The Development of Electrochemical Theories of the Course of Reactions of Carbon Compounds.

THE EIGHTEENTH FARADAY LECTURE, DELIVERED BEFORE THE CHEMICAL SOCIETY ON JULY 16TH, 1947.

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THERE are many tributaries to the river of scientific progress, and their contribution to the broad stream persists in spite of inevitable loss of individual form.

So, the modern theories of molecular structure and chemical reactions which flourish in the domain of physical chemistry, thermodynamics, and wave mechanics, are derived from many sources. It is my intention to speak of only one of these, namely that provided by the generalisations of their experience which organic chemists have been able to make in terms of the electronic conception of valency.

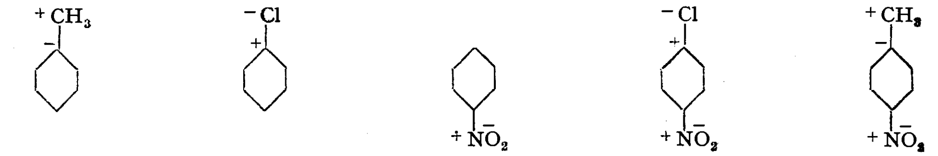
That these generalisations were a real forward step cannot be doubted, but the form in which they were expressed has naturally been altered in accordance with the successive advances in our knowledge of the fundamentals of chemical kinetics and atomic and molecular theory.

The identity of the ideas has not yet been lost, however, and the qualitative approach still affords a valuable framework for the elaboration of detail by means of the more searching methods of analysis which are now available. But the section of the subject that I have indicated is small only in relation to the whole; it is very complex in itself and is the outcome of developments in varied fields of work. It will be convenient to follow the thread suggested by the lecturer's contacts with the topic and by precedent and parallel investigations, but it is certain that, by a change of emphasis, many different lectures could be delivered under the same title.

After the discovery of the electron by Sir Joseph Thomson and the successive stages in the formulation of the electrical theory of the constitution of matter, the conceptions of the nature of chemical affinity and valency bonds were gradually adjusted, and attempts were made to explain the chemical properties of molecules as assemblages of electrons and positively charged nuclei. Some kind of electronic theory of valency became almost axiomatic, but, as the development showed, there was ample scope for divergent views of details of structure, of the nature of the forces involved, and of the interpretation of physical and chemical properties. The idea of covalency, the sharing of electrons by two nuclei, was adumbrated by Ramsay in 1908. Thomson and Stark developed more detailed theories, and were among the first to attack problems of organic chemistry on an electronic basis.

The speculative elaborations of Stark (" Die Elektrizität im chemischen Atom ", Leipzig, 1915), who also advanced electronic explanations of optical properties, have not survived in their original form. Many of his suggestions may, however, be traced in later theories. A second epoch may be roughly defined as that of Kossel (*Z. Physik*, 1920, **1**, 395) and of Lewis (*J. Amer. Chem. Soc.*, 1916, **38**, 762; " Valence and the Structure of Atoms and Molecules ", Amer. Chem. Monograph, 1923), characterised, at least in its earlier phases, by somewhat rigid conventions in regard to the chemical bond, and by great advances in our knowledge of the relation of structure to physical properties. In the third and present period the applications of wave mechanics are yielding more precise information in regard to the distribution of electrons in the molecules. In certain cases that distribution can even be determined from experimental observations of the reflexion of *X*-rays by crystals. These matters lie outside the purview of the present lecture. Indeed, the symbols which we still employ are largely independent of stereo-electronic considerations. The exceptions are those used for the polar molecules, to the study of which Debye has made such outstanding contributions, and for the ions, that is to say the bound and free ions. At every stage of the electrochemical theory these are our trusted guides.

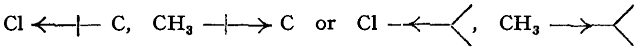
Langmuir pointed out that trimethylamine oxide, formed from electrically neutral NMe_3 and an uncharged oxygen atom, must be $Me_3\overset{+}{N}—\overset{-}{O}$ by the arithmetic of the electrons, and Sidgwick extended the idea to include many compounds containing the co-ordinate link $\overset{(+)}{A}\longrightarrow\overset{(-)}{B}$ (" The Electronic Theory of Valency," Oxford, 1927). The existence of these dipolar groups has been fully established by experiment and has been correlated with a range of physical and chemical properties. The knowledge has been used to confirm the assumed orientation of electrostatic doublets produced by simple substitutions. For example, on theoretical grounds Thomson showed that such a doublet should be present in the group C–Cl, and this is confirmed by the fact that methyl chloride has an electric moment, $1{\cdot}97 \times 10^{-18}$ e.s.u., in the gaseous state. The direction of the moment is shown by a comparison of the dipole moments (e.s.u.) of chlorobenzene, nitrobenzene, and *p*-chloronitrobenzene, because NO_2, a dipole like an amine oxide, must be $\overset{+\,-}{NO_2}$.



$0{\cdot}4 \times 10^{-18}$ $1{\cdot}5 \times 10^{-18}$ $3{\cdot}9 \times 10^{-18}$ $2{\cdot}6 \times 10^{-18}$ $4{\cdot}5 \times 10^{-18}$

(All in benzene solution.)

It is clear that the separate dipole moments due to C–Cl and C–NO_2 are in opposite directions in the molecule, or in other words they are in the same direction with respect to the nucleus. Substitution of methyl for hydrogen in the aromatic nucleus produces a small dipole moment in the opposite sense. We denote these displacements by the symbols :



Both Thomson and Lewis assumed that such doublets would exert an effective field, either directly or by induction through a chain of atoms, and gave in illustration the greater strength of the chloroacetic acids as compared with acetic acid. The operation of the electrical field on the carboxyl group will obviously enhance the stability of the anion produced by electrolytic dissociation. As expressed by Lowry the sheath of electrons moves towards the chlorine atom and thus bares the nuclei of the oxygen atoms, enhancing their repulsion on the attached proton.

$$\mathrm{Cl} \longleftarrow \mathrm{CH_2}\overset{\longleftarrow}{\text{——}}\mathrm{CO_2} \longleftarrow \mathrm{H}$$

Lewis pointed out that the effect diminishes as the chlorine atom is removed from the carboxyl. Thus α-chloropropionic acid is about as strong as chloroacetic acid, but β-chloropropionic acid is much weaker. γ-Chlorobutyric acid is still weaker, and the effect is hardly discernible in δ-chlorovaleric acid.

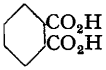
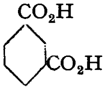
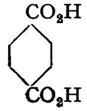
Ionisation constants of aliphatic acids.

