Fifteenth Faraday Lecture.

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Relations between Stereochemistry and Physics.

NEARLY a hundred years ago, shortly before Christmas in the year 1837, a paper on " Induction " was read before the Royal Society, the 11th series of Faraday's experimental researches. The paper had been completed on the 16th of November and handed in on the 30th, and contains in its second part the discovery of the dielectric action of insulators. Although we know now that Cavendish had already observed the effect, this was at that time entirely unknown. It is a wonderful task, here in these rooms, where, right up to the present day, the spirit of Faraday has been so successfully guarded and nurtured, to be allowed to describe to you how the tree which Faraday planted has grown, and what rich fruits the chemist can now gather from it. Faraday was not one of those physicists who are satisfied with the discovery of new phenomena, and their exact description. The basis on which all his discoveries are built is a lively and detailed picture of how an action is propagated from place to place, and what alterations the smallest particles of matter experience. Perhaps such a basis is hard to find in the work of so many other researchers only because, in their published works, they coyly withhold the disclosure of the necessarily incomplete and hypothetical pictures with which they actually work. At any rate, in Faraday's case we are enabled, by means of his open and thorough notes, to follow the whole development of his discoveries, and the pictures which filled his mind during their growth.

Thus, his discovery of the dielectric constant leads him at once to a picture of what happens in the individual molecules of an insulator when they come under the influence of an electric field. He supposes that they come into a constrained condition, which only remains as long as the external field is applied, and consists in the particles being polarised, that is, as Faraday expresses it, " the particles assuming positive and negative points or parts." In point of fact, this is exactly the conception we have to-day of the dielectric action of simple atoms. If we take the helium atom as an illustration, it has in its normal state an electron cloud with centrally symmetrical density distribution. In an electric field, the nucleus is displaced in one direction, the electron cloud in the opposite, with some alteration in its density distribution. In this way arises the polarised state, which Faraday imagined. It is not unimportant that we should be clear on the fact that the atomic distortions experimentally producible are always very small. The dielectric constant observed in gaseous or liquid helium, for instance, can be accounted for if in a field of 300 volts per cm. the displacement of the nucleus is 2×10^{-16} cm., that is, less than one hundred millionth of the diameter of the atom.

If we transfer our attention from simple atoms to molecules, we must nowadays recognise that deformation is not the only cause of the observed dielectric action. When a piece of iron is attracted by a magnet, and the question is asked " Why does this occur ? " the answer is—The iron becomes magnetically polarised, in the same way as an insulator becomes electrically polarised in an electric field. But if the further question is asked " How does this polarisation arise ? " we reply that in iron elementary magnets (nowadays the spinning electrons) exist, and are oriented by the field. Strangely enough, for many years no one, in considering electrical polarisation, thought of the possibility that perhaps molecules could also be electrically polar in their natural state of equilibrium. In this case the polarisation obviously could not come entirely from the deformation of the molecules, but an orientation of the whole molecule would also play a part. That the existence of polar molecules is in itself probable, is clear if we think of the facts of electrolysis. HCl, for example, is dissociated in water into H^+ and Cl^-, and one may hazard a guess that the molecule which is formed by these two ions coming together even after the reaction will

show an excess of positive charge on the hydrogen side, and an excess of negative on the chlorine side. This would not have been a new idea even for Faraday. When he wants to form a picture of how electrolysis probably takes place in water, he speaks of a molecule of HO (for that was what water was then considered to be) which has oppositely charged sides and is rotated by the electric field.

