

Some Considerations on the Nature of Catalysis.

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ONE of the misfortunes of our time is the frequency with which public pronouncements are made to the effect that Science has no concern with values, and is an affair of bare truth and cold logic. In reality scientific laws constitute an expression of experience which has an essentially æsthetic character (compare Croce, "Estetica"; Collingwood, "Principles of Art," *passim*; Poincaré, "Science and Method," I, iii).

Scientific expression of experience may be roughly divided into the mathematical and the qualitative, the former having close analogies with music, the latter with the plastic arts.

The mathematical fundamentals are not directly derivable from anything else in experience: they resemble the subjects of a sonata, which may be woven and developed into forms of infinite variety and charm, but in the last resort must be appreciated for their own sake if the whole is to be significant. Two phenomena may for example be correlated in terms of the fundamental equation of wave mechanics, but, since, as far as is known, this equation is not expressible in terms of anything else,* the basic statement must be regarded as pleasing in itself if the analysis of Nature with its aid is to make any appeal.

Qualitatively, on the other hand, the nature of things can be expressed in terms of principles, analogies, models or other schemes which make an appeal to the mind because they appear to be related to ordinary perceptual experience; and the object of science is to order phenomena into a picture possessing the maximum, not only of coherence, but of what the artist calls significant form.

The qualitative method may be less powerful than the mathematical, but it is advantageous for the preliminary ordering of varied and complex sets of observations.

In this lecture I want to try and see how far chemical research has been able to give us an æsthetically satisfactory picture of the diverse group of phenomena which our early training has caused most of us to refer to as catalytic.

At a meeting of an eminent society, one of the elder statesmen once got up and discouraged further discussion by observing that he had heard innumerable theories of catalysis in his life, but never one which he could not disprove. One may feel that he, or those who tried to satisfy him, were seeking the impossible. There is no theory of catalysis. The only question is whether we understand catalytic phenomena well enough to arrange them into a picture of which we like the pattern.

Now, I have just spoken of liking patterns. People do like patterns, and that is why some Persian carpets are rightly regarded as among the most beautiful things in the world. The qualitative idea of pattern is therefore important and significant to us, and one in terms of which we willingly express our experience about the nature of things.

One of the fundamental facts about the world is that it is made up of a series of patterns of different kinds or orders; that the symmetry of these patterns is of vital importance in determining what happens in the world; and that the patterns themselves are struggling for preservation against a primordial chaotic motion which is ever tending to destroy them. These simple notions must first be examined.

To start at the beginning, one of the first of all questions is whether the world is made up of continua or of discrete systems. Whether a world of continua is thinkable at all is a question which might be worth exploring, but this is not the place, since we know that experimental science has decided in favour of discrete systems.† Given discrete

* The steps by which this equation can be led up to are only rough analogies, as indeed are the parallels with macroscopic experiments which suggested Maxwell's field equations.

† Wave mechanics is not a non-discrete theory. Even in its more general forms the number of co-ordinates has to be chosen with reference to the number of "particles": and numbers of nodes are related to quantum states.

units, the possibility of arranging them in spatial patterns follows. The units themselves are capable of interaction : the inwardness of this is again a profound philosophical question, but one outside the province of chemistry. Given interaction, it leads static systems of discrete units to group themselves into designs possessing elements of symmetry. For the units group themselves in such a way as to leave the interaction least play : that is, to assume a state of minimum potential energy. The differential coefficients of the potential energy function with respect to certain space co-ordinates are zero, a condition most naturally satisfied when the system has appropriate elements of symmetry in its arrangement. In a static world molecules would group themselves regularly into extended patterns constituting crystal lattices. More than one design with a relative minimum of potential energy can usually exist, so that polymorphism is the natural lot of matter.