		K.
	$CH_3{\cdot}CO_2H$	$2{\cdot}1 \times 10^{-5}$
(Br)	$CH_2Cl{\cdot}CO_2H$	$1{\cdot}55 \times 10^{-3}$ (Br, $1{\cdot}38 \times 10^{-3}$)
	$CHCl_2{\cdot}CO_2H$	5×10^{-2}
	$CCl_3{\cdot}CO_2H$	2×10^{-1} (?)
	$CH_3{\cdot}CH_2{\cdot}CO_2H$	$1{\cdot}4 \times 10^{-5}$
(Br)	$CH_3{\cdot}CHCl{\cdot}CO_2H$	$1{\cdot}47 \times 10^{-3}$ (Br, $1{\cdot}08 \times 10^{-3}$)
(Br)	$CH_2Cl{\cdot}CH_2{\cdot}CO_2H$	$8{\cdot}59 \times 10^{-5}$ (Br, $9{\cdot}8 \times 10^{-5}$)
	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$	$1{\cdot}6 \times 10^{-5}$
(Br)	$CH_3{\cdot}CH_2{\cdot}CHCl{\cdot}CO_2H$	$1{\cdot}39 \times 10^{-3}$ (Br, $1{\cdot}06 \times 10^{-3}$)
	$CH_3{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2H$	$8{\cdot}94 \times 10^{-5}$
(Br)	$CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$	3×10^{-5} (Br, $2{\cdot}6 \times 10^{-5}$)
	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$	$1{\cdot}5 - 1{\cdot}6 \times 10^{-5}$
(Br)	$CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$	$2{\cdot}04 \times 10^{-5}$ (Br, $1{\cdot}9 \times 10^{-5}$)
	$CH(CH_3)_2{\cdot}CO_2H$	$1{\cdot}5 \times 10^{-5}$
	$C(CH_3)_3{\cdot}CO_2H$	$9{\cdot}8 \times 10^{-6}$
	$CH_3{\cdot}[CH_2]_4{\cdot}CO_2H$	$1{\cdot}45 \times 10^{-5}$
	$CH_3{\cdot}[CH_2]_5{\cdot}CO_2H$	$1{\cdot}46 \times 10^{-5}$
	$CH_3{\cdot}[CH_2]_6{\cdot}CO_2H$	$1{\cdot}44 \times 10^{-5}$
	$CH_3{\cdot}[CH_2]_7{\cdot}CO_2H$	$1{\cdot}44 \times 10^{-5}$

Dippy and R. H. Lewis (*J.*, **1937**, 1008) noted an almost linear relation between the dipole moments and the electrolytic dissociation constants of a number of acids.

In the series of the dibasic acids we can study the effect of one carboxyl on the strength of another at varying distances.

Ionisation constants of dibasic acids.

	K_1.	K_2.
$CO_2H·CO_2H$	7×10^{-2}	$3–7 \times 10^{-5}$
$CO_2H·CH_2·CO_2H$	$1·46—1·63 \times 10^{-3}$	$2·1(1·4) \times 10^{-6}$
$CO_2H·CH_2·CH_2·CO_2H$	$8·1 \times 10^{-5}$	$3·7 \times 10^{-6}$
$CO_2H·[CH_2]_3·CO_2H$	$4·7(6·9) \times 10^{-5}$	$2·9 \times 10^{-6}$
$CO_2H·[CH_2]_4·CO_2H$	$3·7 \times 10^{-5}$	$2·4 \times 10^{-6}$
$CO_2H·[CH_2]_5·CO_2H$	$3·23 \times 10^{-5}$	$4·4 \times 10^{-6}$
$CO_2H·[CH_2]_7·CO_2H$	$2·5 \times 10^{-5}$	$2·4 \times 10^{-6}$
$CO_2H·[CH_2]_8·CO_2H$	$2·7 \times 10^{-5}$	$2·5 \times 10^{-6}$
	$1·3 \times 10^{-3}$	$3·4—5·8 \times 10^{-6}$
	$2·9 \times 10^{-4}$	$2·4 \times 10^{-5}$
	$1·5 \times 10^{-4}$	
$Ph·CO_2H$	$6·5 \times 10^{-5}$	

It is apparent that $·CO_2H$ behaves like $\mathrm{C}\rightharpoonup\mathrm{Cl}$. As Thomson's electrostatic argument suggests,* it must be represented as $\rightharpoonup\overset{\delta+}{\mathrm{C}}\ \overset{\delta-}{\mathrm{O}}_2\mathrm{H}$, and it is electron-attracting. But after dissociation the group becomes $\rightharpoonup\overset{-}{\mathrm{C}}\mathrm{O}_2$; there is now no question of a dipole,† but only of a negative charge which should repel electrons and conversely hold protons even at a distant point. The second dissociation constants clearly show that this anticipated reversal of the effect occurs.

The values quoted for K_2 are not always strictly comparable with one another, or with those for K_1. The second dissociation constants were in some cases determined at 100° by the method of inversion of sucrose (cf. Smith, *Z. physikal. Chem.*, 1898, **25**, 220). It may be noted that E. Q. Adams (*J. Amer. Chem. Soc.*, 1916, **38**, 1503) has shown that if the first dissociation had no effect on the second, K_2 should be one-fourth of K_1. When the carboxyl groups are far removed from one another, this relation was found to hold approximately (cf. Chandler, *J. Amer. Chem. Soc.*, 1908, **30**, 694).

The case of isomeric acids differing in stereochemical configuration is particularly convincing.

Ionisation constants of stereoisomeric dibasic acids.

	K_1.	K_2.
$CH·CO_2H$ $\|\|$ $CO_2H·CH$	$9·8 \times 10^{-4}$	$2·7 \times 10^{-5}$
$CH·CO_2H$ $\|\|$ $CH·CO_2H$	$1·3 \times 10^{-2}$	$2(2·6) \times 10^{-7}$
$CMe·CO_2H$ $\|\|$ $CO_2H·CH$	$8·5 \times 10^{-4}$	9×10^{-6}
$CMe·CO_2H$ $\|\|$ $CH·CO_2H$	$3·8 \times 10^{-3}$	$2·4 \times 10^{-7}$ (100°)

The *cis*-acids are much the stronger as monobasic acids but they are far weaker in the second ionisation step. The ratio of K_1 to K_2 for fumaric acid is about 36 and for maleic

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* However, in opening a discussion on these topics in 1923 (Faraday Society) Sir Joseph Thomson classed Cl, OH, NH_2, and CH_3 together $(\overset{+}{\mathrm{C}}—\overset{-}{\mathrm{Cl}})$ and distinguished their effect from that of CN and NO_2 $(\overset{-}{\mathrm{C}}—\overset{+}{\mathrm{C}}\mathrm{N})$. This view appears to have been based on some kind of alternation and disregards the inductive transmission of the field of a doublet. Thus $\overset{+}{\mathrm{C}}\overset{-}{\mathrm{N}}$ distributes a positive field over the atoms to which it is attached and, of the groups mentioned, $\overset{-}{\mathrm{C}}\overset{+}{\mathrm{H}}_3$ is the only one that produces a negative field.

† This is not true of the sulphonic ion, SO_3^-. Thus K_2 for *p*-sulphobenzoic acid is $1·4 \times 10^{-4}$ ($>K$ for $Ph·CO_2H$, $6·5 \times 10^{-5}$). There is other evidence that SO_3^- distributes a ***positive*** electric field over an attached group, and this is clearly due to its constitution $—S^{++}O_3^{---}$, the nearer double positive charge being more effective than the more remote triple negative charge.

