

CXI.—*Ionisation and Chemical Combination.*

By JAMES WALLACE WALKER.

THERE is a sentence in Ostwald's *Lehrbuch*, 1893, II, 1, 786, which runs: "Eine sehr grosse Zahl chemischer Vorgänge beruht auf der Bildung von Ionen aus neutralen Körpern und umgekehrt." This statement is the key to the development of a very large portion of the views which have been expressed regarding the mechanism of chemical change during the past decade. From a brief summary of these opinions, as given by Walden (*Zeit. physikal. Chem.*, 1903, 43, 394), it is evident that the tendency at present is to throw more and more stress on the rôle played by the ions in chemical change. We find reactions of all kinds ascribed to them, whether the recognised methods of demonstrating their existence indicate their presence or not, and possibly the majority of chemists will now subscribe to the statement of Arrhenius (*Lehrbuch der Elektrochemie*, 1901, 171): "Man kann sogar so weit gehen, zu behaupten, dass nur Ionen chemisch reagieren können." That the ionised condition—whatever views may be held regarding its nature—is one in which different kinds of matter are peculiarly liable to mutual interaction is sufficiently manifest, and, although the degree of ionisation of a liquid generally diminishes to an almost infinitesimal amount when the liquid reaches a high degree of purity, the contention that there are still sufficient ions present to account for its manifestations of chemical change when brought into contact with another substance is one which it is by no means easy to combat, however unsatisfactory it may appear when applied to individual cases. Further, the work of various investigators on the influence of a trace of moisture on reactions between gases has demonstrated the effect which an undetectable trace of one kind of matter may have on systems which, without it, are incapable of change, and so, by analogy, has strengthened the position of the extreme ionist. The exceedingly interesting observations of Kahlenberg and his pupils (*Zeit. physikal. Chem.*, 1903, 46, 68) that hydrogen chloride and trichloroacetic acid react readily with some metals in certain non-ionising media have therefore been met, as it were, in anticipation, by the advocates of this theory, which assumes the presence of ions because a reaction takes place. However, to take refuge behind a mathematical abstraction which, from the nature of the case, is incapable of experimental demonstration, is a position that is decidedly unsatisfactory when another method of representation of the same phenomena suggests itself, at least until that other method has been shown experimentally to be untenable. A second and even more

vulnerable point of weakness in the theory is the tacit assumption of the absence of any extensive ionisation when no reaction is observable. Even with regard to the first, the argument would have a certain amount of force that in one of two otherwise parallel instances, neither of which exhibits ionisation, a reaction is found to take place with great readiness, whilst in the other it does not do so at all. An instance of this nature came under my observation in the behaviour of ethereal solutions of hydrogen chloride and of trichloroacetic acid towards zinc. The first evolves hydrogen vigorously even when no moisture is present, the latter not at all. The amount of ionisation is so small as to be immeasurable in both solutions, and the cases are so far parallel that in aqueous solution both acids are ionised to a very great extent. Is it legitimate, therefore, to assume ionisation in the first ethereal solution only? The second line of attack is of course open to the objection that the absence of reaction is due to the absence of the necessary kind of ions. But if instances can be brought forward which are so similar that the nature of the ions may in all be assumed to be the same, and if reaction takes place in some cases and not in others, it would seem advisable to look round for another method of representing the mechanism of the reactions in question. Such a method is found in the conception of potential valency as the determining factor in many chemical reactions, and, although very frequently brought forward, it has never received what seems to me due consideration, possibly because it has not been supported by any great weight of experimental evidence. In this and the following communications I hope to bring forward some observations which point to the necessity of such an assumption in special cases, as well as to discuss the closely-allied question of ionisation and chemical combination from the standpoint of cause and effect.

The possibility of a close relationship between these two series of phenomena, the combination of a solvent with the dissolved substance and the electrical conductivity of the resulting solution, was advanced even in the early days of the electrolytic dissociation theory by Ostwald (*Lehrbuch*, II, 1, 801). He states clearly, without laying special stress on the statement, that ionisation may be accompanied by a process of hydration, and, although this suggestion was at first neglected, a very intimate connection between the two series of phenomena has recently begun to be insisted on, notably by Bruhl, who sees in chemical combination not the concomitant or even the more or less accidental precursor of ionic dissociation, but the necessary condition for the existence of the latter.

