[CONTRIBUTION FROM THE HARRIMAN RESEARCH LABORATORY, ROOSEVELT HOSPITAL, AND THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY.]

THE ELECTRON CONCEPTION OF VALENCE. VII. THE THEORY OF ELECTROLYTIC DISSOCIATION AND CHEMICAL ACTION.

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In the further development of the electron conception of valence,[1] a careful study of the relation which the phenomenon of electrolytic dissociation bears to this theory is of interest. Some of the simpler relations were pointed out in previous papers. The study of electrolytic dissociation in solution furnishes experimental methods for determining the distribution of some of the charges on some of the atoms of the molecules which show such ionization. These methods for locating the charges are confined to substances which conduct the electric current to a readily measurable extent in solution, and are, therefore, of limited value only for determining the charges on the atoms. The VI Paper of this series showed the importance of the solvent in ionization phenomena, a fact which had been emphasized by Werner, Walden and others.

The relation between the changes occurring in chemical reactions and the degree of electrolytic dissociation of one or more of the reacting substances will be taken up in this paper. For convenience of presentation, the conclusions reached in this study will be given at once and then some of the lines of evidence upon which these conclusions are based will be presented. *The changes occurring in chemical reactions do not depend upon the electrolytic dissociation of the reacting substances. The chemical changes are accompanied very often by electrolytic dissociation phenomena. but the latter parallel the former (or vice versa) and do not necessarily precede or cause them.*[2]

In the first place, it may be pointed out that the explanations of certain reactions, which at one time had been assumed to be purely ionic in character, have in recent years considered the un-ionized molecules as taking part in the reactions. Among those who have adopted this view may be mentioned Acree,[3] Goldschmidt,[4] Bredig,[5] Snethlage,[6] Dawson and

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[1] For the earlier papers of this series cf. *School of Mines Quarterly*, **30**, 179 (1909); THIS JOURNAL, **32**, 1637 (1910); **33**, 1140 (1911); **35**, 1810 (1913); **36**, 209 (1914); **37**, 274 (1915); *Orig. Comm. 8th Intern. Congr. Appl. Chem.*, **6**, 212 (1912); *J. prakt. Chem.* (*N. F.*), **88**, 97 (1913); *Proc. Am. Phil. Soc.*, **53**, 25 (1914).

[2] Similar views were brought forward by J. W. Walker (*J. Chem. Soc.*, **85**, 1082 (1904)) in several papers on "Ionization and Chemical Action."

[3] *Am. Chem. J.*, **37**, 410 (1907); **49**, 345 (1913).

[4] *Z. physik. Chem.*, **81**, 30 (1913).

[5] *Ibid.*, **85**, 170 (1913); *Z. Elektrochem.*, **20**, 489 (1914).

[6] *Z. physik. Chem.*, **85**, 211 (1913).

Powis,[1] Taylor,[2] and Stieglitz.[3] The theory of electrolytic dissociation does not postulate that only ions react.[4] In fact, it has always been taken for granted by all except the most extreme followers of the theory of electrolytic dissociation, that reactions take place between un-ionized molecules.

In the second place, certain physical properties of substances, which, early in the history of the electrolytic dissociation theory, were considered to be dependent upon ionization have since been shown to be independent of it. Thus, the color of a salt in solution was assumed to be made up of the different colors of the ions and the un-ionized molecule. Later work showed that ionization changes do not affect the color of the substance. J. Lifschitz goes into these relations in some detail in a review entitled "Die Aenderungen der Lichtabsorption bei der Salzbildung organischer Säuren."[5] This fact will also be brought out more in detail with some organic substances (the indicators) where the color changes have been shown to be due to other reasons. The rotation of polarized light by salts has also been shown to be independent of the ionization.[6]

The explanations advanced at different times with regard to the color changes of indicators will serve to illustrate the views which are to be brought forward. Ostwald in 1894[7] attributed the different color of an indicator in acid or alkaline solution to the different colors of the ions and un-ionized molecules. If the indicator substance itself was an acid, the color in acid solution would be that of the un-ionized molecule, while in alkaline solution the color would be that of the negative ion. If the indicator substance was a base, the color in alkaline solution would be that of the un-ionized molecule, in acid solution that of the positive ion.

This theory was shown not to be general enough to include the observed phenomena, and was replaced by the "chemical" theory first suggested (for phenolphthalein) by Bernthsen and developed by Stieglitz,[8] who was the first to bring the chemical theory into harmony with Ostwald's theory of the sensitiveness of indicators, and especially by Hantzsch,[9] who showed the ionic theory of indicators to be highly im-

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[1] *J. Chem. Soc.*, 103, 2135 (1914).

[2] *Z. Elektrochem.*, 20, 201 (1914).

[3] THIS JOURNAL, 35, 1774 (1913).

[4] Cf. Arrhenius, *Z. physik. Chem.*, 2, 247 (1889).

[5] "Sammlung chemischer und chemisch-technischer Vorträge," Vol. 21, Nos. 5–7 (1914); cf. p. 198 for the discussion with inorganic salts.

[6] Cf. A. A. Noyes, "Congress of Arts and Sciences," Universal Exposition, St. Louis, 4, 322 (1904).

[7] "Die wissenschaftlichen Grundlagen der analytischen Chemie," p. 104.

[8] THIS JOURNAL, 25, 112 (1903).

