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THE FACTORS AFFECTING THE STABILITY OF ADDITION COMPOUNDS IN SOLUTION AND THEIR INFLUENCE UPON IONIZATION EQUILIBRIA (Part I).¹

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It is unfortunate that any attempt to modify the currently accepted ionization theory inevitably introduces a great many complicating factors, especially when solutions of finite concentration are considered. Compound formation between solvent and solute, changes in molecular complexity of solvent and solute, complex ion formation, etc.—all these are influences about which so little is definitely known that it soon becomes impossible to treat the subject satisfactorily in a strictly quantitative manner. Before any real advances can be made toward a new and more comprehensive theory it will consequently be necessary to examine very closely the effect of these various factors upon the simple equilibrium postulated at present between “ionized” and “non-ionized” solute.

Some preliminary steps in this direction have been made in earlier

¹ This article was practically completed in 1917 (see Kendall, Booge and Andrews, *THIS JOURNAL*, **39**, 2303 (1917)); its publication has been delayed by the absence of both authors on war work and by the subsequent postponement of the additional experimental tests which it was desired to impose upon the views here put forward. The first section of this confirmatory experimental work is now presented in the succeeding article.

In the interim, many investigators in this field have followed Milner, (*Phil. Mag.*, **35**, 214 and 354 (1918)) and Ghosh (*J. Chem. Soc.*, **113**, 449 and 627 (1918)) in postulating complete ionization in solutions of strong electrolytes. Mention may be made in particular of recent articles by A. A. Noyes and MacInnes (*THIS JOURNAL*, **42**, 239 (1920)), and by Langmuir (*ibid.*, **42**, 287 (1920)). The whole question of the abnormality of strong electrolytes, as related to the ionization hypothesis advanced in this and previous papers, will be dealt with in detail in a subsequent article of this series, so that it would be premature to dwell upon the matter at this point. As may be gathered from the contents of this communication, however, the present authors are not in agreement with the fundamental assumption of Ghosh that the *only* equilibrium to be considered in a solution of a strong electrolyte RX in water is the electrostatic equilibrium between simple “free” and “bound” ions R^+ and X^- , but insist upon the additional necessity of taking into account the existence of solvent-solute complexes in all conducting solutions and their influence upon ionization. Inter-ionic attractive forces must undoubtedly be recognized in any final quantitative treatment of the problem, but no satisfactory solution can possibly be obtained if all other factors are totally neglected. In this connection it may be profitable to repeat the opinion clearly expressed in a recent paper by Wells and Smith (*THIS JOURNAL*, **42**, 185 (1920); see also previous articles by G. McP. Smith in *ibid.*,) that our failure to elucidate ionization equilibria has been mainly due to our refusal to take into account the occurrence of complex chemical reactions between the different ionic and molecular species in the solution. The factors affecting such reactions are further discussed in the present communication.

articles of this series.² The basis of the hypothesis there advanced is that ionization in solution is preceded by the formation of solvent-solute complexes, and that the disintegration of these into ions of opposite charge results from the diminished electrostatic attraction between the constituent radicals. The extent of ionization in any solution will consequently depend upon (a) the extent of compound formation; *i. e.*, the degree to which reactions of the type $AB + CD \rightleftharpoons AB \cdot CD$ ³ proceed from left to right in a mixture of AB and CD in the liquid state; and (b) the extent of the dissociation of these compounds into ions of opposite charge; *i. e.*, the degree to which reactions of the type $AB \cdot CD \rightleftharpoons A^+ + (B \cdot CD)^-$ proceed from left to right in the same mixture.

If the amount of compound formation is large and if these compounds are, ionically, extremely unstable, then the solution will exhibit a high conductivity. On the other hand, where there is little combination or where the compounds formed are comparatively stable ionically, the conductivity of the mixture can be but small.

We shall therefore be able to *predict* the extent of ionization in any solution when we have once established what factors affect the formation and the ionic stability of solvent-solute complexes in general. The first half of this problem has already been discussed,⁴ and it has been demonstrated experimentally that the extent of formation of addition compounds between solvent and solute (in other words the stability of complexes *with respect to their components*) increases uniformly with the differences in character (*i. e.*, in the positive or negative nature of the constituent groups) of these components. It is particularly noteworthy that complexes other than the simplest possible type $AB \cdot CD$ are formed in quantity only when AB and CD are decidedly diverse.

