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ADDITION COMPOUND FORMATION IN AQUEOUS SOLUTIONS. THE STABILITY OF HYDRATES AND THE DETERMINATION OF HYDRATION IN SOLUTION.[1]

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In a number of communications recently appearing,[2] addition compounds of organic acids with organic substances containing oxygen have been described and compared. This series of investigations is now practically completed. Aldehydes and ketones, acids, phenols and esters have been exhaustively examined, and the results in each case have been found to conform to simple and definite rules. The only important classes of organic substances containing oxygen not yet considered are the alcohols and the ethers. It is our intention to take these up in detail later, the former class indeed being of especial interest in connection with the general mechanism of esterification[3] and its relation to the reverse process of ester hydrolysis.[4] For both alcohols and ethers, however, a few systems with strong inorganic acids have already been investigated by the freezing-point method in the researches of McIntosh and his co-workers.[5] It is therefore possible for us at the present time to make a critical survey of the entire field. Sufficient results have been accumulated to allow us to indicate, in brief, the true "raison d'être" of the complete work, and at the same time to extend the generalizations which have been deduced to systems in which water is one component.

It is not intended to convey the impression that the arguments advanced in the following articles are entirely new, or that the view point arrived at is altogether original.[6] Speculations upon the topics discussed

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[1] It was the intention of the authors to defer publication of this and the following article until a third and concluding instalment had been completed. Owing to the fact that Prof. Kendall has been commissioned to proceed to Europe on government service, however, further progress of this work is delayed for an indefinite period. The investigation is consequently appearing in its present form, and the final sections, which continue the argument left unfinished at the end of the second paper, will be added as soon as possible.

[2] Kendall, THIS JOURNAL, 36, 1222, 1722 (1914); 38, 1309 (1916); Kendall and Carpenter, *Ibid.*, 36, 2498 (1914); Kendall and Gibbons, *Ibid.*, 37, 149 (1915); Kendall and Booge, *Ibid.*, 38, 1712 (1916).

[3] THIS JOURNAL, 38, 1323 (1916).

[4] *Ibid.*, 38, 1736 (1916).

[5] McIntosh, THIS JOURNAL, 30, 1104 (1908); Maass and McIntosh, *Ibid.*, 33, 70 (1911); 34, 1273 (1912); 35, 535 (1913); McIntosh and Evans, *Ibid.*, 39, 1073 (1917); see also Baume, *J. chim. phys.*, 12, 208 (1914).

[6] A comparison of the results of these articles with those obtained by previous workers will be entered into more fully in a succeeding communication. The references here given, while numerous, are by no means complete.

below have, in fact, constituted for decades one of the favorite recreations of almost all chemists who have revolted against a purely mechanical conception of solutions. Nevertheless, it will be found that we have now available, for the first time, systematic deductions from our experimental data which enable us to postulate definitely what effect variation of any of the factors concerned will exert upon the course and extent of the reactions under consideration. The main conclusions reached are consequently not to be regarded as mere hypothetical possibilities, to be accepted or rejected according to the mental attitude of the reader, but as immediate derivations from facts experimentally established, the consistency of which with these facts can in each case be subjected to direct test.

Résumé of Previous Results.

When an organic substance containing oxygen—*e. g.*, a compound of the type RR′C = O, ROR′, or R.COOR′—is added to an acid HX, the existence of an addition product in the liquid mixture can always be demonstrated. The evidence throughout has accorded with the hypothesis of an oxonium salt formation.

In the majority of cases combination is extensive, and the conditions necessary for the actual isolation of the compound can be readily derived from the freezing-point curve of the system. The *stability* of the compound (or the degree to which its components exist in combination in the liquid state) can also be deduced from the "sharpness" of its maximum on this curve. The following rules are perfectly general:

(*a*) Increase in the strength of the acid (*i. e.*, in the *negative* character of the radical X) increases the stability of the compound. Thus CCl_3.COOH gives stable addition products with nearly all substances examined;[1] with CH_2Cl.COOH and CH_3.COOH only one case of compound formation (with dimethylpyrone) has been obtained. The numerous addition compounds of dimethylpyrone with acids fall off regularly in stability as we go down the order of acidic strengths.[2]

(*b*) Increase in the "basic characteristics" of the organic substance (*i. e.*, in the *positive* nature of the radicals R and R′) also increases the extent of compound formation. Thus CCl_3.COOH combines more firmly with CH_3.COO.C_2H_5 than with C_6H_5.COO.C_2H_5, while with C_6H_5.COO.C_6H_5 its compound is not of sufficient stability to be isolated. Other examples abound throughout the series.

These two rules may be conjoined in the statement that the stability of an addition compound increases with the differences in the character (*i. e.*, the positive or negative nature of the constituent groups) of its two

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[1] No fewer than 35 compounds have been isolated.

[2] THIS JOURNAL, 36, 1241 (1914). The phenols only are exceptional; see p. 2306.

components.[1] Thus substances of similar acidic strengths (*e. g.*, $CH_3.COOH$ and $C_6H_5.COOH$, or $C_6H_5.OH$ and $CH_3C_6H_4OH$) exhibit no appreciable trace of compound formation. If the acidic strength of one of the substances is increased, however, by the introduction of a negative group, combination becomes evident. Thus $CCl_3.COOH$ gives an equimolecular compound with $C_6H_5.COOH$, so also does $C_6H_5.OH$ with $C_6H_5(NO_2)_3.OH$.

Further evidence as to the extent of compound formation in the liquid state may be obtained, even in systems from which no compound can actually be isolated, by observing the freezing-point depressions of a fixed substance A on addition of fixed mol fractions of different substances B. The *deviations* from the *ideal depression* afford, in point of fact, a legitimate basis for a *strict* comparison of compound stability.[2] The rule given above is again found to be valid in all cases. Thus in systems of the type $CCl_3.COOH–R.COOR'$ the degree of combination varies with the ester as follows: $C_6H_4OH.COO.C_6H_5 < C_6H_5.COO.C_6H_5 < C_6H_5.COO.CH_2.C_6H_5 < C_6H_5.COO.CH_3 < C_6H_5.COO.C_2H_5 < CH_3.COO.C_2H_5$. Weaker acids give with the same esters much less stable compounds throughout.

One point remains to be noted—that, with uni-univalent components, formation of *complex* addition compounds (*i. e.*, compounds other than equimolecular) becomes apparent only when the differences in character of the components are extreme. Thus $CCl_3.COOH$ gives more than one compound with aldehydes and ketones containing strongly positive groups. In systems of the type $CCl_3.COOH–R.COOR'$, compounds other than equimolecular[3] are existent in the liquid mixture, but are not of sufficient stability to make their appearance upon the freezing-point diagram.[4]

The Stability of Hydrates.

The above results may now be extended to the field for which they were primarily collected, namely to a consideration of the factors affecting the formation and stability of *hydrates*. In the present article we shall confine our examination to systems of the types: water–acid and water–base. Some preliminary observations upon the more obscure type: water–salt are added, but the further study of salt hydrates is deferred to another paper.

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[1] For acids or bases, such differences in character are clearly indicated by differences in the acidic or basic strengths in aqueous solution. With other classes of substances, the effect of the introduction of various groups can, in general, be predicted by comparison with corresponding acids or bases.

[2] All *special* factors (*i. e.*, the melting point and heat of fusion of the compound) are here eliminated. See THIS JOURNAL, **38**, 1730 (1916).

[3] Equi-equivalent, if the ester is a derivative of a dibasic acid.

[4] This will be discussed in a second article on catalysis, at present in preparation.