[9] *Ber.*, 39, 1090 (1906) and numerous articles since. Cf. also among others, Vorländer, *Lieb. Ann.*, 320, 116 (1902); *Ber.*, 36, 1485 (1903).

probable. The newer view considers every change in color of an organic substance to be due to an intramolecular rearrangement. Indicators form a special group in so far as the intramolecular rearrangements in their case are tautomeric in character and include, therefore, in most cases the shifting of a hydrogen atom in passing from one form to the other. The production of ions is secondary in the tautomeric changes, and if the ions are colored, it is because the un-ionized molecules from which they are derived are colored. The equilibrium between the tautomeric forms of a substance depends upon a variety of factors such as solvent, temperature, small amounts of certain added substances such as acids or bases, etc. To illustrate this, a few results obtained with ethyl acetoacetate may be quoted. The equilibrium between the tautomeric forms varies greatly in different solvents, the extreme values given by K. H. Meyer[1] being 0.4% enol form present in 3-5% aqueous solution at 0°, and 48% in hexane at 20°. Hantzsch[2] recently showed the important part played by solvents in affecting the equilibrium between the tautomeric forms of some indicators, and, therefore, the color changes of indicators. The action of acid and of alkali on the equilibrium between tautomeric forms is well known.[3] Similar actions take place with indicators in aqueous solution, one form predominating in the presence of acids, the other (tautomer) in the presence of bases. In practical titrations, the indicator substance is present in such small concentration that the color change which accompanies the transformation of one tautomer into the other is very marked with the relatively small amount of added substance necessary to produce it.[4] Other changes of conditions may be considered similarly for the indicators as a special class of tautomeric substances. In general, it may be stated that the various factors which influence the equilibrium between tautomers also influence the equilibrium between the different tautomeric forms of indicators, and that the question of the electrolytic dissociation of the indicator substances does not enter into the theory of their color changes as assumed in the earlier theory, although it appears to be connected with one of the factors involving the sensitiveness.

Esterification and saponification reactions are catalyzed by acids or bases. Until recently, the hydrogen or hydroxyl ions were assumed to be the catalysts, but the evidence brought forward recently showed that catalytic action by the un-ionized molecule must also be assumed. These reactions will now be taken up, but in order to develop the sub-

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[1] *Ber.*, **45**, 2843 (1912).

[2] *Z. Elektrochem.*, **20**, 480 (1914); *Ber.*, **48**, 158 (1915).

[3] For example, cf. Hantzsch, *Ber.*, **43**, 3052 (1910) for the action of alkalis on ethyl acetoacetate.

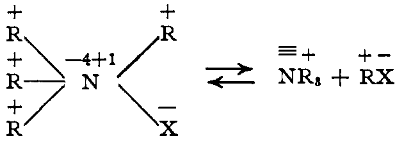
[4] In this connection cf. A. A. Noyes, THIS JOURNAL, **32**, 815 (1910).

ject logically, it will be necessary to describe a number of simpler reactions first. These reactions will be considered from the standpoint of the primary formation of addition compounds followed by their decomposition. Kekulé, in his textbook,[1] brought forward the view of primary addition followed by decomposition in organic reactions. Van't Hoff,[2] in 1878, came to similar conclusions with regard to some reactions which had been considered to be direct substitution reactions before. Michael has brought out much experimental work showing the same relations, and considers addition to play a greater part in reactions than has generally been assumed. Similarly, Emil Fischer[3] stated recently,

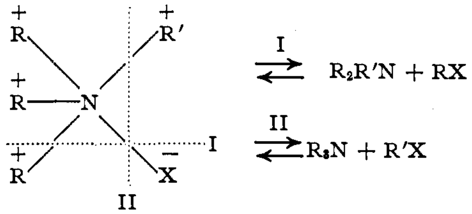
> " . . . es bricht sich immer mehr die Ueberzengung Bahn, das allgemein, auch bei gewöhnlichen Substitutionsvorgängen vorübergehende Additionen stattfinden, wie es schon Kekulé u. a. für wahrscheinlich erklärt haben."

A number of other workers might be quoted to the same effect.

It is well known that amines and alkyl halides combine to form substituted ammonium halides under certain conditions, and that under different conditions (rise in temperature, or addition of alkali) the latter decompose into amine and alkyl halide. An equilibrium exists in these reactions between amine, alkyl halide, and ammonium salt which may be represented by the formulas



The course taken by the reaction depends upon the equilibrium relation and whether any of the substances may be removed from the sphere of action. If more than one species of alkyl radical is present, the reaction may proceed in different ways as shown by the following equilibria:



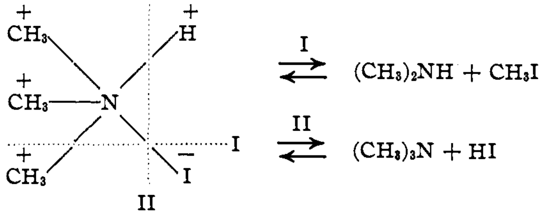
If more than two kinds of alkyl groups are present, the number of possibilities is increased correspondingly. In general terms, each of the positive groups is capable of uniting with the negative group, and there will be as many possible equilibria as there are different species of positive

[1] Vol. 1, 142 (1859).

[2] "Ansichten über die organische Chemie," 1, pp. 225, 244.

