possible to think in terms of Kekulé structures (and Dewar structures of course also) : but these structures do not have the independent objective existence which Kekulé supposed. Instead, we think of them as possible ways in which we could start with the π-electrons on their separate atoms and then pair them together to form bonds. There are many ways of doing this : each of them corresponds to a Kekulé or other structure : and all must be regarded as existing at the same time, losing their individuality in the resonance that I have been describing. In some respects it is not unlike the way in which yellow and red make brown, a new colour which is not like either of its parents, though it may be regarded as derived from both. At this distance of time it is nothing less than amazing that Kekulé could have argued as he did.

FIG. 7. *A somewhat schematic representation of a π molecular orbital in benzene. The charge-cloud consists of two regions, of streamer-like character, above and below the molecular plane, and extending over all six carbon atoms.*

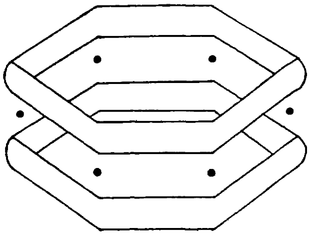
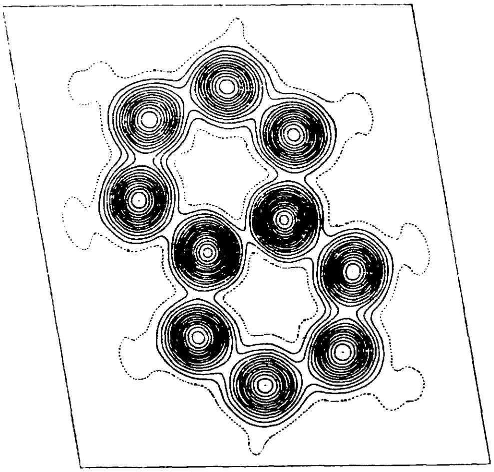
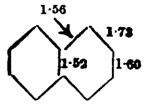


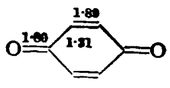
FIG. 8. *Charge-density contours for naphthalene. (Prof. J. M. Robertson; reproduced by kind permission from* Acta Cryst.)



But there is more to say about all this. In benzene all the C–C bonds are similar; but in naphthalene they are not. Their actual values may be found experimentally from the accurate *X*-ray diagrams of charge density such as Fig. 8, obtained by Professor J. M. Robertson. What can we say theoretically about patterns of this kind ? In the first place, as Dr. N. H. March has shown, it is possible to calculate, in advance, diagrams of the total charge distribution which very closely resemble that of the Figure. In particular, it is possible to assign to each of the C–C bonds a numerical magnitude—what Lennard-Jones called its bond order. This is 1, 2, and 3 for single, double, and triple bonds, with intermediate fractional values for other types of bond. If the bond order p is large, the bond can be said to possess more double-bond character than if it is small. In this way we see new light on another very old question, bond fixation. Despite great attempts to do so, the older classical chemists were unable to show unequivocally that in a molecule such as naphthalene, the 1–2 bond was really either double, or single. It appeared to be more double than single; and so the attempt was made to speak of bond fixation

(I*a*)





(I*b*)

Bond orders

Now however we see that bond fixation is never absolute. All that we can say is that there is a relative degree of double-bond fixation : and we can give figures to show how large this is. Thus in naphthalene (I*a*) there is much less bond fixation than in benzoquinone (I*b*), though even in the latter molecule it is not absolute.

Now if two bonds differ in bond order, we should expect them to differ in bond length. The lengths of the C–C, C=C and C≡C bonds are 1·54, 1·34, and 1·20 Å respectively. It should therefore be possible, as Pauling first showed, to draw a curve relating order and length, and use this curve to predict unknown bond lengths once the corresponding bond orders have been calculated. It is significant that when a smooth curve is drawn through the points corresponding to single, double, and triple bonds, benzene (order 1·67, length 1·39 Å) and graphite (order 1·52, length 1·42 Å) fit excellently on to it. Fig. 9 is a composite diagram showing all the calculated orders and observed lengths for the molecules listed underneath it. There can be no doubt but that this graph justifies the concept of fractional bond order, and shows how we may use the theory to predict bond lengths. The two broken lines of the diagram are drawn parallel to the central one, at a distance 0·02 Å from it. When it is realised that almost all the observed point lie within the band thus formed, and that the experimental accuracy of most of these points is only $\pm 0{\cdot}02$ Å, we can see how satisfactory the wave-mechanical argument really is. In larger molecules the agreement seems to be even better than in small, as the situation shown in Figs. 10 and 11 for ovalene illustrates very nicely. This is an agreeable situation, but one that is unfortunately not very common in Science.

The concept of fractional bond order is one of the most fruitful of the concepts which wave mechanics has introduced and developed. As we shall see later, it may be used very profitably in the study of certain types of chemical reactivity, as well as in discussions of structure such as that I have just given. But of course it was not original to wave mechanics. Had not Ingold described a mesomeric effect and had not Robinson and Lapworth attempted graphically, by the now familiar curved arrows, to represent some flow of bonding power from one region to another in a molecule ? Yet I believe it is perfectly true to say that without this contribution from the theoretician, it would have been very difficult to see really what was involved in the curved arrows and the mesomerism.