Meanwhile two other properties of solvents were being considered in the same causal relationship, namely, the association of the solvent and its dielectric power. Dutoit and Friderich (*Bull. Soc. chim.*,

1898, [iii], 19, 321) concluded from their investigation on solutions in ketones and nitriles, as well as from the results observed by others in various other solvents, that a non-associated liquid has no ionising power. From the extensive series of researches which have been carried out in recent years by various investigators, among others by Walden, Kahlenberg, Carrarra, and Euler, on solutions other than aqueous, a summary of which is given by Walden (*Zeit. physikal. Chem.*, 1903, 43, 388), it appears that this view regarding the connection between its degree of association and the ionising power of a liquid is not generally applicable. Lincoln (*J. Physical Chem.*, 1899, 3, 486), in discussing the possibility of such a connection between the two phenomena, states that some solvents, which show at most only very slight association, yield solutions that conduct quite well, whereas others, the molecules of which are to some extent polymerised, do not form conducting solutions. The question of the non-association of certain liquids is, however, one regarding which different views may still be held. Ramsay, assuming the simplest molecular formula for some, was able to compute the relative complexity of others, but it may well be doubted whether any ordinary liquid consists for the most part of simple molecules, although with our present hard and fast conceptions of the strictly limited valency of certain elements it seems necessary to assume that the hydrocarbons of the marsh gas series at least must be so constituted. Some experiments on heats of solution, described elsewhere by the author (*Proc. Roy. Soc. Canada*, 1902, 7, [iii], 105), may be considered as throwing doubt at least on this assumption. Certainly, however, the accepted degree of association of a liquid seems to have no very intimate connection with the question as to whether it can or cannot yield conducting solutions. It is otherwise with respect to the dielectric power of a liquid, for, although there does not seem to be direct proportionality between the magnitude of the latter and the extent to which the liquid can ionise a substance dissolved in it, still, in general, liquids with high dielectric constants have been found thus far to yield solutions of the highest conductivity.

Although the accepted molecular complexity of a liquid is not a criterion of its ability to yield conducting solutions, there is a chemical property which may well be considered as essential to the exhibition of this phenomenon, namely, the presence of atoms in its molecule which show a marked tendency to enter into certain combinations where they exhibit a higher valency. As is well known, association is not dependent on the presence of such atoms. The range of substances which may be expected to be ionising media is therefore greatly extended. The possibility of chemical combination being a precursor of ionic dissociation seems to have been first experimentally con-

sidered by Konowaloff in an investigation on "Properties of the solutions which amines form with acids" (*Wied. Annalen*, 1893, 49, 733). In these cases the power of conducting the current is shown to be closely connected with the reactions which take place between acid and base.

Two causes, however, may have operated against the application of this idea of combination as the cause of ionisation, derived from the special case considered by Konowaloff, to the more common one of aqueous solution. Firstly, the molecular conductivity of electrolytes in the latter almost invariably increases with dilution, whilst that of the amines decreases in the same circumstances. This objection, however, lost its weight, although no definite conclusion was drawn regarding the causes operating to produce ionic dissociation, when it was shown by Kahlenberg and Lincoln (*J. Physical Chem.*, 1899, 3, 12) that in some instances which they treat as cases of simple solution, but where chemical combination undoubtedly occurs between the solvent and the solute, the molecular conductivity increases with dilution, whilst in others it diminishes. The second and main cause which prevented any analogy being drawn between solutions of amines in acids and of substances in aqueous solution was the lack of appreciation of the closeness of the resemblance between oxygen and its companions in the seventh group in the periodic table, although this had been very decidedly pointed out by van't Hoff (*Ansichten über die Organische Chemie*, 1877). So long as water was regarded as a saturated compound, in so far as ordinary chemical combining power is concerned, hydration could scarcely be considered, and was certainly not universally considered, to be a distinctly chemical phenomenon, and one likely to play an important rôle in the production of solutions possessed of the power of conducting electricity. In fact, although the higher valency of the oxygen atom had been repeatedly suggested as a simple means for associating a large number of otherwise more or less disconnected facts, Collie and Tickle (*Trans.*, 1899, 75, 716), when proposing the oxonium theory to account for the existence of the compounds of dimethylpyrone with acids, expressed the opinion that the tendency for oxygen to form definite compounds in which its higher valency is evident can at best be feeble, and that isolation of the compound can only be expected in favoured cases. A summary of the opinions regarding, and of the investigations on, this subject has recently been given by Walden (*Ber.*, 1901, 34, 4185, and 1902, 35, 1764), as well as by Schmidt (*Ueber die basischen Eigenschaften des Sauerstoffs und Kohlenstoffs*, 1904). The very great import of the conception, in its bearing on the mechanism of chemical reaction, was pointed out by Collie and Tickle, and the subsequent work of Baeyer and

others shows that amongst organic compounds the isolation of the desired derivatives may be an easier problem than was at first anticipated.