In the present article the study of the second half of the problem—the factors affecting the stability of solvent-solute complexes *with respect to their ionic dissociation products*—is initiated. In their simplest form⁵

² Kendall, Booge and Andrews, *THIS JOURNAL*, **39**, 2303 (1917); Kendall and Booge, *ibid.*, **39**, 2323 (1917). These articles also give references to the extensive work of previous investigators upon various aspects of the problem. Two typographical errors in the equations given in the former paper may be corrected here. On p. 2309, read $1/T_0$ instead of T_0 in Equation 2. On p. 2313, read 1200 *c* instead of 12000 calories in the equation on line 9.

³ In the first articles of this series (*e. g.*, Kendall, *THIS JOURNAL*, **36**, 1242 (1914)) the mechanism of this type of reaction was discussed in a very inadequate manner, an ionic basis being postulated. However, as has been pointed out by Dehn (*ibid.*, **39**, 2647 (1917)), a reaction is not necessarily ionic because it is instantaneous. A more logical view has been briefly outlined in a later article (Kendall and Booge, *ibid.*, **39**, 2328 (1917)), and in favor of this view the earlier argument may now be definitely discarded.

⁴ For a résumé see Kendall, Booge and Andrews, *loc. cit.*, p. 2304.

⁵ The arguments which follow immediately below are independent of the actual formula of the complex or of its mode of ionization.

the reactions here involved may be written, $AB \cdot CD \rightleftharpoons A^+ + (B \cdot CD)^-$. The case where AB and CD are identical molecules (or AB·CD is an associated pure liquid) may first be briefly considered.

The Ionization of Pure Liquids.

Any liquid, the simple molecules of which contain unsaturated atoms, will exhibit to a greater or less degree the phenomenon of association.⁶ As a consequence of this association, the moments of the electrical doublets present in the simple molecules are considerably increased, and the constraints upon the electrons correspondingly diminished. The higher the degree of association, therefore, the less firmly are the constituent groups of the complex molecules held together, and the more readily will disintegration into ions of opposite charge take place. We should expect, then, that self ionization is in general a property characteristic of highly associated liquids. In a series of liquids of similar type, arranged in order of ascending molecular complexity, a regular increase in specific conductivity should be apparent.⁷

Such is in fact the case. Ideal non-associated liquids (such as the saturated hydrocarbons) possess practically zero conductivity.⁸ Other normal organic substances (for example, benzene, chloroform, ether) are extremely poor conductors, the specific conductivity at 25° being of the order 10^{-4} . When we examine the associated organic liquids,⁹ somewhat higher values are recorded in the literature: *e. g.*, formamide, $\kappa_{25^\circ} = 4.7 \times 10^{-5}$; acetone, $\kappa_{25^\circ} = 2.27 \times 10^{-7}$; formic acid, $\kappa_{25^\circ} = 6 \times 10^{-6}$; methyl alcohol, $\kappa_{25^\circ} = 1.45 \times 10^{-6}$. Even water, however, with an association factor probably between 2 and 3 at ordinary temperatures, has very little conductivity when perfectly pure; $\kappa_{25^\circ} = 0.55 \times 10^{-7}$.

It is only when we come to consider fused salts,¹⁰ where the apparent molecular complexity may be as high as 8 to 10, that we find examples of "pure" substances highly dissociated into ions. The following table¹¹ indicates clearly how specific conductivity varies with association in a

⁶ See Kendall and Booge, *loc. cit.*, p. 2327.

⁷ The effect of other factors, which will be considered later, must however be borne in mind in the application of this rule. The viscosity of each liquid is a property to be taken into account in any comparison. (See particularly Walden, *Z. physik. Chem.*, **55**, 246 (1906)).

⁸ Scudder, "Conductivity and Ionization Constants of Organic Compounds," D. van Nostrand Co., 1914.

⁹ Walden, *Z. physik. Chem.*, **46**, 103 (1903). It is probable that the presence of small traces of difficultly removable impurities renders the values given in most cases considerably too high. See Schlesinger and Martin, *THIS JOURNAL*, **36**, 1592 (1914); also the experimental section of the succeeding article.

¹⁰ Walden, *Z. Elektrochem.*, **14**, 723 (1908); Landolt-Börnstein, "Tabellen," 1912, p. 1078.