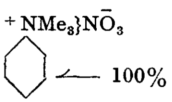
acid about 50,000. Attention should be paid to the order of the phenomena only, as, apart from the experimental difficulties, the interpretation is complicated by the possibility of differences of solvation of the acids and their ions.

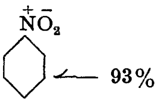
Many of these facts were established by the work of Walker, Ostwald, and Bone, Sprankling, and Sudborough fifty to sixty years ago, and Ostwald gave the acceptable explanation of them in general terms (*Z. physikal. Chem.*, 1889, **3**, 177).

The whole problem of the strengths of acids and bases (where the effects are naturally reversed) can be satisfactorily treated along similar lines, but, as Flürscheim was the first to show (*J.*, 1909, **95**, 718; 1910, **97**, 84), steric hindrance must be taken into account in many cases, for example in *o*-substituted benzene derivatives. We may regard the dissociation constant of a carboxylic acid as a measure of the electrical field over the dissociating group, provided that approach of solvent molecules is not hindered by steric conditions.

I have dwelt at some length on this clear case because of its historical importance and in order to place in juxtaposition with it, experimental results from which it can be seen that exactly analogous phenomena control the nitration of certain benzene derivatives in the *o*-, *p*-, or *m*-positions with respect to a substituent. With the acids we have an ionic equilibrium and the effect of an electric field is not surprising. But in the nitration case we have an effectively irreversible process and no obviously ionic reaction.

The work of Vorländer showed that the direct attachment of an 'onium group to the benzene nucleus gives substances that nitrate exclusively in the *m*-position (*Ber.*, 1919, **52**, 262, 274; Vorländer and Siebert, *ibid.*, p. 283). This may be compared with the *m*-nitration of nitrobenzene (benzoic acid, benzenesulphonic acid, etc.):





The "'onium" atom need not be nitrogen but may be sulphur, selenium, phosphorus, arsenic, antimony, bismuth, lead, or even iodine [Vorländer and Büchner, *Ber.*, 1925, **58**, 1898 (I); Vorländer and Schroedter, *ibid.*, p. 1900 (Bi, Pb); Michaelis and Soden, *Annalen*, 1885, **229**, 324 (a P compound not quite analogous); Ingold, Shaw, and Wilson, *J.*, 1928, 1280 (P, As, Sb); Baker and Moffitt, *J.*, 1930, 1722 (S, Se)].

The interpretation given by Vorländer laid emphasis on the direct union of the "'onium" atom to the nucleus and is no longer considered valid.

In 1902 Schultz and Bosch (*Ber.*, 1902, **35**, 1292) stated that phenylbenzylethylamine nitrated in the *m*-position in the benzyl group, and Noelting and Kregeczy (*Bull. Soc. chim.*, 1916, **19**, 355) recorded the *m*-nitration of benzyldiethylamine, both in strongly acid solution. The significance of these isolated observations was not quickly recognised, mainly because there was no orientation theory that was generally considered satisfactory. A few years later interest was wakened and an active discussion arose in this country on the question of the actual substance that nitrates in the *m*-position. Was it the base or the salt? This was settled in favour of the latter view by Ing and the lecturer (*J.*, 1926, 1655) who found that benzyltrimethylammonium nitrate furnished nearly 90% of the *m*-nitro-derivative. In this quaternary salt the existence of free base is naturally impossible. The paper was entitled "The orienting influence of free and bound ionic charges", and the *m*-nitration in this and other cases was attributed to an electrical field produced by the cation over the molecule. The result was of great importance because it demonstrated that the charged centre need not be directly connected to the nucleus.

In a footnote it was stated that the work would be extended to β-phenylethyltrimethylammonium nitrate and γ-phenylpropyltrimethylammonium nitrate in order to determine the influence of the length of chain separating the charged centre and the nucleus. Even in the former case the nitration was chiefly in the *p*-position. Quantitative details of these and other examples were later provided by the extensive work of Ingold and his school.

It was found that, when a cationic charge is separated by a methylene group from the benzene ring, the nature of the 'onium atom is significant. Other things being equal the heavier atoms are the less effective, possibly because the distance from the aromatic nucleus is increased by their larger radius and the nuclear positive charge is more diffuse. Examination of the results demonstrates conclusively that the proportion of *m*-nitration is dependent on the intensity of the positive electric field over the nucleus.

m-*Nitration of 'Onium Salts*, Ph·R.

R = $CH_2{\cdot}NMe_3^+$, 88;[1] R = $CH_2{\cdot}CH_2{\cdot}NMe_3^+$, 19%;[2] R = $CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3^+$, about 5%;[3] R = PMe_3^+, 100%;[4] R = $CH_2{\cdot}PMe_3^+$, 10%;[4] R = $AsMe_3^+$, 98%;[4] R = $CH_2{\cdot}AsMe_3^+$, 3·4%;[4] R = $SbMe_3$, 86%;[4] R = SMe_2^+, 100%;[5] R = $CH_2{\cdot}SMe_2^+$, 52%;[5] 2-phenylbenzopyrylium salts[6] and 2-phenylquinoline metho-salts,[7] only *m*-nitro-derivatives were isolated, and in high yield.

[1] Ing and Robinson, *loc. cit.*; Goss, Ingold, and Wilson, *J.*, 1926, 2240. [2] Goss, Hanhart, and Ingold, *J.*, 1927, 250. [3] Ingold and Wilson, *J.*, 1927, 810. [4] Goss, Ingold, and Wilson, *loc. cit.* [5] Baker and Moffit, *loc. cit.*; Pollard and Robinson, *J.*, 1930, 1765, found $Ph{\cdot}CH_2{\cdot}SEt_2^+$, *m*-nitration, 28%. This fall, as compared with the benzyldimethylsulphonium salt, is probably due to reduction of the positive 'onium field of sulphur by a negative field due to the methyl groups. [6] Le Fèvre, *J.*, 1929, 2771. [7] Le Fèvre, *J.*, 1930, 2236.

Flürscheim and Holmes (*J.*, 1926, 1562) and Pollard and Robinson (*J.*, 1927, 2770) found cases in which the electrostriction of the cations by added salts diminished the percentage of *m*-nitration. Thus benzyldiethylamine in an excess of sulphuric acid gives 53·5% of the *m*-derivative. When ammonium sulphate was added the proportion fell to the region of 33%. The nitration of benzylpiperidine in nitric acid (*d* 1·5) gives about 70% of the *m*-nitro-base, and addition of trimethylammonium nitrate or rubidium nitrate, salts which are soluble in nitric acid, caused progressive reduction as more of the salts was added, until only about 20% of the *m*-derivative was produced. It was suggested that the accessibility of, for example, a sulphonium cation to electrostriction may be a part of the cause of the less intense field (as compared with a corresponding ammonium cation) that it exerts over the aromatic nucleus.

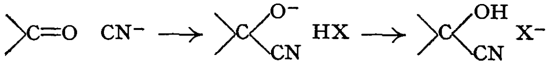
It was pointed out long ago by Holleman ("Die direkte Einführung von Substituenten in den Benzolkern", 1910, p. 469) that predominant *op*-substitution occurs at a higher rate and under milder conditions than predominant *m*-substitution.

