

Summary.

The results of previous work upon addition compound formation have been summarized, and the general rules already established for organic mixtures have been extended to aqueous solutions. Since water can function either as a weak acid or a weak base, the extent of hydration in solution should be found to increase with the acidic or basic strength of the solute.

A review of the known hydrates of acids and of bases shows that, in accordance with this prediction, only the stronger acids and bases form isolable compounds with water. Freezing-point determinations with a series of acids of widely divergent strengths confirm the general validity of the rule. The different factors which must be taken into consideration in the determination of hydration in solution by the freezing-point method have been critically discussed.

The question of salt hydrates is only briefly touched upon in this article, but will be taken up more fully in subsequent papers.

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THE MECHANISM OF THE IONIZATION PROCESS.

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In the preceding article it has been shown that there are two phenomena which proceed in parallel for acids and bases¹ of all strengths in aqueous solution—*ionization* and *combination with the solvent*. Slightly ionized substances exhibit no appreciable hydrate formation; as ionization increases combination becomes evident; where ionization is extensive marked compound formation also occurs.

Obviously there must be *some* connection between the two: divergence of opinion can arise only with regard to the nature of their correlation. It is important to note, at the outset, that the orthodox representation of the dissociation equilibrium $RX \rightleftharpoons R^+ + X^-$, suggests no reason at all for any dependence between hydration and ionization. The latter is regarded as a solute phenomenon entirely and the solvent is relegated to the role of "dead space." A preliminary discussion of the unsatisfactory basis of this viewpoint has been given in a previous communication,² where an alternative hypothesis to that of spontaneous dissociation, namely dissociation *by the solvent*, was advanced. The main purpose of

¹ For salts the present data do not justify any definite conclusions, although throughout the mercuric salts (where ionization varies considerably) the same rule is apparently valid.

² Kendall, *THIS JOURNAL*, 36, 1073-5 (1914).

the present series of investigations has been to obtain additional data to test more rigorously the relative merits of these two assumptions. In view of the results obtained, the second may now be stated somewhat more definitely,¹ as follows; "Ionization is preceded by combination between solvent and solute and is, indeed, a consequence of such combination."

This is not, strictly speaking, a *new* conception of the mechanism of the ionization process,² and to some chemists may appear self-evident. The great majority, however, are still conscious or unconscious adherents of the original dissociation theory, which ignores "solvation" altogether. The current text-books touch very incompletely upon the enormous amount of work that has been done upon this subject, and almost unanimously confine the discussion of hydration in solution to a paragraph in which it is "referred to very briefly as a possible explanation of certain peculiarities in the mobilities of some of the ions."³

Hydration of ions is now practically universally recognized.⁴ Hydration of the undissociated molecule of an electrolyte in solution is less generally admitted, except among the more enthusiastic followers of the hydrate theory, who would reject ionization absolutely and refer all solution phenomena to compound formation between solvent and solute.⁵

¹ In the paper cited above an attempt was made to coördinate the author's conclusions with those drawn by Walden, "that the process of disaggregation of the polymerized solute molecules also causes, and induces, the process of ionic cleavage." (Walden *THIS JOURNAL*, **35**, 1661 (1913).) From the results now obtained, however, it appears hardly possible to reconcile the two views of the ionization process, and consequently some of the statements of the earlier article stand in need of revision. For example, the solvent is now considered to act *chemically* and to enter *directly* into the dissociation equation (p. 1078). Walden's conception of neutrons, used in the discussion on pp. 1086-7, could also profitably be discarded.