But the world is not static. Even at the absolute zero the order established must be a compromise between the interaction and the zero-point energy, a fact responsible for the strange properties of liquid helium (London, *J. Physical Chem.*, 1939, **43**, 49). And at higher temperatures the thermal motion of the units tends to disturb or destroy the order. First, the orientation of the crystal state is lost, then the aggregation of the liquid state is lost, and finally chemistry ends with the resolution of the molecular patterns into atoms. At still higher temperatures alchemy replaces chemistry and the atomic patterns are resolved into their own constituents, often called ultimate particles, though whether these in their turn are also ordered designs, and so on in an infinite regress, it is useless to ask.

The phase change from gas to liquid takes place discontinuously at a sharply defined temperature, and that from liquid to crystal at another. These changes are largely influenced by the presence of nuclei—the first and simplest example of a catalytic phenomenon. Let us for a moment consider the nature of these phase changes. In a gas the molecules are moving too fast to aggregate together into a liquid, but since the molecules exert attractions on one another, there is a slightly greater chance, calculable by the Boltzmann principle, of finding two or more molecules close together than of finding them quite randomly spaced. There will thus be a few aggregates in the gas, but they will be temporary and rare. They increase in number and size as the temperature falls, and we might expect a continuous passage to something like a liquid, if a new factor did not enter. Order begets order, and the larger an aggregate becomes the greater is its attraction for fresh molecules, because it contains several attracting centres reinforcing one another. But just because it is larger, the aggregate is more likely to lose molecules and disperse. Two factors thus oppose one another : and either one or the other must be the greater at a given temperature. As long as the reversal tendency is called forth more strongly than the aggregating tendency by a small increase in size an equilibrium is reached. But as the temperature falls there comes a point at which a small increase favours the further aggregation more than it favours the reversal, and we have a discontinuity where small aggregates in equilibrium with single molecules begin to grow indefinitely. The relation of the liquid to the solid state is similar, only that here it is a question not of aggregation but of orientation. The forces between molecules tend to arrange them in symmetrical arrays which thermal agitation breaks up. But by Boltzmann's principle small elements of temporary orientation not only can but must exist in a liquid—and these are doubtless responsible for some of the X-ray structural effects observed in liquids. Once again order begets order, because, when one molecule is striving to set itself in a symmetrical way in relation to a second, its efforts are rendered easier if neighbouring molecules already conform to the regular design.* Thus here also there exists a limiting size for the orientated elements beyond which they will grow steadily rather than remain in equilibrium.

Catalysis enters into these phase-change phenomena in the following way. At a

* The principle of order begetting order, which follows from simple considerations of potential energy, is of course inherent in the a/v^2 term of van der Waals's equation and in the potential functions used by Bragg and Williams in their treatment of order-disorder transitions in alloys (*Proc. Roy. Soc.*, 1934, *A*, **145**, 699).

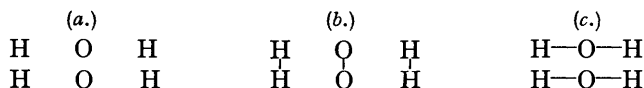
given temperature, in the less ordered phase there will always be a small equilibrium proportion of elements of the more ordered phase. In a liquid there are tiny patches of orientation fluctuating according to the hazards of the thermal motion. If we wait long enough, orientated patches of very improbable size may momentarily appear, and as soon as one beyond the critical magnitude is formed the whole liquid will crystallise. The only temperatures at which crystallisation is impossible however long we wait are those where even an infinite crystal will dissolve away into liquid. At any lower temperature crystallisation occurs after a time interval depending upon the improbability of building up an orientated patch of the requisite size. This is where the catalytic effects come in. In a supercooled liquid, where the probability of crystallisation is still small, the change can be induced by the addition of a nucleus of appropriate size, and, what is more striking, by particles of any foreign substance, such as dust, which adsorbs molecules of the liquid in such a way as to present an orientated patch of the appropriate size (Hinshelwood and Hartley, *Phil. Mag.*, 1922, **43**, 78). Similar considerations apply to the condensation of vapours. There are also polymorphic changes in solids. In a lattice the pattern with the lower potential energy does not always remain the stabler, because its spatial relations may become inconsistent with the necessary thermal motions of the molecules. It may, for example, be too close-packed to allow appropriate vibrations to occur with the proper amplitude, or there may be more complex reasons, such as those recently studied in the case of resorcinol (Robertson and Ubbelohde, *Proc. Roy. Soc.*, 1938, *A*, **167**, 136). When polymorphic changes occur, they are catalysed by nuclei in a way similar to that already described for condensation and for melting.