This is easy to understand in the series which has been discussed because the recent work of Bennett and Ingold and their collaborators has indicated that the effective nitrating agent, at least in sulphuric acid solution, is the nitroxyl ion, NO_2^+. Obviously this will be repelled by a positive field and will enter the molecule the more easily the less intense the field. The relation indicated by this example is general and is often diagnostic of an ionic type of reaction. In regard to the actual rates in different cases Wibaut (*Rec. Trav. chim.*, 1915, **34**, 241) found the order $C_6H_5{\cdot}CH_3 > C_6H_6 > C_6H_5Cl > C_6H_5Br$ in acetic anhydride solution. Using the method of competitive nitration, Ingold and Shaw (*J.*, 1927, 2918) calculated from their results that each *o*- and *p*-position in toluene is roughly thirty times as reactive as in benzene, and each *m*-position about twice as active as one of the positions in benzene. The ratio $R_{C_6H_5R}/R_{C_6H_6}$ was found to be R = I, > 1; R = Br, 0·2; R = Cl, 0·01; R = F, 0·002. Ingold, Lapworth, Rothstein, and Ward (*J.*, 1931, 1959) working under somewhat different conditions increased the figures for toluene and found that one of the *m*-positions is about three times as active as one position in benzene. Although the assumptions made in the calculations hold only approximately and may be arguable, the general trend of the phenomena was established. It is in agreement with the theory outlined that the *m*-position of toluene should be activated (see below).

Excluding the cases (conjugated systems) considered later, all the data on benzene substitution can be shown to be in harmony with these principles. If we withdraw electrons from the nucleus as by substitution of halogens, nitro-groups, carboxyl groups, etc., for hydrogen in the side-chain we augment *m*-nitration. Introduction of methyl groups into the side-chain augments *op*-nitrations. Nitration has been studied very extensively but enough is known of sulphonation and halogenation to demonstrate that the orientation in these processes follows the same general lines. In order to be able to discuss why *m*-nitration occurs under the influence of a positive electric field, it is necessary to study other aspects—the reagents, and the behaviour of unsaturated systems.

The Classification of Reagents as Anionoid and Cationoid.—These terms introduced by Lapworth (*Manchester Phil. Soc.*, 1925; cf. *Nature*, 1925, **115**, 625) implied that certain electrically neutral molecules exhibit reactions of ionic type. Thus the hydroxyl ion combines with a proton to form water, and when water combines with a proton to form the solvated hydrogen ion, the process is evidently analogous. Hence the water molecule is said to be anionoid or to be an anionoid complex. The terms are equivalent to electron-donor and electron-acceptor and also to Ingold's expressions nucleophilic and electrophilic, respectively.

When a neutral molecule is attacked by an ion, the site of a cationoid or anionoid position is easily located, and it was just such a case that led Lapworth to develop his system of incipient alternate polarities. The reference is to the formation of cyanohydrins which were conclusively demonstrated, qualitatively and by kinetic studies, to result from the attack of cyanidion on a carbonyl group. The resulting complex ion then takes a proton from a suitable source, such as water or an alcohol, or even from a molecule of hydrocyanic acid:



$$>\mathrm{C{=}O}\quad \mathrm{CN^-} \longrightarrow\ >\mathrm{C}\genfrac{}{}{0pt}{}{\mathrm{O^-}}{\mathrm{CN}}\quad \mathrm{HX} \longrightarrow\ >\mathrm{C}\genfrac{}{}{0pt}{}{\mathrm{OH}}{\mathrm{CN}}\quad \mathrm{X^-}$$

Thus pure hydrocyanic acid does not combine with aldehydes or ketones, but the alkali from a glass vessel is sufficient to start the succession of processes.

Hence the carbon of the carbonyl group is said to be " cationoid ". All the characteristic reactions of carbonyl compounds conform to this view. By analogy we also class many similar groups as cationoid, for they evidently undergo the same type of reactions. These include carboxyl and especially the carboxylic ester group, the cyano- of nitriles, nitrosyl and nitroxyl groups.

The cationoid character of the carbon of $^-$CO$^-$ could be deduced theoretically from the fact that oxygen has a greater affinity for the negative charge than carbon, but there is no such guide in the case of the carbon–carbon double bond, and a conclusion had to be based on what was already known of the characteristic behaviour of olefins. This knowledge was sufficient for the purpose but it was eked out by specifically designed tests, among which may be mentioned Gilman's demonstration that olefins are inert towards organometallic compounds.

Consideration of the reactions of the olefins showed that in general and under ordinary conditions, they are easily attacked by cations and cationoid reagents but are relatively inert to anions and anionoid reagents. They were therefore regarded as anionoid. But this only means that their additive reactions are *usually initiated* by electron-donation to reagents; there must always be a subsequent process in the course of which the second carbon of the system evinces cationoid character.

In the formation of cyanohydrins it is clear that the group $>\mathrm{C{=}O}$ becomes $>\overset{+}{\mathrm{C}}\text{—}\mathrm{O^-}$, and any part of this full displacement of an electron pair is conveniently represented by the symbols $>\overset{a}{\mathrm{C}}\overset{\curvearrowright}{=}\mathrm{O}$ or $>\overset{\delta+}{\mathrm{C}}{=}\overset{\delta-}{\mathrm{O}}$. Similarly any part of the full displacement of a pair of electrons in an olefin can be represented as $>\underset{a}{\mathrm{C}}\overset{\curvearrowright}{=}\underset{b}{\mathrm{C}}<$. The difference is that whereas the carbonyl is cationoid at (*a*) the olefin is anionoid at (*b*). There is complete analogy between the reactions of the olefins and those of the aromatic compounds which tend to retain their type, and therefore benzene, and all similar substances, are also classed as anionoid.

Saturated carbon, midway between lithium and fluorine, has little or no intrinsic tendency to be either anionoid or cationoid. Therefore alkyl groups exhibit either behaviour in accordance with the electrochemical character of the group or atom to which they are united. Thus a chlorine atom holds the covalency electrons tenaciously and tends to separate as an ion. An attached alkyl group is consequently cationoid. But metals easily relinquish electrons and hence the alkyls of organometallic compounds are anionoid.

$$\mathrm{R(\text{—}Cl}\qquad \mathrm{R\text{—})MgX}$$

The annexed table requires little further explanation and can, of course, be greatly extended.

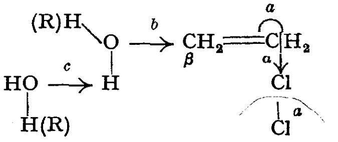
Anionoid.	Cationoid.
Nucleophilic.	*Electrophilic.*
Electron-donating.	*Electron-accepting.*
Active anions (OH^-, CN^-, etc.).	Active cations ($H_3{}^+O$, $\phi N_2{}^+$).
Anionoid complexes with unshared electrons (R_3N, ROH, etc.).	Atoms with incomplete electron configurations (neutral O; Co, Pt, etc.; BF_3, $AlCl_3$).
Reducing agents ($Fe^{++} \longrightarrow Fe^{+++}$).	Oxidizing agents [$Fe(CN)_6{}^{---} \longrightarrow Fe(CN)_6{}^{----}$].
Metals as electron sources.	Halogens, nitric acid (in nitration), sulphuric acid (in sulphonations).
R in R_2Zn, RMgX, etc.	R in RCl, R_2SO_4, $\vdots NR^+$, etc.
$:\mathrm{C}\overset{\curvearrowright}{=}\mathrm{C}:$, $\overset{\curvearrowright}{C_6H_6}$, etc.	$:\mathrm{C}\overset{\curvearrowright}{=}\mathrm{O}$ (at carbon), etc.
Free radicals.	Free radicals.