[3] *Ber.*, 40, 495 (1907).

groups. The fact that a number of possibilities exists, does not necessarily mean that all the reactions will occur to appreciable extents. The ones which will be observed are those for which the reactions proceed with the greatest velocities and where one or more of the products is removed from the sphere of action. As an example of the former, one of the reactions described by Wedekind[1] may be quoted: Benzylallylphenylmethylammonium iodide (prepared from allyl iodide and benzyl phenylmethylamine, or from benzyl iodide and allylphenylmethylamine, or from one of the other iodides and the corresponding amine) when heated alone or in aqueous solution formed benzyl iodide and allylphenylmethylamine, the halogen uniting with the radical containing the largest number of carbon atoms. To illustrate the latter, trimethylammonium iodide in the presence of alkali forms trimethylamine and hydrogen iodide, because the latter combines with the alkali.



The reaction proceeds to the right according to (II). An interesting reaction belonging to this type is that between cyanogen bromide and a tertiary amine in which addition takes place to form the trialkylcyanammonium bromide, which then decomposes into dialkylcyanamine and an alkyl bromide, the alkyl group of smallest molecular weight combining with the bromine.[2]

These reactions involve no electrolytic dissociation, but depend upon the formation of an onium compound of nitrogen. After being formed, these ammonium compounds may show electrolytic dissociation in suitable solvents, but this follows their formation.

This type of reaction forms the keynote of the reactions to be discussed, and it will be shown that it serves to correlate a number of apparently separate reactions, including esterification and saponification.[3] That these reactions have not generally been considered from this point of view is doubtless due to the fact that the onium or salt-forming property of oxygen is not very marked, and the oxonium compounds are not as readily isolated under ordinary laboratory conditions as the corresponding nitrogen onium compounds.

Some of the reactions of ethers are analogous to the reactions of the

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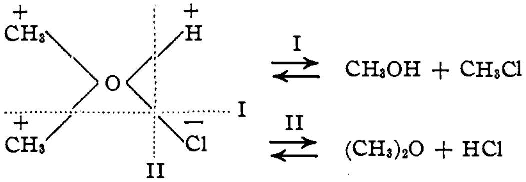
[1] *Ber.*, 35, 766 (1902); cf. Claus, *Ibid.*, 17, 1324 (1884); 19, 2785 (1886).

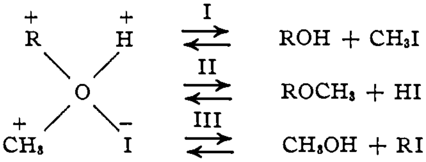
[2] J. v. Braun, *Ibid.*, 33, 1438 (1900)

[3] Cf. Henrich, "Theorien der organischen Chemie," p. 322 (1912).

amines just described. Dimethyl ether and hydrogen chloride at low temperatures readily form an oxonium salt, which decomposes at slightly higher temperatures.[1]

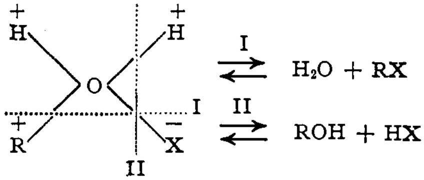


The equilibrium in the latter case follows (II). For reactions involving equilibria of a type similar to (I), it is only necessary to refer to the Zeisel method for determining methoxyl groups by heating the compound in question with hydrogen iodide. These reactions may be formulated as follows:



The substance $ROCH_3$, when treated with an excess of hydrogen iodide will, according to the law of mass action, form the oxonium salt, which in turn will be in equilibrium with the substances represented in (I) and (III). The excess of hydrogen iodide in the reaction mixture will form water and methyl iodide from the methyl alcohol (in III) according to the next group of reactions to be described. The net result of the reaction will be the formation of methyl iodide according to Equations I and III, directly in the former, secondarily from the methyl alcohol in the latter, each molecule of methyl iodide corresponding to a methoxyl group present originally. The relative amounts of ROH and RI formed will depend upon the relative velocities of the reactions of Equations I and III, and also upon the conversion of ROH into RI by the hydrogen iodide (next group of reactions).

The group of reactions, similar to those just considered, except that a hydrogen atom is combined with the oxygen instead of a radical, will be considered next. This group of reactions, in which an alcohol and an acid interact, may be formulated as follows:



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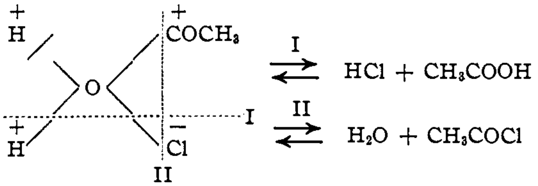
[1] Friedel, *Ber.*, 8, 548, 642, 777, 1193, 1348 (1875).

Addition of alcohol or HX, or removal of H_2O or RX would tend to make the reaction proceed to the right according to Equation II, the reverse conditions according to Equation I. The preparation of methyl chloride by passing HCl into a boiling solution of methyl alcohol in the presence of zinc chloride illustrates this reaction. HCl is continually added, CH_3Cl is removed by boiling, and H_2O by the zinc chloride.

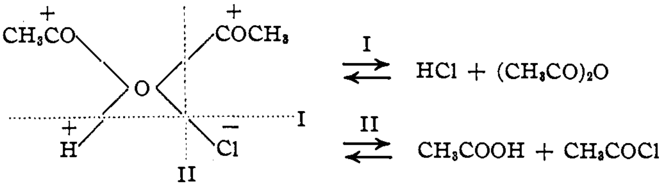
The formation of ethers from alcohols and other similar reactions may be explained by means of the equations already given. The course of the reaction is fixed in every case by the principle of mass action and the relative velocities of a number of possible reactions.