² For previous expressions of similar purport see especially Ciamician, *Z. physik. Chem.*, **6**, 405 (1890); **69**, 100 (1909); Konovaloff, *Ann. Phys.*, [3] **49**, 733 (1893); Werner, *Z. anorg. allgem. Chem.*, **3**, 294 (1893); Abegg, *Ibid.*, **39**, 330 (1904); Walker, McIntosh and Archibald, *J. Chem. Soc.*, **85**, 1082, 1098 (1904); Bousefield and Lowry, *Phil. Trans.*, **204**, 281 (1904); *Trans. Faraday Soc.*, **1**, 197 (1905); **3**, 125 (1907); *J. Chem. Soc.*, **105**, 1824 (1914); Arrhenius, "Theories of Chemistry," p. 83 (1907); Hantzsch, *Z. physik. Chem.*, **61**, 307 (1907); Carrara, Ahrens' *Sammlung*, **12**, 416, 441 (1908); Fitzgerald and Lapworth, *J. Chem. Soc.*, **93**, 2163, 2200 (1908); **107**, 857 (1915); Sachanov, *Z. physik. Chem.*, **80**, 20 (1912); Nelson and Falk, *THIS JOURNAL*, **27**, 285, 1733 (1915); Washburn, "Principles of Physical Chemistry," pp. 186, 292.

The germ of the idea, however, antedates all of these communications, being clearly existent in the Kekulé-van't Hoff formulation of addition compound formation as an intermediate stage in all reactions (Kekulé, *Ann.*, **106**, 140 (1858); van't Hoff, "Ansichten über organische Chemie," **1**, 225, 244 (1878)). What is essentially new throughout the present work is the experimental method of attack employed.

³ Washburn, *THIS JOURNAL*, **31**, 322 (1909).

⁴ See Arrhenius, "Theories of Solutions," pp. 184-195.

⁵ Armstrong and Worley, *Proc. Roy. Soc. London*, **87A**, 604 (1912).

Thus Kahlenberg, while denying the existence of ions in a solution of acetic acid in water, considers that all the acid is combined with all the water, and that it is the compound which conducts the electric current.¹ This is the antithesis of the view of Ostwald and van't Hoff,² in which the solvent functions merely as a screen and the solute behaves exactly as if alone and in the gaseous state. The two extreme views appear, at first sight, to be quite incompatible.

The present hypothesis offers itself, however, as an intermediary: it emphasizes neither ionization nor compound formation exclusively but takes both into consideration and endeavors to correlate the two. As Walker³ has recently pointed out, the rival theories are, in reality, not irreconcilable but supplementary. The Thirty Years' War between them has been waged largely on account of misunderstandings, and it now seems opportune to propose a peace. The chief points at issue will be taken up in succession below and interpreted in terms of the hypothesis here advanced.

The Cause of Conductivity in Solutions.—This has been the most vigorously contested portion of the whole field. Many factors are known to influence conductance in solutions, but which are to be considered of basic importance varies with the viewpoint. The examination by Walden⁴ of a particular solute (tetraethylammonium iodide) in a great number of widely different solvents has shown that there are two factors here with which conductivity is undoubtedly *fundamentally* related—the dielectric constant of the solvent and the unsaturated condition of its simple molecules.⁵ The ionists, referring conductance to the solute alone and regarding the solvent as “passive,”⁶ have always emphasized the former property and its influence upon the dissociation equilibrium.⁷ Their opponents, treating *solvent* and *solute* as essentially equal and interchangeable terms,⁸

¹ Kahlenburg, *Trans. Faraday Soc.*, **1**, 42 (1905).

² See “Discussion on the Theory of Solution,” *British Assn., Reports*, **60**, 311–38 (1890).

³ Walker, *British Assn., Reports*, **81**, 356 (1911).

⁴ Walden, *Z. physik. Chem.*, **46**, 103 (1903); **54**, 129 (1906).

⁵ See Stieglitz, “*Qual. Chem. Anal.*,” **1**, 61–66; H. C. Jones, *Am. Chem. J.*, **25**, 232 (1901). When different solutes are considered, the nature of the solute of course enters in as an additional factor. The viscosity of the solvent (see Jones, *Am. Chem. J.*, **32**, 409, 521 (1904); Walden, *Z. physik. Chem.*, **55**, 207 (1906)) is not a property of *primary* significance, although it modifies the actual conductivity values obtained. Association of the solvent, also (Dutoit and Aston, *Compt. rend.*, **125**, 240 (1897); Crompton, *J. Chem. Soc.*, **71**, 925 (1897); Walden, *Z. physik. Chem.*, **46**, 103 (1903)), is a consequence of unsaturation, and not a separate factor.