¹¹ Compare Turner, *J. Chem. Soc.*, **99**, 895 (1911).

typical series of chlorides.¹² Unfortunately a strict comparison at one fixed temperature is impossible.

Substance.	Association Factor. ¹³		Specific Conductivity.	
			Mhos.	
NaCl.....	9	(810°)	3.34	(800°)
KCl.....	7	(778°)	2.19	(800°)
AgCl.....	2.25	(451°)	1.83	(500°)
PbCl ₂	2.05	(512°)	2.39	(500°)
SbCl ₃	1.55	(80°)	1.09	× 10 ⁻⁴ (80°)
POCl ₃	1.3	(0°)	2.2	× 10 ⁻⁶ (25°)
AsCl ₃	> 1.0	(25°)	1.24	× 10 ⁻⁶ (25°)
HCl.....	> 1.0	(-100°)	2.0	× 10 ⁻⁷ (-100°)
SO ₂ Cl ₂	1.02	(25°)	1.8	× 10 ⁻⁷ (25°)
CCl ₄ ; SiCl ₄	1.00	(25°)	about 1	× 10 ⁻⁸ (25°)
SnCl ₄ ; SbCl ₅				
S ₂ Cl ₂ ; PCl ₃				

Specific conductivity in a pure liquid, therefore, is primarily dependent upon the association factor. To go further we must ask the question: upon what does the degree of association of a pure liquid depend? Examination of the available data shows that here, *just as in two component systems*, the formation of complexes is conditioned primarily by the differences in character (*i. e.*, in the positive or negative nature) of the several groups concerned. Thus in a substance where we have a highly electro-positive and a highly electronegative conjunction, ideal opportunity is afforded for the production of highly associated molecules.¹⁴ When differences in character are less pronounced, less association occurs. We can, indeed, trace a general trend towards increasing or decreasing molecular complexity (so far as our elementary knowledge of association factors allows) as we proceed through any particular series of compounds

¹² The term "associated" is hardly adequate to express the condition of fused salts such as NaCl and KCl, the term *polar* being far more pertinent (compare Hildebrand, *THIS JOURNAL*, **38**, 1463 (1916)). The fact that the electron has already passed between the atoms has been regarded by most recent investigators, indeed, as establishing that such substances are not associated at all, but completely ionized. The transfer of an electron, however, does not necessitate the independence of the radicals involved, and the use of the term *completely ionized* to include both *free* and *bound* ions is liable to lead to serious confusion of ideas (compare Harkins, *Proc. Nat. Acad. Sci.*, **6**, 601 (1920)). Neither *ionized* nor *associated* alone gives a true representation of the state of affairs in a fused salt such as NaCl; the physicist may center his attention upon the passage of the electron and the lack of a definite bond between any two particular ions, while the chemist may lay more stress upon the forces exercised by any one radical upon all oppositely-charged radicals surrounding it and the consequent "pooling of affinity." The two views are not exclusive but supplementary.

¹³ The association factors given are the mean of those obtained by the surface tension method of Ramsay and Shields (*J. Chem. Soc.*, **63**, 1099 (1893)) and by the specific cohesion equation of Walden (*Z. physik. Chem.*, **65**, 129 (1909)). Other methods of estimating association give here, in several instances, very divergent results (see Walden, *Z. Elektrochem.*, **14**, 723 (1908)).

¹⁴ See Kendall and Booge, *loc. cit.*, pp. 2327-8.

arranged in order of the electro-affinity of the variable radical. Thus hydrogen fluoride is highly associated even in the gaseous state and at ordinary temperatures, hydrogen chloride is highly associated only when liquefied, while hydrogen bromide and iodide are only slightly associated even as liquids at low temperatures.¹⁵ In the same way, comparing analogous compounds of succeeding elements in the periodic system, we have "association factors" as follows: $\text{NaCl} > \text{MgCl}_2 > \text{AlCl}_3 > \text{SiCl}_4$; and also, $\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$. Other illustrative examples will readily suggest themselves.¹⁶

Ionization in Solutions.