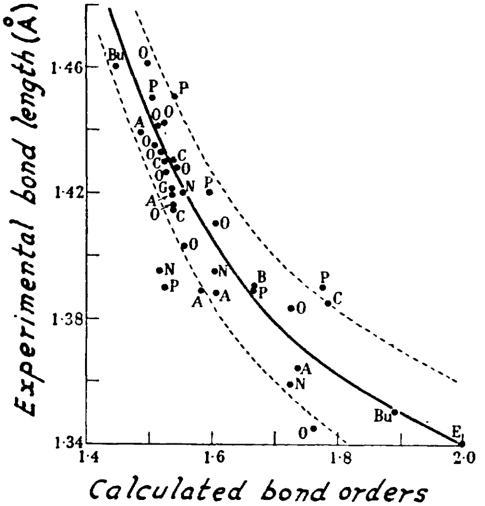


FIG. 9. *Curve showing relation between calculated bond orders (by use of molecular-orbital approximation) and observed bond lengths in conjugated hydrocarbons.* A = *anthracene,* Be = *benzene,* Bu = *butadiene,* C = *coronene,* E = *ethylene,* G = *graphite,* N = *naphthalene,* O = *ovalene,* P = *pyrene.* (*Reproduced from the* Proc. Roy. Soc., *A*., *by kind permission.*)

There is one other famous discussion of older days to which I want to refer before we leave the discussion of π-electron chemistry. This is the famous " aromatic sextet " rule. Within two or three years of G. N. Lewis' papers on the electron-pair bond it came to be realised that in stable benzenoid systems there appeared to be a total of six electrons forming some sort of stable grouping. In 1918 Sir Robert Robinson stated that " the characteristics of all benzenoid systems is to be sought in the hypothesis that six electrons are able to form a group which resists disruption." This group is the aromatic sextet, and it is found in heterocyclic molecules such as pyridine, furan, and pyrrole just as much as in benzene, and the *cyclo*pentadienyl anion. At this distance of time, long before π-electrons had been thought of, the hypothesis of an aromatic sextet can only be regarded with admiration. But, at the hands of people like Hückel, this hypothesis has received an exceedingly simple explanation in terms of the molecular orbitals of the ring. Fig. 12 shows the energy levels for the π-electrons in a ring containing 5, 6, or 7 identical atoms. (If one or more of the atoms differs from the others, the details of Fig. 12 are changed, but not the main argument which follows.) All levels below the central broken line may be regarded as bonding, and there will be a tendency to fill them with as many electrons as they can contain. All levels above that line are anti-bonding, and a molecule will try to shed any electrons which may happen to have been forced into these levels because there were no other lower levels available. It is clear from the Figure that all three systems can accommodate six electrons in bonding orbitals. Hence the explanation of $C_5H_5^-$, C_6H_6, and $C_7H_7^+$. The whole discussion is so simple as to be almost obvious. But that, surely, is one of the characteristics of a good explanation.

There are very many examples to illustrate the general rule, that a six-ring of carbon atoms will not readily give or receive additional electrons, and that a five-ring will accept and a seven-ring will donate an electron. For example it is now known that in fulvene (II) there is a dipole moment of about 1 D due to migration of electrons from the ethylenic double bond into the five-membered ring. In azulene (III) the dipole moment is probably larger, owing to donation from the seven-membered and simultaneous acceptance by the five-membered ring. The non-existence of the hypothetical molecule pentalene (IV) is probably due just as much to the fact that both five-membered rings are seeking for electrons, and that there is no source of supply, as to the more sophisticated explanations that can, and have, been given. This suggests that a possible stable molecule of this type would be a polymethylpentalene, where the electron demands of the central rings were met by the donor methyl groups round the perimeter. In the same way the ferrocene system—or molecular sandwich, if we adopt the term introduced by Orgel and Dunitz—in which an iron atom lies midway between two parallel C_5H_5 groups, is readily understood if it is written as $C_5H_5^-{\cdot}Fe^{++}{\cdot}C_5H_5^-$ (the detailed relations of the ions here cannot, however, be explained without more intimate study, of the kind recently described by W. E. Moffitt). But the system itself is of very general character, as is shown by the existence of similar sandwiches in which Fe is replaced by Ti, Zr, V, Nb, and Ta.

FIG. 10. *Ovalene* $C_{32}H_{14}$, *showing the naming of the* 12 *essentially different* C–C *bonds.*

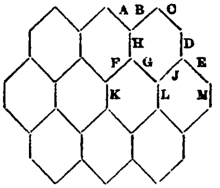
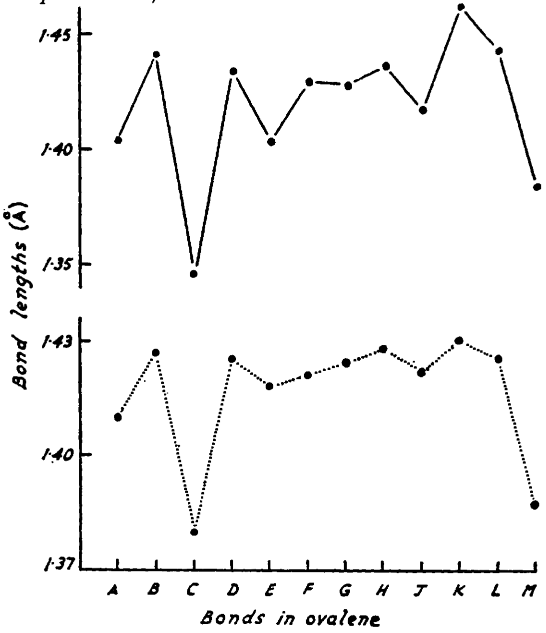