In the system water–acid, the conditions are evidently exactly analogous to those already discussed for acids in pairs.[1] With water functioning as an extremely weak acid, we may at once postulate the following rules:

(*a*) No indication of hydrate formation with exceedingly weak acids.

(*b*) A regular increase in the extent of combination in the liquid state as the strength of the acid is increased.

(*c*) Extensive compound formation with the transition and strong acids. The isolation of stable hydrates in the solid state will here become possible.

(*d*) Increase in the complexity as well as in the stability of hydrates with the strength of the acid.

Experimental data exist in plenty, scattered throughout the literature, to indicate the general validity of these rules. It has been thought advisable, however, since many of the older observations are contradictory and inconclusive,[2] to obtain more convincing additional proof by "quantitative" examination of a series of acids of widely divergent strengths. The results of this examination will be found in a later section; the previous "qualitative" data may first be summarized.

1. **Weak Organic Acids.**—These give no isolable hydrates. Not a single exception is to be found among the myriads of such acids listed in Beilstein, *unless* the acid has also the character of a phenol or a base.

(*a*) **Phenols.**—Phenol itself has been stated to yield a hemi-hydrate.[3] Orcinol and phloroglucinol also combine with water. Similarly, acids containing one or more phenolic groups (*e. g.*, *p*-oxybenzoic acid, several dioxybenzoic acids, and gallic acid) give isolable hydrates, even although they are in some cases weaker acids than benzoic.

These cases are certainly confusing, but the abnormal nature of the results obtained with phenols has already been noted several times in the course of these investigations.[4] It is presumably due to some special factor (such as the existence of the phenols in two tautomeric forms of widely different acidic strengths) not as yet taken into account.

(*b*) **Amphoteric Electrolytes.**—The abnormality here is to be ascribed to the "self-neutralization" of the acid. The hydrates of such sub-

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[1] THIS JOURNAL, 36, 1722 (1914).

[2] Eutectic mixtures ("cryohydrates") and mixtures of constant boiling point have frequently been recorded as definite compounds. This type of error is not yet extinct, thus Alexander Scott ("Introduction to Chemical Theory," 1911, p. 255) still obtains crystals of $NaCl + 10H_2O$ by cooling brine to —23°!

[3] Smits and Maarse, *Proc. K. Akad. Wetensch. Amsterdam*, 14, 192 (1911).

[4] THIS JOURNAL, 38, 1317, 1322 (1916). The phenols have also been shown to yield abnormally stable addition compounds with dimethylpyrone, a base of approximately the same strength as water. THIS JOURNAL, 36, 1240 (1914)).

stances[1] belong indeed to the class of salt hydrates, and will as such be considered later.

2. **Transition and Strong Organic Acids.**—These afford numerous instances of hydrate formation, especially when there is present a highly negative radical such as Cl, Br, NO_2, or SO_3H. A few illustrative examples may be cited from the pages of Beilstein.

Aliphatics.	
$CCl_3.SO_3H + H_2O$	Vol. 1, p. 370
$CBr_3.CO.COOH + 2H_2O$	588
$(COOH)_2 + 2H_2O$	638
$COOH.C \vdots C.COOH + 2H_2O$	729
$r\text{-}(CHOH.COOH)_2 + H_2O$	798
$(COOH.CH_2)_2.C(OH).COOH + H_2O$	835

Aromatics and heterocyclics.	
$C_6H_3.(SO_3H)_3 + 3H_2O$	Vol. 2, p. 117
$C_6H_2.(NO_2)_3.(SO_3H) + 2H_2O$	127
$C_{10}H_7.SO_3H + H_2O$	201
$C_6H_3.(NO_2).(COOH)_2 + H_2O$	1822
$C_4HO.Cl(NO_2).(COOH) + H_2O$	Vol. 3, p. 705
$C_4H_3S.CO.COOH + H_2O$	757

Most of the above are typical strong acids. Racemic and citric acids, however, with dissociation constants[2] at 25° approximately fifty times as large as that of acetic acid, belong to the intermediate class of "transition acids." Mesotartaric acid also gives a monohydrate.

3. **Inorganic Acids.**—Here again it is found that the weak acids yield no hydrates,[3] while the transition and strong acids give frequent cases of compound formation. The following examples will suffice to show that combination becomes highly complex for the strongest acids considered:

Transition acids.

H_2PO_3[4]; 0.5 H_2O; H_2O
H_3PO_4[5]; 0.1 H_2O; 0.5 H_2O
H_3AsO_4[6]; 0.5 H_2O
HF[7]; H_2O (?)

Strong acids.[8]

HCl; H_2O; 2 H_2O; 3 H_2O
$HClO_4$; H_2O; 2 H_2O; 2.5 H_2O; 3 H_2O; 3.5 H_2O
HBr; H_2O; 2 H_2O; 3 H_2O; 4 H_2O
HI; 2 H_2O; 3 H_2O; 4 H_2O
HNO_3; H_2O; 3 H_2O
H_2SO_4; H_2O; 2 H_2O; 4 H_2O

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[1] Examples (from Beilstein) among aliphatics, aromatics and heterocyclics, respectively, are: $C_3N_3H_3O_3 + 2H_2O$; $N(C_2H_5)_2.C_6H_4.COOH + 2H_2O$; $CH_3.C_5H_3N.COOH + H_2O$. Sulfanilic acid gives *two* isolable hydrates (Philip, *J. Chem. Soc.*, 103, 284 (1913)).

[2] Walden, *Z. physik. Chem.*, 8, 433 (1891); 10, 563 (1892).

[3] A number of references to a hexahydrate of H_2S are to be found in the literature (see Gmelin-Kraut, "Handbuch anorg. Chem.," I, 1, 399), but actual analyses of the solid phase show compositions varying all the way between H_2S, 5 H_2O and H_2S, 24 H_2O (de Forcrand, *Compt. rend.*, 94, 967 (1882); 106, 1402 (1888); 135, 959 (1902)). It is most probable, therefore, that we have here a case of mixed crystal formation, as might indeed be expected with two substances of such similar character.

[4] Rosenheim and Pritze, *Ber.*, 41, 2708 (1908); Sänger, *Ann.*, 232, 40 (1885).

[5] Smith and Menzies, THIS JOURNAL, 31, 1893 (1909).

[6] Anger, *Compt. rend.*, 134, 1059 (1902); Menzies and Potter, THIS JOURNAL, 34, 1452 (1912).

[7] Metzner, *Compt. rend.*, 119, 683 (1894). The actual existence of this hydrate is doubtful. See Abegg, "Handbuch anorg. Chem.," [2] 4, 45.

[8] Landolt-Börnstein, "Tabellen," 1912, 469–472.

All this evidence, it must be noted, is of weight merely because of the enormous number of substances included. The transition and strong acids listed above *must* be largely combined with water when in solution, otherwise their hydrates could not separate out from the liquid phase. Weak acids, as a class, *cannot* be combined with the solvent to any considerable extent, or some hydrates would certainly be known. For any single case, however, the actual isolation of a hydrate is essentially a hit-or-miss procedure. Compounds may be present in the solution and yet not be isolable either by evaporation (owing to instability at high temperatures) or by freezing (owing to persistent supercooling at low temperatures). It is necessary, therefore, to supplement the above data by means of some method which will definitely indicate the relative extent of hydration of a series of acids *while in solution.* For this purpose the much used and abused freezing-point depression method[1] has been employed. This possesses certain disadvantages and limitations, as will be seen below, but in previous papers[2] it has shown to afford reliable comparative data regarding the existence of compounds in solution, and such results are all that we require here. The *exact* estimation of hydration in the liquid state is beyond our power at present.