Now, chemical reactions are often accompanied by changes of phase, and not infrequently the phase change impresses some of its characteristics upon the reaction as a whole. In the type of reaction: Solid I = Solid II + Gas, such as is found in the decomposition of calcium carbonate or of silver oxalate, or the dehydration of copper sulphate pentahydrate, the rate of the whole chemical change is determined by the formation and growth of the nuclei of the new solid phase. We encounter such typically catalytic phenomena as the acceleration of the reaction by the addition of solid product, or even of suitable foreign solids upon the surfaces of which orientated layers of molecules of the new phase can be formed with lower activation energy than they could in regions where their potential energy was not lowered by the ordered nature of their environment. One might expect to find a relation between the effectiveness of solid additions and the closeness with which their crystal lattice and interatomic distances on certain planes resemble those of the solid reaction product. That such correlations should exist is very strongly suggested by the work of Bunn on adsorption and orientated overgrowths (*Proc. Roy. Soc.*, 1933, *A*, **141**, 567). It is also interesting to note that the effectiveness of nuclei may be modified by the presence of adsorbed ions or gases, a fact of significance in reactions of such practical importance as the decomposition of explosives and the reduction of silver halides in photographic emulsions. The principle that a chemical change may be largely determined by the growth of the new phase is further exemplified in the decomposition of arsine, strongly catalysed by a surface upon which arsenic is deposited.

So far, we have been dealing with those extended patterns which present themselves in condensed phases. But even in gases we have to consider those more elementary designs which the atoms form in their molecules. An assemblage of hydrogen atoms and oxygen atoms could, at a high temperature, remain nearly all in a state of complete chaos. But at lower temperatures two kinds of pattern formation occur in the gas, the hydrogen atoms and oxygen atoms respectively grouping themselves into pairs, on the one hand, or pairs of hydrogens ranging themselves symmetrically about single oxygens, on the other hand.

In Fig. 1 the systems (a), (b), and (c) are of decreasing potential energy in the order

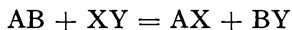
FIG. 1.



shown. At higher temperatures the thermal motion is violent enough to throw a proportion of the groups into the less stable forms (*b*) and (*a*). At temperatures below 1000° the balance is almost all in favour of (*c*). Yet the rearrangement of design (*b*) into design (*c*) may occur but slowly, and we have a typical chemical process which becomes subject to some very remarkable catalytic influences.

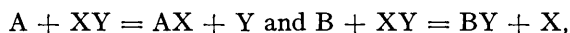
When liquids solidify, the principle that some degree of order creates fresh order leads to a discontinuous phase change. When, however, $2\text{H}_2 + \text{O}_2$ pass into the higher ordering of the system $2\text{H}_2\text{O}$, there is nothing in the statics of the process to encourage further regrouping of the same kind. Hence we do not observe a transition temperature but a continuous variation of equilibrium with temperature. In spite of the contrast in the equilibrium relations there is an interesting analogy in the dynamics of the two processes. Consider a polymorphic change, for example, of monoclinic to rhombic sulphur. One way in which it can, and sometimes does, occur is by the evaporation of one form and condensation of the vapour on the other: that is to say, complete resolution of an existing pattern and the reconstruction *de novo* of the other. But the process does not usually take place like this. Instead, at the interface, atoms or molecules detach themselves from one phase and reorientate themselves on the new structure without ever being free. Energy must be imparted to the lattice to initiate the disturbance, but in an amount much less than the heat of vaporisation.*