The conception regarding the mechanism of chemical reaction, according to which combination, in virtue of potential valency, precedes any manifestation of chemical change, is at least equally with that of ionic dissociation, as the necessary forerunner of reaction, in harmony with thermodynamical principles. It is not therefore necessary to attribute reaction between the most diverse kinds of substances entirely or mainly to a previous ionisation of these substances, especially when the existence of intermediate compounds, which may or may not be ionised, is so easily shown in many instances not only by actual isolation, but also by the irregular change of some physical property of their solutions. The actual isolation of an intermediate compound in special circumstances may, however, be rejected as proof of its actual participation in a given reaction under ordinary conditions, hence the frequent resort to dynamical studies as a means of determining the mechanism of certain reactions. An interesting class of reactions for study along both of these lines is that involving the interaction of the halogen hydrides and substances of the type $R(OR_1)_n$, where neither R nor R_1 contains atoms to which change of valency is usually assigned, and where therefore the formation of an intermediate compound could only be attributed to the higher valency of oxygen, as in Friedel's compound of hydrogen chloride and dimethyl ether (*Bull. Soc. chim.*, 1875, 24, 241), and in the compounds of the ethers with the other halogen hydrides (*Ber.*, 1875, 8, 1352, and *Amer. Chem. J.*, 1898, 21, 64). The ethereal salts of such inorganic acids as phosphorous and boric acids were selected, and attempts were made to isolate compounds at very low temperatures, where their stability would probably be increased, as well as to measure the velocity of such reactions as $PCl_3 + C_2H_5 \cdot OH = PCl_2 \cdot O \cdot C_2H_5 + HCl$, also at low temperature, and in some indifferent solvent which might be assumed to have little attraction for either of the products of dissociation of the complex $PCl_2(OHCl \cdot C_2H_5)$. This investigation had proceeded some way and indications of the existence of compounds of this nature obtained, when it was observed by my assistants, Mr. McIntosh and Dr. Archibald, that a few substances of this type form good conductors when dissolved in the liquefied halogen hydrides, which have been lately shown by Steele and McIntosh (*Proc. Chem. Soc.*, 1903, 19, 223) to be ionising media for some ordinary electrolytes. Since the conductivity could only be ascribed to ionisation following on combination between solvent and solute, the method suggested itself as a very simple one for determining whether, in analogous cases at least, combination had taken place or not. The results of this investigation form the subject of another communication.

Even dynamical studies, however, do not yield a conclusive answer as to the nature of a reaction, but only elucidate that stage of it, the velocity of which is measured. The results may indicate that the chemical change proceeds by way of ionisation or by the formation of an intermediate complex, but, nevertheless, in neither case is the other excluded as an operative cause during a previous or a subsequent stage. For example, in the Friedel-Crafts reaction, lately studied in this laboratory, it has been shown by Steele (Trans., 1903, 83, 1470) that, when benzyl chloride acts on an excess of toluene in the presence of aluminium chloride, the reaction is unimolecular, indicating the formation of a compound between the reagents. The method, however, gives no information as to whether this complex in its subsequent action reacts in the ionised condition or not, nor does it tell us whether the compound is formed by an ionic reaction from its constituents or by their direct union in virtue of potential valency. And, conversely, had the reaction been found to be bimolecular, it would not have excluded the possibility of the formation of an intermediate compound in some stage of the process. The considerations put forward in the foregoing pages gave rise to the following investigation.

EXPERIMENTAL.

It has been shown by Kahlenberg and Lincoln (*J. Physical Chem.*, 1899, 3, 19) that solutions of ferric chloride in *o*-nitrotoluene are fairly good conductors of an electric current, whilst solutions of the same salt in anisole conduct very poorly. This is in accord with the general behaviour of nitrohydrocarbons and of ethers. Gattermann has already indicated that both of these classes of substances combine with aluminium chloride, and a more detailed description of the compounds will be given in another communication. Measurements of the electrical conductivity of aluminium chloride in *o*-nitrotoluene and in anisole gave the following results at 18°, V , the volume, being expressed in litres, and μ , the molecular conductivity, in reciprocal ohms.