Theoretical Basis of the Method.—The simple Raoult-van't Hoff equation for the depression of the freezing point is valid only for infinitely dilute solutions; its application to solutions of finite concentration, although frequently attempted,[3] necessarily conduces to unwarranted and sometimes ridiculous conclusions.[4] The true expression for the temperature of fusion of a solution, valid for *all* concentrations, is readily derived from the fundamental relation

$$d \log_e (1 - x)/dT = -Q/RT^2 \qquad (1)$$

(x is the mol. fraction of solute in the solution in equilibrium with solid solvent at the absolute temperature T; Q is the differential molar heat of solution;[5] R the gas equation constant, 1.988).

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[1] For references see Roozeboom, "Heterogene Gleichgewichte," **2**, 196–328; Baur, "Hydrates in Aqueous Solution," Ahrens' *Sammlung*, **8**, 466 (1903); Washburn, "Hydates in Solution," *Tech. Quart.*, **21**, 363–78 (1908); Noyes and Falk, THIS JOURNAL, **32**, 1011 (1910).

[2] *Ibid.*, **36**, 1733 (1914); **38**, 1731 (1916).

[3] Biltz, *Z. physik. Chem.*, 40, 218 (1902); H. C. Jones, "Hydrates in Aqueous Solution," 1–157 (1907). In the latter work the equation is applied to solutions as concentrated as 5.0 *N*, where the depression is 76.000°(!). For further criticisms see Findlay, *Trans. Faraday Soc.*, **3**, 153 (1907).

[4] Compare Washburn, *Tech. Quart.*, **21**, 367 (1908).

[5] The number of calories of heat evolved on solution of one mole of solid solvent in an infinitely large quantity of solution of concentration x at temperature T.

If the solution is ideal[1] and Q is independent of T, we obtain by integration:

$$\log_e (1 - x) = (Q/R).(1/T - T_0) \qquad (2)$$

(T_0 is the freezing point of the pure solvent.) If, on the other hand, any compound formation occurs on admixture, then the temperature of fusion will be abnormally depressed, for part of the solvent will have been removed by combination and the *actual* mol fraction of solute will be greater than that calculated from the weights of the two components taken. The larger the extent of compound formation, the greater will be the deviation from the ideal value. The exact degree of "solvation" for any particular concentration (*i. e.*, the average number n, of solvent molecules combine with each molecule of solute) may be found by determining what value must be given to n to make x, as calculated for the system $A + A_nB$, fall upon the ideal curve.[2] The comparison of the curves obtained with a series of different solutes affords, therefore, a ready means of establishing their relative degrees of solvation in solution.

Application of Aqueous Solutions of Electrolytes.—Here our systems are, in general, far from ideal, and we cannot pretend to estimate hydration without taking into account the many disturbing factors influencing x and T. Since the significance of these factors and the magnitude of the effects produced have been very inadequately recognized by recent investigators,[3] each is briefly considered in order below.[4]

Factors Due to the Solvent Alone.—Water being a highly associated liquid, the use of the value $H_2O = 18.016$ in the calculation of mol. fractions leads to values for x which are much too low.[5] Our utter lack of knowledge regarding its true degree of association would, at first sight, appear to bar all solution of the difficulty. Fortunately, however, the variation in x with the molecular weight assumed for the solvent is largely counterbalanced upon the right-hand side of Equation 2 by the fact that

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[1] *I. e.*, if the molecular states of the two components in the solution are independent of x or T. See also Findlay, "Osmotic Pressure," p. 30; Hildebrand, THIS JOURNAL, 38, 1453 (1916).

[2] See Washburn, "Physical Chemistry," p. 174.

[3] One or more factors are usually disregarded entirely, with the consequence that all values derived from the observed freezing-point depressions (*e. g.*, degrees of ionization or hydration), sometimes laboriously calculated to several places of decimals, are apt to be altogether illusory.

[4] This digression is necessary before we can proceed to the examination of the experimental results of the next section. Clearly, if we can establish the method of correction for each factor, or fix the limits within which such correction becomes negligible, then (and only then) we can return to our main problem with the assurance that we have a firm basis on which to build our conclusions.

[5] Certainly 1000 g. water are not equivalent to exactly 55.5 moles, as is often assumed. (See Washburn, *Tech. Quart.*, 21, 381 (1908); Noyes and Falk, THIS JOURNAL, 32, 1013 (1910).)

Q (the *molar* heat of solution) is similarly affected. Roozeboom,[1] indeed, has pointed out that, if x is less than 20%, the ideal freezing-point curves are practically identical[2] whether the solvent is assumed to consist of simple or double molecules. The actual differences calculated from Equation 2 for the case of water are given in the following table (Δ is the depression of the freezing point in degrees).

Moles solute in 1000 g. water.	(a) water = H_2O. x.	Δ.	(b) water = $(H_2O)_2$. x.	Δ.	Difference in Δ.
0.5607	0.01	1.0335	0.01980	1.0284	0.0051°
1.1328	0.02	2.0697	0.03922	2.0498	0.0194°
2.9214	0.05	5.194	0.09524	5.070	0.124°
6.1674	0.10	10.460	0.1818	9.980	0.480°

The variation in the "ideal curve" with the association factor of the solvent is, therefore, obviously far beyond ordinary experimental errors throughout the above range. When it is remembered that the association factor is certainly much greater than 2 at temperatures below zero,[3] and also varies considerably with concentration of solute, it will be evident that the arbitrary assumption, universally made in freezing-point investigations, that the ideal curve is that for water = H_2O, renders all subsequent calculations only approximations. In the present examination, nevertheless, where the relative positions of the curves for different solutes with respect to the ideal curve are all that we require to establish, it will suffice to express all mol fractions under this assumption, since the error at any one concentration will be practically identical throughout the series.[4]

The fact that the heat capacities of water in the solid and liquid states are not the same involves a small variation in Q with the temperature. This leads to a considerable complication in the integrated ideal equation.[5] If, however, we substitute the numerical values for the constants and expand the equation in ascending powers of x, we obtain the relation[6]

$$\Delta = 103.20\,(x + 0.428\,x^2). \qquad (3)$$

Higher powers of x may be neglected, without an error exceeding 0.001°, if x is less than 7%.

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[1] Roozeboom, "Heterogene Gleichgewichte," 2, pp. 306–7.

[2] The side of the unit square in the diagram under discussion by Roozeboom represents a temperature interval of 100°. Subsequent investigators, however, have implicitly confided in the accuracy of the above statement even for freezing-point measurements reading to 0.001–0.0001°.

[3] "The Constitution of Water," *Trans. Faraday Soc.*, 6, 71–123 (1910).

[4] The variation in the association factor of the solvent with concentration of solute will be the same for all normal solutes. Provided the solute concentration is small, this will still be substantially the case even when hydration occurs, since the consequent increase in x (tending to decrease association) will be partially counterbalanced by the decrease in T (tending to increase association).

[5] Washburn, THIS JOURNAL, 32, 667 (1910).

[6] Washburn, "Physical Chemistry," p. 173.

Factors Due to the Solute.—The ionization of the solute in the solution will increase the total number of solute molecules. If we know the degree of ionization at any concentration, we can at once make the requisite correction in the calculation of x. The difficulty here lies in the exact estimation of the extent of ionization. The conductance ratio, at the concentrations here considered, cannot indicate the true degree of dissociation of the electrolyte. A large correction for viscosity is necessary, which will at best be only approximate.[1] Each solution furthermore requires, for strict accuracy, conductivity and viscosity data for its own particular temperature of fusion, whereas all existent measurements are for fixed temperatures (usually 0° or 25°).

