[FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF LIVERPOOL.]

A THEORY OF CHEMICAL REACTION AND REACTIVITY.

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During the last ten years a great number of papers have been published describing the absorption spectra of organic compounds, and the majority of these publications have dealt with the constitution of these compounds, the assumption being made that there exists a definite correlation between the primary structure of the molecule and the type of light absorption which it exerts. One of the oldest theories of constitution is the quinonoid theory, which categorically attributes visible color to compounds which possess a constitution analogous to that of ordinary benzoquinone. It is hardly necessary to point out the danger that attends the use of a physiological sensation of color as a criterion of constitution in this connection. There often exist pairs of compounds which to the eye have exactly the same color and yet when their absorptive power towards light is spectroscopically examined it is found that the compounds are materially different. As a matter of fact the application of accurate spectroscopic methods to the problem very soon revealed considerable difficulties and proved that the quinonoid theory is by no means as secure on its foundations as had previously been supposed. Some of these difficulties have been recognized by Hantzsch, who has put forward theories which differ to a certain extent from the old quinonoid theory. Hantzsch, however, still maintains that there is a definite correlation between light absorption and structure, and when he succeeded in preparing five differently colored alkali metal salts from one colorless acid he attributed essentially different formulas to them all.[1] But it was not long before Hantzsch also found himself in difficulties, because after he had obtained a number of different modifications of *m*-nitroaniline he was obliged to confess that there are not enough different formulas to go round.[2] It is not necessary here to specify the essential points of Hantzsch's theories and sufficient has already been said to indicate that the fundamental basis of them, and the older (quinonoid) theory, is the assumption of the existence of an absorption structure correlation. It may be pointed out, however, that there is not one particle of evidence to show why any one of the structural formulas devised by Hantzsch should possess a color different from that of any other. Indeed, recent investigations into the problem of light absorption by organic compounds by no means favor the view that there is any direct relation between absorption and constitution, if such relation is held to mean that when a colored salt is obtained from a colorless acid or base the parent substance

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[1] Hantzsch, *Ber.*, 42, 966 (1909); Hantzsch and Robison, *Ibid.*, 43, 45 (1910).

[2] *Ber.*, 43, 1662 (1910).

has changed its constitution in the salt. The principal outcome of this work is the establishment of a definite relation between light absorption and chemical reactivity. The evidence obtained is so strong that it is necessary to formulate a new theory to account for the observed phenomena, a theory which must at the same time embrace all those experimental facts which appear to support the color constitution relation. It is proposed in this paper to develop this theory from the chemical side, and only briefly to indicate its bearing upon the problems of light absorption.

It follows from the Zeeman effect, that is to say, the resolution of spectrum lines into doublets, triplets, etc., in a powerful magnetic field, that the particles or atoms producing these lines must possess magnetic fields of their own. In a paper dealing with the pressure shift of spectrum lines, Humphreys[1] discusses these atomic fields and shows that they are capable of explaining the phenomena of the Zeeman effect and also of the shift of spectrum lines under the influence of pressure. While these atomic fields have been taken into consideration in explaining such physical phenomena as the above, their influence upon the properties of molecules does not seem to have received notice. These fields must possess both a polar and a quantity factor, and it would follow that atoms which are markedly different in their chemical properties must differ markedly in the polar factor of their force fields. When two such atoms approach one another sufficiently closely, the force lines due to their respective force fields will tend to condense together with loss of energy and with the formation of a condensed field. A potential gradient will thus be set up and it seems possible that if this gradient be sufficiently steep a transference of one or more electrons will take place from one atom to the other, whereby a true chemical compound of the two will be established. Primary valency would thus only mean the transference of one or more electrons along the potential gradient which is set up by the condensing together of the force lines arising from the electromagnetic fields of two atoms of opposite type that are brought close together. On these lines, therefore, it may be said that the chemical reaction or combination between the two atoms is due in the first instance to the force fields appertaining to the two atoms.

Turning now to the compound that is produced, it is evident that the general stability will depend upon the condensed force field between the two atoms. Before such a compound can be decomposed or resolved into its elements this force field must be opened up, and, therefore, the greater the number of force lines that are condensed within the field the more stable will be the compound and the greater the amount of energy required to decompose it.