In all the classes the various representatives can be arranged in order of reactivity, and one general principle is that unshared electrons are better donors, the smaller their number.

This is connected with a closer approximation to the rare gas configuration. A negative charge on the reagent molecule naturally enhances the ease of electron donation, but even a positive charge need not entirely suppress the process. Conversely a positive charge enhances the activity of an electron acceptor, an example being the catalysis of carbonyl reactions by acids, due to the complex $:\overset{\curvearrowright}{C{=}O}\overset{+}{H}$. And again a negative charge does not always inhibit carbonyl activity completely. It was only gradually realised that the potentiality for covalency transformations is given by unshared electrons, or electrons in defect of a normal configuration, and that the charges either help or hinder the reactions.

The symbols suggested for electron displacements, together with Sidgwick's for the co-ordinate link, can conveniently be used to illustrate the course of reactions and one example will suffice. This is the formation of glycol chlorohydrin (or an ether, $R{\cdot}O{\cdot}CH_2{\cdot}CH_2Cl$) from ethylene, chlorine, and water (or an alcohol, $R{\cdot}OH$).

The lecturer (Institut International de Chimie Solvay, Quatrième Conseil, Brussels, 1931; Gauthier-Villars, Paris, 1931, p. 460. The use of R·OH as well as H_2O was mentioned in subsequent lectures and was known to Professor Noyes) suggested the following cycle :



$(R)HO{\cdot}CH_2{\cdot}CH_2Cl$ Cl^-
$(R)HOH_2^+$

(*a*) The anionoid ethylene donates electrons from C_α to cationoid chlorine, from which a chloridion is gradually produced.

(*b*) When the process of electron depletion of C_β has reached a certain stage, C_β acquires cationoid reactivity and is attacked by anionoid water (or an alcohol molecule) the mass of which greatly exceeds that of the chloridions. A small proportion of ethylene dichloride is always formed.

(*c*) Finally the complex loses a proton to a solvent molecule.

This mechanism serves to explain the formation of $CH_2Cl{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2Cl$ when the concentration of the chlorohydrin rises.

The idea was criticised by W. A. Noyes, who preferred to postulate the formation of hypochlorous acid or an alkyl hypochlorite and its addition to ethylene. Subsequently, however, evidence accumulated from many directions which rendered untenable the hypothesis that hypochlorous acid or its esters are intermediates.

The rate-determining reaction is that between chlorine and ethylene; moreover hypochlorous acid is found to be far less reactive than chlorine. Again in certain similar reactions the hypochlorous acid type of view cannot be suitably adapted because the intermediate required is unknown and would probably be extremely unstable. To take one instance, bromine reacts with ethylene in the presence of aqueous sodium nitrate so as to form β-bromoethyl nitrate, $CH_2Br{\cdot}CH_2{\cdot}ONO_2$. The result conforms to the mechanism suggested but can hardly be due to formation of $BrNO_3$ (Terry and Eichelberger, *J. Amer. Chem. Soc.*, 1925, **47**, 1067; A. W. Francis, *ibid.*, p. 2340). Bartlett and Tarbell (*ibid.*, 1936, **58**, 466) made an elegant kinetic study of the addition of methyl hypobromite to stilbene, and reached the following conclusions.

" (1) The rate of bromination of stilbene in methyl alcohol solution is sharply diminished by bromide ions but not by hydrogen ions.

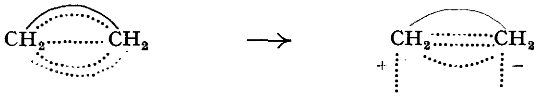
" (2) Therefore, although stilbene methoxy bromide is the principal product, methyl hypobromite is not responsible for its formation.

" (3) The kinetics of the reaction is consistent with a mechanism of reaction in two steps, in which molecular bromine is the active agent."

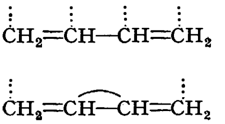
And here the lecturer wishes to take the opportunity to insist on the original form of his hypothesis and to deprecate the later versions which postulate a fully polarised ethylene $\overset{+}{C}H_2{-}\overset{-}{C}H_2$ and halogen cations, *e.g.*, $\overset{+}{Br}$. Similarly the second phase involves the neutral solvent molecule, *e.g.*, water, and not the hydroxyl ion as has sometimes been assumed. It is probable that the polarisation swings of ethylene in the resting or even the activated state indicated by $CH_2\overset{\curvearrowright}{=}CH_2$, represent only a small fraction of the full displacement of an electron pair. If it were otherwise the substance would be far more prone to polymerise than is found to be the case, and it would also react with anionoid reagents. But once the electron donation from an ethylene molecule has commenced, strain is relieved, and the process can be continued. Hence the full displacement is assumed to occur only in the course of the reaction. Again the process is not one of interaction with halogen cations but with halogen molecules, because the concentration of the former, if they are present at all, must be extremely low and the kinetics would be inexplicable. Finally the concentration of hydroxyl ions in the strongly acid solution is certainly exiguous.

The Conjugated Systems.—(1) *Polyenoid.* In 1911 Hugo Kauffmann (" Die Valenz Lehre ", Enke, Stuttgart) developed a theory of partial and distributed valency which he applied with success to the problem of auxochromes and to the constitutions of benzene and the triphenylmethane dyes. He appears, however, to have regarded chemical affinity as a special kind of force and speaks of the valence fields becoming electric fields, if electrons are interposed. In other respects too, and particularly in the development, Kauffmann's views differed from those that the lecturer developed from 1916 (*J.*, 1916, **109**, 1032, 1041; 1917, **111**, 959; 1918, **113**, 643; *Mem. Manchester Phil. Soc.*, 1920, **64**, No. 4) and which were translated in 1922 into definite electronic symbols (Kermack and Robinson, *J.*, 1922, **121**, 427).

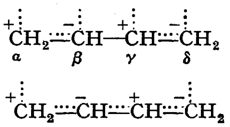
It was postulated that a valency bond could be subdivided, to an unknown but large extent, and it was further assumed that molecules are polarised by such partial division of the bonds. The polarised complexes enter into reactions. Thus taking four subdivisions of a bond, for convenience only, the activation of ethylene was represented as



With this polarised form the reaction, say addition of bromine, could be initiated and it was supposed to be completed in the course of the process by further division and rearrangement of the valencies. This view differed from that of Thiele in that the partial valencies were derived from the normal valencies and were not additional to them. The schemes for butadiene illustrate this contrast of which the most significant aspect is the assumption of polarisation :



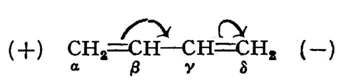
Thiele.