Again we are fortunate in the fact that at high concentrations, where errors become large, their actual effect is minimized. The ionization of all except very strong electrolytes is exceedingly small at such concentrations, so that even the *total* effect upon the calculated value of x is inconsiderable and the *uncertainty* in the correction represents an infinitesimal factor. For weak electrolytes the ionization α is obtained directly from the equation[2]

$$c.\alpha^2/(1 - \alpha) = k.$$

(c = weight concentration of solute; k = dissociation constant.) For the strong electrolytes considered, a correction[3] has been made for viscosity with the help of the best data available.[4] The ionization values so derived, while still necessarily somewhat inaccurate, cannot be so far in error as to affect the relative positions of the curves.[5]

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[1] The assumption that, for aqueous solutions, ionic mobilities are exactly proportional to the fluidity has been shown to be incorrect. The variation is more nearly expressed by some fractional power (p) of fluidity, the divergence of this power from unity increasing with the mobility of the ion. See Green, *J. Chem. Soc.*, **93**, 2049 (1908); Johnston, THIS JOURNAL, **31**, 1010 (1909); Washburn, *Ibid.*, **33**, 1461 (1911); Kraus, *Ibid.*, **36**, 35 (1914). In view of the uncertainty in the viscosity correction, minor factors affecting the calculation of ionization in concentrated solutions, such as complex ion formation and change in ionic hydration (see Washburn, *Trans. Am. Electrochem. Soc.*, **21**, 125 (1912)) need not be considered here.

[2] This equation (Kendall, THIS JOURNAL, **36**, 1083 (1914)) has been shown to hold exactly for concentrations up to weight normal; the slight extension here cannot involve any significant error. A similar equation is available for the transition electrolytes here studied (see Kendall, *Loc. cit.*, p. 1084).

[3] For acids, in view of the high mobility of the hydrogen ion, conductivity will not vary nearly so rapidly as fluidity. Green (*Loc. cit.*) has investigated the relation in the case of HCl by addition of sucrose and obtained $p = 0.55$.

[4] Determinations at 0° have been used wherever possible, in preference to those at higher temperatures.

[5] This is demonstrated, in the case of HCl (see diagram, below) by showing the two limiting curves: (*a*) ionization uncorrected for viscosity; (*b*) ionization corrected proportionally to viscosity. It will be seen that neither assumption changes the position of HCl appreciably with respect to weaker acids.

A second possible disturbing factor is *association* of the solute in solution. This will tend to place the true value of x below that calculated on the assumption of simple molecules. Since, however, the mol fraction of the solute is always small, extensive association is not to be expected, except for very abnormal substances.[1] Even the highly-associated methyl and ethyl alcohols appear to exist solely as simple molecules in aqueous solution up to a concentration of 5 mol %.[2] Hence with careful choice of solutes, appreciable errors due to this factor need not be apprehended.

Factors Due to Both Components.—The most important factor for consideration here is the heat of admixture. In the integration of Equation 1 it is assumed that Q is independent of concentration. This is true only if the heat of dilution is zero throughout the whole composition range. Since such is notoriously not the case for aqueous solutions of electrolytes, the necessary modification of the integrated Equation 2 and the magnitude of the correction involved must be taken into account here.

These questions have been discussed in detail by (among others) Abegg,[3] van Laar,[4] Roozeboom,[5] Bancroft[6] and Callendar.[7] Where the heat of dilution is exceedingly great (*e. g.*, in the system H_2SO_2–H_2O) the requisite correction may be so enormous as to render uncorrected values absolutely meaningless.[8] Most investigators, nevertheless, still unite in neglecting the heat of admixture factor entirely,[9] even for depressions measured to 0.001°.

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[1] Peddle and Turner (*J. Chem. Soc.*, **99**, 685 (1911)) have examined the molecular complexity of a great number of organic acids and bases in water, and find marked association only with aromatic compounds. Even for these it is probable that the association in dilute solution is much less than indicated by the above authors. For example, benzoic acid is represented by them (p. 695) as having the same association factor in water as in benzene, a result out of all agreement with coefficient of distribution determinations (Nernst, *Z. physik. Chem.*, **8**, 110 (1891)).

[2] Washburn, "Physical Chemistry," p. 174. It is very conceivable, however, that agreement with the normal curve is here the result of several disturbing factors (association, hydration, heat of dilution) counteracting one another.

[3] *Z. physik. Chem.*, **15**, 244 (1894).

[4] *Arch. Néerland*, [II] **8**, 264 (1903).

[5] *Ibid.*, [II] **6**, 430 (1901); also "Heterogene Gleichgewichte," **2**, 287–303. The correction indicated by Roozeboom is, however, far too large, since the statement that the ratio of the actual to the ideal temperature of fusion is Q/Q_o (*Ibid.*, p. 293) is equivalent to the integration of Equation 1 without regard to the nature of the variation of Q with x.

[6] *J. Phys. Chem.*, 10, 319 (1906). The corrections indicated here (pp. 326–7) are similarly far too large. See Bates, THIS JOURNAL, **37**, 1424 (1915).

[7] *Proc. Roy. Soc. London*, **80A**, 493 (1908).

[8] See Bancroft, *Loc. cit.* A recent article by Gibbons, however (*J. Phys. Chem.*, 21, 48 (1917)), shows that the methods of correction for such cases are still very imperfectly understood.

[9] See H. C. Jones, "Hydrates in Aqueous Solution," passim; Washburn and MacInnes, THIS JOURNAL, **33**, 1702 (1911); Hall and Harkins, *Ibid.*, **38**, 2658 (1916).

We are unable to calculate, for any particular solution, the *exact* correction to be applied, since no direct measurements of Q are available. Even if Q were known, Equation 1 could not be integrated unless we were able to express Q as some simple function of x. For present purposes, however, it will be sufficient to indicate the magnitude of the correction for a single case: HCl when $x = 0.05$. We must here employ the (integral) heat of dilution values of Thomsen.[1] These may be represented by a simple general formula, from which we can derive the relation[2]

$$Q = Q_o - 12000 \text{ calories.}$$

(Q_o is the differential heat of solution, when c, the concentration expressed as moles HCl to moles H_2O, is zero.) Substituting for Q in (1) and integrating, we obtain for $x = 0.05$ the value $\Delta = 5.32°$.[3] Since the uncorrected depression of the freezing point at this concentration[4] is 5.19°, the maximum correction is only 0.13°.[5]

For most substances the heat of dilution is much smaller than for HCl, and the correction is correspondingly reduced. Abegg,[6] indeed, found that "the corrections for the heat of dilution of acetic, formic and tartaric acids, for depressions up to 15°, are at the utmost of the same order of magnitude as the experimental errors in the freezing-point determinations."[7] Hence in the present investigation, where the substances examined have relatively small heats of dilution[8] and x is less than 5%,

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[1] "Thermochemische Untersuchungen," **3**, 12. These values are for 18°, and should of course, each be corrected to fusion-point temperature to be strictly applicable. The changes so made, however, cannot be large (compare Nernst, "Theoretische Chemie," 1909, p. 166), and will in any case, since the heat of dilution decreases with T, tend to reduce the correction indicated above.

[2] See Callendar, *Loc. cit.*, p. 496.

[3] Certain simplifying assumptions made in order to facilitate the integration render this a maximum value.

[4] See table above.

[5] For smaller values of x the correction falls off rapidly. Thus for $x = 2.5\%$, the maximum correction is 0.02°.

[6] *Loc. cit.*, pp. 247–8.

[7] It must be noted that Abegg's experimental errors amount to 2% in some cases (see Noyes and Falk, THIS JOURNAL, **32**, 1017 (1910)). With the more refined methods at present employed (Adams, THIS JOURNAL, **37**, 481 (1915)), allowing results accurate to ±0.0001°, the heat of dilution factor will certainly be significant at much lower concentrations.