The next group of reactions which will be considered along the same lines contains in the formulas of the substances a group such as acetyl or benzoyl in place of a simple radical R. With acetyl chloride, for example, the following relations may be given:



The same products are formed by starting with acetic and hydrochloric acids. Removal of water and addition of HCl increases the amount of acid chloride formed.[1]

If, in place of a second hydrocarbon radical (R) or of hydrogen, another acetyl group is introduced, the reactions may be formulated as follows:



These reactions represent the customary method of preparation of acid anhydrides from acids (or their salts) and acid chlorides. An excess of acid is used and the HCl formed is driven off by heat. Both of these factors tend to increase the formation of the anhydride.

Similar formulations hold for all acetylations, whether of hydroxyl groups or of amino and imino groups. Two equilibria may be represented with the oxonium or ammonium compound taking part in both, and the factors involved in these equilibria determine according to the law of mass action which products will be formed in greater amounts. If the

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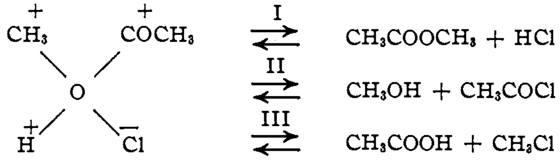
[1] Cf. Friedel, *Compt. rend.*, **68**, 1557; *Ber.*, **2**, 80 (1869).

mass action effect does not enter into the question, owing to lack of excess of one or more of the constituents, or if it enters equally for two reactions, if a greater number is possible, then the relative velocities of the different reactions will determine the relative amounts of the substances formed.

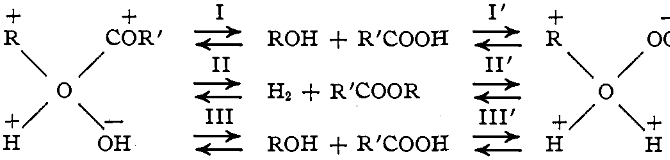
An interesting group of reactions is that in which one alkyl group and one acetyl group (for example) are involved, as follows:



This is evidently the group to which simple esterification and saponification may belong. Three equilibria are possible as indicated. With a large excess of alcohol, there would be a tendency for the substances represented by (I) and (III) to be formed. With primary and secondary alcohols the reaction has been found to proceed according to Equation I; on the other hand, with tertiary alcohols reaction III takes place with formation of alkyl halide. Also, if an ester such as ethyl acetate is heated with gaseous hydrogen halide, acetic acid and ethyl halide are formed. The velocity of this reaction is greatest with hydrogen iodide, smallest with hydrogen fluoride, decreasing with decrease in the atomic weight of the halogen.[1] In these last experiments, the reaction yielded the products shown by III because the hydrogen halide was present in excess. This group of reactions takes place if water is absent, or present in inappreciable quantities only.

In all of these reactions, in the equilibria between the oxonium compounds, and the possible products of the reactions only very small concentrations of the former need be assumed to be present at any time under ordinary conditions of working. They may therefore be considered to be intermediate products, the decomposition products being the substances actually obtained.

If alcohol and acid, or ester and water, are brought together, the following relations hold:



If the dissociation takes place according to (I), (I'), or (III), (III'), al-

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[1] Sapper, *Ann.*, 211, 178 (1882).

cohol and acid are formed, if according to (II), (II′), water and ester.[1] Excess of alcohol or acid will increase the proportion of ester and water formed; removal of water increases the proportion of ester, etc. The equilibrium constants of the reaction between these substances will depend in each case upon the equilibria with the oxonium salt. The velocity of the reaction to form the oxonium salt and the velocity of the decomposition of the oxonium salt are small, as a rule. The addition of small amounts of HCl, H_2SO_4, or other acid increases the velocities of esterification and saponification greatly. These increases in velocity are connected with the ability or the velocity with which oxonium salts are formed.

A better understanding of these relations may be obtained by first considering some simpler analogous reactions. Dry ammonium chloride, when heated, slowly dissociates into ammonia and hydrogen chloride.[2] When moist, very much more rapid dissociation takes place. In the latter case there is a partition of the HCl between the NH_3 and the water. If this is true of dissociation, it should also be true of combination. Dry HCl adds slowly to dry NH_3 to form an onium salt. It should also add slowly to H_2O. Ordinarily, however, water is made up of "double" and perhaps more complex molecules in which onium oxygen is already present; $H_3O.OH$, etc. A number of other facts, some of which will be given later, together with the experiments just indicated, suggest as a possible explanation of these phenomena that onium compounds react more rapidly than do the same constituents when not combined in the onium form. In other words, the positive and negative components of an onium compound add to some other atom, or atoms, in the onium manner, rapidly in comparison with the rate of addition of the same constituents when not combined in this way. The parallel phenomenon of electrolytic dissociation illustrates the same principle. Ammonium chloride ionizes instantaneously into $\overset{+}{NH_4}$ and $\overset{-}{Cl}$. It may also add in the onium manner as the same parts, to magnesium chloride, for example. One of these actions does not necessarily depend upon the other. Both depend upon a certain property of ammonium chloride. In the one case this property is measured by the electric current which the two parts (carrying opposite electric charges) are capable of transporting, in the other by the amount of the compound formed by the addition of the oppositely charged parts to a certain atom. Similarly, dry HCl adds slowly to dry NH_3; HCl reacts rapidly with water con-