Robinson.

Here the signs on C^{β} and C^{γ} represented the polarity of the partial valencies from which the central partial bond was derived. It was an error to retain these signs after the part bond was formed, but the convention gave the right results in more complex systems.

Although these ideas were based from the commencement on the electronic theory of valency, use was made for some years of the partial polarised valency expressions. It was realised that the partial valencies labelled (—) represent available electrons, or part of an electron, and that those labelled (+) represent corresponding electron defect. Therefore the equivalent electronic symbol for polarised butadiene is :



$$(+)\quad \underset{\alpha}{CH_2}{=}\underset{\beta}{CH}{-}\underset{\gamma}{CH}{=}\underset{\delta}{CH_2}\quad (-)$$

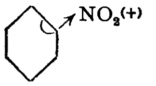
This implies that a certain electron value, possibly quite a small fraction of one electron, becomes free on C^{δ} and that the resulting electron defect on C^{γ} is made up by the transfer of a corresponding electron fraction from the $C^{\alpha\beta}$ bond to $C^{\beta\gamma}$, and that this produces a corresponding electron defect on C^{α}. A very important feature of this representation is that, apart from the inevitable electron defect on one carbon atom, the number of quantised electrons in the configurations of the carbon atoms is unchanged. The mechanism of addition to this system will then be precisely analogous to that already discussed for ethylene. It will be noticed that the process transfers electron defect from C^{γ} to C^{α} but this event does not *always* occur. The left-hand arrow need not come into operation and, as experience shows, we may observe $\gamma\delta$ (or $\alpha\beta$) additions. It is obvious, and was clearly stated, that a double bond can transmit *any* effect of electron accession or recession and one or more double bonds can therefore be interpolated in any system AB such that the quality of reactivity exhibited is due to a displacement of electrons from A to B, directly, or through an external circuit.

Much later Fuson (*Chem. Reviews*, 1935, **16**, 1) called this the " Principle of Vinylogy ". It is a theoretical potentiality which is not always realised in practice. The effects may be greatly damped, and there are special exceptions such as R·Cl, R·CH=CH·Cl, the cause of which is apparent.

The polarised complexes of which butadiene is the type are called *polyenoid*. They include benzene and other aromatic hydrocarbons.

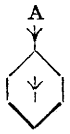
We are now in a position to consider why an electric field over the benzene nucleus should produce *op*-substitution or *m*-substitution according to its direction and intensity (Allan, Oxford, Robinson, and Smith, *J.*, 1926, 409).

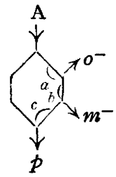
The reagent in nitration is cationoid; * it is looking for electrons. Therefore the first stage of the nitration of benzene could be represented as :



The second stage is the removal of the proton at the point attacked. That is also important but need not enter into the present discussion.

Now suppose we have a group (A) which promotes electron accession to the nucleus and a general drift or repulsion of electrons as shown in the figure. Its effect will be a maximum at the carbon atom to which it is attached and less work will be needed to effect the polarisation (*a*) than (*b*) or (*c*) :





Thus *o*-substitution can be expected. If the reagent approaches the *m*-position substitution may occur through the independent operation of (*b*) but it will be far less facile. But if the reagent approaches the *p*-position and enters into tentative union with it, the defect on the *m*-carbon can at once be made up by a conjugative process (*d*) which will be favoured by the same circumstances that helped (*a*) :

Thus the push from (A) promotes *o*-substitution directly and *p*-substitution by conjugation. It is important to note that the process (*b*) cannot be assisted in a similar fashion, because in the expression

the number of electrons in the configuration of the *m*-carbon is increased.

We have seen that methyl is an (A) group; the percentage of *m*-nitration of toluene is 4 and the ratio of *o*- to *p*-nitration is about 3 : 2 (*o*-, 59%; *p*-, 37%).

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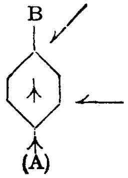
* It is not certain that NO_2^+ is the sole nitrating agent; electrically neutral cationoid complexes are probably operative under appropriate conditions.

A group (B) which attracts electrons is equivalent so far as the field effect is concerned to an imaginary (A) group at the *p*-position :

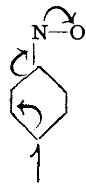


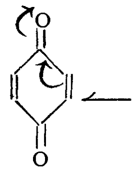
Hence by the argument already given we anticipate *op*-substitution with respect to (A). That is, *m*-substitution with respect to (B), or displacement of that group by the substituent. The latter phenomenon is often encountered.

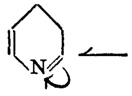
Naturally this use of the imaginary (A) group must not be pressed too far. The group (B) is real and by its positive electric field it renders all the nuclear electrons less available and reduces the ease and velocity of the substitution reaction.

(2) *Catio-enoid.* The cationoid reactivity of the carbon of a carbonyl group has been attributed to the electronic displacement $>C\overset{\curvearrowright}{=}O$. This can be conjugated with a double bond and thereby the quality of reactivity of a carbonyl is transferred to a carbon of the ethenoid system $\underset{\gamma}{C}\overset{\curvearrowright}{=}C-\underset{\alpha}{C}\overset{\curvearrowright}{=}O$. It is another example of the $\alpha\gamma$ rule. Thus a cyanidion attacks the γ-carbon (usually denoted as β) in an unsaturated ketone. Consideration of these and similar cases led Lapworth (1920) to formulate his theory of alternate polarities expressed : $\overset{+}{C}=\overset{-}{C}-\overset{+}{C}=\overset{-}{O}$. In this way he merely indicated the polarities which the various atoms seemed to display at the moment of reaction. The device led to some useful and interesting results but it was certainly taken too literally, and Lapworth's clearly stated reservations were often overlooked by other workers. Later (1922) he adopted a view similar to that suggested by the lecturer, but this was presented in a very general form which was somewhat difficult to assimilate.

In the aromatic series, catio-enoid systems may lie outside the nucleus, partly in the nucleus, or wholly in the nucleus. They give rise to typical reactions with *anionoid* reagents:

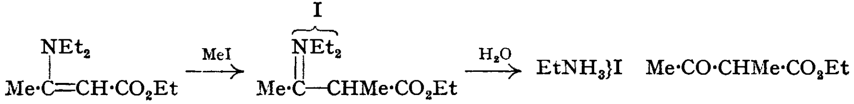




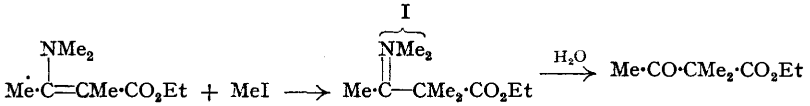


Examples are the hydrolysis of nitrosodimethylaniline and 1-chloro-2 : 4-dinitrobenzene, the amination and hydroxylation of nitrobenzene, quinones, and pyridine, etc. etc.