[8] This condition excludes the logical series of the chloroacetic acids, which have proved so helpful in previous work. The heat of dilution is here a considerable factor, as is shown both by direct measurement (see Petersen, *Z. physik. Chem.*, **11**, 174 (1893)) and by the freezing-point curves of Pickering (*J. Chem. Soc.*, **67**, 683 (1895)). While these latter data are far from accurate, yet they demonstrate that the depressions deviate largely from the normal, the curves exhibiting, indeed, points of inflexion. The conditions for such a characteristic in systems where heat of dilution is taken into account have been discussed mathematically by van Laar (*Verslag. Akad. Wetenschappen Amsterdam*, June, 1903).

it may safely be assumed that the heat of dilution factor is negligible.

A final disturbing influence, the formation of solid solutions, needs only short consideration here. Equation 2 is quite inapplicable to systems where the components do not separate out pure; observed depressions are smaller than the ideal and may even be converted into elevations. We have thus sure evidence, from the results given below, that none of the substances investigated form solid solutions with ice,[1] since in every case the *initial* portion of the freezing-point curve[2] coincides with the ideal within the limits of experimental error.

Availability of the Method in View of the Above Factors.—The disturbing influences are, evidently, collectively sufficient to preclude all possibility of obtaining *exact* values for the hydration of any particular solute by the freezing-point method.[3] We can so limit our experimental conditions, however, as to be able to derive reliable *comparative* data for a series of solutes, the relative hydrations of the different substances investigated being indicated by the relative positions of their freezing-point curves with respect to the ideal.

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[1] Acetic acid is a possible exception. Ballo (*Z. physik. Chem.*, 72, 439 (1910)) claims to have shown that the slight positive deviations from the ideal curve, for this acid and its homologs, are due not to association but to solid solution. Inclusion of mother liquor in the samples of crystals analyzed may account for these results.

[2] Where Δ is less than 1.0°. At such concentrations all other disturbing factors cannot exceed errors of observation.

[3] It might appear that some alternative method—for example, the vapor-pressure depression method recommended by Washburn (*Tech. Quart.*, 21, 379–81 (1908))—could profitably be substituted. It is true that the theoretical basis of this latter method is simpler, x (the actual mol fraction of solute in a solution) being obtained directly from the ratio *depression of vapor-pressure/vapor-pressure of pure solvent.* Vapor-pressure measurements possess the further advantage that they can be carried out isothermally over the whole concentration range, whereas with the freezing-point method no two determinations refer to the same temperature. The practical difficulties of investigating minute differences of vapor pressure with sufficient accuracy have also recently been completely solved (Frazer and Lovelace, THIS JOURNAL, 36, 2439 (1914); Washburn and Heuse, *Ibid.*, 37, 309 (1915)). Nevertheless, the employment of the vapor-pressure method for aqueous solutions of finite concentration, such as are considered here, is at present not possible. We require to know the exact value for the association factor of water in order to interpret our results, and we have no counterbalancing function (such as Q in the freezing-point method) to offer a means of escape. The very simplicity of the relation renders it useless.

"Three-component" methods—such as that of solubility lowering favored by Philip (*J. Chem. Soc.*, 91, 711 (1907)) and Senter (*Trans. Faraday Soc.*, 3, 146 (1907))—are quite uncertain in their general application, however serviceable they may appear in special cases (see Rothmund, *Z. physik. Chem.*, 69, 545 (1909)). Methods based upon transference measurements during electrolysis (Washburn, THIS JOURNAL, 31, 322 (1909)) can establish only ionic hydrations. In spite of its inherent disadvantages the freezing-point method constitutes, therefore, our sole means of attacking the present problem with any hope of a successful issue. Fortunately the method is, experimentally, exceeding simple, and results of the requisite accuracy are readily obtained.

The necessary limitations are: (*a*) the mol fraction of the solute must be small; (*b*) the heat of dilution must not be excessive; (*c*) the solute must not be associated; (*d*) the solvent must separate out pure as the solid phase. For strong electrolytes, even within these limits, our results will still be rather uncertain, owing to the difficulty in the exact estimation of ionization in concentrated solutions.[1]

A serious effort has been made to respect all of the above conditions in the experimental section which follows. The mol fraction of the solute is always less than 5%. The heat of dilution is either known to be small, by direct measurement, or may safely be assumed so from the data for substances of similar constitution and acidic strength.[2] Among organic substances, only aliphatics are included.[3] Data for strong electrolytes are appended merely to illustrate the fact that the conclusions drawn are valid throughout the whole range of acidic strengths; the main work deals with weak and transition electrolytes.

There is consequently no reason to doubt that the interpretation of our results is in any way unjustified through neglect of special disturbing factors. These are, for all practical purposes, entirely eliminated. The order of the curves upon the diagram (see that below) represents, therefore, the true order of the hydration of the different solutes.[4] No calcula-

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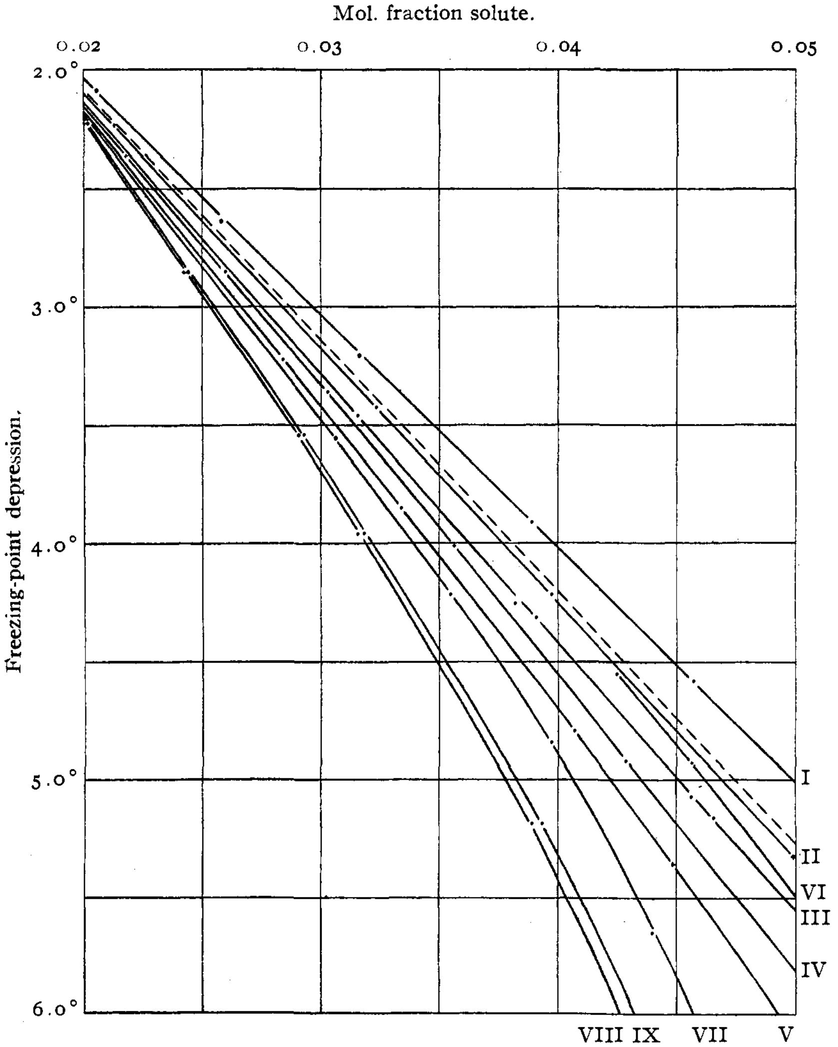
[1] For strong electrolytes still another question arises, which can be but briefly discussed here. Are we entitled to assume that all solute molecules (ionized and non-ionized) exercise a normal depression of the freezing point? If so, then "the mass action law becomes a thermodynamic necessity" (Lewis, *Proc. Amer. Acad. Arts Sci.*, 43, 288 (1907)); Washburn, THIS JOURNAL, 33, 1461 (1911); Bates, *Ibid.*, 37, 1421 (1915)), whereas we know that for strong electrolytes it does not even approximately hold. The present tendency is to fix the responsibility for any abnormality mainly upon the non-ionized portion (Noyes, THIS JOURNAL, 30, 351 (1908); Walker, *Chem. News*, 104, 104 (1911); Lewis, THIS JOURNAL, 34, 1631 (1912)). According to Washburn and MacInnes (*Ibid.*, 33, 1705 (1911)) the resulting divergence will be in a *positive* direction so as to produce too small a freezing-point depression. If this is the case, then, even although we cannot estimate its quantitative influence upon the curves for strong electrolytes considered below, yet we need have no fear that the conclusions based on these curves, as they stand, can be significantly affected. The corrected curves would, indeed, deviate still more widely from each other, since the abnormality is opposed to the hydration effect and could only mask *negative* deviations from the ideal curve, not induce them (compare Washburn and MacInnes, *Loc. cit.*, pp. 1704–6).