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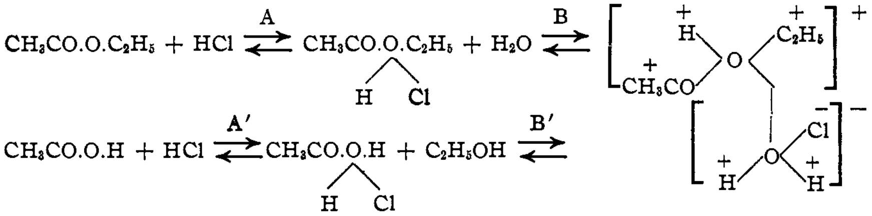
[1] To this group belong the formation of tetramethylammonium salts of acetic and nitric acids (as well as betaines from the tertiary amine and ester); Willstätter and Kahn, *Ber.*, **35**, 2757 (1902); Duvillier and Buisine, *Ann. chim. phys.*, [5] **23**, 322, 331 (1881).

[2] H. B. Baker, *J. Chem. Soc.*, **65**, 611 (1894); **73**, 422 (1898).

sisting partly of double molecules containing oxonium combinations, and these oxonium chlorides then react rapidly with ammonia to form ammonium chloride. In brief, the catalytic action of the water may depend upon the presence of the oxygen in the onium form, which renders these compounds capable of reacting more rapidly to form other onium compounds.

The action of HCl as catalytic agent in esterification and saponification will now be taken up briefly. It is, of course, impossible to state with definiteness just what compounds are formed in a system as complex as the one under consideration. All that will be done is to give a series of reactions as a possible type of the course of the changes. These may readily be modified to conform to different experimental facts. The main purpose of the presentation is to call attention to the general principles underlying this type of reaction. The formulation for the reaction between ethyl acetate, water, acetic acid, ethyl alcohol, and hydrogen chloride, is as follows:[1]



$$CH_3CO.O.C_2H_5 + HCl \overset{A}{\rightleftarrows} CH_3CO.\underset{H\quad Cl}{\overset{}{O}}.C_2H_5 + H_2O \overset{B}{\rightleftarrows}$$

$$CH_3CO.O.H + HCl \overset{A'}{\rightleftarrows} CH_3CO.\underset{H\quad Cl}{O}.H + C_2H_5OH \overset{B'}{\rightleftarrows}$$

In the first place, it will be observed that in the reaction between ester or acid and HCl, the oxonium salt is considered to be formed with the hydroxyl oxygen. This agrees with the view of Goldschmidt. Experimental measurements do not offer a solution to the question whether the hydroxyl or the ketone oxygen is involved in the salt formation.[2] The hydroxyl or ether oxygen was chosen here in order to bring the reaction into line with the reactions described in the earlier parts of this paper. The ester or acid hydrochloride is an onium compound and, therefore, reacts rapidly to form a new onium compound by the addition of negative chlorine and positive complex to some atom capable of forming an onium combination, in this case the oxygen of the water or of the alcohol. In this way reactions B and B′ form the substance indicated, containing two onium oxygen atoms.[3] The brackets do not necessarily indicate electrolytic dissociation of the complex, although this is a possible accompaniment of the reaction, but are only intended

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[1] An explanation of esterification similar to the one given here was suggested by Goldschmidt, *Z. physik. Chem.*, 70, 642 (1910); Goldschmidt and Thuesen, *Ibid.*, 81, 65–6 (1912).

[2] Stieglitz, This Journal, 35, 1776 (1913).

[3] For the experimental proof of the existence of ternary compounds of this type cf. Baumé and Pamfil, *J. chim. phys.*, 12, 260 (1914).

to show in the one case the negative group combined with the upper oxygen in the formula, in the other case the positive group combined with the lower oxygen. The concentration of this complex substance at any one time is undoubtedly small. This scheme accounts for the following facts: (1) The hydrogen chloride bears the same relation to the acid and to the ester. It, therefore, catalyzes the reaction in both directions. (2) The onium compound formation depends upon the strength of the acid catalyst. This is measured by the degree to which it breaks up in solution to form ions, a "physical" property similar to the "chemical" property of onium addition which controls the rate of reaction with water or alcohol. (3) Increasing the concentration of water favors the production of acid; increasing the concentration of alcohol favors the production of ester.

It is evident that the reactions might have been considered to take place between hydroxonium chloride and ester or between ethyl hydroxonium chloride and acid.[1] In this case also, an intermediate complex compound similar to the one given would be formed. Other schemes might be formulated, but the one given seems to fit in most satisfactorily with the simpler reactions and principles given before. It is evident also that the organic acid itself may catalyze the reaction by forming double molecules, which as oxonium compounds would react more rapidly with alcohol than the simple molecules.[2]

In considering the experimental evidence bearing upon the views outlined, it will be sufficient to indicate the large amount of material gathered in recent years regarding oxonium salts. A number of groups of organic substances containing oxygen have been shown to form salts with both organic and inorganic acids.[3] The results indicate that both the nature and the strength of the acid and the character of the organic compound influence the readiness of formation and the stability of the

[1] Suggested by H. Goldschmidt, *Z. Elektrochem.*, **14**, 581 (1908).