(3) *Hetero-enoid.* H. Decker (Decker and Klauser, *Ber.*, 1904, **37**, 523; Decker, *Ber.*, 1905, **38**, 2893) suggested that tervalent nitrogen could be conjugated with a double bond, and employed the Thiele symbol : $C=\overset{\frown}{C-N}\colon$. The experimental basis of the divided addition concerned only the action of acids and therefore the mobile proton. The lecturer (*J.*, 1916, **109**, 1038) showed that alkyl groups could be used to mark the position of combination as in the examples :



$$\begin{array}{c}NEt_2\\ |\\ Me\cdot C{=}CH\cdot CO_2Et\end{array}\xrightarrow{MeI}\begin{array}{c}I\\ \frown\\ NEt_2\\ \|\\ Me\cdot C{-}CHMe\cdot CO_2Et\end{array}\xrightarrow{H_2O} EtNH_3\}I\quad Me\cdot CO\cdot CHMe\cdot CO_2Et$$

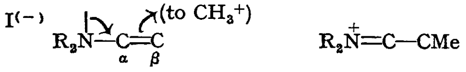


$$\begin{array}{c}NMe_2\\ |\\ Me\cdot C{=}CMe\cdot CO_2Et\end{array} + MeI \longrightarrow \begin{array}{c}I\\ \frown\\ NMe_2\\ \|\\ Me\cdot C{-}CMe_2\cdot CO_2Et\end{array}\xrightarrow{H_2O} Me\cdot CO\cdot CMe_2\cdot CO_2Et$$

This latter case excludes the hypothesis

$$>C{=}CH\cdot CO_2Et + RI \longrightarrow\ >C{=}CR\cdot CO_2Et + HI.$$

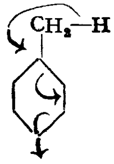
The basic nitrogen attached to the double bond has transferred, to unsaturated carbon, its own power of combining with a cationoid methyl group. The facts were established in the partial valency period and expressed in terms of that hypothesis. The electronic translation (1922) is much simpler and more convincing.



The unshared electrons (lone pair) of the nitrogen atom are used to increase the covalency with the nearest unsaturated carbon Cα. This must release electrons of the double bond to Cβ which can thus bind the methyl group. At the same time the nitrogen acquires a positive charge to balance the iodion, for it started with unshared electrons which became shared in the process.

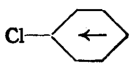
It is quite clear that this system must be definitely anionoid or electron donating. For though olefins are anionoid the tervalent nitrogen is far more strongly so, and here the nitrogen atom endows the unsaturated group with something of its own quality. Furthermore this type of conjugation is possible if the nitrogen atom is replaced by any atom which carries unshared electrons, and the order of activation will be that of the proton-affinity (or basic strength) of the hetero-atom: the greater that affinity the more reactive will be the anionoid carbon. Thus $N^- > O^- > N > O > I > Cl$ to mention a few of the possibilities. The *C*-alkylation of the sodio-derivative of ethyl acetoacetate which is derived from the enolic form, is seen to be analogous to the *C*-alkylation of the β-aminocrotonic esters. The most important examples are in the aromatic series, *e.g.*, the phenoxide ion, the aromatic amines, phenols and their ethers, halogenobenzenes. All the characteristic nuclear reactions of phenols and amines, *e.g.*, bromination, nitration, condensation with carbonyl compounds, etc., are with cationoid reagents, and all occur exclusively in the *op*-position. The conjugations

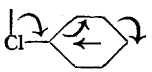
provide a much more definite mechanism of activation than that previously considered, and they take precedence over other effects. It has been suggested by J. W. Baker and Nathan (*J.*, 1935, 1845) that a methyl group can release electrons in a somewhat similar fashion :



The relation of this suggestion to the use of unshared electrons in the systems under discussion is not yet clear.

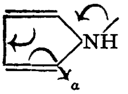
The case of chlorobenzene is very interesting because its nitration, for example, is far less facile than that of benzene itself. This was to be expected, for chlorine is known to be an electron-attracting group as we have already seen :

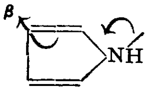




All the electrons of the nucleus are less available than they are in benzene. But even at this low level of reactivity the conjugative process determines where the donor electrons are to be found (see below, mesomerism).

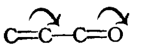
Other important hetero-enoid systems are recognised in such substances as pyrrole, and account for the correspondence of its reaction types with those of phenol and dimethylaniline :





The α-positions are like the *p*-position in aniline, whereas the β-positions resemble the *o*-positions in aniline. They are all reactive as shown by the formation of tribromoaniline on the one hand and tetraiodopyrrole on the other.

The recognition of two kinds of conjugated changes of covalency with simultaneous increase or decrease of the unshared electrons of atoms such as oxygen or nitrogen as in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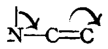
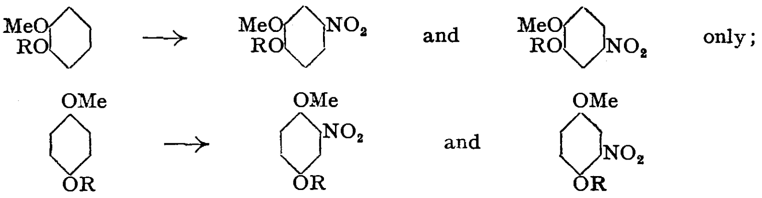
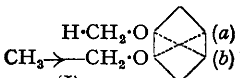


must be regarded as one of the milestones on the road we have travelled.

An Example of the Interaction of the Conjugated Polarisation and General Electric Effects.—A very important aspect of the lecturer's views was experimentally illustrated by a carefully selected case (three preceding papers were discussed by Allan, Oxford, Robinson, and Smith, *loc. cit.*; Lea and Robinson, *J.*, 1926, 411; Oxford and Robinson, *J.*, 1927, 2239; Fawcett and Robinson, *J.*, 1927, 2415; Clarke, Robinson, and Smith, *J.*, 1927, 2647; Smith, *J.*, 1931, 251). This was the mono-nitration of alkyl ethers of catechol and quinol (OMe, OR) which proceeds quantitatively. The proportions of the products can be determined accurately by thermal analysis.



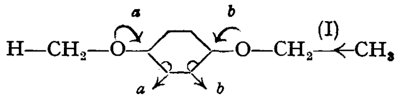
If we consider the case of the ethyl ether of guaiacol, there are two hetero-enoid systems directing *p*-substitutions as indicated by the dotted lines :



(I)

The oxygen of the methoxyl group directs the substituent to (*b*), that of the ethoxyl group to (*a*). In the ethoxyl group a hydrogen of the methoxyl group is replaced by methyl, and this, as we know from strengths of acids and bases and from the dipole moment of toluene, will repel electrons relative to the effect of hydrogen. Hence the system terminating in (*a*) should be reinforced and the directive power of ethoxyl should exceed that of methoxyl; which is actually found to be the case. Taking MeO, 100 we find EtO, 135. But on increasing the size of R in OR, the directive power rises to a maximum and then falls : Pr$^{\beta}$O, 150; Pr$^{\alpha}$O, 128; *n*-BuO, 123.