For the homogeneous regrouping



there exist the corresponding two mechanisms—complete resolution followed by reconstruction, on the one hand, or, on the other, a rearrangement something like what we see when we watch the bits of glass in a kaleidoscope, without any of the atoms ever becoming free. Although AX and BY may be more stable than AB and XY, the latter are more stable than the intermediate states, so that rearrangement will not generally occur until some considerable disturbance of the original structures has been brought about by the hazards of thermal motion. Hence the existence of what are called energy barriers, or activation energies.

Owing to the saturable quality of chemical forces, AB and XY are normally not very much interested in each other. If, however, some of the AB molecules have split up into atoms of A and B, these incompleting patterns wander round seeking a complement, and when they meet molecules they will readily enter into the reactions



after which the dispossessed X and Y wander round in their turn to prey upon AB molecules, the incomplete patterns eating their way into the less stable to form the more stable groupings. This is called a chain reaction. The possibility of this seesaw-like action whereby, once an unsatisfied and voracious atom is introduced, each of the less stable forms is cut into, giving a stable one and leaving another unsatisfied fragment to continue the process, is in a sense an example of order begetting order, though the action affects only the dynamics of the transformation and not the equilibrium.

Regarded in this light, chain reactions are by no means unexpected or fanciful things. They might even be much commoner than they are, for, often, it may be shown that once initiated they should proceed almost indefinitely. What militates against their more frequent occurrence is not the difficulty of the initiation process, but the fact that often the competing rearrangement process has an energy barrier so much lower than that required to produce free atoms or radicals that this less spectacular alternative mode of reaction completely by-passes the chain reaction.

The existence of these two types of reaction gives rise to some interesting and important catalytic phenomena.

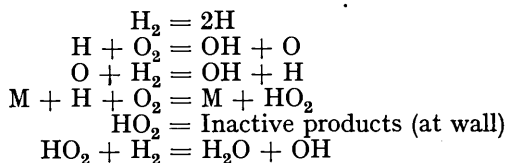
Such phenomena will be called forth, on the one hand, by agencies which generate, or

* Compare, *e.g.*, the recent study of the mercuric iodide transformation; Eade and Hartshorne, *J.*, 1938, 1636.

introduce, or favour the survival in the system of the kind of unsaturated and unsatisfied atomic groupings which lead to the propagation of chains; and, on the other hand, by all agencies which influence the energy barrier to be crossed in the ordinary transformation by internal regrouping.

Into reacting systems may be introduced atoms or radicals similar to those which take part in the normal chain reaction, for example, hydrogen atoms into the system $2\text{H}_2\text{-O}_2$. In the well-known catalytic action of nitrogen peroxide in sensitising explosions of hydrogen-oxygen mixtures one possible mode of action is by the initial production of oxygen atoms, though more complex fragments such as HNO may also play their part. One quite plausible mechanism for the homogeneous reaction between oxygen and hydrogen is that shown in Table I, in which there is seen to be room for a great variety

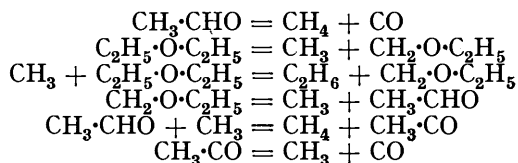
TABLE I.



of positive and negative catalytic influences—surfaces which facilitate the primary dissociations on the one hand, or the catalytic removal of radicals on the other; substances which generate hydrogen atoms, oxygen atoms, or hydroxyl radicals; substances such as halogens, which, by removing such atoms or radicals, exert a spectacular anticatalytic action.

As an example from organic chemistry we may take the fact that ether decomposes partly by a chain mechanism involving radicals, whereas acetaldehyde does not. In the presence of ether, the rate of decomposition of the aldehyde is several times greater than normal since fragments from the ether decomposition intervene in the reaction of the aldehyde (Table II).