The polar character of a molecule is clearly a kind of first step towards dissociation, and it can be expected that interesting connections with the chemical structure will exist. To be able to discuss these connections, however, we must first find a method of separating the effect of deformation from that of orientation; for in the dielectric constant as such only the sum of the two enters. We have such a method to-day in the observation of the variation with temperature. It is easily understood that the orientation will be progressively less complete as the disturbances from thermal agitation become greater. The law governing this temperature effect is completely analogous to that, discovered by Curie and theoretically explained by Langevin, governing the temperature variation of paramagnetic susceptibility. It was only necessary to carry over the same considerations to the case of dipole orientation, as was done by me some twenty years ago and by J. J. Thomson a little later. The deformation, we can show, does not vary appreciably with temperature, and the possibility of separating the two effects is thus given. To be sure, one must exercise some care in the experiments. One cannot simply without further consideration work with liquids. In these, the molecules are so close that they disturb one another strongly, especially if they are polar. We must therefore work with gases. If under these conditions it is found that, although the density is kept constant, the dielectric constant decreases with increasing temperature, then the molecule is polar. Its polarity can be measured by its dipole moment, and for this quantity values of the order of magnitude 10^{-18} e.s.u. are always found. That is what would be expected, for the charge of an electron is $4\cdot77 \times 10^{-10}$ e.s.u., and the extension of a molecule is of the order of 10^{-8} cm. It is of some interest to obtain an idea how much of the dielectric action is to be ascribed to deformation, and how much to orientation. H_2O is a typical polar molecule with a moment of $1\cdot85 \times 10^{-18}$ e.s.u. and we can calculate that in this case 95% of the dielectric action arises from orientation and only 5% from deformation. In his first work in 1837 Faraday had already tried to measure the dielectric constants of a series of gases, chemically as different as possible. He felt that this quantity ought somehow to depend on the chemical constitution of the molecule. He had even made an experiment on the influence of temperature on the dielectric constant of air. His method, however, was too inexact, and he could not find any effect.

Although measurements on the temperature effect are the most accurate means of determining the degree of polarity of the molecule, most dipole moments are at present measured by other methods. This is because measurements of the dielectric constants of gases are not very easy, since we are dealing with a quantity very little different from unity. The dielectric constants of dilute solutions of polar molecules in a non-polar solvent can be measured much more easily. The solutions can readily be made so dilute that the polar molecules no longer exert appreciable forces on one another. There only remains to be considered a possible influence of the surrounding solvent on the dipole moment. This is, however, as experiment has shown, in general very small, and has only recently been definitely established by exact measurements. Thus measurements on dilute solutions are often sufficient for the discussion of questions of molecular structure. But here also it is not enough simply to measure the dielectric constant; there remains still the problem of differentiating the effects of orientation and of deformation. This can be done, however, by a method which does not presuppose any knowledge of measurements at different temperatures. If we think of the experiments as being carried out at different frequencies, we should expect eventually to reach a frequency so great that the dipoles no longer follow the field. This is in fact the explanation given by the dipole theory for the anomalous dispersion which Drude first found in a series of liquids in the region of short electric waves. Now the dielectric constant is, according to Maxwell, identical with the square of the index of refraction, and this law is exactly true if both quantities are measured at the same

frequency. The deformation alone can thus be determined from the refraction, which gives us the possibility of estimating from the measured dielectric constant the part due to orientation.

Perhaps I may now be allowed to illustrate by a few examples what connections the dipole moment shows with the spatial structure of the molecules.