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[1] *Astrophys. J.*, 23, 233 (1906).

In the general case of any molecule it is clear that the independent existence of the several force fields due to the atoms composing the molecule must represent a metastable condition. A certain amount of condensation of the force lines of the various force fields must take place with the escape of energy and the establishment of a closed molecular force field which will determine the properties of the molecule. If a molecule of one compound reacts with a molecule of another compound such reaction takes place by virtue of their respective force fields. If these fields are of opposite type the force lines of the two will condense together with the result that an addition compound of the two is formed. Just as in the case of the two atoms dealt with above, this addition compound will possess potential gradients and if these be sufficiently steep there will follow a transference of one or more electrons between the constituent atoms with the formation of new chemical individuals.

Perhaps an example will make this more clear, but in quoting such an example it must be remembered that reactions which take place by means of ions are for the moment excluded for reasons that will presently be made clear. We may take a perfectly general case of an acid HX and a base YOH. According to the present theory the first stage of the reaction will be the formation of the addition compound YOH,HX, arising from the condensing together of the force lines of the molecular fields of YOH and HX. Within this complex a potential gradient will exist and if this is steep enough the electrons will rearrange themselves with the formation of XY,H_2O. Another way of stating the same fact is to say that the change within the complex will take place if the system XY,H_2O has less energy than the system YOH,HX. If it has less energy, then a new chemical individual XY is formed and we say that a chemical reaction has taken place.

A very important fact may be noticed here in passing, namely, that a chemical reaction will only occur when the gradient within the complex first formed is sufficiently steep to cause the electrons to migrate. The complex between the two original molecules will of course be formed whether or no a true chemical reaction occurs, for the formation of the complex depends only upon the force fields of the two molecules that are brought together. In this way we are enabled to recognize a very large gradation between the condition when a chemical reaction occurs between two molecules and the condition when, owing to their force fields being exactly the same, the molecules have no mutual influence whatsoever. This recognition of mutual influence between two molecules when no specific chemical reaction occurs is of great importance both in pure chemistry and in the phenomenon of light absorption.

According to the above view the reaction between molecules depends upon their force fields. But it has been already shown that these force fields normally must be more or less closed, according to the measure of the polar and quantity factors of the several fields of the constituent atoms. The reactivity of any molecule must vary inversely as its force field is closed. If, owing to the inherent properties of the atomic fields, the force lines can form a completely closed system, then the molecule will possess no reactivity. If two such molecules with completely closed fields are brought together it is evident that they can have no influence upon one another, and, further, this absence of influence will be entirely independent of what their chemical properties in solution would lead us to expect. It would seem that in this fact is to be found the explanation of the absence of any reaction between HCl and NH_3, 2 H_2 and O_2, 2 CO and O_2, etc., in the complete absence of water. The first case is peculiarly interesting since the known acidic and basic properties of these two gases would at once lead us to expect that they should immediately combine to form NH_4Cl. The other cases mentioned might be criticised from the point of view that in each of them the molecules of at least one diatomic gas have to be resolved into atoms before the chemical reaction can proceed. The HCl and NH_3 reaction is free from that possible objection, for it is purely one of addition, and yet it does not take place if the gases are dry. According to the present theory the reason why these two gases do not combine together lies in the fact that the molecules of both possess completely closed force fields and, therefore, they can have no influence upon one another. An exactly similar explanation holds good for the converse case, namely, that NH_4Cl vapor does not, when dry, dissociate into HCl and NH_3. The molecules of NH_4Cl must possess a completely closed field which is not readily opened up and, therefore, when the substance is converted into vapor the molecules do not dissociate.

On the other hand, although a certain amount of condensing together of the force lines due to the atomic fields must occur *ex hypothesi*, yet by no means must the resulting force fields always be entirely closed. When the maximum possible condensing together of the force lines has occurred with the maximum possible escape of energy, there may be left over an uncompensated balance of force lines. This residuum will determine the properties of the given molecules and will give rise to what has long been recognized by chemists as residual affinity. Although this residual affinity has proved itself a very useful friend to chemists, yet it has always been of a somewhat mysterious, not to say mystic, nature which in moments of doubt as to the true dogma has from time to time been invoked to play the role of a *deus ex machina* and relieve the exigencies of the situation.