⁶ In other words, influencing the extent of ionization only *indirectly* by determining the nature of the medium in which the solute dissociates.

⁷ Walden, *Loc. cit.*; Kraus and Bray, *THIS JOURNAL*, **35**, 1422 (1913).

⁸ Armstrong, *Brit. Assn., Reports*, **58**, 357 (1888); Kahlenberg, *Trans. Faraday Soc.*, **1**, 51 (1905).

have concentrated attention more upon the significance of the latter factor in connection with compound formation.¹

Any unsaturated solvent will evidently possess the power to form complexes not only with itself—association—but also with *any* suitable (*i. e.*, also unsaturated) solute.² If the formation of such binary compounds is a prerequisite of conductance, then we should expect those solvents which readily furnish addition products (*e. g.*, water or ammonia) to supply the best conducting solutions. This is the actual case, but *how* such complexes conduct without ionization is a point which the disbelievers in the dissociation hypothesis have allowed to remain in obscurity.³

The strict ionic theory is equally indefinite. While conductance in solutions is accounted for by assuming dissociation of the solute into separate charged ions, no reasonable *motive* for such dissociation is recognized. Many text-books still seem to consider the Nernst-Thomson rule⁴ a satisfactory and sufficient explanation, although Nernst himself admits⁵ "man muss also annehmen dass anderweitige Wirkungen, deren Natur uns noch unbekannt ist, auf Trennung hinarbeiten," and points to the kinetic energy of the components of the molecule as a possible factor. Walden⁶ and others⁷ also claim that the *initial* formation of ions cannot logically be ascribed to the mere diminution of their electrostatic attraction *after* formation, and indicate further influence (particularly chemical reactions between solvent and solute) which must be taken into consideration.

Recent contributions to our theories of interatomic forces (the work of Thomson⁸ and Lewis⁹ may be especially mentioned) suggest a rational solution of the difficulty. High dielectric constant and marked unsaturation in a solvent are not distinct, but intimately related phenomena,¹⁰ as might indeed have been predicted from their universal co-appearance.

¹ Brühl, *Z. physik. Chem.*, **27**, 319 (1898); Armstrong, *Chem. News*, **100**, 114 (1909).

² The absence of a quantitative measure of "unsaturation" has prevented any extensive use of this conception. It is often presented in the vague terms of "affinity" (see Carrara, *Gazz. chim. ital.*, **371**, 525 (1907); Creighton, *J. Franklin Inst.*, **182**, 745 (1916).

³ See, for example, Armstrong, *J. Chem. Soc.*, **67**, 1122 (1895); Armstrong and Worley, *Proc. Roy. Soc. London*, **87A**, 616-7 (1912).

⁴ The combined statements of Thomson (*Phil. Mag.*, [5] **36**, 313 (1893)) and Nernst (*Z. physik. Chem.*, **13**, 535 (1894)) relating the attraction between oppositely charged particles to the dielectric constant of the medium in which they are immersed.

⁵ Nernst, "Theoretische Chemie," 6th ed., p. 379 (1909).

⁶ Walden, *THIS JOURNAL*, **35**, 1661 (1913).

⁷ See Carrara, "Elektrochemie der Nichtwässrigen Lösungen," Ahrens' *Sammlung*, **12**, 417 (1908); Creighton, *J. Franklin Inst.*, **182**, 759 (1916).

⁸ Thomson, *Phil. Mag.*, [6] **27**, 757 (1914).

⁹ Lewis, *THIS JOURNAL*, **35**, 1448 (1913); **38**, 762 (1916).