First of all, monatomic molecules are non-polar, and also diatomic molecules which are built up of two identical atoms, such as O_2, N_2, etc. If two unlike atoms are combined, however, the dissymmetry expresses itself in the production of a moment. Examples of this are HCl, HBr, HI, the moments of which have been measured by C. T. Zahn. Among triatomic molecules both polar and non-polar are to be found : H_2O, H_2S, SO_2, for example, have moments, while CO_2 and CS_2 show no moment. We shall expect, then, that the atoms of the first-named molecules form a triangle, while in the second group the atoms are on a straight line. This has been actually confirmed by the analysis of the band spectrum of H_2O. NH_3 behaves similarly to H_2O, and according to Watson's measurements PH_3 and AsH_3 do also. All these molecules are polar; they must therefore be in the form of a pyramid, at the apex of which one of the atoms N, P, or As is placed. In the case of NH_3 this is again confirmed by the structure of its band spectrum. The investigation of the series CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4, which was carried out by Sänger, gave results in complete agreement with the stereochemical pictures, according to which the four valencies of the carbon atom are directed towards the corners of a tetrahedron. CH_4 and CCl_4 are unpolar; the intervening members of the series have electric moments. If we remember that a diatomic molecule is always polar when made up of two unlike atoms, we arrive at a model, for example, for CH_4, in which the individual C–H bonds are each polar, but because of their spatial distribution their resultant is zero. If that is so, then the complicated aliphatic hydrocarbons, irrespective of whether the chain is branched or not, should all be unpolar. Smyth has proved that this is in fact so for the nine possible isomerides of heptane. Double or treble bonds between two carbon atoms are also themselves unpolar, as the examples ethylene and acetylene show. However, if a double bond occurs not exactly in the middle of a chain, but to one side, that is sufficient, as Smyth showed, to produce an electric moment. The electric measurements provide a good and simple method to distinguish between *cis*- and *trans*-isomerides. As Errera showed, only *trans*-dichloroethylene is unpolar, corresponding to its symmetrical structural formula ; *cis*-dichloroethylene on the other hand has a considerable moment. An obvious suggestion is to attempt to build up the total moment of the molecule from individual moments which are localised in the various atomic bonds, in the same way that forces are compounded according to the parallelogram law into a resultant. For this to be possible it is necessary that each bond should have a characteristic moment, the alterations in which, caused by more distant atoms, can be neglected. This is often very approximately true, as Wolf showed in a series of ketones, which all have nearly the same moment, corresponding to the C=O group. A good example of the vectorial composition of moments is provided by the dichlorobenzenes. Most strikingly, *p*-dichlorobenzene is unpolar like benzene itself ; in the case of the meta-compound, however, weak, and in that of *o*-dichlorobenzene stronger perturbations are found, which are obviously due to the close proximity of the two C–Cl bonds. A similar perturbation, only in still stronger form, is probably the reason that methyl chloride and chloroform have not the same moment. There would be equality, if the moments of the bonds were quite independent of each other and the tetrahedron were regular. That cases may occur where two equal moments in the para-position do not compensate each other is shown by Williams's measurements on quinol diethyl ether, which is definitely polar. The reason is obviously that the two valencies of the oxygen atom which join the C_2H_5 group to the benzene ring are at an angle to each other. This is in agreement with the fact that water, methyl ether, and ethyl ether are also polar. It is also in certain cases possible to distinguish electrically between positive and negative groups. Thus *p*-chloronitrobenzene has a moment equal to the difference of the moments of chlorobenzene and nitrobenzene, obviously because the two substituents have the same, probably negatively charged, end outwards. On the other hand, methyl *p*-aminobenzoate has a moment

equal to the sum of those of aniline and methyl benzoate, on account of the differing electrical characters of the two attached groups. It has been possible during the last few years to show that certain molecules have a moment which is not constant, but varies with temperature. The typical example is 1 : 2-dichloroethane, where the two CH_2Cl halves can rotate with respect to each other; this takes place, however, not quite freely, but with a preference for the *trans*-position of the two Cl atoms, as is shown by a more exact examination. Increase in temperature, then, causes all relative rotations to become more equally probable, and the moment becomes larger.