FIG. 11. *Comparison between computed and observed bond lengths in ovalene.* —— *X-Ray measurements of Prof. J. M. Robertson*; – – – – *Molecular-orbital calculations of Miss Buzeman (Mrs. Taylor). (Reproduced from the* Proc. Roy. Soc., *A, by kind permission.)*



One final example of the aromatic sextet will show how widespread is its use. The hydroxy-*cyclo*heptatrienyl bromide molecule is found in solution in the form (V) where the positive charge seems to lie in the seven-membered ring and not particularly on the hydroxy-hydrogen atom. Similarly the dipole moment of tropone (VI) is much larger than that of a normal carbonyl group, as, *e.g.*, in benzoic acid (VII), indicating the relatively greater importance of ionic structures such as (VIII) for tropone than for benzoic acid.

It may be interesting to point out that there is an aromatic duplet, as well as an aromatic sextet, though this is less often noticed. Some recent calculations of charge in the methylene*cyclo*propene molecule (IX) show that charge has left the three-membered ring and migrated to the exocyclic carbon atom, in distinction to the situation in fulvene (II) where it leaves the exocyclic carbon atom and migrates into the ring.

Chemical Reactivity.—And now we must leave questions of chemical structure in order to deal with the last of my three main applications of wave mechanics : chemical reactivity. This is a wide field and some choice of material is inevitable. I propose therefore to leave out of my account any mention of the interesting and valuable work of Eyring, Polanyi, and M. G. Evans on the reactions of saturated systems : and shall instead deal only with the reactions of π-electron molecules where, on account of the common fundamental possession of these π-electrons, a greater degree of systematization is possible In this field, as in our earlier fields, we shall see how naturally modern wave mechanics has gathered up the older ideas and fitted them into a most promising general scheme.

We must begin, as all discussions of reactivity must, by a reference to the reaction-path diagram (Fig. 13) of Eyring and Polanyi. Here, between the initial and the final stage we may distinguish (*a*) the perturbed (or polarised) stage in which the reacting systems, while still separate and distinct from each other, have nevertheless begun to polarise each other, and (*b*) the transition stage (or activated complex) in which the two molecules have merged together and we are compelled to think of them as a single system. If we could calculate the details of this energy curve, we should know almost all that was needed about the reaction. But, as I stated earlier, such a hope is doomed to disappointment. Instead, we shall ask, in more modest mood, what influences are responsible for the changes in energy associated with (*a*) the perturbed and (*b*) the transition state. If we can get an answer to these questions—as indeed we shall see that we can—then we can make good our claim that wave mechanics has helped us to see and to feel what is going on in a reaction of this kind.

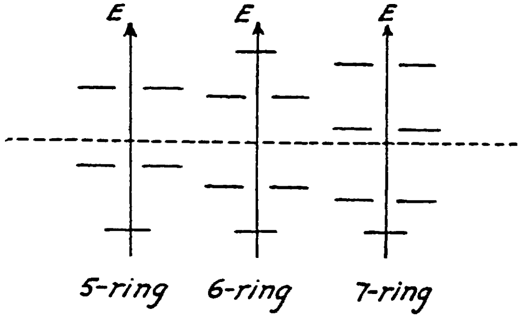
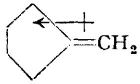
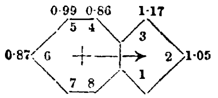


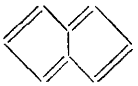
FIG. 12. *Calculated energy levels for the π-electrons in 5-, 6-, and 7-membered rings. All levels below the broken line are bonding, those above it are anti-bonding. The tendency to acquire the aromatic sextet of electrons in all three cases follows from the fact that there are just three bonding levels, which can hold six electrons. (Many of the levels, as shown in the diagram, are doubly degenerate. Each such level will hold 4 electrons in all.)*



(II)



(III)



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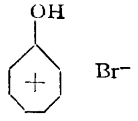
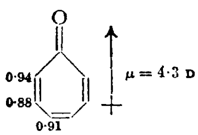
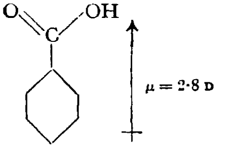


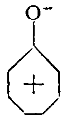
(V)



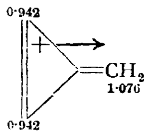
(VI)



(VII)



(VIII)



(IX)

(In these formulæ arrows denote the direction of migration of the π-electrons, and the numerical values at each atom give the total number of π-electrons associated with that atom. Values not shown follow from symmetry.)