[2] Rosanoff, two years ago, presented the results of an experimental study of esterification (as a part of his general studies on catalysis, THIS JOURNAL, **35**, 173 (1913)) by himself and his collaborators before the New York Section of the American Chemical Society. The reactions were found to follow the trimolecular law of reaction velocities closely, two molecules of acid and one of alcohol taking part, and any factors which increased the polymerization of the acid increased the velocity. Permission to communicate these facts here was granted by Professor Rosanoff, who expects to communicate the complete results very soon.

[3] Among those who have worked in this field may be mentioned Collie and Tickle, *J. Chem. Soc.*, **75**, 710 (1899); Collie, *Ibid.*, **85**, 973 (1904); v. Baeyer and Villiger, *Ber.*, **34**, 2679, 3615 (1901); **35**, 1201 (1902); Hoogewerff and van Dorp, *Rec. trav. chim.*, **21**, 353 (1902); Thiele and Strauss, *Ber.*, **36**, 2375 (1903); Vorländer, *Ann.*, **341**, 1 (1905); Plotnikow, *J. Russ. phys. chem. Ges.*, **36**, 1088 (1904); **40**, 64 (1908); Stobbe, *Ann.*, **370**, 93 (1909); K. A. Hofmann, *Ber.*, **43**, 178, 183, 2630 (1910); McIntosh, THIS JOURNAL, **32**, 542 (1910); Maas and McIntosh, *Ibid.*, **34**, 1273 (1912); **35**, 535 (1913); Gomberg and Cone, *Ann.*, **376**, 183 (1911); J. Kendall, THIS JOURNAL, **36**, 1222, 1722 (1914); Kendall and Carpenter, *Ibid.*, **36**, 2498 (1914); Kendall and Gibbons, *Ibid.*, **37**, 150 (1915).

oxonium salts. The formation of oxonium salts need not be considered to be connected with the electrolytic dissociation. The readiness of formation of the oxonium salt often parallels the electrolytic dissociation in aqueous solution of the acid, but there is no direct evidence for such ionization in the mixtures studied. What is undoubtedly true is the fact that the properties of these acids are such that, when brought into aqueous solution under suitable conditions, electrolytic dissociation is observed, and when brought in contact with certain organic substances, possibly under different conditions, oxonium salts are formed. Furthermore, the oxonium salt itself may well ionize in solution.[1] On the other hand, while the formation of oxonium salts is not necessarily preceded by the electrolytic dissociation of any of the reacting substances, these same compounds might be formed by the suitable ions in solution reacting. Either the charged parts of un-ionized molecules may act, or ionized charged parts may act. Electrolytic dissociation is a special case of charged atoms, and the reaction is fundamentally the same.

It would be possible also to consider reactions such as sulfonation, nitration, aldol condensation, coupling, the Grignard, and probably others, in a similar way, but it is impossible to go into these in a paper such as this. Primary formation of addition compounds, followed by their decomposition in different ways as controlled by the law of mass action and the relative velocities of the different possible reactions form the basis of these views.

The theory of electrolytic dissociation has proven of greatest value in studying the reactions of inorganic chemistry, especially those taking place in aqueous solutions. An attempt to suggest a somewhat different point of view for these reactions will, naturally, meet with opposition, unless it can be shown that this new view not only retains all that is good of the old, but also brings out new relations, or explains, correlates, or accounts for reactions not satisfactorily dealt with on the older view. The latter considers that in aqueous (and also other) solutions, the ions of the substances present are the active factors in chemical reactions. The electron conception of valence considers that each atom in a molecule carries electric charges; the theory of electrolytic dissociation does not go beyond this, but on the other hand does not go as far and takes into account only some of the charges on the atoms of the molecules.

The point of view proposed here is that the ions in solution are formed from the substances, generally because of certain properties of the solvent, and also that due to certain, probably the same, properties of the solvent, the velocity of chemical change of the substances is increased. Both

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[1] Cf. Walden. *Ber.*, **34**, 4189 (1902); **35**, 1764 (1903).

phenomena depend upon properties of the solvent but not upon each other. If the properties of the solvent affect both sets of reactions (the so-called chemical and physical) alike, there should be a perfect parallelism between the two sets of phenomena and one might then be considered to depend upon the other; otherwise this parallelism will not appear. For simple uni-univalent salts this parallelism apparently exists, and it is therefore not surprising that the "chemical" phenomena have been assumed to depend upon the "physical" phenomenon of electrolytic dissociation. For more complex salts, including the so-called double salts and many of the compounds included in Werner's classification, this parallelism does not exist and a number of hypotheses have been suggested to account for these deviations.

In the VI Paper of this series, it was shown that in the electrolytic dissociation of uni-univalent salts of the first order[1] onium combination with the solvent was a necessary preliminary. In the earlier part of this paper it was suggested on the basis of experimental facts, that onium compounds react more rapidly than do compounds not in onium combination. This may be the more fundamental phenomenon (onium compound formation by the solvent) upon which both electrolytic dissociation and reactivity depend. The fact that the electrolytic dissociation may be measured quantitatively in several different ways and that definite numerical values may be assigned to these degrees of ionization has resulted in this being considered the fundamental property and the chemical changes based upon them.

As stated before, there is no intention of suggesting that ions cannot react chemically. The broader view is proposed, namely, that every chemical reaction is one between charged atoms. Since ions form only a special case of charged atoms, they would be included. At the same time, many of the explanations of reactions which have heretofore been attributed to ions, may find a more rational explanation in other ways. This will now be illustrated by a group of reactions of inorganic chemistry.