TABLE II.

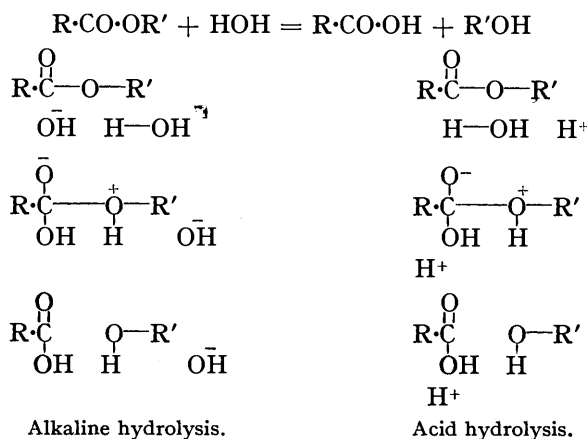


In all these examples we see how the rearrangement of pattern is facilitated by the introduction of unsatisfied fragments which set up this seesaw process of redistribution. In gases and on surfaces, and in general at higher temperatures, it is atoms and radicals which most readily fulfil this function. In solutions there exists a class of partially complete structures in the form of ions. Among these the hydrogen ion is pre-eminent because of the number and variety of structures to which the hydrogen atom may become attached by covalent linkages.

We have been taught by Brönsted and by Lowry that acids are substances capable of yielding, and bases of harbouring, protons. A vast number of reactions depend upon the addition or removal of the elements of water to or from other molecules or different parts of the same molecule, or upon the addition, removal or migration of hydrogen atoms. Now, if substances are added which can harbour or yield protons at call, then, just as in the chain reactions considered above, a relatively complex evolution depending upon the simultaneous satisfaction of several conditions in different molecules, or in different parts of the same molecule, may be replaced by a series of simpler processes in which the rearrangement of design occurs piecemeal, by a sort of nibbling action of incomplete structures demanding protons, or by the protons themselves derived from acids. As an example we may take the classical reaction of ester hydrolysis. According to the ordinary equation (Table III), the direct uncatalysed reaction would be a rearrangement

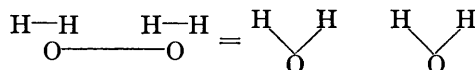
in which water is split up and the fragments added in two different places. In presence of hydroxyl ions or of hydrogen ions, or substances ready to yield them, schemes become possible (Table III) in which the rôle of the water is much simplified in that it yields

TABLE III.

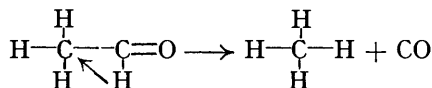


only one fragment, the complementary fragment coming from the catalyst. The catalysing ion is not so much regenerated as replaced by another ion left over from the water, a process presenting a distinct analogy with the radical or atom type of chain reaction. The fact that ions here play the part that atoms or radicals play in gas reactions is due partly to the internal electrical inhomogeneity of most molecules—a factor of great significance in determining their reactivity, as has been brilliantly shown in the electronic theories of organic chemistry. This may not be the whole story of acid-base catalysis, but it certainly seems to be an important part of it.

The evolutions which would be required in the one-stage reaction



are too complex for the parade ground of Nature, which prefers not to waste efficiency in the mastering of purely decorative company drill, so that in this example the chain mechanism has an easy preponderance. But in other examples this will not necessarily hold, and a comparatively simple evolution such as



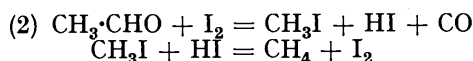
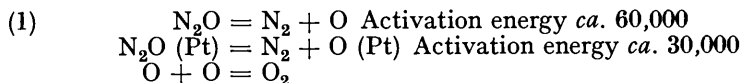
can compete effectively with the chain process. But before the change of pattern can occur the molecule must suffer dislocation and be supplied with energy—a potential barrier must be overcome.