[2] See Landolt-Börnstein, "Tabellen," 1912, p. 885, *et seq.*

[3] See Note 1, p. 2312. Even among aliphatic acids it is necessary to reject those containing strongly acidic radicals, since these afford opportunity for salt formation with the basic carbonyl group (Kendall, THIS JOURNAL, 36, 1722 (1914)). No organic acid is *entirely* free from this objection, yet the choice of material here is such as to minimize any possible effect.

[4] In order to demonstrate the behavior of *abnormal* solutes, the data for acetic acid (which is either associated or forms solid solutions) and hydrofluoric acid (which furnishes both double molecules and complex ions) have been added for comparison. A shift from the expected position is evident in each case.

tions of actual hydration values (by the method indicated on pages 2308–9) have been attempted, however, since it is obviously idle to expect results so derived to possess any real significance.[1]



Broken line shows ideal curve.
I = acetic acid.
II = β-oxypropionic acid.
III = α-oxypropionic acid.
IV = citric acid.
V = tartaric acid.
VI = hydrofluoric acid.
VII = phosphoric acid (uncorr.).
VIII = hydrochloric acid (uncorr.).
IX = hydrochloric acid (corr.).

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[1] Numerous previous investigators have exhibited little hesitation on this score. For a full list of references see Dhar, *Z. Elektrochem.*, 20, 57 (1914).

Experimental.

The following acids have been employed in the investigation:

Acetic................ $k_{25} = 0.0000185$;[1] $k_0 = 0.0000168$.[2]
β-Hydroxypropionic.... $k_{25} = 0.000031$.[3]
α-Hydroxypropionic.... $k_{25} = 0.000138$.[3]
Citric................. $k_{25} = 0.00082$;[4] $k_0 = 0.00069$.[5]
d-Tartaric............ $k_{25} = 0.00097$;[6] $k_0 = 0.00091$.[5]
Hydrofluoric.......... $k_{25} = 0.00065 + 0.000025\ (1 - \alpha)/\alpha$;[7] $k_0 = 0.00090 + 0.00007\ (1 - \alpha)/\alpha$.[8]
Phosphoric............ $k_{25} = 0.0070 + 0.0013\ (1 - \alpha)/\alpha$.[9]
Hydrochloric.......... $k_{25} = 1$ (at $v = 10$).[10]

As will be seen from the dissociation constants, we have here a continuous series from the typical weak acid to the typical strong acid.[11] The freezing-point depression curves for water on addition of these acids for concentrations up to 5% (molecular) are given in the tables below, also in the diagram.

In the experimental work the ordinary Beckmann apparatus and method were employed. In view of the disturbing factors affecting all results, it was not attempted to estimate temperatures to a greater accuracy than 0.01°, and for such measurements no special precautions were necessary. Supercooling was limited to 0.1-0.2°. The concentration errors incurred thereby thus fall within those involved in the titration of solutions. Solutions were standardized against known barium

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[1] Kendall, *J. Chem. Soc.*, 101, 1275 (1912).

[2] Baur, *Ann.*, **296**, 95 (1897).

[3] Ostwald, *Z. physik. Chem.*, **3**, 418 (1889).

[4] Walden, *Ibid.*, 10, 568 (1892).

[5] White and Jones, *Amer. Chem. J.*, 44, 197 (1910). Both citric and tartaric acids would certainly, at the higher concentrations employed, deviate to some extent from the simple dilution law and begin to exhibit the "anomaly of strong electrolytes" (see Wegscheider, *Z. physik. Chem.*, **69**, 6 (1909)). The ionization changes so produced would, however, be too small to affect the results here.

[6] Walden, *Z. physik. Chem.*, **8**, 466 (1891).

[7] Ostwald, "Allg. Chemie," Leipsic (1893); see Kendall, THIS JOURNAL, **39**, 21 (1917). The measurements of Fox (*Z. anorg. Chem.*, **35**, 135 (1903)) and of Deussen (*Ibid.*, 44, 300 (1905)) are in good agreement.

[8] Deussen, *Loc. cit.*

[9] Rothmund and Drucker, *Z. physik. Chem.*, 46, 850 (1903); see Kendall, *J. Chem. Soc.*, **101**, 1294 (1912). The results of Noyes and Eastman at 18° (*Carnegie Inst. Publications*, **63**, 262 (1907)) are also substantially reproduced by the same formula.

[10] See Stieglitz, "Qual. Chem. Anal.," 1, 104; also footnote 2, same page.

[11] Considerable difficulty was experienced in acquiring a complete series of acids of suitable strengths; the above represents not the ideal, but the best available material. Few organic acids are sufficiently soluble in water at low temperatures, except hydroxy and amino acids. Use of the latter is out of the question, since extensive salt formation is evident in concentrated solutions (see Washburn, *Tech. Quart.*, 21, 377 (1908)).

hydroxide, and the results transposed to weight concentrations by means of density determinations.

In the following tables, α represents the degree of ionization, x the calculated mol fraction of solute, Δ the observed freezing-point lowering. Wherever possible, the work of previous investigators has been included.[1]

1. **Acetic Acid.**[2]—Fractional "glacial" acid was employed, m. p. 16.4°.

Conc. (wt. molar)...	0.514	1.08	1.159	1.462	1.807	2.240	2.660	2.957
α..................	0.006	0.004	0.004	0.003	0.003	0.003	0.003	0.002
x..................	0.922	1.915	2.052	2.578	3.159	3.890	4.569	5.065
Δ..................	0.938	1.922	2.088	2.641	3.206	3.910	4.584	5.078

2. **β-Hydroxypropionic Acid.**—The acid was obtained pure from a specimen of β-iodopropionic acid by the action of moist silver oxide.