In <i>o</i> -nitrotoluene.		In anisole.	
$V=1.15$	$\mu=0.6$	$V=0.31$	$\mu=0.026$
2.30	0.8	0.62	0.026
4.60	1.1	0.78	0.023
9.20	1.5	0.99	0.019
18.40	2.2	1.25	0.018
36.80	3.7	1.55	0.012
73.60	4.3	1.97	0.010
147.20	1.9		

In preparing these solutions, a quantity of aluminium chloride was distilled into the tube forming the conductivity cell, which was then

instantly corked up and weighed. The salt was dissolved in each case in 4 c.c. of the solvent, and from this solution the others were made by dilution in the ordinary way. No account has therefore been taken of the volume of the aluminium chloride. The molecular conductivity of the solution in *o*-nitrotoluene increases regularly with dilution, and, although the most dilute solution shows a large decrease, calculation indicates that, if, as is most probable, moisture would destroy the conducting power, a very small amount would be sufficient to produce the observed effect. With anisole, on the contrary, the molecular conductivity diminishes continuously with increasing volume, and this phenomenon will be discussed later. When these solutions are now compared with regard to their powers of reaction, it is seen that, as far at least as the Friedel-Crafts reaction is concerned, there is no connection between ionisation and reactivity, for, whilst *o*-nitrotoluene along with other nitrohydrocarbons is distinguished by its indifference in this respect, anisole is found to be extremely reactive (*Ber.*, 1890, 23, 1199), and yet its conductivity is found to be less than the 1/100th part of that of the *o*-nitrotoluene solution. The conclusion seems obvious that in this case reaction is conditioned by some factor other than ionisation. Evidently also, since both substances combine with aluminium chloride, what ionisation there is is consequent on chemical reaction; no antecedent ionisation can be detected either in *o*-nitrotoluene, anisole, or aluminium chloride.

A further observation of considerable interest was made when the solution of aluminium chloride in anisole was treated with benzoyl chloride, that is, was made to undergo the Friedel-Crafts reaction. The solution contained 1.286 grams of the chloride in 6 c.c., and when examined in the cell employed in the preceding experiment its resistance was found to be more than 50 times greater than that of 1/50 *N* potassium chloride. When, however, 1 c.c. of benzoyl chloride was added and the ensuing reaction had ceased, its resistance at the same temperature was found to be somewhat less than that of the same potassium chloride solution. The amount of benzoyl chloride added is slightly less than equivalent to the aluminium chloride, but, assuming it to be equivalent, the molecular conductivity of the resulting compound of the ketone with aluminium chloride has been calculated: $V = 0.727$, $\mu = 2.0$; $V = 1.142$, $\mu = 2.3$.

The first conclusion from this experiment is that there has again been chemical action with a consequent large increase of electrical conductivity, and therefore also presumably of ionisation; the second, that, with an appropriate solvent, anisole yields solutions which conduct quite as well as the solutions in *o*-nitrotoluene, although thus far it has been looked on as a practically non-ionising medium. Further, although it was examined only at two concentrations, the

conductivity seems to increase with dilution in the normal manner. Another remark, which has reference to the cause of the chemical reaction, may be added, namely, that, although the ionic concentration is now considerable, further addition of benzoyl chloride causes neither further change of conductivity to any marked extent, nor does it produce further chemical change. A similar result to the above was obtained by substituting acetyl for benzoyl chloride. Unfortunately, the occurrence of well-known reactions prevents the employment of these acyl chlorides as solvents for aluminium chloride, but thionyl chloride was substituted. No quantitative experiment was performed, but it was observed that, whilst some aluminium chloride in this solvent had a resistance in the same cell of 35,000 ohms, the addition of a little naphthalene caused it to fall to about 2500 ohms. In this case also, ionisation seems to be greatly increased by reaction, although not to the same extent.

Metathetic Reactions between the Alkyl Halides.—In attempting to prepare some simple compounds of the alkyl halides with aluminium chloride, it was observed that, whilst this salt is apparently only slightly soluble in ethyl iodide or chloroform separately, it is rapidly dissolved when added to a mixture of these two substances. The liquid at once becomes dark red, and in a short time an abundant crystalline deposit of iodoform separates. Similar results were obtained when methyl iodide was substituted for ethyl iodide and carbon tetrachloride for chloroform, carbon tetraiodide being the solid product in the latter case. The aluminium chloride evidently combines very readily with a mixture of two of these substances forming a very dark red compound, which, in the case of ethyl iodide, is quite soluble, but in the case of methyl iodide could be seen as a dark, supernatant layer. A relatively small quantity of aluminium chloride was sufficient to convert a large amount of methyl iodide into carbon tetraiodide or iodoform. Although instances of double decomposition between aluminium halides and a single alkyl halide are on record, and in the case of carbon tetraiodide this reaction is the one employed for its production from carbon tetrachloride and aluminium iodide (*Annalen*, 1874, 172, 173), an apparently catalytic reaction proceeding with such facility between two substances which, under ordinary conditions are so indifferent to each other as ethyl iodide and carbon tetrachloride, seemed to warrant a little further investigation. The first point of interest is the manifest display of the higher valency of the halogen atoms in the formation of the soluble or liquid double compounds. No results have been obtained thus far in the few attempts made at a closer characterisation of these compounds. The matter is one of considerable difficulty, since one of the products of their dissociation is gaseous and very likely readily split off, and