There are various mechanisms by which this energy barrier may be lowered. The most important class is where something is present which has an attraction for the reaction product, strong enough to aid the abstraction of part of the atomic grouping from its original setting, but not strong enough to retain it permanently. Table IV shows some examples. Nitrous oxide decomposes on the surface of platinum: the attraction of the platinum surface aiding the removal of oxygen atoms from the nitrous oxide molecules, without, however, being able to prevent a steady escape of oxygen molecules into the gas phase.

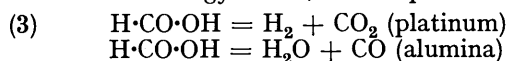
The second reaction in the table is general to most organic compounds with an active hydrogen atom near to a carbonyl group. The overall result is a catalytic decomposition by the iodine.

In the third example the easy accommodation of hydrogen on platinum, or of water molecules on the hydrate-forming oxide, guides the reaction in the one or the other course.

TABLE IV.



Over-all activation energy *ca.* 30,000 compared with 47,000 for direct reaction.



The importance of the accommodation of the reaction products on solid surfaces is reflected in a marked correlation between catalytic activity and surface spacings. The latter are also important in another way: in that, when their pattern is properly adapted to that of one of the reactants, they may facilitate its resolution into atoms or radicals which enter into further reactions:

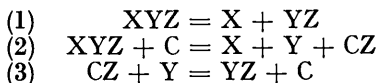


In these examples the interaction of catalyst and substrate by which the energy barrier is lowered is enough to give rise to intermediate compounds or adsorption complexes. But, seeing that the changes can in fact occur without the intervention of any catalyst at all, it is not surprising that they are often facilitated by encounters with substances which simply exert perturbing forces without giving rise to well-defined intermediate states at all.

If A-B is resolved into A and B when activation energy *E* is communicated to it, then, since anything which exerts strong forces on A-B will put it in a state where the potential energy of A with respect to B is no longer a minimum, the energy barrier for the decomposition may well be lowered.

To this class of actions, possibly, belongs the marked positive catalysis of the decompositions of acetaldehyde, chloral (Verhoek, *Trans. Faraday Soc.*, 1935, **31**, 1521), propaldehyde (J. H. Strawson, unpublished results), and ethyl bromide (J. E. Hobbs, unpublished results) by nitric oxide, whose radical-like character makes it exert forces on a variety of atomic groups. Our general picture of such a process is as follows (see Table V):

TABLE V.



In reaction (1), if the catalyst C exerts forces of the type which might tend to the series of reactions (2) and (3), then in presence of C reaction (1) may take place with a lowered activation energy. We see that a variety of mechanisms are possible which differ in degree rather than in kind. Sometimes more than one operate at the same time, and the preponderance of type shifts when one passes from one compound to a closely related compound—a fact responsible for much controversy and misunderstanding.

The lowering of activation energy by the influence of foreign molecules may not be an unmixed blessing, especially if the lowering is only produced by the co-operation of several members of the catalytically active species, as may happen in the case of reactions catalysed by surfaces or by the action of a solvent atmosphere. Suppose, to take a simple example, that *n* molecules of a solid heterogeneous catalyst, or *n* molecules of a solvent grouped round a reactant molecule, can by their united pulls reduce the activation energy from an original value E_0 to *E*, each contributing a reduction *e*, so that

$$\Delta E = ne$$

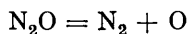
Now they will only exert the proper forces when they are properly placed, or when they are in the right phases of their own vibratory motions, and the chance that all co-operate will be proportional to the quantity p^n , where p is some fraction less than unity. The probability of reaction, although increased in the ratio $e^{ne/RT}$, is reduced in the ratio p^n . In the usual notation of reaction kinetics, $\Delta E = ne$, and $P/P_0 = p^n$. Eliminating n , we find $\Delta \log P \propto \Delta E$.