It is clear that any discussion of this sort must start by distinguishing the heterolytic and the homolytic type of reaction. In the first, at least one of the reagents is essentially ionic, and in the second both are normally uncharged free radicals, though of course there may be some polarity in them associated with the presence of polar groupings. The distinction between these two types of reaction is, of course, equally preserved in the wave-mechanical analysis. We shall find it convenient to deal with the heterolytic type first.

A large number of heterolytic reactions are covered by two rules : (i) a positive (*i.e.*, electrophilic) reagent will attack that part of the molecule where the negative charge is greatest, and (ii) a substituent in any conjugated system such as benzene induces alternately greater and less reactivity at the successive atoms on either side. The first of these rules is the original rule of Robinson and Lapworth, the second is one form of the law of alternating polarity, or alternating affinity, associated first with the name of Flürscheim. Both of these rules may now be put in wave-mechanical language. Thus Professor Longuet-Higgins and the present writer have shown that when a positive charge approaches one position (C_r say) in a conjugated molecule, its electric field may be supposed to pull any electrons that are free to move, towards C_r. These are the π-electrons, and the pull towards C_r may be translated into the statement that this particular atom has an enhanced electronegativity. It is not difficult to calculate the energy change associated with this change of electronegativity, and so we can estimate the change in π-electron energy when the original cation approaches C_r. It turns out that the term which dominates this change of energy is none other than the total π-electron charge on C_r before the reaction started. This means that the early stages of the reaction are governed by the charge distribution. But this is precisely our rule (i). For nucleophilic reagents the attack comes most easily at that carbon atom where the number of π-electrons is least.

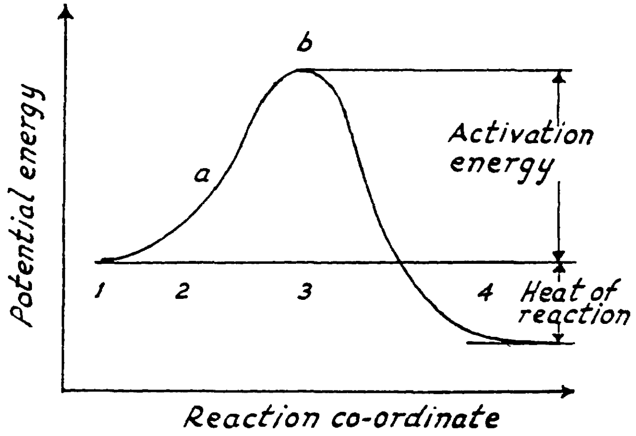
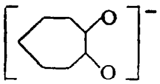
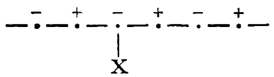


FIG. 13. *A potential-energy curve for a chemical reaction, showing the four stages* (1) *initial reactants,* (2) *perturbed* (*polarised*) *or* (*a*) *stage,* (3) *transition* (*activated*) *or* (*b*) *stage, and* (4) *final products.*

Before going further we may give two illustrations of this. The first is the reactivity of azulene. According to structure (III) the largest concentration of π-electrons is around atoms $C_{(3)}$ and its equivalent $C_{(1)}$. We should therefore expect that nitration would take place at these positions. In fact this prediction was made before Anderson, Nelson, Tazura, and others showed experimentally that not only nitration, but also bromination and acetylation, occurred at the 1-position. In the same way R. D. Brown and M. J. S. Dewar were able to predict nucleophilic activity in tropolone (X) and tropone (VI).



(X) Tropolone anion



(XI)

The second example that I have chosen is one where accurate numerical comparisons are possible. It is well known that the silver cation very readily forms complexes with nitrogen compounds. Fyfe has measured the equilibrium constant K_f for a series of amines, where the reaction is

$$Ag^+ + 2\text{Amine} \rightleftharpoons (\text{Ag Amine}_2)^+$$

and

$$K_f = (\text{Ag Amine}_2)^+/(Ag^+)(\text{Amine})^2.$$

We may expect that, other things being equal, equilibrium will lie more to the right if the N atom, which is to form an ionic bond to the metal atom, carries as large a number of electrons as possible. The charge on the N atom in such molecules as pyridine, quinoline, and acridine can easily be calculated, and even if the values shown in Fig. 14 are not absolutely correct, they are almost certain to be relatively so. It will be seen that when the experimental values of log K_f are plotted against the theoretical charge, a good straight line results. This is just what would have been expected, and shows us that we may use complex-forming ability as a kind of "charge probe." And surely the conclusion of all this is that we are beginning to understand the distribution of electrons in these heteronuclear molecules in a deeper sense now than would ever have been possible before.

The second fundamental rule—rule (ii) above—was expressed in the law of alternating polarity. Here it has proved possible to give a very general theoretical discussion. It has been shown, for example, that if we take a long conjugated polyene chain such as (XI) and then replace one of the H atoms by a substituent X, there will be migrations of charge which lead to a final situation in which the atoms are alternately positively and negatively charged as we move away from X in either direction : and in which the net charges on the atoms diminish with distance from X. For example, if X attracts charge from its adjacent carbon atom, the resulting migrations of π-electron charge in the conjugated chain will follow the distribution of signs shown. Now this is precisely the law of alternating polarity for a straight chain. For benzenoid systems it still holds, though since we can get to the *para*-position in benzene by two routes, the dying-away effect is less pronounced. Fig. 15 shows the π-electron charges induced in stilbene (where originally they are all closely equal to 0) by an amino-substitution in the 4-position of one ring. It is surely most interesting that we can not only trace the alternating charge effect, but also see that in the ground state, the effect of the substituent is hardly appreciable in the far benzene ring. In certain of the excited states, however, this may not be the case.