¹⁰ Stieglitz, "Qual. Chem. Anal.," **1**, 66; Walden, *Z. physik. Chem.*, **55**, 683 (1906); Abegg, *Z. anorg. allgem. Chem.*, **39**, 348 (1904).

We can therefore combine the two existent views, each of which expresses part of the truth, to obtain a more complete representation of the processes involved in the production of a conducting solution.

A brief outline of the successive steps is all that will be given below.¹ The fundamental assumptions upon which the argument is based are fully discussed in both of the papers cited immediately above (to which frequent reference should be made), their reproduction *in extenso* is therefore not necessary here.

The Mechanism of the Ionization Process.

Unsaturation in a molecule consists in the presence of electrons which are not rigidly fixed but free to move under the influence of an electric field.² In a simple water molecule the oxygen atom is unsaturated and there are (presumably) at least two electric doublets, as represented by the formula $H^+ \longrightarrow O^- \longleftarrow H^+$. The six free electrons of the oxygen atom will move into such position (or orbits)³ as to exert a maximum attraction upon the positive parts of these doublets, and an unequal distribution of electric charges will result.

When two such molecules come into close proximity the unequal distribution of the charges will be greatly accentuated. The mutual attraction may consequently become sufficient to lead to the formation of complex molecules—*association*. It makes no difference whether we regard such complexes as held together by primary or residual valence (*i. e.*,

whether we write $(H_2O)_2$ as $\begin{array}{ccc} H & & H \\ | & & | \\ HO & \longrightarrow & OH, \text{ or } O \text{ --- } HOH \end{array}$; in either

case the associated molecule possesses a larger electrostatic moment, and the constraints upon the electrons are correspondingly weakened.⁴

Association can evidently proceed further, with the production of still more complex molecules. The higher the degree of association, the larger the electrostatic moment and the weaker the constraints holding the charges—in other words, the higher the *dielectric constant*.

¹ The nomenclature of Thomson has been employed. Polar terminology, however, can readily be substituted by the reader.

² Strictly speaking, of course, no molecule is perfectly saturated. It is convenient, however, to employ the term in a relative sense to distinguish compounds such as CH_4 from others such as NH_3 , H_2O .

³ See W. A. Noyes, *THIS JOURNAL*, 39, 879 (1917).

⁴ No matter what formula is chosen this statement holds, but as an aid in visualizing the question, the oxonium structure given above may be examined more closely from another point of view. It will be noticed that whereas the (H_3O) group is, as a whole, *positive*, and the OH group *negative*, yet the two oxygen atoms which are directly in conjunction both possess more than sufficient electrons to neutralize their positive nucleus—in other words, both have an excess negative charge. Hence it is evident that the complex will show a tendency to dissociate ionically at this point. The same considerations apply equally well to other complexes.

Considerable attractive forces are exerted by such associated molecules upon the molecules of any *solute* RX, especially if the solute molecules also furnish strong fields of electric force.¹ The effect is cumulative as the molecules come into close proximity, each increasing the electrostatic moment of the other. The mutual attraction may again become sufficient to lead to the formation of complexes, which we can regard either as of the type $R(H_2O)_n \rightarrow X$, or of the type $(H_2O)_n \cdots RX$ (according as primary or residual valence is assumed).² In both cases, as before, the constraints holding the electrons are still further weakened. Such complexes are consequently much more unstable than their simple component molecules, and disintegration at any point³ becomes possible.

We have, therefore, this distinction. In the simple solute molecule the two radicals are, in general, attracted to each other so strongly that no dissociation is observable. In the solvent-solute complex, on the other hand, the attractive forces are so diminished (either by actual separation of the radicals or by the counter-attractive forces of the solvent molecule) that dissociation can readily occur. *Union with another molecule, therefore, promotes ionization.*⁴

A careful study of the articles of Thomson and of Lewis will answer most of the questions that may be suggested by the above condensed statements. One point, however, must be discussed a little more fully here, since it bears directly upon the experimental work of the present series of papers.