This is a form of the well-known correlation of activation energy and temperature-independent factor, for which various kinds of explanation may prove to be possible according to the particular case considered. But, in general, one might well expect that the more violent the activation process the less need will there be for other more subtle conditions to be fulfilled. This has been expressed by the following analogy : when a safe is opened by a key, little energy is needed, but precise geometrical conditions must be fulfilled : when, on the other hand, it is blown open, much more energy is used, but the exact geometry of its lock ceases to be of much importance (Hinshelwood, *Bull. Soc. chim.*, 1935, 2, 1786).

A similar dependence upon a simple algebraic function of the action energy of the *logarithm* of the temperature-independent factor follows from certain assumptions about the *time* relations in the reaction (Fairclough and Hinshelwood, J., 1937, 538), which are, in detail, of course, quite different from those discussed above. But the underlying principle is the same in each case, the *logarithmic* form of the relationship, whatever be the exact algebraic function of E , arising from the quite general assumption that the reaction depends upon certain *rarely fulfilled conditions*—in Fairclough and Hinshelwood's treatment the occurrence of a collision of abnormally long duration ; in the above, the suitable state of several surface atoms or solvent molecules.

Whatever be the precise mechanism of any given reaction, what is always necessary is that the activation energy should be communicated to the molecules, and this brings us to the question of the catalytic effects associated with energy transfers.

Nitrous oxide decomposes into its elements by a primary process



which occurs as the aftermath of a collision in which the necessary energy is given to the molecule. Collisions not only of nitrous oxide molecules among themselves but with molecules of argon, carbon dioxide, and other gases are effective, and the different substances are specific in their action. The efficacy of halogens in this respect is of a different order of magnitude from that of the other gases, and is probably dependent upon the mechanism described above. The halogens yield free atoms which seize the oxygen of the nitrous oxide, giving halogen oxides, stable with respect to their atoms, though not with respect to their molecules ; *e.g.*, $\text{N}_2\text{O} + \text{X} = \text{N}_2 + \text{XO}$ and then $2\text{XO} = \text{X}_2 + \text{O}_2$. The instability of XO with respect to its elements in the molecular form is of course no argument whatever against such a mechanism. Explanations of this kind do not, however, contribute anything to the understanding of the action of such gases as carbon dioxide or nitrogen, whose efficiency must be connected with their capacity for communicating energy directly to the reacting molecules. There are interesting, though by no means simple relations between these phenomena and those of energy transfer occurring in sound waves. Eucken has pointed out that the molecules between which such transfers occur most readily are often those where there is a potential mutual chemical reactivity (Eucken and K uchler, *Physikal. Z.*, 1938, 39, 831) : but the full knowledge of the laws governing these exchanges is still lacking. In particular, it may be mentioned that a quite remarkable difference sometimes exists between hydrogen and deuterium in their power of energy transference.

When a molecule is set in vibration by collision, there are different normal modes in which it may vibrate, and various combinations of these normal modes, so that the amplitudes of the vibrations in particular linkages may have very widely varying values immediately after the collision, and also varying subsequent histories. Now we have seen that energy transfers on collision are highly specific and depend upon the mutual forces, so that the collision complex may be thought of as a sort of temporary chemical

compound with more or less well-defined properties, and with its constituents tending to assume preferred relative orientations. As a result, it is not hard to imagine that the molecules may emerge from collisions with certain modes of motion preferentially excited, and that the particular mode preferred may depend upon the nature of the other partner in the collision. Further, it is conceivable that not one but several preferred modes, corresponding roughly to the location of the bulk of the energy in different links, may become excited according to the conditions of the initial encounter. Wherever the energy is placed, it will, of course, after subsequent collisions soon be redistributed. But from the point of view of chemical reaction what matters is the fate of the activation energy in the time between two collisions. This determines the chemical life of the activated molecule and the whole kinetic character of the reaction.

