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THE THEORY OF ACIDITY

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During the past five years there has been published by Hantzsch a series of papers[1] on the nature of acidity, whose results are markedly at variance with accepted ideas on the subject. In the recent papers of Hall and Conant[2] on "superacid solutions" there is presented evidence from much more precise indicator studies and from potential measurements of the essential correctness of some of Hantzsch's conclusions. These results may be completely explained by methods which derive from Brönsted's important treatment of the problem,[3] and which will be developed in the present article.

According to the classical ionization theory the quantitative measure of acidity is hydrogen ion concentration, and a non-ionized solution cannot have the properties of an acid. The experimental evidence for this conclusion is the unquestionably close parallelism between ionization and acidity in solutions in a single solvent, and the fact that such non-ionized solutions as hydrogen chloride in benzene do not react or react only very slowly with metals and carbonates.[4] Hantzsch's conclusion, on the other hand, is that practically non-conducting solutions may be acid, even that such solutions may be much more acid than highly ionized aqueous solutions. His evidence is that dilute solutions of certain acids in non-ionizing solvents produce the same effect upon indicators as do more concentrated solutions of the same acid in water; and that the rate of decomposition of diazoacetic ester, an acid catalyzed reaction, is greater in the non-ionized solution than in an equally concentrated aqueous solution of the same acid.

The evidence for high acidity in the non-ionizing solvent depends upon homogeneous reactions; the evidence against high acidity depends upon heterogeneous reactions for which both reactant and product are insoluble in the medium. The formation of protective coatings seems almost certain, and it is clear that Hantzsch's conclusions rest upon sounder evidence than do the accepted theories.

The essential features of Hantzsch's results may be summarized as

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[1] Hantzsch, (a) *Z. Elektrochem.*, **29**, 221 (1923); (b) **30**, 194 (1924); (c) **31**, 167 (1925); (d) *Ber.*, **58**, 612 (1925); (e) **58**, 941 (1925); (f) **59**, 793 (1926); (g) **59**, 1096 (1926); (h) **60**, 1933 (1927); (i) *Z. physik. Chem.*, **125**, 251 (1927).

[2] (a) Hall and Conant, THIS JOURNAL, **49**, 3047 (1927); (b) Conant and Hall, *ibid.*, **49**, 3062 (1927).

[3] (a) Brönsted, *Rec. trav. chim.*, **42**, 719 (1923); (b) *J. Chem. Soc.*, 119, 574 (1921); (c) *J. Phys. Chem.*, **30**, 777 (1926).

[4] See Stieglitz, "Qualitative Chemical Analysis," The Century Co., New York, **1922**, Vol. I, Chap. 5, for a complete discussion.

follows: 1. Acids (HCl, HBr, $HClO_4$) which are both highly ionized and strongly acidic in aqueous solutions, are even more strongly acidic yet practically un-ionized in hydrocarbons and similar solvents, and differ among themselves greatly in their acidity; whereas dilute aqueous solutions of the different acids have the same acidity at the same concentration. 2. Acids (acetic, formic) which are weak in water are much weaker in the hydrocarbon type of solvent. 3. Many solvents containing oxygen, notably ether, give solutions of extremely low acidity. Some acids which are strong in water (nitric, trichloro-acetic) are quite weak in ether, and only those acids (HBr, $HClO_4$) which are the most acid in chloroform and similar solvents have an acidity in ether which approaches the value in water.

Hantzsch's explanation of the first of these results seems very probable: that water is a base in much the same way that ammonia is a base; that an acid dissolved in water exists as an oxonium salt just as an acid dissolved in ammonia exists as an ammonium salt.[5]

Strong acids are then less acid in water than in solvents of lower basicity, and still less acid in the more basic ammonia, and they all have the same acidity in a given basic solvent, because this is now the acidity of oxonium (OH_3^+) or ammonium ion regardless of the acid used. This may be better expressed in terms of Brönsted's adaptation of Werner's theory in the light of the principle of complete dissociation. The formation of ions and the resultant conductivity, according to Brönsted, are due not to the reaction $HClO_4 \rightleftarrows H^+ + ClO_4'$ but to the reaction $HClO_4 + H_2O \rightleftarrows OH_3^+ + ClO_4'$. This process can take place only by virtue of the fact that oxonium ion holds its hydrogen ion more firmly than does perchloric acid, that OH_3^+ is less acid than $HClO_4$.