The theory of hydrolysis of Werner[2] and Pfeiffer[3] may be combined with the views developed in this paper. They consider hydrolytic reactions to be dissociation reactions which may be formulated as follows: $RHX \rightleftharpoons R + HX$. In terms of the electrolytic dissociation theory, the equation would be written $\overset{+}{RH} + \overset{-}{X} \rightleftharpoons R + \overset{+}{H} + \overset{-}{X}$. The hydrolysis depends mainly upon the affinity of R and H for each other. A special case may be quoted from Werner. With metallic hydroxides, the hy-

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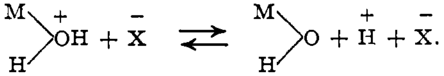
[1] Werner "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," III edition, 1913, p. 89.

[2] "Neuere Anschauungen," pp. 232–237 (1913).

[3] *Ber.*, 40, 4036 (1907).

drolytic dissociation may be represented by the equation



$$\begin{matrix}M\\H\end{matrix}\!\!>\!\overset{+}{O}H + \overset{-}{X} \rightleftarrows \begin{matrix}M\\H\end{matrix}\!\!>\!O + \overset{+}{H} + \overset{-}{X}.$$

The aquo-metal ammines react in this way. For instance, the electrolytic dissociation of aquopentamminecobalti salts in aqueous solution would be represented by the equilibrium

$$[Co(OH_2)(NH_3)_5]X_3 \rightleftarrows [Co(OH_2)(NH_3)_5]^{+++} + 3\overset{-}{X},$$

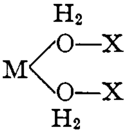
while the hydrolysis would be represented by the equilibrium

$$[Co(OH)_2)(NH_3)_5]X_3 \rightleftarrows [Co(OH)(NH_3)_5]X_2 + HX.$$

Just how much to the right this reaction proceeds will depend upon the equilibrium relationships and upon the concentrations of the substances. If one of the substances is removed from the sphere of action, as for instance HX by the action of a base, more of the product of hydrolysis, in this case hydroxopentamminecobalti salt, will be formed. The general formulation is as follows:

$$X_2[A_5MCl] + H_2O \rightleftarrows X_2[A_5MH_2O]Cl \rightleftarrows X_2[A_5MOH] + HCl$$

The reactions between some metallic salts, ammonium salts, and ammonia in aqueous solution will be considered now. Many of the bivalent metals such as nickel, magnesium, etc., form hydroxides insoluble in water but soluble in solutions of ammonium salts. The generally accepted explanation for the solubility in solutions of ammonium salts or for the nonprecipitation by ammonia, if ammonium salts are present, is that the ammonium ion of the ammonium salts drives back (or represses) the electrolytic dissociation of the ammonium hydroxide so that the hydroxide ion is not present in sufficient concentration to exceed with the metal ion the solubility product of the metal hydroxide.[1] The explanation of these reactions which will be developed here depends upon the hydrolysis reactions and equilibria outlined and upon the structures of salts in solution developed in the VI Paper.

A bivalent metal halide, MX_2, will be chosen as example. In water solution the compound  $M<\begin{matrix}\overset{H_2}{O}—X\\\underset{H_2}{O}—X\end{matrix}$ will be present and negative X combined with O carrying a predominatingly negative charge will ionize into $[M(OH_2)_2]^{++}$ and $2\overset{-}{X}$. It is probable that a substance of this sort will take up more (generally four) molecules of water in onium combination with the metal element. The complete formula may be written

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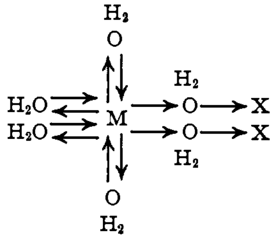
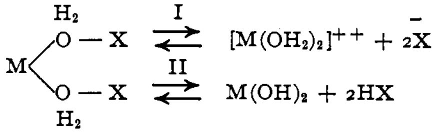
[1] Cf. Loven, *Z. anorg. Chem.*, 11, 404 (1896); Herz and Muks, *Ibid.*, 38, 138 (1904).



Since the last four H_2O molecules are not directly involved in the theoretical views to be developed, the formulas will be written without them. The substance $M(OH_2)X_2$ may undergo hydrolytic dissociation as shown in Equilibrium II.



The reaction which will be observed depends upon the equilibria (affinity relationships) of (I)[1] and (II) and upon the addition or removal of any of the products. For instance, Equilibrium II will proceed to the right if a base is added. The addition of the base removes HX and causes more $M(OH_2)_2X_2$ to undergo hydrolysis until ultimately only $M(OH)_2$ will be present. This reaction will take place especially if $M(OH)_2$ is insoluble, but it is important to note from these equations that it is due to the removal of HX by the base rather than direct metathesis. The simplest way of looking at the change, if only the initial and final substances and their formulas are used, is $MX_2 + 2M'OH = M(OH)_2 + 2M'X$; but this, for one thing, leaves out of account the action of the solvent. Written in the ionic form $\overset{++}{M} + 2\overset{-}{OH} = M(OH)_2$, while apparently going back to more fundamental relationships, does not show what direct part, if any, the solvent plays. By means of the equilibrium reactions as formulated, the part the solvent plays is made evident. Furthermore this reaction is brought into line with a great number of others (a number of which were given in the earlier part of this paper), and also shown to belong to the group of hydrolytic reactions, to which the theoretical explanations developed by Werner apply.