On the present theory, the whole of the reactivity and chemical properties of atoms and molecules is due to the force fields which have been proved to exist in the immediate neighborhood of the atoms. Chemical union between atoms, chemical reaction between molecules, both are due to these force fields, and valency itself would seem not to be the *causa causans* of such reactions but to be a resultant effect. Valency in its stoichiometrical meaning is due to the interatomic rearrangement of the electrons when the potential gradients within the addition complexes first formed are sufficiently steep and the electronic transference results in a smaller energy content of the product. The so-called residual affinity is the uncompensated residuum when the maximum possible condensation of the force lines of the molecule has taken place. When this residuum is vanishingly small the given molecule exhibits no evidences of chemical reactivity, but when, as is more usually the case, the residuum has a finite value the molecule does possess an observable and measurable reactivity.

Among chemical compounds which possess a balance of uncompensated force lines or residual affinity water may be mentioned as a very typical example. The extraordinary power possessed by water of forming addition complexes with other molecules is too well known to need emphasizing here, but one or two points in connection with the hydrating power of water may be described. In the first place Humphreys, in his paper referred to above, showed that one of the results of the existence of the electromagnetic fields is the tendency of the mutually attracting faces of the atoms to be brought near together, and of the mutually repelling faces to be kept comparatively far apart. When, therefore, a molecule of a salt hydrates itself, owing to the formation of a closed force field between water and salt molecules, it is obvious that the distribution of the molecules must be symmetrical. Barlow and Pope[1] have shown that in such cases as $Na_2CO_3H_2O$ and $Na_2CO_37H_2O$, $NiSO_46H_2O$ and $NiSO_47H_2O$ the addition of the water molecules takes place entirely along one axial direction of the crystal, that is to say, only one axis of the crystal grows on hydration. This, as readily can be seen, is an absolutely necessary sequitur from Humphreys' deduction. Indeed, it would seem that the conception of electromagnetic force fields gives a complete and rational explanation of all Barlow and Pope's observations, but this cannot be entered into here.

Again, the question of the hydrolysis of salts may be considered in connection with the present theory. When a salt hydrates itself there is formed a complex field due to the condensing together of the force lines of the two components, salt and water. In this complex there are two gradients to be considered, one between the component atoms of the salt and the other between the salt and the water. As long as the former is very steep, as it is in the case of the salts of strong acids and bases, then the tendency to hydrolyze will be a minimum. If, how-

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[1] *J. Chem. Soc.*, 89, 1675 (1906).

ever, the former gradient is shallow, the gradients between the salt and water become relatively steeper. In such a case a rearrangement of the electrons will occur with the formation of acid and base from salt and water. The hydrolysis of a salt has been taken as a typical example of a chemical reaction, for it shows the rationale of the phenomena on the lines of the present theory.

From what has already been said, it is obvious that if the closed force field of a molecule be opened or unlocked its reactivity will be enhanced. This unlocking may be brought about in two ways, namely, by the use of a substance possessing residual affinity or by the action of light. If the molecules of a compound, the force fields of which are closed, be brought into the neighborhood of the molecules of another compound possessing residual affinity the force lines of the latter will interpenetrate the closed fields of the former, with the result that they will be opened and endowed with enhanced reactivity. The simplest case to consider is that of the solution of the closed force-field molecules in a solvent possessing residual affinity. The free force lines of the solvent molecules will interpenetrate the closed fields of the solute molecules, with the result that these will now be capable of reacting with any other suitable substance dissolved in the same solvent. Clearly, however, the case is an absolutely general one. The tendency of molecules possessing residual affinity will always be to open up the closed fields of other molecules whenever the two molecular types are brought together, whether an actual solution is formed or not, with the result that the previously closed fields become endowed with reactivity. The bearing of this upon chemical phenomena may be considered from three points of view.