These conclusions are further supported by the work of Hall and Conant, and the significance of the concept of basicity of solvent for the question of acidity is very clearly presented in their diagram and discussion.[6]

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[5] Aside from Hantzsch's work, the theory that water is a base in this sense is supported by the following lines of evidence. The overwhelming similarity in the properties of water and ammonia, which shows so clearly for instance in Franklin's work on ammonia solutions, indicates strongly that the acidity relations are similar in the two solvents. But acids in ammonia solution are ammonium salts. There is evidence in the work on oxonium salts that the maximum coördination number of oxygen is three; that saturated oxygen compounds can add one hydrogen ion just as can ammonia and its substitution products. Fajans and Joos, *Z. physik*, **23**, 1 (1924), have shown that the interpretation of the refractive index of aqueous acids demands the assumption of the existence of such an ion as OH^+_3. Hantzsch, *Z. physik. Chem.*, **65**, 41 (1908), has shown that the cryoscopic effect in sulfuric acid of water and ammonia is the same. Volmer, *Ann.*, **440**, 200 (1924), has demonstrated by x-ray analysis the crystallographic identity of ammonium perchlorate and the monohydrate of perchloric acid, which is therefore shown to be oxonium perchlorate.

[6] Ref. 2 b, page 3069.

If, however, basicity of solvent were the only factor, all acids, and not merely the strong ones, should appear stronger in chloroform than in water, which is not true. Brönsted[3c] has already suggested the importance of dielectric constant in this connection, and it is possible to account for Hantzsch's results as they have been enumerated by taking this into account.

It has been clearly shown by Brönsted[3a] that the only logically consistent general measure of acidity is hydrogen-ion potential (which is proportional to P_H) or the closely related hydrogen-ion activity. The use of activities instead of potentials is convenient, but it should be made very clear that this use does not express or even imply any knowledge of concentration. Hydrogen-ion activity is by definition an exponential function of hydrogen-ion potential, and hydrogen-ion potential represents the work concerned in the reversible removal of hydrogen ions (protons) from a given system, or their addition to it. High activity means loosely bound hydrogen ions, low activity firmly bound hydrogen ions. Reaction proceeds by the transfer of hydrogen ions from higher to lower activity, and we have no means of knowing whether actual protons are ever present either as an intermediary or as a by-product in such transfers. It may, however, be reasonably expected that the concentration of free hydrogen nuclei in a solution should be at least as small as the concentration of free electrons, that is, negligible; and this point of view will be taken in what follows.

Since it is only the ratios of activities that can be measured, it is necessary always to set up a purely arbitrary scale of numerical values of activity. It has been convenient when considering the variation of activity with concentration in a single solvent to set up a different arbitrary scale for each solvent, in such a way that the activity coefficient, the ratio of activity to concentration, approaches one as the solution becomes infinitely dilute. This usual convention is, however, very unsatisfactory when solutions of the same solute in more than one solvent are considered,[7] and the quite different convention is adopted in this paper that the same scale of activities is used for all solvents. It follows then that two solutions of the same hydrogen-ion potential, that is, of the same true acidity, will have the same hydrogen-ion activity, no matter what the solvent, but it follows also that the activity coefficient will not in general approach one for infinitely dilute solutions. When numerical values become available it will probably be desirable to define the scale of activities in such a way that the activity coefficient approaches one for very dilute solutions in some one solvent, say water; the activity coefficient in another solvent will then approach a value which will in general be greater or less than one.

With this understanding it is possible to attack mathematically the

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[7] See Scatchard, THIS JOURNAL, 47, 2105 (1925).

problem of the effect of solvent upon acidity. The following symbols will be used: HX = acid, for example HCl, or $HClO_4$; S = solvent, for example water, ether, chloroform; c = concentration; a = activity; f = activity coefficient; c_a = stoichiometric concentration of HX.