Conc. (wt. molar)...	0.521	1.202	1.849	2.291	2.910
α..................	0.008	0.006	0.004	0.004	0.003
x..................	0.937	2.130	3.235	3.977	4.993
Δ..................	0.960	2.231	3.426	4.220	5.320

3. **α-Hydroxypropionic Acid.**—(Lactic acid).[3]

Conc. (wt. molar)...	0.552	0.594	1.075	1.344	1.793	2.189	2.24	2.608	2.69
α..................	0.016	0.015	0.011	0.010	0.009	0.008	0.008	0.007	0.007
x..................	0.999	1.075	1.92	2.386	3.154	3.820	3.91	4.564	4.656
Δ..................	1.075	1.163	1.99	2.616	3.460	4.262	4.31	5.073	5.158

4. **Citric Acid.**

Conc. (wt. molar)...	0.434	0.705	1.209	1.45	1.70	2.01	2.41
α..................	0.039	0.031	0.024	0.022	0.020	0.018	0.017
x..................	0.806	1.293	2.182	2.60	3.029	3.557	4.285
Δ..................	0.839	1.35	2.36	2.849	3.363	4.010	4.920

5. ***d*-Tartaric Acid.**[4]

Conc. (wt. molar)...	0.407	0.509	0.747	0.940	1.09	1.59	1.88	2.31	2.56
α..................	0.047	0.042	0.034	0.031	0.029	0.024	0.022	0.020	0.018
x..................	0.761	0.946	1.37	1.715	1.986	2.841	3.343	4.066	4.483
Δ..................	0.790	1.000	1.459	1.862	2.154	3.225	3.850	4.79	5.355

6. **Hydrofluoric Acid.**[5]

Conc. (wt. molar)...	0.266	0.494	0.746	1.001	1.649	2.331	2.482	2.882
α..................	0.087	0.076	0.073	0.071	0.070	0.070	0.070	0.070
x..................	0.518	0.95	1.42	1.89	3.08	4.30	4.56	5.26
Δ..................	0.54	0.955	1.38	1.88	3.19	4.55	4.94	5.89

[1] Most of the earlier observations were found, on plotting, to lie too irregularly to be of service here. Several series, however, furnish reasonably smooth curves and have been utilized to amplify the present results.

[2] Points by Loomis (*Ann. Phys.*, [3] 60, 540 (1897)), Abegg (*Z. physik. Chem.*, 15, 218 (1894)), Roth (*Ibid.*, 43, 556 (1903)) and Roloff (*Ibid.*, 18, 583 (1895)) are added to complete the curve.

[3] Points by Abegg (*Loc. cit.*) are included for this and the two following acids.

[4] Points by Raoult (*Z. physik. Chem.*, 1, 186 (1887)) are included.

[5] Paterno and Peratoner, *Atti accad. Lincei*, [4] 6, 306 (1890). Only a small portion of this curve is represented in the diagram in order to avoid confusion. The upper part lies very near to the ideal curve throughout.

7. Phosphoric Acid.[1]

Conc. (vol. molar)	0.2	0.4	0.6	0.8	1.0	1.401	1.62	1.810	2.0
α (uncorr.)	0.256	0.198	0.188	0.179	0.175	0.170	0.167	0.164	0.161
α (corr.)	0.263	0.210	0.205	0.199	0.203	0.209	0.212	0.215	0.218
x (uncorr.)	0.455	0.872	1.304	1.735	2.171	3.061	3.546	3.973	4.399
x (corr.)	0.458	0.880	1.322	1.764	2.222	3.160	3.677	4.139	4.603
Δ	0.485	0.868	1.292	1.775	2.370	3.555	4.213	4.842	5.550

8. Hydrochloric Acid.[2]

Conc. (vol. molar)	0.1	0.2	0.4	0.6	0.75	0.9	0.991	1.245	1.520	1.698
α (uncorr.)	0.950	0.906	0.890	0.865	0.841	0.815	0.796	0.768	0.740	0.722
α (corr. I)	0.951	0.908	0.894	0.871	0.848	0.823	0.812	0.787	0.752	0.746
α (corr. II)	0.952	0.910	0.897	0.875	0.854	0.830	0.812	0.787	0.762	0.746
x (uncorr.)	0.351	0.685	1.356	2.004	2.426	2.910	3.154	3.895	4.672	5.147
x (corr. I)	0.351	0.686	1.359	2.010	2.436	2.922	3.169	3.916	4.702	5.186
x (corr. II)	0.351	0.687	1.361	2.014	2.443	2.933	3.182	3.935	4.728	5.216
Δ	0.355	0.712	1.442	2.250	2.852	3.540	3.960	5.184	6.57	7.64

The significance of the above results will be immediately apparent on reference to the diagram, where the temperature-composition curves for all the acids considered here are plotted.[3] The order of the curves corresponds exactly with the order of the acidic strengths, for any fixed concentration the deviation from the ideal curve being greater the stronger the acid. The only exceptions are acetic acid and hydrofluoric acid, which lie abnormally high, a behavior only to be expected from their abnormal molecular states in concentrated solution.

For acids in aqueous solution, therefore, the anticipated results have been completely realized. Hydration increases in extent with the acidic

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[1] H. C. Jones, "Hydrates in Aqueous Solution," p. 100; Chambers and Frazer, *Am. Chem. J.*, **23**, 515 (1900). Two series of values for α and x are given in the above table, the former calculated from conductivity values at 0° (Jones, *Loc. cit.*) uncorrected for viscosity, the latter corrected by the viscosity data of Moore (*Phys. Rev.*, 3, 321 (1896)), assuming $p = 0.55$ (see note 3, p. 2311). It will be evident from the run of the ionization values with concentration that even this "fractional" viscosity correction is too great, hence it has seemed preferable to show, in the diagram, the *uncorrected* curve. The position of this is admittedly somewhat too low (the corrected curve lies near to that for tartaric acid) but it is impossible, in cases where the viscosity change is so large, to apply any really satisfactory correction. (Compare Kraus, *Z. Elektrochem.*, **20**, 524 (1914).)

[2] H. C. Jones, "Hydrates in Aqueous Solution," p. 93; Jones and Pearce, *Am. Chem. J.*, **38**, 683 (1907); Roloff, *Z. physik. Chem.*, **18**, 576 (1895). In the calculation of α and x the conductivity measurements of Jones (*Loc. cit.*) and the viscosity data of Taylor and Ranken (*Proc. Roy. Soc. Edinburgh*, **25**, 231 (1904)) have been employed. The values under corr. I are obtained by the use of the fractional-power formula indicated on p. 2311 (see note 1); those under corr. II are corrected proportionally to viscosity. The two extreme curves are shown in the diagram; the essential point is that any error in viscosity correction cannot appreciably affect the position of the curve.

[3] The initial portions of all curves coincide within the limits of experimental error. Hence, in the diagram, only depressions greater than 2°, where deviations begin to become considerable, are shown.

strength throughout the entire series.[1] Before we proceed to discuss the consequences of this relationship, the corresponding data for bases in aqueous solution may be briefly considered.

The Hydration of Bases.

Systems of the type: water–base are clearly amenable to identically the same general values as have been developed for those of the type: water–acid. With water functioning as an exceedingly weak base, we may predict:

(*a*) No indication of hydrate formation with extremely weak bases.

(*b*) A regular increase in the extent of combination in the liquid state as the strength of the base is increased.

(*c*) Extensive compound formation with the transition and strong bases.

(*d*) Increase in the complexity as well as in the stability of hydrates with the strength of the base.