In the first place the enhancement of the reactivity of the substance brings us at once to catalysis and indeed gives us an explanation of this phenomenon. Catalysis may be looked upon as the enhancement of the reactivity of one or more of the components of a reaction and a catalytic agent is a substance which, from the nature of its residual affinity, has the power of opening up the closed fields of the reactant molecules to a greater extent than they otherwise would be under the prevailing conditions. Conversely a negative catalyst is an agent which has the power of closing the force fields to a greater extent than they otherwise would be. Some advantage is held by this theory of catalysis because it gives a rational explanation of the positive and negative effects without the somewhat cumbersome conception involved in the ordinary theory of negative catalysis, namely, that a negative catalyst is one which destroys a positive catalyst assumed previously to be present.

A second point arises when the difference in type is considered of the force fields of the two groups of molecules, solute and solvent. It is clear that if the solute possesses basic characteristics the most suitable solvent for the purpose of opening it up will be one the residual affinity of which is acid in type, and, conversely, a solute of acid type will most readily be opened up by a basic solvent. On the other hand, a solute the force field of which is not pronouncedly basic or acid will tend to be opened both by an acid and by a basic solvent, but the manner in which the opening up takes place will be different in the two cases. The potential gradients existing within the closed system of the solute will be attacked differently by the force lines of a basic and of an acid solvent. This will result in a difference between the reactivity of the solute in the two cases and, indeed, the solute will present amphoteric properties. An amphoteric substance, on the present theory, is to be defined as one the closed field of which is opened in a different manner by a basic and an acid solvent. A typical example of an inorganic amphoteric compound is aluminium hydroxide, the reactivity of which is different in acid and basic solvents, while an example of an organic amphoteric compound is nitrobenzene, the force field of which is opened quite differently by sulfuric acid and by dimethylaniline.

A third aspect of the opening-up process concerns the case when the solute possesses at least one steep potential gradient, and the residual affinity of the solvent differs markedly from that of the two atoms of the solute between which the potential gradient exists. Such cases as this occur more particularly in inorganic chemistry with the acids, bases, and salts. If the opening-up process be carried to the farthest possible extent the logical consequence will be the complete resolution of the solute molecule into two entities, each of which will be fully solvated owing to the new conditions under which the force lines have formed condensed systems with those of the solvent. As a result of the existence of the potential gradient in the original molecule one or more electrons will have migrated from one atom to the other, and, therefore, the two entities formed by the complete resolution of the closed field of the solute molecule will carry equal and opposite charges of electricity. Ionic dissociation, therefore, is a logical sequence of the force-field theory. The theory, however, gives a different perspective of chemical reaction and reactivity from that presented by the ionic dissociation hypothesis. Whereas the latter attributes all chemical reactions between dissociated salts to the ions, as if herein were to be found the driving force of such reaction, the electromagnetic force-field theory attributes all reactions and reactivities to the opened-up systems of the molecules independently of whether ions are formed or not. The formation of ions according to this theory is a secondary phenomenon running concurrently with the primary cause of reaction.

The second method of opening up the closed fields is by the influence of light. Due as they are in the first place to the rotation of the electrons of the constituent atoms, it follows that the force fields must be capable of absorbing those rays of light which have the same vibration frequency as that of the electrons. The light in being absorbed does work upon the closed fields and opens them, and this gives a rational explanation of the selective absorption of light. An example of the opening up of the closed molecular force field by means of light is found in the union of hydrogen and chlorine. When in the dark and at ordinary temperatures, the force fields of these gases are closed and they have no action upon one another. Under the influence of ultraviolet light the reaction to form HCl proceeds owing to the opening of the closed fields by the light, and the amount of combination is a function of the amount of the light energy that is absorbed.

In considering the work done by the light upon the molecules by which it is being absorbed, it was pointed out that the effect produced is to open up the closed fields of these molecules. When a substance is dissolved in a solvent it is clear that there must be set up generally an equilibrium condition. Some of the molecules will have their closed fields opened while others will not, and so an equilibrium is established, and upon this equilibrium the reactivity of the system depends. When such a system absorbs light the tendency will be for the light to increase the number of molecules having their fields open. The equilibrium previously existing is, therefore, shifted towards the reactive side, a new photodynamic equilibrium being established. The whole of the phenomena of photocatalysis can thus be explained on these lines.