When a physicist sees in what a wonderful manner the spatial structure-formulæ set up by the chemists correspond to the actual structures, he must become filled with a desire to seek new methods which would allow of the determination of these structures, not only in their general plan, but also in their individual dimensions. It would be presumption if, in the rooms of the Royal Institution, I dared to speak longer of the attainment of this objective for the crystalline state than is necessary to express my sincere admiration for what has been achieved here by W. H. Bragg and in Manchester by W. L. Bragg. However, with your permission, I will give some account of the application of the method of interference to individual free molecules. That a single molecule, if fixed in space, would produce interference patterns when irradiated with X-rays is at once clear. The inter-atomic distances are of the same order of magnitude as the wave-length of the X-rays, and the path differences of scattered rays from the various atoms are therefore large enough. It is also unessential for the effect whether the atoms are ordered in a lattice or form any other fixed geometrical figure. But if the molecule, during the experiment on scattering, takes on, one after the other, all possible orientations, then the interference pattern will of course change with the orientation, and one might guess that all the characteristic maxima and minima would be thereby destroyed. This fear is, however, incorrect, as a short calculation shows, and as Ehrenfest proved simultaneously with myself. Even when all orientations are equally probable, maxima and minima of the intensity of the scattered radiation should still be observed if observations are made in the direction of increasing angle between primary and secondary rays. The first experiments were carried out a few years ago on carbon tetrachloride vapour. Carbon tetrachloride was chosen because the distribution of intensity becomes simpler as the number of inter-atomic distances in the molecule gets smaller. Now the CCl_4 molecule is supposed to be a tetrahedron; there are thus only two distances, C–Cl and Cl–Cl. Further, theory shows that each inter-atomic distance produces a scattered intensity proportional to the product of the scattering factors of the two end atoms, and these scattering factors are, at least for small angles, proportional to the number of electrons in the atom. This means that the intensity of the C–Cl interference pattern is relatively small, and the molecule behaves almost as if in it one single inter-atomic distance, namely, the Cl–Cl distance, occurred four times. The choice of vapour rather than the much denser liquid for the experiments naturally causes experimental difficulty on account of the low scattered intensity. But this is not to be avoided. In liquids we obtain not only interference between rays coming from the various atoms of the molecule. The radiation from a whole molecule interferes as well with that from the neighbouring molecules, and in experiments with liquids a superposition of effects occurs, which means that inferences concerning the molecular structure cannot be drawn simply and in a manner easy to follow. In a vapour at atmospheric pressure the intermolecular interference is no longer observable, and the whole interference pattern is exactly that which would be given by a single molecule, only its intensity is proportional to the total number of irradiated molecules.

In the experiment on carbon tetrachloride, three distinct interference maxima at 36°, 67°, and 110° angle of scattering were obtained, when Cu radiation of wave-length 1·54 Å. was employed as primary radiation. In order to interpret such a photograph exactly we may not consider the atoms as scattering points as is done in the most simple form of the theory. The scattering is caused by the electrons, and these occupy in the atom a space whose diameter is of the same order of magnitude as the wave-length used. Interference will therefore occur between the various beams which come from different regions of a

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single atom. This can be allowed for by the use of a factor known as the atomic form factor, which is to-day exactly enough known for all atoms. Besides this, X-rays are not only scattered coherently, with the same wave-length as incident; part of the scattered radiation consists of incoherent waves, which have an altered wave-length and correspond to the Compton effect. This Compton radiation gives a continuous background, increasing slowly in intensity with increasing angle of scattering, but without maxima and minima. If these details are taken into consideration, it is possible to carry out really accurate measurements of the inter-atomic distances. In this way Bewilogua, using the angular situations of the three maxima mentioned above and of the three corresponding minima of the intensity, found six values for the distance Cl–Cl which gave an average of 2·99 Å., and singly varied less than $\pm$ 1% from this average. Recently van der Grinten has made and discussed new measurements on carbon tetrachloride. In particular, care was taken that the incident radiation should be strictly monochromatic, by obtaining it by reflexion at a rock-salt crystal. The intensity curve which he obtains experimentally falls very accurately on the theoretically calculated curve over its whole length, so that one can now regard the tetrahedral character of the CCl_4 molecule as also proved by the physical inter-ference measurements.

But not only X-rays will produce molecular interference patterns. As is well known, streams of material particles can also, according to L. de Broglie, interfere with one another. For this reason Mark and Wierl allowed cathode rays to be scattered by carbon tetra-chloride vapour, and showed that interference bands were produced exactly similar to those from X-rays. The only difference is that the de Broglie wave-length corresponding to the usual voltage of 30,000 is about 20 times smaller than that of the X-rays normally employed. The maxima and minima occur therefore at about one-twentieth of the previous angles. Wierl deduces from his measurements a value for the Cl–Cl spacing in exact agreement with that found by Bewilogua. The scattering power of an atom is many times larger for cathode rays than for X-rays. On this account an exposure which would take several hours with X-rays can be made in a fraction of a second with cathode rays. Theory prophesies, however—and the measurements so far obtained have confirmed it—that the interference bands obtained with cathode rays will be less distinct than those obtained with X-rays.