From what has already been said it will be evident that a mixture of two ideal saturated substances (*e. g.*, two hydrocarbons) cannot give a conducting solution, also that the specific conductivity of a solution of an unsaturated substance in a saturated liquid (*e. g.*, hydrogen chloride in a hydrocarbon) will be, in general, exceedingly small.¹⁷

A mixture of two unsaturated substances, however, affords several possibilities. The results of actual experiment may be separated into three types. In the first, the specific conductivity of the mixture is not widely different from that of its components (usually very small); in the second, the conductivity is markedly greater, but still not exceptionally high; in the third, the conductivity is very great, even if the mixture is formed from two practically non-conducting substances.

The first case is typical of all mixtures in which the two components are similar in character (*i. e.*, for acids and bases, where the acidic or basic strengths are of the same order). Here there will be little or no increase in molecular complexity through compound formation on admixture; the chief effect rather will be mutual dissociation of any complex molecules of the pure components.¹⁸ Hence the conductivity of the solution will not differ greatly from that of its original constituents, and (except in the case of mixtures of fused salts) will always be small. As examples may be cited

¹⁵ See Turner, *J. Chem. Soc.*, 99, 890 (1911).

¹⁶ For full references on this topic see the monograph "Molecular Association," by Turner, (Longmans, Green and Company, 1915).

¹⁷ In any case it will be *less* than that of the unsaturated component when pure, since the degree of association of this component (hence also its tendency towards ionization) will be diminished with the decrease in its concentration.

¹⁸ An apparent exception is the case where both substances are highly associated (*e. g.*, in such a system as phenol: cresol), when compounds of the general type $(\text{AB})_x \cdot (\text{CD})_y$ are undoubtedly formed (see Dawson and Mountford, *J. Chem. Soc.*, 113, 923 (1918)). The *average* molecular complexity of such a mixture, however, (and hence its specific conductivity also) will not differ greatly from that of its pure components, since extensive disassociation of these is also involved. The complexes here existent are to be regarded, indeed, not as *addition* but as *substitution* compounds, as will be shown in detail in a subsequent article.

(a) two very weak electrolytes, water and methyl alcohol;¹⁹ (b) two very strong electrolytes, trichloro-acetic acid in hydrogen bromide.²⁰ Numerous other instances may be found by reference to Scudder's "Conductivity and Ionization Constants of Organic Substances."

As the characters of the two substances begin to diverge, the extent of compound formation between them will become appreciable. Unless the divergence is very marked, however, the formation of complexes will be limited to the simplest type, and the degree of dissociation of this into its components in the liquid state will be considerable. In other words, the addition of AB to CD involves the production of only a small amount of a new molecular species AB.CD, the least complex (and consequently possessing the least tendency towards ionic disintegration) of all possible compounds. While, therefore, the conductivity of the solution may considerably exceed that of its components, it will still not be especially high. As examples may be given any weak acid or base in water, and hydrogen chloride in formic acid.²¹

If the two substances are decidedly diverse, extensive compound formation will occur on admixture. The complexes formed will include not only the simple type AB.CD but also other and larger molecular species of the general formula $(AB)_x.(CD)_y$. Disintegration of these complexes into ions of opposite charge, taking place very readily, will render the solution an exceedingly good conductor. As examples may be given any strong acid or base in water, and methyl alcohol in hydrogen chloride.²²

The essential features of a solution of high specific conductivity are, therefore: (a) unsaturation in both components; (b) a decided difference in the character of the two components. The first is necessary to enable compound formation to occur at all, the latter is the "driving force" which regulates the increase in molecular complexity (and hence in ionization) on admixture. The following additional examples will illustrate the uniform gradations experimentally observable as these factors are separately varied: (a) *unsaturation*; hydrogen chloride in octane is a non-conductor, in benzene an exceedingly poor conductor, in ether a fair conductor, in alcohol a good conductor, in water an excellent conductor; (b) *diversity*; in liquefied hydrogen chloride²⁰ as solvent, acetic acid is a good conductor, formic acid not so good, chloro-acetic and cyano-acetic acids poor conductors, trichloro-acetic acid a non-conductor. The conductivity decreases regularly as the acidic strength of the solute approaches that of the solvent. Similarly Walden,²³ considering the

¹⁹ Carrara, *Gazz. chim. ital.*, [I] 27, 422 (1897).

²⁰ Walker, McIntosh and Archibald, *J. Chem. Soc.*, 85, 1100 (1904).