another is a somewhat soluble solid. Further, there are grounds for believing that the aluminium chloride is partially converted into iodide during the reaction. This introduces a further complication. Meantime an outline of the course of the reaction in two cases will be given.

To a mixture of 5 grams of chloroform and 20 grams of ethyl iodide was added 0.385 gram of aluminium chloride. The substances were therefore present in the molecular ratio 1 : 3 : 0.07. The reaction was performed in a flask closed with a stopper which carried a fine capillary tube to allow the ethyl chloride produced to escape and to prevent the entrance of air and moisture. After several hours, practically all trace of liquid had disappeared, leaving only iodoform in the flask. The yield was almost quantitative. To a mixture of 12 grams of carbon tetrachloride and 48 grams of ethyl iodide, 1 gram aluminium chloride was added. The substances are in the molecular ratio 1 : 4 : 0.1. The salt was dissolved rapidly and a brisk effervescence set in, due to the escape of ethyl chloride. In less than half an hour the comparatively small quantity of residual liquid was decanted from the heavy, red, crystalline deposit which had formed very rapidly. The latter was quickly washed with alcohol and water and was identified as pure carbon tetraiodide. The reaction with methyl iodide is much slower than with ethyl iodide, doubtless owing to the slight solubility of the intermediate compound, and consequently the carbon tetraiodide was obtained in much larger crystals. Experiments were also made in order to determine if the same reaction could be induced by phosphorus trichloride, silicon tetrachloride, and boron trichloride, but the results were negative. Ethyl bromide was also substituted for ethyl iodide in the expectation that carbon tetrabromide would be obtained with the same facility. The aluminium chloride dissolved forming a red liquid, but when left for two days in a flask arranged as before there was no appearance of crystals. After six weeks, a few crystals in the form of transparent plates had separated, but very little liquid had evaporated. The reaction in this case is evidently excessively slow.

Electrical Conductivity in the Alkyl Halides.—Solutions of various substances, which in other media conduct well, have been examined in the alkyl halides by Dutoit and Aston (*Compt. rend.*, 1897, 125, 243), Kahlenberg and Lincoln (*J. Physical Chem.*, 1899, 3, 19), and Patten (*J. Physical Chem.*, 1903, 7, 161), but have been found to show no electrical conductivity. Kahlenberg and Lincoln employed ferric chloride as the solute, and therefore there was but little expectation that, since it gave negative results, a positive one would be obtained with aluminium chloride, the more so as these liquids, in view of their very

low dielectric power would not be expected from the Nernst-Thomson generalisation to yield conducting solutions. Their very pronounced chemical activity, however, in presence of that salt made it essential to test the point experimentally. With methyl, ethyl, and *n*-propyl iodides, as well as ethyl bromide and chloroform, considerable conductivity could readily be detected, but only in the case of ethyl bromide was the resistance of the solution, saturated with aluminium chloride, found to be less than 2000 ohms in the same cell as was used previously. Accordingly this alone was examined quantitatively with the following result: $V=1.6$, $\mu=0.7$; $V=3.2$, $\mu=0.4$.

The conductivity is low and decreases with dilution. The lower conductivity in ethyl iodide was most probably due to slight solubility, since, when a little chloroform or carbon tetrachloride was added so as to bring the excess of salt into solution, the resistance diminished greatly. Quantitative determinations by this method were excluded by the deposition of solid on the electrodes. The results seem to point to the conclusion that the catalytic reaction just described is an ionic reaction, and this in media where previously the existence of ions had not been demonstrated. One consideration, however, throws doubt on this conclusion. In a mixture of ethyl bromide and carbon tetrachloride, the aluminium chloride seems to conduct just as well as if ethyl iodide was substituted for the bromide, and yet, as was shown, the corresponding reaction with the bromide is very much slower. Further, the observed ionisation is itself the result of chemical combination when a mixture of alkyl halides is employed as solvent. The facts agree much better with the hypothesis of an intermediate compound which undergoes rearrangement to a more stable system, the method of rearrangement depending on a molecular, and not on an accidental, ionic dissociation of the complex.