This supposed phenomenon of preferential kinds of energy transfer may possibly be the cause of a number of interesting subtleties in reaction kinetics which may be summarised as follows.

(1) Some reactions, such as the decomposition of nitrous oxide or of acetaldehyde, appear to be kinetically a superposition of more than one unimolecular change leading to the same products: this would be accounted for if different types of activated molecule had their characteristic mean chemical lives. (2) In such examples the relative contributions from the different types of molecule to the total observed reaction will depend upon the pressure. Accordingly, the mean activation energy is found to vary with pressure. On this point two more detailed observations are relevant: (a) The variation with acetaldehyde is small and its reality has been called in question: the variation has, however, been confirmed by R. E. Smith with deuterioacetaldehyde, where it is qualitatively similar and more pronounced. (b) The observed activation energy sometimes rises as the pressure falls. This cannot be explained by the well-known idea that the probability of reaction increases with the energy content of the molecule, since, as the pressure falls the molecules which contribute more and more to the total observed change are those with the relatively smaller reaction probabilities. Thus a qualitative rather than a merely quantitative difference between types of activated molecule is indicated. (3) With nitrous oxide the relative efficiency of argon, nitrogen, and carbon dioxide is a function of the pressure. It is as though argon and nitrogen were effective in producing the kind of active molecule which contributes most at lower pressures (longer chemical lives), but are helpless to produce those which contribute to the high-pressure change (shorter lives). The action of carbon dioxide, on the other hand, is more or less uniform over the corresponding pressure range.

These various phenomena have been referred to because they are catalytic in the sense of relating to the influence of one molecule on the chemical behaviour of another. The explanation to which allusion has been made, though not a definitely accepted one, is of interest in relation to the general thesis of this lecture, since, in connection with the mysteries of energy transfer, reference was made to possible preferred orientations of molecules at the moment of impact. Is it too fanciful to see here also the operation of the pattern-forming tendency even in the fleeting intimacy of the collisional encounter?

The experimenter usually seeks the simplest systems with which to illustrate the principles of his science, especially when he is interested in the verification of mathematical laws. But a strange disillusion often attends the mathematical analysis of even the simplest real systems, and, by way of compensation, some of the more complex systems may show well-defined phenomena whose qualitative significance far outweighs any numerical uncertainty in their interpretation. In this connection reference may be made to recent studies of polymerisation reactions, which lead to the formation of that type of molecule all-important in animate Nature.

The most complex of all the structures of Nature, and the most elaborate in their function, are those of living matter. To arrive at the understanding of processes such as those of vital synthesis and growth is a great problem, the incentive to attack which is made all the greater by the many dimly seen yet fascinating analogies with the simpler processes of the inanimate world. The adaptation of reactions to the surface patterns of catalysts has its analogy in the functioning of enzymes. The highly specific pharmaco-

logical action of complex organic compounds is often probably a question of the relation between the spacings in protein patterns and the spacings of certain active groups. Indeed, to use teleological language, is not one of the chief purposes of the countless organic compounds simply to provide Nature with a scaffolding of almost infinite variability by which her real weapons can be deftly and accurately applied to their mark? We have seen how pattern may beget pattern, and order may create order, and this reminds us of the fascinating problems of growth, of differential growth which is the basis of the morphology of natural things, of normal and of disordered growth and all that these mean for human life. We have seen that the pattern-begetting principle has both static and dynamic aspects, and we are led to wonder whether there is not a connection between this and the mysterious action of viruses.

But here we are becoming lost in speculation, valuable as a stimulus to further experiment: of doubtful utility in itself. To have paused for a moment, however, to reflect how many of the phenomena of chemistry are simply consequences of the eternal struggle between order and chaos, two principles so like the *yin* and *yang* of ancient Chinese wisdom, is perhaps not wholly unjustifiable, for generalities are only dangerous if they inhibit detailed work or discourage technical virtuosity. And under modern conditions this danger is not a very present one.