The actual behavior of the bases, as collected from the literature, may be seen from the following tabulation:

Base.	Dissociation constant (25°).[2]	Hydrates isolated.
NH_3	0.000018	0.5 H_2O; H_2O[3]
$NH_2(CH_3)$	0.000039	3 H_2O[4]
$NH_2(C_2H_5)$	0.000044	0.5 H_2O; 5.5 H_2O
$NH(CH_3)_2$	0.000057	H_2O; 7 H_2O
$NH(C_2H_5)_2$	0.000098	0.5 H_2O; 8 H_2O
$Sr(OH)_2$	0.03 (at $v = 10$)	H_2O; 2 H_2O; 8 H_2O[5]
$Ba(OH)_2$	0.03 (at $v = 10$)	H_2O; 3 H_2O; 8 H_2O; 16 H_2O[6]
NaOH	1 (at $v = 10$)	H_2O; 2 H_2O; 3.5 H_2O; 4 H_2O; 5 H_2O; 7 H_2O[7]

[1] As stated in a previous note, few acids are available for freezing-point determinations at the high concentrations here investigated, and the series examined is, therefore, not so extensive as might be desired. In order to overcome this difficulty, corresponding measurements of boiling-point elevations are being carried out with a more representative series of acids, the increased solubility at 100° allowing a much wider choice of material. A preliminary examination of the work of previous investigators indicates results of precisely the same character as those here obtained, *i. e.*, deviations from the ideal curve increasing regularly with the acidic strength. Thus boric acid follows the normal curve exactly up to concentrations of 6 weight molar (Kahlenburg, *J. Phys. Chem.*, **5**, 378 (1901); Nasini and Ageno, *Z. physik. Chem.*, **69**, 482 (1909)). Citric acid, on the other hand, gives abnormally large elevations; *d*-tartaric is again slightly more divergent than citric (Juttner, *Z. physik. Chem.*, **38**, 112 (1901); Johnston, *Trans. Roy. Soc. Edinburgh*, **451**, 193 (1908)).

[2] For ammonia and the alkyl-substituted amines the dissociation constants are those obtained by Bredig (*Z. physik. Chem.*, **13**, 322 (1894)), corrected according to Hantzsch and Davidsohn (*Ber.*, **31**, 1633 (1898)) for the velocity of the hydroxyl ion. The values for the strong inorganic bases are taken from Stieglitz ("Qual. Chem. Anal.," 1, 106).

[3] Rupert, THIS JOURNAL, **31**, 866 (1909); **32**, 148 (1910).

[4] Pickering, *J. Chem. Soc.*, **63**, 141 (1893).

[5] Müller-Erzbach, *Ber.*, **20**, 1628 (1887); **22**, 3180 (1889).

[6] Abegg, "Handbuch der anorg. Chem.," [2] **2**, 259 (1905).

[7] Pickering, *J. Chem. Soc.*, **63**, 890 (1893).

Very weak bases yield no isolable hydrates, unless acidic groups are also present in the molecule.[1] Ammonia gives with water two simple compounds, stable at very low temperatures. Increase in the basic strength by substitution of alkyl groups is accompanied by a regular increase in the complexity of the hydrates obtained.[2] The strong inorganic bases, finally, yield very stable and sometimes very complex hydrates.

Unfortunately we are not able to supplement the above data, as in the case of acids, by a series of freezing-point depression curves, owing to dearth of suitable material. Careful preliminary experiments upon the substituted amines examined by Pickering[3] indicated that our ignorance of their respective degrees of hydration *as amines* introduces so much uncertainty into the true position of each freezing-point curve that any estimation of their relative degree of hydration *as bases* is thus rendered impossible. The strong inorganic bases, at any rate, exhibit large divergences from the ideal curve.[4]

The Hydration of Salts.

The method of treatment here is less obvious than in the case of acids and bases, since there is no such direct connection between the two components RX and HOH on which to found generalizations. Fortunately, however, this field has already been covered in some detail by the extensive work of Werner[5] and of Abegg and Bodländer.[6] Werner finds that the stability of an "aquo-salt" decreases as the strength of the acid or the base increases. Abegg and Bodländer also claim that hydration decreases with increasing electro-affinity, *i. e.*, that the salts of *weak* acids and bases are most extensively hydrated.

The evidence in favor of these statements afforded by actually isolable hydrates of simple salts may first be indicated. Thus the salts of the strong alkalies are mostly anhydrous, while those of the weaker alkaline earths are usually hydrated; the still weaker trivalent bases (*e. g.*, $Fe(OH)_3$, $Al(OH)_3$) give salts which are exceedingly rich in water of combination.

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[1] Thus many of the alkaloids, although very feebly basic, give stable hydrates. Such cases do not constitute exceptions to the general rules here drawn.

[2] The *actual* basic strengths of the alkyl-substituted amines are uncertain, since we do not know what proportion of the solute combines with water in solution to form the true base. In any case the true dissociation constants are larger than those given above, which are calculated under the assumption that all of the solute is in combination. With the tertiary amines it is probable, indeed, that by far the greater part is non-hydrated, hence their *apparent* basic strengths are quite abnormal (see Walker, *Z. physik. Chem.*, **57**, 602 (1906)).

[3] Pickering, *J. Chem. Soc.*, **63**, 141 (1893).

[4] Jones, "Hydrates in Aqueous Solution," pp. 41, 48.

[5] Werner, *Z. anorg. Chem.*, **3**, 294 (1893); *Ber.*, 40, 4133 (1907); "New Ideas on Inorganic Chemistry," pp. 206–8.

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

Similarly nitrates are generally less hydrated than chlorides, chlorides less than bromides or iodides, these less than sulfates, sulfates less than acetates or carbonates. Exceptions are abundant, however, and an inspection of all available results appears to offer little prospect of any universally valid rules being thus derivable at present.

Comparison of the freezing-point depression curves also provides no conclusive evidence regarding relative degrees of hydration. It is true that when we compare the abnormalities of the curves as they stand, we obtain series such as the following:[1]

$$Ce < Rb < K < NH_4 < Na < Li$$

$$NO_3 < Cl < Br < I$$

In most instances, nevertheless, the final position of each curve is so indefinite owing to the uncertainty of conductivity, viscosity and heat of dilution at high concentrations that deductions of real significance are out of the question.

It would be difficult, in any case, to substantiate whether for salts, as for acids and bases, there is a uniform increase of ionization with hydration. Nearly all uni-univalent salts are practically equally dissociated in solution (whatever the strengths of their constituent acid and base), yet hydration values—as far as we can judge from present data—are widely divergent. It is a very striking fact, nevertheless, that with mercuric salts, the one series in which ionization varies considerably,[2] *all* highly-ionized salts yield hydrates (*e. g.*, $Hg(NO_3)_2.8H_2O$, $Hg(ClO_4)_2.6H_2O$, $HgF_2.2H_2O$) while *all* slightly-ionized are non-hydrated.

It does not seem profitable, in view of the confusion at present existing, to attempt to follow the subject further at this point, or to seek to correlate or contrast the opinions of Werner and of Abegg and Bodländer with those here advanced, in spite of their evident interdependence.[3] A more promising, if indirect, means of progress is open to us in the systematic study of acid and basic salts—two subjects as yet almost untouched. If experimental work now under commencement succeeds in deducing general rules for the extent of compound formation in systems of the types: HX–RX and ROH–RX, then, by comparison of the results with those already obtained for systems of the types: $HX–H_2O$ and $ROH–H_2O$, it may prove possible for us to formulate generalizations for the more complex type: $RX–H_2O$. Meanwhile the bearing of the conclusions here established for acids and bases upon our present theory of solutions will be discussed in an article immediately following.

[1] Drucker, *Z. Elektrochem.*, 20, 80 (1914).

[2] See Abegg, "Handbuch anorg. Chem.," 2, 556.

[3] The connection of the results of these workers with those of the present series of communications will be taken up in a later article, after the various factors affecting ionization and hydration have been more fully discussed.

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 from 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 bases[1] 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 $RX \rightleftarrows R^+ + X^-$, 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

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[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).