Ionisation in the Friedel-Crafts Reaction.—Since the solutions of aluminium chloride in the alkyl halides had been found to be conducting liquids, it seemed quite likely that further chemical action might, as in the case of anisole, produce liquids of higher conducting power. Accordingly, to a solution of aluminium chloride in ethyl bromide, which showed in the same cell as before a resistance of 2770 ohms, a little benzene was added. A reaction immediately occurred with an evolution of hydrogen bromide, but after this had ceased the resistance of the solution was found to have decreased to 220 ohms. Similarly, to a solution of aluminium chloride in ethyl bromide, which showed a resistance of 1630 ohms, a little naphthalene was added, when the resistance fell to 92 ohms.

These results are conclusive enough as regards the dependence of

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ionisation on chemical reaction, but they do not indicate in any way the dependence of chemical reaction on ionisation.

Some points of equal interest were observed in what is so far a somewhat roughly quantitative study of these cases. A solution was prepared containing 1 gram-molecule of benzene to 1 gram-molecule of aluminium chloride, the solvent being ethyl bromide. A slight evolution of an acid gas occurred immediately when the solvent was added, and a straw-coloured liquid remained when the whole of the salt had disappeared. This was diluted in the ordinary way as the measurements of conductivity were made. A corresponding series was made with naphthalene.

Benzene.		Naphthalene.	
$V=0.907$	$\mu=4.2$	$V=1$	$\mu=3.9$
1.814	1.5	2	2.3
3.628	5.7	3	4.9
7.256	4.3	4	5.4
		8	3.5

The volume is assumed to be the sum of that of the ethyl bromide and of the benzene or naphthalene, and the molecular conductivity μ is calculated on the aluminium chloride present. In both cases, its value is observed to pass through a minimum with increasing volume—in fact, even the observed conductivity does so—and then through a maximum, and there is an indication that the position of those points in the case of benzene may be identical with their position in the case of naphthalene. With the latter, the evidences of chemical change are very marked. Thus, at $V=1$, the colour was very deep red, at $V=2$, still deep red, at $V=3$, medium red, at $V=4$, quite pale, and at $V=8$ almost colourless. As will appear in the sequel, points of sharp colour change correspond with these positions of maxima and minima in the curves of molecular conductivity. In the following experiments, aluminium chloride was added in small quantities to a solution of benzene or naphthalene in ethyl bromide, and repeated measurements of the conducting power of the solution were made in the same cell as before, while the salt slowly dissolved. In this way, the position of the points of maximum and minimum conductivity could be gauged with a fair degree of accuracy even in the first experiments.

I. Benzene; 0.4311 gram in 4 c.c. of ethyl bromide.

AlCl ₃ .	Resistance in ohms.		V.	μ.
0.0532 gram	3300	colourless		
	3000	„	11.3	1.38
0.1788 „	400	„		
	390	„	3.4	3.2
0.2500 „	355	„		
	367	„ slight fume	2.4	2.4
0.3214 „	750	„		
	1800	„		
	3400	„ { almost all } { dissolved }	?	[0.13]
	2000	pale yellow		
	1900	„	1.87	0.35
0.4170 „	207	deeper yellow		
	197	„	1.44	2.7
0.5185 „	101	„	1.16	4.3
0.8570 „	43	effervescence	0.7	6.0
1.1630 „	35	„	0.52	5.5

The appearances accompanying these remarkable changes in conductivity are much less pronounced in the case of benzene than in that of naphthalene, but are still quite distinctly evident. Thus, neither colour nor acid fume is observed until the first maximum is reached, when a slight acid fume becomes perceptible. This continues and the solution remains quite colourless until the minimum is just passed, when a yellow colour appears quite suddenly. This continues to deepen, still without any effervescence of acid gas, until more than an equivalent weight (0.7378 gram) of aluminium chloride, calculated on the benzene present, has been added. Apparently in this neighbourhood a maximum of conductivity is again reached. The position of the minimum coincides very nearly with a volume of 1.87 litres, and, taking the highest resistance recorded when only a trace of salt was left undissolved, the molecular conductivity is found, with only a slight error, to be 0.13, or about one-thirtieth of the previous maximum. Whether these sharp changes of conductivity point to the formation of definite compounds between the aluminium chloride and the benzene, or the ethyl bromide or both, will be discussed after the observations with naphthalene have been described.