FIG. 14. *The variation of diamine formation constant* K_f *with theoretical charge on the* N *atom. This shows that we are now able to calculate relative values of the charge on* N *atoms in large molecules. A curve of this kind could be used to predict* K_f *values for other similar molecules. A, Pyridine; B, isoquinoline; C, quinoline; D, acridine.*

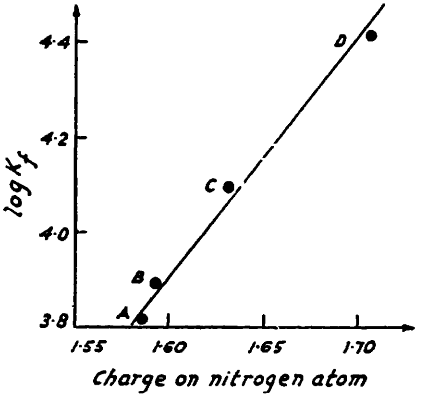
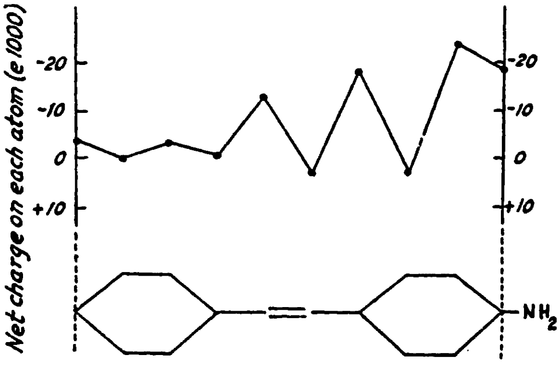


FIG. 15. *Charge distribution for the* π*-electrons in* 4-*aminostilbene. The charges shown in the top diagram relate to the carbon atoms directly underneath in the lower diagram. This diagram shows the alternating character of the charge distribution, and also the minute effect in the farther ring.*



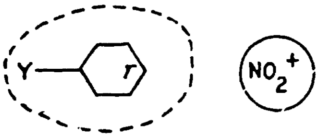
The discussion which has just been given shows very clearly that in heterolytic reactions, the factor which really controls the polarised stage (*a*) of Fig. 13 is the charge distribution. We may reasonably now ask what controls stage (*b*), the activated complex stage. Here the answer has been provided by Wheland, who has shown that estimates of the difference in activation energy as between one position of attack in a molecule and some other position in the same molecule or in some other molecule, may be found by the following localisation process.

Let us consider the approach of an NO_2^+ group towards atom C_r of an aromatic system (XII*a*). As Ingold has shown, this is the first step in an aromatic nitration. In the transition state we may imagine a bond formed from C_r to the NO_2^+, as in (XII*b*). This bond requires that C_r becomes a tetrahedral atom, so that the resonating region of the molecule is effectively restricted to that part within the broken line. Further, since the new bond uses two electrons, the total number within the resonating region is now two less than it was before. Consequently the π-electron energy is altered, and the extent of this alteration provides a good measure of the activation energy, since the other energy effects which most certainly exist—change of σ-bond energy, change of hybridization at C_r, formation of C_r–NO_2 bond—may be presumed to be constant both for different atoms *r* and even for different molecules. If we may describe the difference in π-electron energy between (XII*a* and *b*) as the localisation energy, then differences in localisation energy should be closely similar to differences in activation energy.

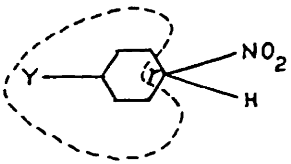
A single example, taken from Wheland's work, will suffice. If Y in (XII*a*) is itself a nitro-group, we are concerned with the nitration of nitrobenzene. We could imagine that the second nitro-group approached to the *ortho-*, *meta-*, or *para*-position in (XII*a*). Wheland shows that the localisation energies necessary to produce the transition states (XII*b*) are 1·886, 1·852, and 1·861 respectively, measured in terms of a certain fundamental resonance integral β. The lowest of these is the middle one, showing that *m*-dinitrobenzene is formed more easily than the *o*- or *p*-isomer; and, by comparison with the figure for benzene itself (1·814 β) we can see that the first nitration of benzene requires less activation energy than the second.

All this fits together very nicely : and considerable extensions, to deal with attack at a bond rather than an atom, and also with the Diels–Alder diene addition, have been made by R. D. Brown and others. We are justified in claiming that in heterolytic reactions the dominant factor in stage (*b*) of Fig. 13 is the localisation energy. By good fortune it turns out that predictions made on the basis of polarisation calculations, as in stage (*a*), almost always agree with predictions on the basis of localisation calculations, as in stage (*b*). This agreement justifies us in our belief that the model with which we try to understand this type of reactivity, is adequate and basically correct.