The mechanism of the opening up of a closed force field may now be dealt with in greater detail. The general statement has been made that a given closed field may be opened by the influence of a solvent or by the influence of light, the action of the light being evidenced by the selective absorption of definite rays. If now the case be considered of a complex molecule, it is clear that the force field of that molecule will be complex. There must exist in such a complex field a network of potential gradients and the influence of the solvent in opening up the field will depend upon the nature of that solvent. It would be expected that the influence of a solvent upon a complex force field would be progressive, and that it would attack various portions of the field in turn. It indeed follows that the opening up of a complex field must take place in definite stages, the number of stages depending upon the complexity of the field. Each of these stages will be influenced by light so that each stage must be characterized by its power of absorbing definite light rays and may be differentiated in this way because the light waves absorbed by the various stages will be different. Each of these different stages mark steps in the opening up of a given force field and, therefore, are functions of a given molecule with a definite primary structure. The number of possible stages will depend upon the complexity of the force field and these stages in turn may be called into play by the use of suitable solvents. Very typical examples of compounds which are opened up in stages are the β-substituted naphthalene compounds, which as a rule in alcoholic solution show three absorption bands. Three stages in the opening up of the force fields must, therefore, coexist in the solvent, each one characterized by its power of absorbing definite rays of light. In concentrated sulfuric acid solution the absorption spectrum is very different, since other stages are called into play, but usually one of these stages at least is common to the two solvents.

Certain experimental evidence may now be presented which gives very clear and decisive support to the theory. Since the opening-up process takes place in stages, and since each stage is characterized by its light absorptive power, it should be possible to follow the course of a chemical reaction and to trace the appearance of the stages by optical methods. Each opened-up stage must possess a definite reactive power towards other molecules. It is probable that a particular and definite stage must be reached before any specific reaction can occur. By this it is meant that if it be desired to induce a definite reaction towards a definite reagent it is necessary in all probability to open up the closed force field to one definite stage. Any earlier stage in the opening up will not endow the system with the required reactivity. In short, it may certainly be assumed that while each stage in the opening up possesses a definite reactivity, a certain limiting stage must be reached before any particular reaction can proceed.

Some years ago Miss Marsden and I investigated the absorption spectra of certain aromatic amino-aldehydes and ketones and we have found that the alcoholic solutions of these compounds exhibit a well-marked absorption band.[1] The addition of a small quantity of alcoholic HCl to any one of these solutions causes the development of a yellow or red color which disappears when more of the acid is added. This color is due to the appearance of a new absorption band nearer to the red than that shown by the parent compound. On the addition of the excess of acid the absorption spectrum changes to that of the hydrochloride of the amino base, which somewhat resembles that of the free base itself. It is clear from these results that the conversion of the amino bases to their hydrochlorides is not simply an addition reaction. There is no doubt that it is not the amino compound such as exists in alcoholic solution which forms the salt, but that the first quantity of acid converts the base into an intermediate form and *it is this intermediate form which reacts with more acid to give the salt.* These results at once extend our view of chemical reaction, in that they undoubtedly prove the existence of a hitherto unrecognized

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[1] *J. Chem. Soc.*, 93, 2108 (1908).

intermediate stage; they also afford a definite proof of the force-field theory, for it was exactly this phenomenon which was shown above to be the direct result of the application of the theory to chemical reaction. The addition of the first quantity of HCl opens the closed fields to a higher stage, which is evidenced by its characteristic light absorptive power, and the field must be opened to this stage before the molecule can react to give the salt. These results also have a bearing on the application of the theory to catalysis. When the above amino compounds are treated with methyl iodide they tend to give their methyl derivatives. The velocity of this reaction is known to be materially increased when some acid is added. The acid has been shown to open up the closed systems to a higher stage with a greater reactivity, and, therefore, it acts as a positive catalyst' in the methylation of these compounds.