Compound formation between solvent and solute has been postulated as the *immediate* cause of ionization. All conducting solutions, consequently, should afford evidence of such compound formation. How far experimental results are in support of this (another vital issue between the ionic and the hydrate theories) is briefly examined below.⁵

¹ This will be the case if the simple solute molecule is also highly unsaturated.

² In concentrated solutions complexes containing more than one molecule of the solute RX must also be considered. For the present, however, the simple types given above suffice to illustrate the points at issue. The state of affairs in concentrated solutions will be taken up in detail later.

³ See note 4, p. 2327.

⁴ Thomson (*Loc. cit.*, p. 770) discusses in this connection only *intramolecular* ionization (*i. e.*, the passage of an electron from one atom to another), and neglects the final breaking up of the molecule. These two steps in the disintegration process are, however, to be regarded as successive effects brought about by causes of exactly similar character. If the first step is already taken before solution (owing to the highly unsaturated condition of the solute molecule) the second will naturally follow more readily.

⁵ An ample list of references on this topic is given by Dhar, *Z. Elektrochem.*, 20, 57 (1914). No comprehensive critical review has appeared since Washburn's "Hydrates in Solution" (*Tech. Quart.*, 21, 360 (1908)), even there only aqueous solutions are considered.

Compound Formation a General Characteristic in Conducting Solutions.

The classical method for establishing the presence of compounds in a solution (introduced by Mendelejeff¹ and still in favor among the followers of his hydrate theory) consists in plotting some physical property of the mixture² against composition³ and noting the position of discontinuities either in the curve itself or in some derived function.⁴ No doubt this procedure will ultimately prove of value as our knowledge concerning solutions progresses,⁵ but the ludicrous and conflicting conclusions drawn from certain aqueous systems⁶ have succeeded not only in discrediting the method but also in creating the belief that compound formation in the liquid state is, even if sometimes an existent, yet in general an unimportant factor. For example, the failure of the Ostwald dilution law for strong electrolytes in aqueous solution has been referred to a great variety of causes,⁷ but rarely have the consequences of the solvent entering into the reaction in any way been seriously considered.⁸ Where such a possibility is mentioned, it is usually followed directly by the statement that, in dilute solutions at any rate, the effect upon the dissociation equilibrium of the solute will be negligible.⁹

For non-aqueous solutions, on the other hand, where the dilution law is scarcely ever satisfactorily followed, it is the custom to ascribe *all* irregularities to the existence of complexes between solvent and solute. Compound formation is recognized, for example, as the disturbing factor in all cases where the molecular conductivity *decreases* with increasing dilution, as in solutions of ether and acetone in the liquefied hydrogen halides.¹⁰

¹ Mendelejeff, *Z. physik. Chem.*, **1**, 273 (1887); *J. Chem. Soc.*, **51**, 778 (1887).

² *E. g.*, density, viscosity, refractive index, magnetic rotation, compressibility, surface tension, heat of dilution, conductivity, etc.

³ Composition has been expressed indiscriminately in volume, weight or molecular percentages, according to the predilections of each particular author.

⁴ For examples see Crompton, *J. Chem. Soc.*, **53**, 116 (1888); Armstrong, *Ibid.*, **53**, 125 (1888); Pickering, *Proc. Chem. Soc.*, **4**, 35 (1888); **5**, 86, 149 (1889); **7**, 105 (1891); **8**, 162 (1892); H. C. Jones, *Ibid.*, **10**, 101 (1894).

⁵ See Denison, *Trans. Faraday Soc.*, **8**, 20, 35 (1912); Morgan and Davis, *THIS JOURNAL*, **38**, 555 (1916).

⁶ In the system $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$, for instance, as many as 102 different hydrates have been "discovered," ranging in composition from $36\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ to $\text{H}_2\text{SO}_4\cdot 4950\text{H}_2\text{O}$. Few of these have been encountered twice by independent investigators, the opportunity for originality being almost unlimited.