In spite of the short time during which the interference method for the investigation of the structures of free molecules has been available, a large number of structures have already been analysed. A few examples may be given, to show which questions have first been answered.

Besides carbon tetrachloride, Wierl investigated the tetrachlorides of silicon, germanium, titanium, and tin. All these molecules are tetrahedral, but the Cl–Cl distance increases with increasing atomic number of the central atom, varying from 2·98 $\pm$ 0·02 Å. for CCl_4 to 3·81 $\pm$ 0·05 Å. for $SnCl_4$. Quite recently, Brockway and Pauling investigated the hexafluorides of sulphur, selenium, and tellurium and demonstrated that the fluorine atoms lie at the corners of a regular octahedron; the F–F distance increases from 2·23 in SF_6 to 2·59 in TeF_6. In quite early experiments Bewilogua examined the molecules $CHCl_3$, CH_2Cl_2, and CH_3Cl as well as CCl_4. My first interest in these experiments was this, that I wished to know how many heavy atoms must be present in a molecule in order to be detectable by interference measurements. It was found that the smallest possible number, two, sufficed. This has since been confirmed by Richter in his photographs with Cl_2, and also by Wierl's electron photographs. One can therefore practically examine any inter-atomic distance in a molecule, in which one is specially interested, by substituting a heavy atom at each end of this length. A more exact discussion of the diagrams resulted in showing that the Cl–Cl spacing, which is in CCl_4 in round figures 3·0 Å., increases to 3·1 Å. in $CHCl_3$ and to 3·2 Å. in CH_2Cl_2. Other considerations make it unlikely that the C–Cl distance alters. It fits in better with the dipole measurements to suppose that the tetra-hedron has become irregular, and the valency angle has been increased, as if the Cl atoms repelled each other. Wierl could not find this increase of spacing in his electron photo-graphs at first, but I hear that Dornte in Berkeley has confirmed the increase from more recent

electron photographs. The *cis–trans*-isomerides of dichloroethylene were investigated, because according to the chemical formulæ *trans*-dichloroethylene should show a larger Cl–Cl spacing than the *cis*-compound. This is in fact the case, the interference photographs show clearly the difference between the two isomerides. Benzene is a somewhat more difficult substance, because it is characterised by three different inter-atomic distances. It could be shown, however, that the interference pattern corresponds to the regular hexagon, and that in the transition from benzene to hexachlorobenzene the shape of the interference curve characteristic for the hexagon remains essentially unaltered, and the maxima and minima are simply displaced towards smaller angles, corresponding to the increased Cl–Cl spacing. It may be noted also that the C–C distance is, according to Wierl, 0·1 Å. smaller in aromatic compounds than in aliphatic. As the last example we may mention the interesting molecule of 1 : 2-dichloroethane, in which the two CH_2Cl groups are free to rotate with respect to each other. Since this rotation alters the Cl–Cl distance, interference photographs can give information concerning details of the rotation. Ehrhard has made *X*-ray photographs, and Wierl electron photographs. The result shows that not all angles of rotation are equally probable, but the *trans*-position of the Cl atoms is preferred.

Through the quantum theory physics has at last found a way of approach to the chemical idea of valency. The stereochemist sees nowadays with satisfaction how new methods of experimental physics confirm his structural formulæ. The process of amalgamation between chemistry and physics is obviously well under way, so much so indeed that we are often not sure whether to call the boundary region physical chemistry or chemical physics. In these circumstances we turn our gaze again to Faraday, who was chemist and physicist at once, chemist even in the sense of a tentative stereochemistry. For this, reliable evidence exists. I was especially struck by a statement in the 14th series of his experimental researches. There he attempts to explain to himself the molecular processes involved in electrolysis, and says of a certain compound which he considers to be $SnCl_2$: " For when a particle of tin combines with two of chlorine, it is difficult to conceive that there should not be some relation of the three in the resulting molecule, analogous to a fixed position, the one particle of metal being perhaps symmetrically placed in relation to the two of chlorine . . ."

For this reason, may I hope that you will regard also the last part of my account as a tribute of respect which I owe to Faraday, the great master, a model for physicists as for chemists ?