Exactly analogous results have been obtained by Mr. Rice and myself in the sulfonation of aromatic phenol ethers.[1] In this case it was found possible to convert the whole of the reacting substance into the intermediate form and to observe its change into the sulfonic acid. In the former case we succeeded only in obtaining a small quantity of the amino base in the intermediate and more reactive form owing to the affinity between this form and the acid. In fact the maximum amount of this stage is obtained when only about 0.2 equivalent of HCl is added. In the sulfonation reaction, when the compounds are dissolved in cold concentrated sulfuric acid they are in many cases entirely converted into the intermediate stage, which frequently is characterized by its absorption of visible light so that the solution is visibly colored. On standing, the system is slowly changed to the sulfonic acid and the progress of the reaction can be followed with the spectroscope. The absorption spectrum of the sulfonic acid differs entirely from that of the intermediate stage, and somewhat resembles that of the original substance in alcoholic solution. It is, perhaps, worth mentioning that if the sulfuric acid solution, before the sulfonation has taken place, is poured onto ice the original compound is recovered in a pure state. These two investigations establish beyond any doubt the existence of the intermediate stage in a chemical reaction such as was deduced from the force-field theory.

The fact that the existence of the various stages in the opening up can be recognized by their characteristic light absorption enables us to interpret absorption observations with considerable certainty. These phenomena and their explanation will be fully dealt with in a subsequent paper, but reference may be made to one statement given above, namely, that nitrobenzene is an amphoteric substance. Mr Rice and I have found that the nitro derivatives of benzene tend to exist with their force fields

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[1] *J. Chem. Soc.*, 101, 1475 (1912).

very definitely closed.[1] This results from the difference between the affinities of the phenyl nucleus and the nitro group. Such a compound would naturally tend to be affected differently by a strong acid and by a strong base. The absorption of nitrobenzene in solution in dimethylaniline and in concentrated sulfuric acid is entirely different; indeed, the former solution is colored red while the latter is colorless. Clearly, therefore, the manner of opening up the force fields is different; according to whether an acid or basic solvent is used and so we may speak of nitrobenzene as being amphoteric.

It was pointed out above that in the case of inorganic acids, bases, and salts, ionic dissociation is the extreme case in the opening up of their force fields. Now the effect of the selective absorption of light by a solution is to shift the equilibrium between the opened-up molecules and unopened-up molecules towards the reactive side, that is, to increase the former relatively to the latter. It should, therefore, be possible to increase the amount of ionization of a salt in solution by the action of light, and such effect should evidence itself in the catalysis of a given reaction or by an increase in the electrical conductivity of a solution. As a general rule, however, the force fields of inorganic salts are relatively simple and so the wave length of the light selectively absorbed by their solutions will be very short. Very few inorganic salts (except those visibly colored) exert selective light absorption in the region of the spectrum that can be photographed with a spectrograph in air, and therefore the absorption bands must lie beyond the frequency $1/\lambda = 5000$. There are, however, a few cases which can be experimented with and in one of these, namely, the chloroplatinic acids, Boll and Job[2] have found that under the influence of ultraviolet light the electrical conductivity of their solutions is materially increased. This is exactly what the force-field theory foretold.

An important confirmation would be found if it were possible to prove the catalysis of a simple inorganic reaction by the influence of light. As a general rule the velocity of such reactions is so great that the measurement of an increased velocity is precluded. There is one case, however, namely, that of KI and $Hg(CN)_2$, which do not react in aqueous solution to give HgI_2. The aqueous solution of each salt is diactinic to all the rays of light above $1/\lambda = 5000$ and, therefore, their absorption bands must lie at still shorter wave lengths. Such very short waves of light may be obtained from a hydrogen vacuum tube fitted with a fluorite window, and as such very short light waves are absorbed by air all experiments with them must be carried out *in vacuo*. A mixture of the two salts, finely powdered and slightly moist, was placed in a vessel cemented to the fluorite window. This vessel was exhausted so as to allow the rays to reach the

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[1] *J. Chem. Soc.*, **103**, 2085 (1913).

[2] *Compt. rend.*, **154**, 881; **155**, 826 (1912).