II. Naphthalene ; 0.6459 gram in 4 c.c. of ethyl bromide.

AlCl ₃ .	Resistance in ohms.	V.	μ .
0.0302 gram	14000 colourless	20	0.53
0.0577 "	4100 "	10.4	0.95
0.1209 "	1240 "	5.0	1.5
0.3134 "	1950 orange		
	2100 " slight fume		
	2210 "	1.92	0.32
0.3692 "	408 deep red		
	385 "	1.63	1.57
0.4532 "	140 "	1.33	3.5
0.5634 "	85 "	1.06	4.6

In this experiment, there was never any effervescence due to the escape of hydrogen bromide. This point would probably have been reached by adding an equivalent weight of aluminium chloride, namely, 0.6735 gram. A second series of observations was made in order to locate the maximum and minimum points more closely. The continual fall from the first values for μ shows, however, that the maximum had been already reached in the first observation.

AlCl ₃ .	Resistance in ohms.	V.	μ .
0.2300 gram	527 colourless	2.61	1.85
0.2408 "	531 pale pink	2.5	1.75
0.2530 "	558 "	2.37	1.58
0.2823 "	700 "	2.13	1.13
0.3078 "	980 "		
	1480 "	1.95	0.49
0.3187 "	2155 "		
	3390 "	1.88	0.21
0.3247 "	5670 red		
	5900 "		
	5757 "	1.85	0.12
0.3272 "	5210 very deep red	1.84	0.13
0.3350 "	2500 "		
	1970 "	1.79	0.34

In this series of observations, in which the aluminium chloride was added in very small portions, the colour changes are seen to be exceedingly sharp. For example, 1 centigram induces a pale pink tinge in the colourless solution, whilst less than 8 milligrams trans-

forms the pale pink into a very deep red. When the position of the minimum for naphthalene is compared with that for benzene it is found that they lie very close together—about $V=1.85$ —and when the amount of aluminium chloride added up to that point is compared with the quantity of naphthalene present it is found that they are very nearly in the ratio of one molecule of the former to two of the latter. With benzene, however, the agreement is not so close if the position of the minimum value is taken as identical with that for naphthalene. Again, in the second series of observations with the latter substance, the first reading is probably very close to the maximum, since colour develops with the addition of less than 1 centigram of aluminium chloride. If so, this maximum corresponds almost exactly with a molecular ratio of three of naphthalene to one of aluminium chloride. The breaks in the curves would therefore seem to indicate the formation of compounds $3X, AlCl_3$, $2X, AlCl_3$, and $X, AlCl_3$, where X stands for a molecule of hydrocarbon. As a test of the cogency of this conclusion, the proportion of naphthalene present was also varied with the following result.

III. Naphthalene ; 1.2918 grams in 4 c.c. of ethyl bromide.

$AlCl_3$.	Resistance in ohms.	V .	μ .
0.0625 gram	10400 colourless	11.32	0.4
0.1584 „	1800 „	4.46	0.9
0.1910 „	1200 „	3.70	1.15
0.2690 „	800 „		
	800 faint pink	2.63	1.23
0.2816 „	860 „	2.51	1.08
0.3520 „	4230 red		
	4000 „	2.01	0.18
0.4470 „	315 very deep red	1.58	1.87
0.5120 „	177 „	1.38	2.90
0.8695 „	70 „	0.81	4.32

There was still no effervescence due to escape of hydrogen bromide.

IV. Naphthalene; 0.6459 gram in 8 c.c. of ethyl bromide.

AlCl_3 .		Resistance in ohms.	V .	μ .
0.0880	gram	6670 colourless	12.9	0.96
0.1540	„	2580 „	7.37	1.06
0.1937	„	1874 „	5.86	1.16
0.2720	„	980 „	4.17	1.58
0.3630	„	575 „	3.13	2.02
0.5994	„	445 faint pink		
		724 „	1.80	0.93
0.6836	„	1820 very deep red		
		1000 „	1.66	0.65
0.7704	„	277 no effervescence	1.47	1.98