Ammonia has been shown to be analogous to water in its reactions. Onium compounds are formed to a greater or more readily observable extent with it than with water. If ammonia is added to a solution of MX_2, it is evident that a compound $(H_3N\rightleftarrows)_4M(\longrightarrow NH_3\longrightarrow)_2X_2$, or (omitting the four ammonias in onium combination with M) $M(NH_3)_2X_2$, may be formed. The relative amounts of $M(OH_2)_2X_2$

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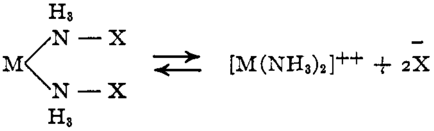
[1] The "intermediate" ion is not given in this equilibrium, but doubtless is present.

and of $M(NH_3)_2X_2$ which will be formed, or the distribution of MX_2 between water and ammonia, will depend upon the relative stabilities of these compounds under the given conditions. The substance $M(NH_3)_2X_2$ undergoes electrolytic dissociation as follows:[1]



Ammonolytic dissociation to form $M(NH_2)_2$ and HX, analogous to the hydrolysis of the hydrated salt, does not seem to occur with these compounds under these conditions.[2] The addition of a base has, therefore, no direct action on a substance of this formula in the way of influencing the equilibrium. Beyond the possibility of a direct metathetical reaction, the base plays no part, as it does in the hydrated salt, even if the hydroxide is not soluble. To sum up, the possible reaction between a base and a substance MX_2 in water in the presence of ammonium salts or ammonia will depend upon the relative amounts of hydrated and ammoniated salt present; if an appreciable amount of the former is present, $M(OH)_2$ may be precipitated; if the salt is entirely present as the latter, no $M(OH)_2$ will be precipitated.

Ephraim[3] recently published some very careful studies on the stability of the metal ammoniates. He determined the temperatures at which the hexa-ammonia (and substituted ammonia) derivatives of a number of salts of the bivalent metals (including Be, Ni, Co, Fe, Cu, Mn, Zn, Cd, Mg) showed definite vapor pressures. The results give a measure of the relative stabilities of these compounds, and consequently also for solutions of them. This gives no direct evidence as to the distribution of any given salt between water and ammonia with both present in solution, but does give a relative measure of the amounts of the ammoniates formed by a number of different salts. For instance, the salt $NiCl_2.6NH_3$ shows a vapor pressure of 500 mm. at 130°, while the salt $MgCl_2.6NH_3$ shows the same vapor pressure at 24.5°. This means that a very much smaller concentration of ammonia would be needed in solution to form the hexa-ammoniate with a nickel salt than would be necessary for a magnesium salt. Consequently, as a result of the distribution of the salt between the ammonia and the water, the concentration of ammonium salt needed to prevent the precipitation of the metal hydroxide if a base is added would be much less for the nickel salt than for the

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[1] Possible intermediate ions are omitted.

[2] Perhaps the mercury ammonia compounds dissociate in this way under suitable conditions.

[3] *Ber.*, 45, 1322 (1912); 46, 3103, 3742 (1913); 47, 1828 (1914); 48, 41 (1915); *Z. physik. Chem.*, 81, 513, 539; 83, 196 (1913).

magnesium. The salts studied by Ephraim may be arranged in a series showing the relative amounts of ammonium salts needed to prevent precipitation if a base is added. This explanation of the action of ammonium salts in preventing the precipitation of the hydroxides of bivalent metals is advanced in place of the usual theory of repression of the electrolytic dissociation of ammonium hydroxide by ammonium salts, as bringing the reactions into line with other equilibrium reactions, and as considering the solvent (including thereby dissolved substances) as the predominating influence in the reaction. These reactions are now being studied quantitatively from this point of view and the results will be communicated later.

It is evidently possible to apply similar views to other reactions. No more will be taken up here in detail, but only the view will be emphasized that chemical reactions need not be considered to depend upon electrolytic dissociation. With the atoms in a molecule all carrying electric charges, certain properties of a solvent make some of these charges evident to experimental methods, while certain, perhaps very often the same, properties of the solvent increase the extent or rate of a reaction. These phenomena are independent of each other but both dependent upon the solvent, or possibly some other underlying cause. Many of the changes which have been considered heretofore as metatheses involve, without doubt, primary addition and subsequent decomposition or splitting off in various ways of the reacting molecules.

NEW YORK, N. Y.

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USE OF IODINE AS A DEHYDRATING AND CONDENSING AGENT.

BY HAROLD HIBBERT.

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The question of devising some simple general method for the dehydration of organic hydroxy compounds has recently (on account of its importance in connection with the rubber synthesis) been made the subject of considerable activity among chemical investigators, as is indicated by the numerous patents taken out on this subject. In the interesting communication of Kyriakides[1] on the "Preparation of Butadiene—1 : 3 Hydrocarbons," some valuable data are quoted to show that the dehydration of various glycols and alcohols can be readily brought about in the "wet way" by heating them with a small amount of a mineral acid of high dissociating power. It would seem that the use of such a reagent offers many advantages over that of such substances as sulfuric acid,[2] potassium

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[1] THIS JOURNAL, 36, 980, 987 (1914).

[2] The use of phosphoric acid for the preparation of unsaturated derivatives (Newth, *J. Chem. Soc.*, 79, 917 (1901)), has so many advantages over sulfuric acid that it is difficult to understand why this reagent is not more frequently employed.