powder and it was then found that very small quantities of HgI_2 were superficially produced where the light fell on the mixture. These experiments must be looked upon as still being incomplete, but as far as they have gone the results are eminently satisfactory. It is in organic chemistry that the force-field theory finds its most obvious application, for so few of the reactions are ionic. For example, the opposite affinities of the nitro group and the phenyl nucleus give the key to the nitration of aromatic compounds. It is clear that when the latter are treated with HNO_3, addition complexes tend to be formed in which the closed fields are opened up. Such addition compounds, if the potential gradients are sufficiently steep, will by transference of electrons give the nitro compound and water. It may readily be possible that the affinity of HNO_3 be not strong enough to open up the closed fields of the aromatic compound and in such a case it naturally will be advisable to use another strong acid as solvent. This explains why glacial acetic acid and concentrated sulfuric acid are so valuable in carrying out the nitration process. The power possessed by sulfuric acid in opening up the fields of aromatic compounds has already been mentioned and it is evident that its influence on the nitration reaction is not simply to be explained as that of a dehydrating agent. Again, the absence of action of HNO_3 upon the paraffins is also accounted for, since the spectroscope shows that there is no mutual influence between the two. Further, toluene is oxidized to benzoic acid by moderately concentrated HNO_3, for its force field is not sufficiently opened to give the nitro derivative, but it is nitrated readily enough in a mixture of HNO_3 and H_2SO_4. One further point of interest in the nitration of aromatic compounds is afforded by such compounds as *p*-dimethyltoluidine, which gives 1-methyl-3-nitro-4-dimethylaminobenzene when treated in HCl solution with $NaNO_2$ but gives 1-methyl-2-nitro-4-dimethylaminobenzene when dissolved in a mixture of HNO_3 and H_2SO_4. The course of the reaction depends on the manner in which the force field of the amine is opened up.

There is some temptation to continue giving instances of phenomena which are simply explained by the force-field theory, as, for example, the unstable highly colored nitrophenol ethers of Hantzsch and Gorke[1] and similar compounds. One might point out that these compounds are simply an opened-up phase in metastable equilibrium. They are prepared from a salt in which the complex radical already exists in an opened-up condition. At the moment of formation the derivatives will also exist in a similarly opened-up condition and if due care be taken such derivatives may be preserved in that condition. In the presence of a suitable catalyst the metastable opened-up force field will condense until that condition is arrived at which is characteristic of the ordinary form of the com-

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[1] *Ber.*, 39, 1073 (1906).

pound. This explanation of the existence of these unstable compounds. many of which have now been prepared, is very much simpler and more rational than that usually adopted, namely, that such bodies are chemical isomers of the stable modifications. The latter explanation generally involves the wandering of a radical, which experience derived from other compounds would not lead us to expect. Again, the present theory accounts at once for the abnormal reactivity of these unstable substances, because they have their force fields opened up to a high stage and they, therefore, obviously will be more reactive than the stable modifications.

The theory may also be applied to the phenomena of allotropy. It has already been shown by Smits that a most reasonable explanation of allotropy is to be found in the existence of definite molecular species, each allotropic modification being an equilibrium mixture of two or more such species.[1] The possibility of the existence of these molecular species is at once furnished by the force-field theory, for such species would simply be constituted by various complexes with their force fields in different states of condensation. The existence of such complexes is a very obvious deduction from the present theory, and, indeed, the theory would lead to the expectation of the phenomenon of allotropy being very wide spread. Our knowledge of allotropy, however, is rapidly being extended, for recent work[2] shows that the power of existing in allotropic modifications is possessed by numerous elements previously supposed to be confined within the limits of one form.

An interesting and somewhat suggestive conclusion is arrived at if the influence of an external magnetic field upon the molecular force fields is considered. The effect of such an external field on the force fields of the atoms of elements is shown clearly enough by the Zeeman effect. That there must result some effect when a molecular force field is brought into an external magnetic field is obvious. Since the former are electromagnetic in type it is clear that they will become keyed with the external field. The molecules will become polarized as it were, and unless the molecules are perfectly symmetrical as regards their force fields, a skew effect will tend to be established, since the external force lines are stationary. Such skew systems of force lines will result in the unequal retardation of light waves passing through the system, and, therefore, a plane-polarized beam of light will undergo rotation as regards its plane of polarization. It would, seem therefore, that the phenomenon of magnetic rotation also finds its explanation in the present theory. The suggestiveness of this is to be seen in the fact that it may be extended to the phenomenon of stereoisomerism and optical rotation generally. If the principle, advanced above, of the skew effect being the origin of the rotation of plane-polarized

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[1] *Proc. K. Akad. Wet. Amsterdam,* 14, 788 (1912).