²¹ Zanninovich-Tessarini, *Z. physik. Chem.*, 19, 251 (1896).

²² Maass and McIntosh, *THIS JOURNAL*, 35, 540 (1913).

²³ Walden, *Trans. Faraday Soc.*, 6, 71 (1910).

conductivity of solutions with water as solute, found that water in liquid hydrogen cyanide is a poor conductor, in formic acid a fair conductor, in sulfuric acid a good conductor.

The examples cited in the foregoing paragraphs furnish valuable cumulative evidence for the presumable validity of the principles underlying the ionization hypothesis here advanced. It must be freely conceded, however, that the greater part of previously recorded work on specific conductivity in non-aqueous solutions has been of a very rough order of accuracy, and it seems scarcely justifiable to base such important generalizations entirely upon isolated measurements of this nature. Consequently, in order to test more systematically the general applicability of the rules regarding ionization outlined above, exact conductivity determinations have been carefully carried out upon several series of typical two-component systems, for each of which the relative extent of compound formation in the liquid state had already been established in earlier articles.

As will be seen by reference to the paper immediately following, the experimental results obtained are in complete accordance with the theory developed, since compound formation and ionization (as given *qualitatively* by specific conductivity)²⁴ proceed uniformly in parallel throughout each of the systems studied. Where the extent of compound formation is known to be minute, the conductivity is almost immeasurable; as compound formation increases in amount, the conductivity becomes appreciable; where combination is extensive, the conductivity is very markedly increased. A fundamental relationship between the two phenomena is therefore confirmed.

In a later article other factors affecting the formation and stability of addition compounds in solution (such as the influence of ionic volume, of valence, and of temperature) will be discussed. Although these factors are subsidiary to the "diversity factor" here examined, occasional minor divergences from the general rules may be referred to their effect, as will be shown by the consideration of some typical examples.

In conclusion here, it is of importance to indicate how far the above views can be correlated with those expressed by previous investigators in the same field. Owing to the scope of the subject, it is not possible to consider all sides of the question in detail, consequently the discussion will, for space considerations, be limited to two most significant topics—Abegg and Bodländer's theory of complex ions, and Werner's theory of bases and acids. Many other workers have dealt equally intimately and ex-

²⁴ Specific conductivity is not in itself, of course, an exact measure of the extent of ionization in a solution; other factors (*e. g.*, viscosity, ionic mobility, molecular volume) must also be considered. The corrections introduced by the consideration of these factors will be the subject of a later paper.

tensively with other aspects of the connection between compound formation and ionization in solutions, but reference to their researches must be made directly by the reader.²⁵

The Theory of Complex Ions.

It has been shown in the preceding pages that, in binary solutions, increasing compound formation is regularly accompanied by increasing ionic instability; "union with another molecule promotes ionization." Suppose now that to a binary solution in which there is but little tendency towards ionization we add a third substance which combines very extensively with one of the original components. Obviously the same reasoning will still apply, the increase in molecular complexity will result in increased ionization.

This is Abegg and Bodländer's well-known theory of electro-affinity²⁶ (which has more recently been restated by Lewis,²⁷ Hildebrand²⁸ and Harkins),²⁹ arrived at from a new angle. Indeed, the whole theory of ionization outlined in this article may be considered, in one sense, as an extension of Abegg and Bodländer's generalizations regarding complex ions to solutions in general.³⁰ While in a simple substance AB the attractive forces between the constituent radicals usually suffice to inhibit marked ionization, the formation of complexes on addition of a second substance CD will weaken these attractive forces and disintegration of the complex molecules into oppositely charged ions will much more readily occur. Similarly for solutions; a "weak electrolyte" in any given solvent becomes a "stronger electrolyte" by combination with a second solute.³¹ As illustrations the following systems may be cited; additional examples are to be found in the article immediately succeeding.

ORIGINAL SYSTEM ("WEAK ELECTROLYTE").	ADDED SUBSTANCE.	RESULTANT COMPOUNDS ("STRONGER ELECTROLYTES").
H ₂ O or SO ₃	SO ₃ or H ₂ O	H ₂ SO ₄ ; H ₂ S ₂ O ₇ ; H ₂ SO ₄ .xH ₂ O
NH ₃ or H ₂ O	H ₂ O or NH ₃	NH ₄ OH
(C ₂ H ₅) ₂ O or HCl ³²	HCl or (C ₂ H ₅) ₂ O	(C ₂ H ₅) ₂ O.HCl; (C ₂ H ₅) ₂ O.2HCl; (C ₂ H ₅) ₂ O.5HCl.