The effect (I) (inductive or general) is evidently also exerted on the oxygen of the methoxyl as the stereochemical conditions suggest that it should be, and the distributed direct effect partly neutralises that exerted through the chain. But in the quinol series this is no longer true :



The push of the methyl now assists (*b*) and actually opposes (*a*). Hence the directive power of EtO (164) is higher than that found in the catechol series. And with larger groups it continues to increase (Pr$^{\alpha}$O, 180; *n*-BuO, 186; *n*-$C_{16}H_{33}O$, 212).

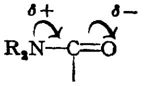
An electron-attracting group is *p*-nitrophenyl, and here the circumstances are reversed. In the catechol series $NO_2·C_6H_4·CH_2O$, 67, and in the quinol series, 38. The distributed pull on the electrons of the oxygen atoms in the former case results in a higher directive power than the pull in the latter case acting on the oxygen of the nitrobenzyloxy-group alone. One apparent exception was noted in the benzyloxy-group (113 in the catechol series, 107 in the quinol series), but the differences are small and the value in the catechol series is suspect. In the course of the Faraday Society discussion in 1923, it was stated that the polarity theories explained everything and predicted nothing. The lecturer thereupon made a prediction as follows .

(1) That the *para*-chlorobenzyloxy-group would have a greater orienting power than *meta*, and

(2) that the *para*-nitrobenzyloxy-group would have a weaker orienting power than the *meta*.

In 1927 the first prediction was justified (*p*-, 82; *m*-, 69), but the *m*- and *p*-nitrobenzyloxy-groups had nearly the same directive powers (67), in the catechol series. The anticipated effect was, however, noted with the nitrobenzamido-groups in the acylated *p*-phenetidine series (EtO, 100; *p*-, 190; *m*-, 226).

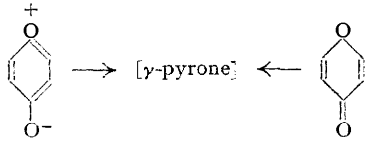
The Neutralised Systems.—If a strongly cationoid group is attached to a strongly anionoid group, *e.g.*, N to CO, electron transfer occurs in the molecule under all conditions :



The result is in this case to diminish the basic character of N and the cationoid character of C of CO and to produce a definite dipole evinced by the physical character of the amides. In a similar way the characters of the carboxylic acids and their derivatives receive a very convincing explanation. As always the groups can be separated by one or more double bonds, and the extent of the neutralisation depends on the affinity of the nitrogen and oxygen, or what corresponds to them in other examples, for their respective charges.

The Condition of Molecules in the Resting State.—Both Lapworth and the lecturer postulated a certain degree of polarisation in normal molecules of an unsymmetrical nature, but paid little attention to the matter because their chief concern was with reactions. The existence of electromeric displacements in the normal molecules of the conjugated complexes was, however, always mentioned in lectures in various centres on these topics and in University teaching from 1922. Indeed, the views expressed in regard to neutralised systems such as the amides, and the references to their physical and chemical properties, were meaningless without this assumption.

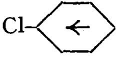
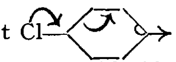
In the case of certain classes of compounds the idea was emphasised, and the pyrones, for example, were recognised as intermediate between the fully polarised hydroxypyrylium betaine and the usual neutral formula (Armit and Robinson, *J.*, 1925, **127**, 1604) :



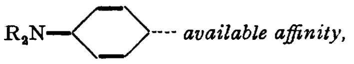
Arndt, Scholz, and Nachtwey (*Ber.*, 1924, **57**, 1903) put forward a similar view of " Zwischenstufe " based on the properties of a series of thiopyrones. They did not interpret their hypothesis in terms of electronic displacements.

Another way of representing the matter is to say that the pyrones are normally

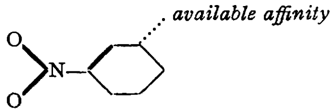
and it will be noticed that this is merely a neutralised system of ester type, $^-$O—CO$^-$, in which a double bond is interpolated in two places. There is, however, the additional circumstance that the pyrylium nucleus is aromatic, and that was considered to be an important factor in producing a closer approximation to the pyrylium betaine than would otherwise be the case.

Ingold and Ingold (*J.*, 1926, 1310) introduced the convenient term " mesomerism " for this electromeric effect in normal molecules, and an outstanding contribution on the experimental side was made by L. E. Sutton. Using the method of measurement of dipole moments he was able to recognise the mesomerism of many aromatic compounds containing hetero-enoid and catio-enoid systems as well as those in which both are present and may be partly neutralised. The direction of the mesomeric displacement was not necessarily in the same sense as the dipole. Thus the dipole in chlorobenzene was in the direction  as the theory of the general effect demands. A small counteracting mesomeric effect  was detected by comparison of the moment of chlorobenzene with that of *tert.*-butyl chloride (*Proc. Roy. Soc.*, 1931, **133**, 668). This work was a remarkable physical confirmation of the validity of the hypotheses which have briefly been expounded, for it was found that all *op*-directive groups examined increased the density of electrons in the aromatic nucleus and all *m*-directive groups decreased it. Methods for determining the occurrence and extent of mesomerism have been developed by Pauling and others, but they belong to the modern period. The device of writing down the possible structures and estimating the contribution which each makes to the actual condition of the molecule is a calculus and not a theory of structure, though it has often been misunderstood as such.

Conclusion.—Many important tributaries have been omitted from this account and the river has not been followed to the sea. Thus the work of Claus, Werner, and Flürscheim had a most important influence on the thoughts of chemists. Flürscheim's development of the theory of alternating and variable affinity was especially valuable. It gave the results now regarded as correct in many cases, as in the hetero-enoid systems :



but failed to meet our requirements in the catio-enoid systems :



The speculations of Vorländer and Fry likewise contained useful detailed suggestions but were eventually seen to be out of the direct line of progress. The lecturer has perforce had to omit all reference to the stereochemical aspects, such as the Mills–Nixon effect, to W. Baker's applications of chelation, to tautomerism, dissociating systems, and molecular rearrangement, as well as to many other topics of great interest. In particular he has not mentioned the neutral free radicals and atoms, which can be anionoid, *or* cationoid, *or* homopolar.

It seems peculiarly appropriate that a Faraday Lecture should deal with molecular electrical phenomena, although they are of a very simple kind, in relation to properties of the derivatives of benzene, a substance which Faraday discovered. We owe to him the first studies of dielectrics and as a twig from this tree we take the measurement of dipole moments. Above all he was a great electrochemist and was convinced that electricity and chemical affinity could be identified. His Laws of Electrolysis, considered from the point of view of atoms and ions, bear much the same relation to the atomic theory of electricity that the Law of Multiple Proportions bears to the atomic theory of the elements.

In the Faraday Lecture of 1881, Helmholtz said : " Now the most startling result of Faraday's Law is perhaps this. If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions which behave like atoms of electricity ".

The logic is inescapable and yet we must admire the acumen and courage of the remark.

Without forgetting the work of Volta, Davy, and Berzelius, and of many other real pioneers in the middle and later periods, we are right to honour the memory of Michael Faraday, the most illustrious of the founders of a science of electrochemistry.