Our discussion of the second type of reactivity can now be quite short; for many of the same basic ideas which have just been described for heterolytic reactions carry over into homolytic, *i.e.*, free-radical, reactions. However, there is one major difference in our consideration of stage (*a*). It is not really a new concept which has been devised, but a very old one which has been brought up to date. At the beginning of the twentieth century, as a result of work by Flürscheim, Thiele, and Werner, there grew up the conviction that any one atom was capable of exerting only a certain definite affinity. If the bonds to this atom were already using up most of this affinity, there would be correspondingly less " residual affinity " left over to initiate any possible substitution or addition reaction. In this way these older chemists were led to the idea of a free valency. Sometimes, as in the central bond of butadiene, the free valencies at the ends of a bond managed to satisfy each other; but at other times, as with the terminal carbons in butadiene, this was not possible, and the molecule would be reactive at these positions. What does wave mechanics have to say about this model ? The interesting point is that it has justified nearly every one of those earlier claims—in the appropriate circumstances. For example, it has shown that there really is a total affinity for an atom : in modern terms there is a maximum possible value for the sum of all the bond orders of the bonds which terminate on that atom. In the case of carbon this maximum value is $3 + \sqrt{3} = 4{\cdot}732$. If we add together the fractional orders of all the bonds in a given molecule, we can soon see by how much the total bond number for any atom is less than the maximum possible. This is the free valence, or residual affinity. It is a reasonable hope that this affinity would be available for the initiation of any additional bonds that might be necessary in the course of a chemical reaction. But it is equally probable that the reactions to which it would be expected to apply best would be free-radical ones, where a radical with an unpaired electron can come quite close to the original molecule, and begin the formation of an incipient bond, without the intervention of large localised charges and their associated Coulomb forces. It is true, of course, that in nearly all cases there will be a small amount of unbalanced positive and negative charge, whose effect would be to modify our simple picture by superposing on it a small heterolytic character. But in cases where, for example, a Ph or CH_3 radical approaches a pyridine molecule, we should expect that the dominating influence would be the free valence. A great merit of this new development is that, since we can now calculate actual bond orders numerically, we can give a numerical value for the residual affinity. In this respect, not only has wave mechanics vindicated the older views : it has extended them by allowing comparisons between different molecules, and different positions in the same molecule.



(XII*a*)



(XII*b*)

Two short examples will make this clear. In naphthalene (I*a*) the total bond number for $C_{(1)}$ is $1{\cdot}56 + 1{\cdot}73 + 1{\cdot}00$ (C–H bond) $= 4{\cdot}29$. Thus the free valence is $4{\cdot}732 - 4{\cdot}29 = 0{\cdot}44$ But for $C_{(2)}$ the total bond number is $1{\cdot}73 + 1{\cdot}60 + 1{\cdot}00 = 4{\cdot}33$, leading to a free valence 0·40 We may therefore expect that the 1-position would be just a little more reactive towards free radicals than the 2-position. But the difference would not be very large. This is a general conclusion. For example it may be shown that in a monosubstituted benzene the free valences at the *o*-, *m*-, and *p*-position will always be such that *o*, *p* > *m*, though once again the differences will not be expected to be large. We should not be surprised therefore that all three positions are usually substituted, and, as Hey and Waters and Weiss have shown, *ortho*- and *para*-compounds are formed rather more easily than the *meta*-compound.

My second example shows the power of this type of calculation to give an accurate numerical account of the relative ease of free-radical attack on a series of molecules. Kooyman and Fahrenhorst at Amsterdam have made experiments in which a CCl_3 radical is used competitively, either to attack keten and continue a chain reaction, or to attack an aromatic hydrocarbon such as anthracene or chrysene. Since the reaction is competitive, by suitable choice of conditions and measurement of the degree of polymerisation, we can compare rates of this reaction with different hydrocarbons. Fig. 16 shows what an excellent straight line links the logarithm of the observed rate with the calculated free valence. It is indeed most gratifying that this relation holds for molecules as diverse as benzene with one ring and dibenzanthracene with five. It seems clear that we begin to understand the really essential factors in stage (*a*) of a homolytic reaction.

FIG. 16.

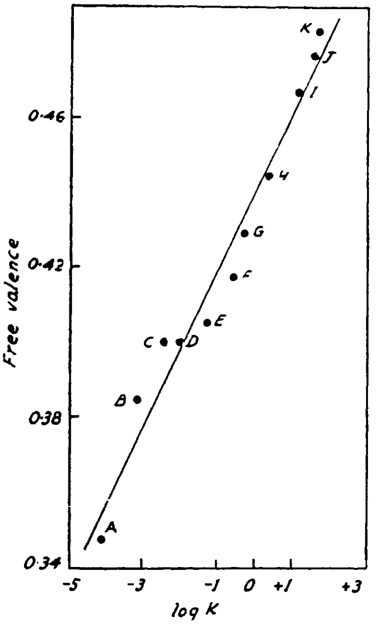


FIG. 17.