²⁵ A representative list of references will be found in an earlier article (Kendall and Booge, *THIS JOURNAL*, **39**, 2324 (1917)). See also Senter, *Trans. Faraday Soc.*, **15**, 4 (1919).

²⁶ Abegg and Bodländer, *Z. anorg. Chem.*, **20**, 453 (1899); **39**, 330 (1904).

²⁷ G. N. Lewis, *THIS JOURNAL*, **38**, 762 (1916).

²⁸ Hildebrand, *ibid.*, **38**, 1464 (1916).

²⁹ Harkins and Hall, *ibid.*, **38**, 216 (1916); Harkins and King, *ibid.*, **41**, 970 (1919).

³⁰ The main points of advance are the inclusion of non-aqueous solutions and the insistence upon the equality of solvent and solute in ionization phenomena.

³¹ Compare the less definite statement of Lewis (*loc. cit.*): "A slightly polar molecule becomes more strongly polar in the presence of another polar molecular type."

³² Maass and McIntosh, *THIS JOURNAL*, **35**, 538 (1913).

ORIGINAL SYSTEM ("WEAK ELECTROLYTE").	ADDED SUBSTANCE.	RESULTANT COMPOUNDS ("STRONGER ELECTROLYTES").
HCN in H ₂ O	Fe(CN) ₂	H ₄ Fe(CN) ₆
H ₂ CrO ₄ in H ₂ O	CrO ₃	H ₂ Cr ₂ O ₇
dimethylpyrone in organic solvents ³³	CCl ₃ .COOH	C ₇ H ₈ O ₂ .CCl ₃ .COOH; C ₇ H ₈ O ₂ .2CCl ₃ .COOH.

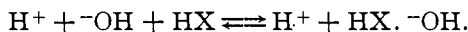
Ionization is thus, essentially, a consequence of compound formation. In certain molecular types, of course, instability may be so extreme that ionic disintegration is appreciable even in the simple molecule (*e. g.*, in the case of liquid iodine,³⁴ $I_2 \rightleftharpoons I^+ + I^-$). In others, conversely, stability may be so great that ionization is still inappreciable even although the molecule is exceedingly complex (*e. g.*, organic substances in general, although even here the ionic instability of "over-loaded" molecules such as hexaphenylethane³⁵ may be noted). In solutions in general, however, there is no difficulty in tracing a clear-cut parallelism between increase in molecular complexity and increase in "ionic instability."³⁶ The analogy of the increasing instability of the atom itself with increasing complexity³⁷ (*i. e.*, the disintegration of radio-active elements of high atomic weight) is not without interest.

Werner's Theory of Bases and Acids.

The particular case of aqueous solutions only will be considered here. A fundamental distinction is drawn by Werner between "anhydro-" and "aquo-" bases and acids.³⁸ "Anhydro-" bases and acids (*e. g.*, NH₄OH; HCl) are not compounds which dissociate directly, but are compounds from which, *by the addition of water*, the true (or "aquo") bases and acids are produced. Thus, for an acid HX, the following ionization mechanism is postulated,



or



The hydrogen ion in the aqueous solution of such an acid is therefore not produced by the dissociation of the acid, but rather comes directly from the water. Bases and salts are similarly treated, and the conclusion drawn that water plays the chief part in ionization.

³³ Plotnikow, *Ber.*, **39**, 1794 (1906); compare Walden, *ibid.*, **34**, 4194 (1901); McIntosh, *THIS JOURNAL*, **32**, 542 (1910).

³⁴ Abegg, "Handbuch der anorg. Chem.," [2] **4**, 256 (1913).

³⁵ Gomberg, *THIS JOURNAL*, **36**, 1144 (1914).

³⁶ Thus in all three cases in the table above where more than one complex is formed, the most simple is the most stable; the equimolecular compound exhibits the smallest conductivity.

³⁷ Subsidiary factors, such as atomic volume, valence, etc., will also induce minor irregularities in this general rule (see p. 1422).

³⁸ Werner, "New Ideas on Inorganic Chemistry," 1911, pp. 200-219.