It is evident that in every instance the minimum is situated at very nearly, if not exactly, the same point, namely, at 0.32 gram of aluminium chloride to 4 c.c. of ethyl bromide, and this independently of the nature of the hydrocarbon and also of its amount. There are not sufficient data to warrant the same conclusion with regard to the point of maximum conductivity, which seems to correspond approximately with 0.23 gram of aluminium chloride to 4 c.c. of ethyl bromide, but if there is a variation it is within comparatively narrow limits. This observation does not bear out the conclusion that the maxima and minima indicate the existence of compounds between the hydrocarbon and the aluminium chloride. It points rather to the presence of some other substance or substances in the ethyl bromide which react first with the aluminium chloride, producing colourless or only slightly coloured solutions. As ordinary ether is an impurity of this nature which might be present, although the ethyl bromide had been very carefully washed with water, the liquid was shaken repeatedly with concentrated sulphuric acid, then with dilute caustic potash, and finally with water. After this treatment it no longer showed the same phenomena when employed as a solvent for naphthalene and aluminium chloride. On the contrary, the first small addition of the latter produced a deep red coloration, whilst the conducting power of the solution was found to be even greater than before, and to increase steadily with increasing concentration of salt.

V. Naphthalene; 0.8074 gram in 5 c.c. of ethyl bromide.

AlCl_3 .		Resistance in ohms.	V .	μ .
0.0220	gram	2730 deep red	30.34	4.44
0.0420	"	1128 "	15.90	5.64
0.0870	"	390 "	7.67	7.84
0.1795	"	161 "	3.72	9.23
0.3335	"	80 "	2.00	10.20
0.3660	"	70 "	1.82	10.48
0.4050	"	60 "	1.65	10.86
0.4880	"	50 "	1.37	10.88
0.5445	"	47 "	1.226	10.40

A very strong indication that ether is the disturbing agent in the previous experiments was found by adding a known quantity of ether to the purified ethyl bromide both with and without naphthalene. In both instances there was a maximum and a minimum of conductivity as the aluminium chloride was gradually added, and, when the concentration of the ether was the same in both, the minimum was reached when identically the same amount of aluminium chloride had been added to each. It was also found that when the amount of ether present was varied, the amount of aluminium chloride required to produce the minimum varied proportionately. Further, the position of the minimum corresponds accurately with the ratio of 1 mol. AlCl_3 to 1 mol. $\text{C}_4\text{H}_{10}\text{O}$. The aluminium chloride therefore combines with the ether entirely before it attacks the ethyl bromide. The position of the maximum is not so well defined; it is conditioned by the equilibrium between the very poor conductor $\text{AlCl}_3, \text{C}_4\text{H}_{10}\text{O}$ and the fairly good conductor $\text{AlCl}_3, x\text{C}_4\text{H}_{10}\text{O}$. The observations in Table II would seem to indicate that x may have the value 1.5. It is very remarkable that the resistance of the solution containing $\text{AlCl}_3, \text{C}_4\text{H}_{10}\text{O}$ is more than ten times greater than that containing $\text{AlCl}_3, x\text{C}_4\text{H}_{10}\text{O}$.

By the addition of aluminium chloride, representatives of two classes of substances, namely, the alkyl halides and the aromatic hydrocarbons, which thus far have been regarded as media incapable of sharing directly in the production of ions, have been shown to become good conductors. The conductivity has been traced to the formation of compounds in virtue of the potential valency of certain atoms which they contain. The formation of these compounds and their comparative stability in the Friedel-Crafts reaction is evidenced by the fact that very little acid is evolved until the concentration of the aluminium chloride passes a certain value. In some instances,

therefore, the proof seems conclusive that chemical reaction is the cause and ionisation the effect of subjecting the substances selected to those reactions to which experience has shown them to be peculiarly liable. This consideration suggested the possibility that these or similar compounds might conduct even when dissolved in the hydrocarbons. No trace of conductivity could, however, be detected in benzene to which aluminium chloride and ethyl bromide had been added. The lower layer which separates when sufficient amounts of the two latter substances are employed is quite a good conductor, but this is not in benzene solution. In a qualitative experiment it was found that bromobenzene can yield solutions possessed of some conductivity.

In various instances it has been shown, as is the case with solutions of aluminium chloride in anisole, that the molecular conductivity diminishes instead of increasing with dilution. Sackur (*Ber.*, 1902, 35, 1248), who examined a few examples of this kind, attributes the latter only to combination with the solvent. This seems to be an arbitrary distinction, however, as there is no reason why progressive combination should not yield a compound more ionised than the original instead of, as he assumes, yielding one less ionised. The foregoing examples of maxima and minima seem to illustrate this.

This investigation will be continued and extended.

MACDONALD CHEMISTRY AND MINING BUILDING,
MCGILL UNIVERSITY, MONTREAL.