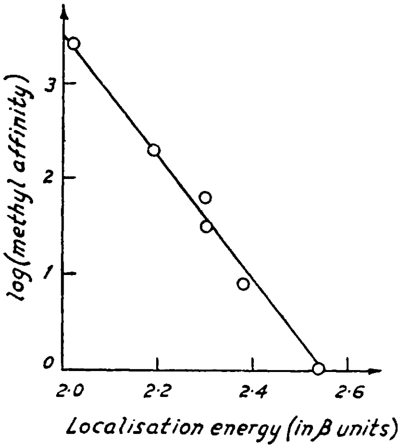


FIG. 16. *Variation of rate of attack by* CCl_3 *radical on various hydrocarbons plotted against calculated free valence. Experimental points were obtained by Kooyman and Fahrenhorst. This curve illustrates the way in which the free valence,* i.e., *residual affinity, governs free-radical reactions. A, Benzene; B, diphenyl; C, phenanthrene; D, naphthalene; E, chrysene; F, pyrene; G, stilbene; H, dibenzanthracene; I, anthracene; J, naphthacene; K, benzanthracene.*

FIG. 17. *Curve showing the linear relation between log (methyl affinity) of a series of aromatic hydrocarbons and the calculated localisation energy. The reaction is* $\mathrm{Me} + \mathrm{A} \longrightarrow \mathrm{MeA}$. *The observed fit of the experimental points on a straight line shows that the transition state is adequately described. It also enables us to decide at what part of the molecule the methyl group becomes attached.*

So far as stage (*b*) is concerned, the analysis is similar to that already described for heterolytic reactions. Let us suppose, for example, that in (XII*a*) we were bringing up a neutral free radical such as methyl to carbon C_r, instead of the positively charged NO_2^+ ion shown in the diagram. Structure (XII*b*) would be essentially the same, except that there would be one additional electron within the resonating part of the molecule. We should, in general, require a different localisation energy from the previous one, though we might expect to find a variation of the logarithm of the rate with the new localisation energy similar to that illustrated earlier for heterolytic reactions in Fig. 14. Fig. 17 shows some very recent results due to Levy and Szwarc. These authors considered the attack of methyl radicals on a variety of hydrocarbons, and were able to infer the existence of a relative methyl affinity for the reaction : $A + Me \longrightarrow MeA$, where A is an aromatic hydrocarbon. The plot in Fig. 17 shows conclusively that there is an almost strictly linear relation between the logarithm of the methyl affinity and the localisation energy. A curve of this kind could evidently be used to predict methyl affinities for molecules as yet not studied experimentally. And so once more wave mechanics has helped us to understand things which otherwise we could scarcely have hoped to regularize in so effective a manner.

There is still much for us to learn about chemical reactivity, and probably there will be new models to improve on the ones which I have just been describing. But whatever they may be in detail it seems almost inevitable that they should be essentially wave-mechanical in their general approach. Indeed no one can reflect on the progress that I have been describing in these last few pages without recognising that, at last, we are on the way to systematizing chemical reactivity just as earlier we were able to systematize valency and stereochemistry.

FIG. 18. *Molecules showing the* K-*region. Anthracene has no* K-*region but phenanthrene and benzacridine have. Carcinogenic activity seems to depend on the electronic distribution in and near this* K-*region*

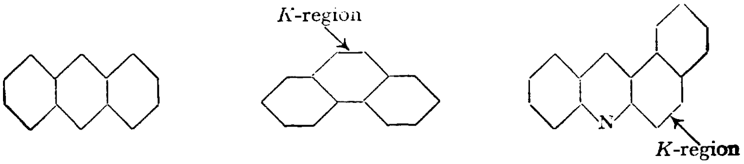
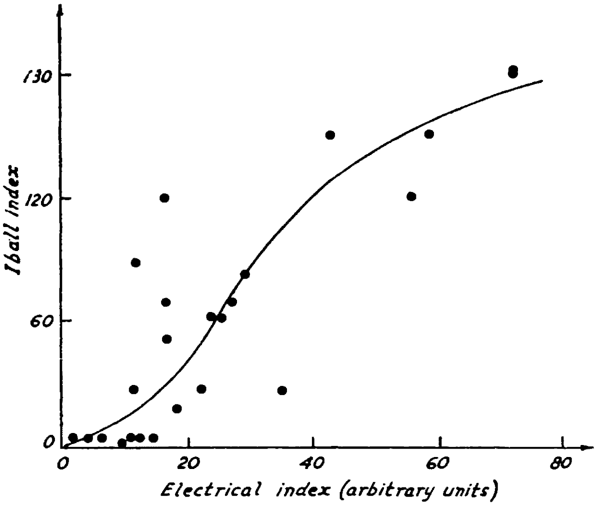


FIG. 19. *The variation of carcinogenic potency with electrical index of the* K-*region for some* 24 *different molecules. Each point represents a different molecule. The electrical index is purely theoretical, the carcinogenic activity, measured by the Iball index, is purely experimental.*