⁷ Wegscheider, *Z. physik. Chem.*, **69**, 603 (1909); Kraus and Bray, *THIS JOURNAL*, **35**, 1424 (1913).

⁸ See, however, Morgan and Kanolt, *Z. physik. Chem.*, **48**, 365 (1904); Biltz, *Ibid.*, **40**, 213 (1902); Abegg, *Z. anorg. Chem.*, **39**, 353 (1904).

⁹ Nernst, "Theoretische Chemie," Sechstauflage, p. 468 (1909).

¹⁰ Steele, McIntosh and Archibald, *Phil. Trans.*, **205A**, 99 (1906); *Z. physik. Chem.*, **55**, 129 (1906). Concurrently with this view, solutions exhibiting the normal *increase*

In many such instances it is even admitted that the solvent-solute complex, dissociating ionically, is responsible for the conductance, as in solutions of ether and dimethylpyrone in HCl or HBr, where the solute is not an electrolyte and migrates to the cathode during electrolysis as part of the complex positive ion.¹

The question may pertinently be raised: How does water differ so radically from other solvents, that we do not conceive of aqueous solutions in a similar way? Water migrates with the ions just as other solvents do; it is surely as reasonable to regard such water, in part at least, as an integral portion of an ionic complex (produced by dissociation of a solvent-solute combination) as to reduce it entirely to the inferior character of an "envelope."² Hydrates in the solid state are, in general, more numerous and more stable than any other solvates; the extent of their formation in solution presumably also exceeds that of most complexes. It certainly is much greater than is ordinarily supposed, the degree of dissociation into components on fusion being extremely small for the hydrates of typical strong electrolytes.³ Even with weak acids and bases complex formation in aqueous solution is still appreciable.⁴

While we cannot, it is true, go so far with the extreme non-ionists as to consider *all* solutions *complete* combinations,⁵ yet the evidence at hand does warrant the conclusion that *some* compound formation between solvent and solute occurs in all *conducting* solutions. In these, indeed, just as in ideal solutions, it is immaterial which component we regard as solvent and which as solute.

The Equivalence of Solvent and Solute.

This is a second fundamental point in the ionization hypothesis outlined above, and one with which the strict ionic theory is again at variance. In molecular conductivity with increasing dilution are regarded as essentially physical mixtures (Walden, *Z. physik. Chem.*, **54**, 145 (1903)). This arbitrary classification becomes difficult to defend when curves possessing both maximum and minimum points are encountered. Silver nitrate in methylamine (Franklin and Gibbs, *THIS JOURNAL*, **29**, 1389 (1907)) and potassium iodide in water (Sloan, *THIS JOURNAL*, **32**, 946 (1910)) may be cited as examples. These also nullify the rule of Ssachanow (*J. Russ. Phys. Chem. Soc.*, **44**, 924 (1912)) that only solvents with low dielectric constants furnish solutions with abnormal conductivity-concentration curves.

¹ McIntosh, *THIS JOURNAL*, **32**, 542 (1910); Maass and McIntosh, *Ibid.*, **35**, 535 (1913). Similarly the high conducting power of solutions of ether in bromine is referred to by Plotnikow (*Z. physik. Chem.*, **57**, 502 (1907); see also *Ibid.*, **48**, 220 (1904)) to a solvent-solute complex. For an example of salts in a non-aqueous solvent see Walker and Johnson, *J. Chem. Soc.*, **87**, 1597 (1905).

² Kohlrausch, *Proc. Roy. Soc. London*, **71A**, 338 (1903); Bousfield, *Z. physik. Chem.*, **53**, 257 (1905); *Phil. Trans.*, **206A**, 101 (1906).

³ Typical examples ($\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) will be discussed in a forthcoming article (J. E. B.).

⁴ As shown in the preceding paper of this series.

⁵ Kahlenberg, *Trans. Faraday Soc.*, **1**, 63 (1905).