While this interpretation is, at first sight, in full accordance with the theory outlined in the present paper, yet on closer examination an important point of difference appears. It is certainly possible to consider water as the *ionizing* substance in all conducting aqueous solutions and to derive thereby a theory of solutions just as satisfactory, in every respect, as that given by the more popular procedure of treating water as merely an inert "medium" for the ionized solute.³⁹ Either extreme becomes equally illogical, however, as soon as we accept the essential and absolute equality of the two components in a conducting solution.

Ionization in a system $RX-H_2O$ is, under such a view, regarded as resulting from the disintegration of complexes of the general type $(RX)_m \cdot (H_2O)_n$.⁴⁰ Cleavage is, of course, *possible* at any point in the complex molecule, and a large number of distinct ionic types may be obtained, the relative concentrations of which will vary with the composition of the solution. There is no *a priori* reason either for the assertion of the ionists that the cleavage necessarily occurs in the RX molecule, or for Werner's claim that dissociation is restricted to the water molecule. In the great majority of conducting solutions, probably, both species of dissociation take place to extents which cannot be neglected, and consequently the simple equation $RX \rightleftharpoons R^+ + X^-$ totally fails to reproduce the ionization equilibria. In extreme cases, indeed, such as a "strong electrolyte" in water, the total number of complex molecular and ionic types present must be very large, and since all complex molecules will be, ionically, more unstable than the simple salt, it is evidently quite incorrect to consider the experimental "ionization values" (as ordinarily determined) as representing the actual concentration of the simple ions R^+ and X^- . Further discussion of this topic must, however, be left for a future communication.

Summary.

In a preceding article, the formation of solvent-solute complexes has been postulated as a prerequisite to ionization in solutions. Under this assumption, we should be able to predict the degree of dissociation in any given solution from (a) the stability of the complexes with respect to their components, and (b) the instability of the complexes with respect to their ionization products.

The first of these points has been dealt with in detail in previous papers, and the rules formulated have here been extended to the association of

³⁹ See Kendall and Booge, *THIS JOURNAL*, **39**, 2333 (1917).

⁴⁰ The structural formula of such complexes and the mechanism of compound formation and ionic disintegration, especially as related to the Lewis-Langmuir theory of valence (Langmuir, *THIS JOURNAL*, **42**, 276 (1920)), will be discussed in detail later. For the present, reference should be made to a few preliminary remarks in an earlier article (Kendall and Booge, *ibid.*, **39**, 2327 (1917)).

pure liquids. In the present communication the study of the second point—the factors affecting the ionic disintegration of solvent-solute complexes in solution—has been started, and additional generalizations⁴¹ deduced. These generalizations have been shown to be in excellent qualitative agreement with the experimental data of earlier investigators. A more stringent test of their validity has been successfully sought by careful conductivity determinations on specially selected systems, as described in the article immediately succeeding.

The connection between the ionization hypothesis here presented and the views of Abegg and Bodländer on the one hand, and of Werner on the other, has been briefly examined and some points of difference indicated.

In a future article the factors affecting the formation and stability of addition compounds in solution will be further discussed, and the problem of strong electrolytes investigated.

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COMPOUND FORMATION AND SPECIFIC CONDUCTIVITY IN SOLUTIONS OF THE TYPES ACID:ESTER, ACID:KETONE AND ACID:ACID.

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As explained in the preceding article,¹ the purpose of this investigation is to test, more stringently than can be done by existent data, the general validity of the hypothesis that ionization in solutions is dependent upon preliminary compound formation between solvent and solute. Careful conductivity determinations through the whole concentration range (pure solvent to pure solute) have here been carried out upon several series of typical two-component systems, for the different members of which the relative extent of compound formation in the liquid state has already been established by a study of their freezing-point curves.

For the first series, systems of the general type $HX:R.COOR'$ were chosen. It has been shown previously² that, in such systems, the extent of compound formation increases regularly as the radicals R and R' of the ester are made more electropositive, or as the radical X of the acid is made more electronegative. A suitable variation of all 3 radicals has been ensured in this work by selecting the following systems for examination:

⁴¹ See pp. 1420-22.

¹ Kendall and Gross, *THIS JOURNAL*, **43**, 1416 (1921).

² Kendall and Booge, *ibid.*, **38**, 1712 (1916).