I have been speaking about past and present contributions of wave mechanics to our understanding of chemistry. But before I conclude I would like to say a little about possible future contributions. One conclusion at least seems quite clear : a very large part of that field which we call biological phenomena must eventually swim into this net. I am not thinking just of the normal metabolic processes such as oxidation, but also of the more abnormal ones. A start has been made with drugs, relating the efficacy of a drug to the distribution of charge within it. But perhaps the best example so far concerns the carcinogenic power of various aromatic hydrocarbons. Some of these molecules are exceedingly effective in causing tumours either by injection under the skin or even painting on the surface of the skin, of animals such as mice and rabbits. A large class of such molecules can be recognised where, following some pioneer work of Schmidt and Swartholm, we attribute the potency to their possession of a *K*-region (Fig. 18). Molecules without a *K*-region are seldom effective, those with it often are active. The activity may usually be increased by a methyl substitution at the periphery of the molecule : it may be reduced by replacement of a CH group by a N atom. Now the electrical properties of the *K*-region may be calculated, as described earlier in this lecture. It turns out, thanks to work by Mme. Pullman and Dr. Daudel in France, and Greenwood in England, that an " electrical index " can be devised. This index depends in a simple way upon the charges and bond orders in the *K*-region. If the index for a given molecule exceeds a certain threshold value, the molecule is likely to be carcinogenic : otherwise it is not. Fig. 19 shows how the carcinogenic potency, measured in terms of the Iball index, varies with the electrical index for the K-region. There is a fair amount of " scatter " among the points. To some extent this is almost inevitable in work of this kind, where different animals must be expected to react differently to similar doses of the carcinogen. But few people would be tempted to deny that some sort of correlation exists. This does not " explain " the mechanism, nor does it give us control, of cancer. But it is one step on the way, a pointer to what will eventually become yet one more field in which wave mechanics plays its part, along with other types of experience, in a fuller understanding of Nature's mysteries.

Conclusion.—And now I have finished with my illustrations : they are all particular, and they are only a tiny gleaning from that larger harvest which has been gathered in these last 25 years. What are we to make of them ? I believe that one characteristic shows most clearly of all. You must surely have been struck by the way in which, all along, modern wave mechanics has taken up ideas of the past, and refurbished them. How astonishingly fruitful have been those semi-formulated concepts of the classical chemists : and how necessary, in a sense, it has been for wave mechanics to give flesh and blood to the spirit which it has inherited. Think of the great names among the past that have come alive again in my short story—Mendeleef, Kekulé, Bayer, Werner, Thiele. Think of more modern ones—Ingold, Robinson, G. N. Lewis. At every turn we have seen how wave mechanics has taken their work and has added to it the quality of a deeper understanding. That of course is always how science proceeds, building the past into the present and enriching it thereby. We do see more deeply now into the meaning of our subject—what is really happening in chemistry. That, and not the calculation of a binding energy or a dipole moment, is the contribution of wave mechanics. Shall I be stretching truth too far if I say that without this contribution we should never have really appreciated the greatness of those giants of former days ?

And yet I must go further, difficult as it is to express what I feel in any succinct and convincing manner. I want to say that theoretical chemistry holds within itself the stuff of intellectual adventure. I know that I shall be saying this in face of certain criticisms. For there is an air of unreality about a good deal of our subject matter today. And it does not require our friends the logical positivists to give us pause. Will you reflect a moment on some of the things I have been saying ? I described a bond, a normal simple chemical bond ; and I gave many details of its character (and could have given many more). Sometimes it seems to me that a bond between two atoms has become so real, so tangible, so friendly that I can almost see it. And then I awake with a little shock : for a chemical bond is not a real thing : it does not exist : no-one has ever seen it, no-one ever can. It is a figment of our own imagination.

So also with some of my other pictures. Hydrogen I know, for it is a gas and we keep it in large cylinders ; benzene I know, for it is a liquid and we keep it in bottles. But what are these snakes of Kekulé, that bite their tails, these molecular orbitals that sprawl over the conjugated part of an organic molecule ? No-one has seen them, no-one ever will, even though I have drawn the diagram in Fig. 7 to show what they are like !

Here is a strange situation. The tangible, the real, the solid, is explained by the intangible, the unreal, the purely mental. Yet that is what we chemists are always doing, wave-mechanically or otherwise. The great Darwin once gloomily described his mind as a " machine for grinding theories out of a mass of experimental facts." With us, as Mendeleef said, the facts are there and are being steadily accumulated day by day. Chemistry certainly includes all the chemical information and classification with which most school text-books are cluttered up. But it is more ; for, because we are human, we are not satified with the facts alone ; and so there is added to our science the sustained effort to correlate them and breathe into them the life of the imagination. It was one of our presidents, Sir Cyril Hinshelwood, who at our recent centenary commemorations, spoke of chemistry as " that most excellent child of intellect and art." And it was another chemist, Kekulé, who could say : " Let us learn to dream, gentlemen, and then perhaps we shall learn the truth." This is why we have chemical theories, and always have had ; this is also why today's journey into the land of wave mechanics is no dull pedant's travel. It is the very stuff of intellectual adventure, in which creative ideas take shape and then illuminate both past and present with a new glory. For some of us, who have come more directly under the spell of the wave equation, it has satisfied us, so that even our long vigil in front of the calculating machine is not altogether unfulfilling. If, in the words of the poet, we have " scorned delights, to live laborious days," as, I fear, many of us have, it is because we have come to feel something about chemistry to which wave mechanics can contribute, and without which chemistry itself would be incomplete.