It is still almost universal practice among the followers of this theory (and few dare to disagree with it at the present date) to consider that the van't Hoff analogy between *infinitely* dilute solutions and gases justifies the total neglect of the solvent in all simple equilibria in solutions of *finite* concentrations.

The enormous value of van't Hoff's conception in the earlier development of physical chemistry cannot be denied, yet it is an unfortunate fact that the undue emphasis which it caused to be laid upon dilute solutions has greatly retarded the study of the far more important problem of solutions in general.¹ Van Laar's mathematical theory of ideal solutions² remains, more than twenty years after its formulation, quite unknown to the greater number of physical chemists, and the kinetic interpretation of osmotic pressure as due to the bombardment of the semi-permeable membrane by the molecules of the solute even yet finds general favor.³ The failure of the simple gas equation $PV = RT$ to represent accurately the osmotic pressure of dilute solutions is perforce recognized, but this failure is "explained" by references to the deviations of compressed gases from Boyle's law and their agreement with the modified equation of van der Waals.⁴ More than fifty analogous equations for osmotic pressure have been put forward,⁵ most of these are capable of reproducing the experimental data satisfactorily—when the additional constants are properly manipulated.

It cannot be too strongly emphasized that osmotic pressure bears no direct relation at all to gaseous pressure, and the true osmotic pressure equation is quite distinct from any possible gas equation. If we neglect a small correction for the compressibility of the solution, it may be written: $\pi V = RT \log_e x$ (where π = osmotic pressure, V = molecular volume of the solvent, x = mol fraction of solvent in the solution). This admittedly reduces to an expression similar to the perfect gas equation when the solution is infinitely dilute, but a formal resemblance between the limiting values of two functions is far from establishing proof of their absolute identity. In actual experimental work, moreover, we never deal with infinitely dilute solutions, so that the analogy between solutions and gases is entirely of philosophical interest. The sole excuse for its survival

¹ See Findlay, "Osmotic Pressure," p. 10.

² *Z. physik. Chem.*, **15**, 457 (1894); **64**, 629 (1908); see also G. N. Lewis, *THIS JOURNAL*, **30**, 668 (1908); Ikeda, *J. Tokyo Coll. Sci.*, **25**, 10 (1908); Washburn, *THIS JOURNAL*, **32**, 653 (1910).

³ W. C. M. Lewis, "Systems of Physical Chemistry," **1**, 198.

⁴ W. C. M. Lewis, *Ibid.*, **2**, 216, *et seq.*

⁵ See Findlay, "Osmotic Pressure," p. 27. It is interesting to note that the most prominent of these (the weight concentration equation of Morse, *Am. Chem. J.*, **38**, 175 (1907)) has recently been abandoned in favor of the ideal-solution equation (Frazer and Myrick, *THIS JOURNAL*, **38**, 1907 (1916)).

at the present time is that it constitutes an exceedingly convenient academic subterfuge for supplying undergraduate classes with a simple, if inexact, formulation of the main properties of solutions: osmotic pressure, depression of vapor pressure, elevation of boiling point, depression of freezing point.¹ In all *exact* equations for these phenomena the concentration of the *solvent* is now recognized as an essential factor. There seems to be no just cause why it should not similarly appear in all exact equations for conducting solutions.

Let us consider a particular case: the system, water-hydrogen chloride. In the liquid state both substances, when perfectly pure, are practically non-conductors.² Both contain unsaturated atoms in the simple molecule, and are in consequence highly associated.³ Both have high dielectric constants.⁴ Upon mixture, we obtain a liquid possessing considerable electrical conductivity,⁵ and we regard this as due solely to the dissociation of hydrogen chloride into its constituent ions. Is there really any reason why the conductance should be referred entirely to hydrogen chloride and not at all to water? Would not a viewpoint under which each component could receive equal credit appear more plausible?