[2] E. Cohen, *Ibid., passim.*

light be accepted, then the explanation of optical rotatory power follows naturally enough. The force field of any molecule which is asymmetric must of necessity itself be asymmetric, with the result that a skew effect will exist in the surrounding ether causing the rotation of the plane of polarized light. Now when the condensation of the force lines due to the several atoms of a completely asymmetric molecule is considered, there must be at least two ways in which such condensation can take place. In each case the same amount of energy will escape and the two skew effects resulting from such condensations will be equal and opposite. We, therefore, will have two entities almost identical if not entirely identical in chemical properties but with equal and opposite powers of rotating the plane of polarized light. The amount of rotation will depend upon the amount to which the force field has condensed. If such condensed force fields be attacked by solvents the rotatory power will tend to be altered. Again the rotatory power will be influenced by temperature, since it is obvious that the influx of energy, whether by increase of temperature or otherwise, will tend to open the fields and alter the skew effect. It equally follows that by the opening up of the condensed fields to a particular stage the skew effect can be nullified, with the result that racemization may ensue.

It is not necessary to emphasize the inherent advantage that this conception possesses over the old notion involved in the Le Bel and van't Hoff theory of the interchange of atoms or groups of atoms. After all, such interchange is abnormal and does not appear to take place in any other case with that readiness with which it is postulated to occur in stereochemistry. As a general conclusion drawn from the field of organic chemistry it may fairly be stated that the wandering of atoms or groups does not take place unless the product of such reaction is more stable than the original compound. The Le Bel and van't Hoff theory postulates the completely reversible interchange of groups in a completely asymmetric molecule. Such, indeed, might be accepted in a perfectly symmetrical system but where the asymmetry is an essential factor of the problem the process is antagonistic to the canons of organic chemistry.

The application of the force-field theory is based entirely on the principle of the rotatory power being due to the skew effect in molecular force fields. The dextro and laevo rotations are both the properties of one single primary structure, no isomerization being necessary to account for these phenomena. Although the present theory differs in one essential respect from the classical one, yet the whole is based on the complete asymmetry of the molecule, which is the real basis of the older theory.

The extension of the principle to all the phenomena of isomerism is sufficiently obvious to need no special discussion. Some emphasis must be laid on the fact that it is by no means necessary that there shall be one way and only one way in which the condensation of a given set of force lines can take place, quite apart from the fact that individual stages in any one condensation process may have the power of metastable existence. The phenomena of geometric isomerism belong to the former category, while the highly colored unstable nitrophenol ethers of Hantzsch and Gorke and similar compounds belong to the latter.

If two differently condensed fields are obtained from one set of force lines, it is possible that the two condensed fields may be opened differently by solvents, and, therefore, the two substances will have different reactivities. Such differences usually are accounted for by attributing different primary structures to the compounds, but it would seem that this is entirely unnecessary.

Summary.

1. The existence of molecular force fields due to the electromagnetic fields of the constituent atoms is dealt with. It is shown that these force fields afford an explanation of chemical reactivity and reaction.

2. To the closed force fields and their opening up by the influence of solvents or light may be attributed all the phenomena of chemical reaction. Ionic dissociation is one special case of the whole.

3. In the existence of definite stages in the opening up of a given complex field, each with its power of absorbing definite light rays, is to be found the explanation of differently colored derivatives from the same compound.

4. The theory leads to the existence of intermediate stages in a chemical reaction and such stages have experimentally proved to exist.

5. When a compound is dissolved in a solvent an equilibrium is set up between the opened-up and non-opened-up molecules of the solute. Such a system has the power selectively of absorbing light rays, the effect of the light being to increase the number of opened-up molecules and thus to shift the equilibrium towards the reactive side. Some preliminary experiments on the photocatalysis of the reaction $Hg(CN)_2 + 2KI = HgI_2 + 2KCN$ afford considerable support to this view.

6. The theory would also seem to afford a reasonable explanation of allotropy, magnetic rotation, stereoisomerism, optical rotatory power, and generally the phenomena of isomerism as a whole.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE AND THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

THE HEATS OF COMBUSTION OF AROMATIC HYDROCARBONS AND HEXAMETHYLENE.

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During the last ten years, extensive series of thermochemical investigations have been carried on in the Harvard laboratories with the help