The ionization mechanism outlined above assumes that complex molecules of the general type $(\text{HCl})_x(\text{H}_2\text{O})_y$ are first formed in the solution, and that these then break up to give radicals of opposite charge. Disintegration of an unstable complex is, of course, *possible* at any point in the molecule, and a large number of different ions may result. In any actual instance, however, one pair will presumably predominate at any one concentration. At present the ionists take it for granted that, in the example here shown, this pair is H^+ and Cl^- throughout, but concede that these ions are hydrated. This concession really spoils their whole case, since there is no *a priori* reason why a "monohydrated chloride ion," for instance, $(\text{Cl}, \text{H}_2\text{O})^-$, might not just as conceivably deserve the alternative title of a "solvated hydroxylion," $(\text{HCl}, \text{OH})^-$.⁶ In the same way any

¹ Readers who are still doubtful should refer to Findlay, "Osmotic Pressure," pp. 49, 69-70; or Washburn, "Physical Chemistry," pp. 155-6.

² Kohlrausch and Heydweiller, *Z. physik. Chem.*, **14**, 326 (1894); Steele, McIntosh and Archibald, *Ibid.*, **55**, 148 (1906). The minimal ionization of pure liquids will be considered in the first part of the succeeding paper.

³ Turner, "Molecular Association," **1915**, p. 84; Steele, McIntosh and Archibald, *Loc. cit.*, p. 154.

⁴ Drude, *Z. physik. Chem.*, **23**, 298 (1897); Schaefer and Schlandt, *J. Phys. Chem.*, **13**, 669 (1909).

⁵ The mixture with maximum conductivity at 15° contains approximately 20% by weight of acid (Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," p. 154.

⁶ The graphic formula $[\text{Cl} - \text{O} - \text{H}]^-$ expresses simultaneously both views.



“hydrated” positive ion (*e. g.*, $(\text{Na}, \text{H}_2\text{O})^+$) might be designated, equally well, a “solvated” hydrogen ion (*e. g.*, $(\text{NaOH}, \text{H})^+$).¹ It is possible, therefore to consider water as the *ionizing* substance in all conducting aqueous solutions.²

Such a procedure is not advocated here, however, although it has, on close examination, exactly as much to recommend it as the current view. It is plainly preferable not to go to either extreme, but to accept the absolute equality of the two components of a conducting solution, and to recognize that the complex ions existent therein (whatever their actual formulas may be), owe their existence directly to “solvent” as well as to “solute.”

The conditions affecting the production of such ions in solutions are further examined in the succeeding article.

Summary.

The results of previous articles in this series have indicated an intimate and general connection between ionization and compound formation in solutions. The hypothesis is here advanced that “ionization is preceded by combination between solvent and solute and is, indeed, a consequence of such combinations.” This viewpoint combines the current ionic and hydrate theories, referring conductance in solutions to the dissociation of solvent-solute complexes into radicals of opposite charge.

The actual mechanism of the ionization process under this assumption, with its relation to phenomena such as unsaturation, association and high dielectric constant, has been briefly discussed. It has been shown that compound formation between solvent and solute may be postulated in all conducting solutions, and that the distinction still commonly retained between the two components is arbitrary and misleading.

The general evidence in favor of the theory of conducting solutions outlined in this paper has been presented in a preliminary form only, attention being centered upon a few fundamental points. The work of previous investigators in this field is considered more fully in the succeeding article, in which the quantitative side of the subject—what modifications are necessary in our present ionization equations under the new view, and how far these modifications are supported by the experimental facts—is also briefly discussed.

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¹ The formula $[\text{Na} - \overset{\text{O}}{\underset{\text{H}}{\text{---}}} - \text{H}]^+$ here conforms to either title. To take another

instance, the ammonium ion may be regarded as $(\text{NH}_3, \text{H})^+$, a hydrogen ion “strengthened” by addition of NH_3 (see Werner and Miolati, *Z. physik. Chem.*, **12**, 35 (1893); Abegg and Bödlander, *Z. anorg. Chem.*, **20**, 484 (1900)).

² The “solvated ions” in such solutions would, of course, be quite distinct from the simpler ions present in pure water.