Regardless of the solvent we have

$$a_{H^+} = K_{HX}\frac{a_{HX}}{a_{X'}} = K\frac{c_{HX}\,f_{HX}}{c_{X'}\,f_{X'}} \tag{1}$$

but if the solvent is basic, we have also

$$a_{H^+} = K_S'\frac{a_{SH^+}}{a_S} = K_S\,c_{SH^+}\frac{f_{SH^+}}{f_S} \tag{2}$$

If, as seems probable, c_{H^+} may be taken as negligibly small

$$c_a = c_{HX} + c_{X'} = c_{HX} + c_{SH^+} \tag{3}$$

since the reaction between acid and solvent is $HX + S \rightleftarrows X' + SH^+$. Combination of 1, 2, and 3 gives

$$a_{H^+} = \frac{1}{2}K_{HX}\frac{f_{HX}}{f_{X'}}\left\{-1 + \sqrt{1 + 4c_a\frac{K_S}{K_{HX}}\frac{f_{SH^+}\,f_{X'}}{f_S\,f_{HX}}}\right\} \tag{4}$$

Since a_{H^+} increases with increasing K_S, this equation records the principle that *decreased basicity of solvent* (greater K_S) *means greater acidity, although it also means less ionization.*

In order to see more clearly the effect of changes in the f terms, which record the effect of changes in dielectric constant, it is advisable to consider the forms to which Equation 4 reduces in the two limiting cases.

When the second term under the radical sign is large compared with one, the equation becomes

$$a_{H^+} = \sqrt{c_a\,K_SK_{HX}\frac{f_{SH^+}\,f_{HX}}{f_S\,f_{X'}}} \tag{5}$$

This is the case of weak acid or weakly basic solvent; the reaction of ionization, $HX + S \rightleftarrows X' + SH^+$, is incomplete, and the acidity depends upon both K_S and K_{HX}, that is, upon the properties of both acid and solvent.

When the same term is small the radical may be expanded and using the linear term only we have

$$a_{H^+} = c_a\,K_S\frac{f_{SH^+}}{f_S} \tag{6}$$

Ionization is large and the acidity depends only upon the properties of the solvent. This represents the leveling effect of the solvent, mentioned by Hantzsch and by Conant and Hall.

We can now make at least a qualitative prediction of the effect of dielectric constant from the known effect of this property upon the activity coefficients. The activity coefficient of an ion is unquestionably greater in solvents of low than in solvents of high dielectric constant. This is demonstrated by the extremely low solubility of true salts in solvents of low dielectric constant, and is predicted by the interionic attraction theory of electrolytes. The changes in the activity coefficients for uncharged molecular species from solvent to solvent are much smaller than the changes of the ionic activity coefficients. It therefore follows of necessity that such a ratio as $f_{HX}/f_{X'}$ or f_S/f_{SH^+} will decrease with decreasing dielectric constant. We shall asume as an admittedly rough approximation that the change in this ratio between two different solvents is independent of the acid or base concerned. There is indeed some reason for believing that specific effects upon the ratio will be considerably smaller than the effect upon the individual activities. This corresponds to the impression that those acids or bases which are themselves much more soluble in organic solvents than in water will have salts which are relatively soluble in organic solvents.

It follows then that the ratio $f_{SH^+}\, f_{HX}/f_S\, f_{X'}$ in Equation 5 will be approximately one for all solvents; that *the hydrogen-ion activity of a weakly ionized acid is independent of the dielectric constant of the medium.* It follows from Equation 6 that *the hydrogen-ion activity of a highly ionized acid will be greater in solvents of low than in solvents of high dielectric constant.* For the intermediate cases decrease in dielectric constant will result in a more or less large increase in hydrogen-ion activity.

But hydrogen-ion activities cannot be measured directly unless or until we know very much more than we do at present about diffusion potentials. Verification of the theory depends upon its extension to some such measurable phenomenon as salt formation with indicators. We shall let I represent the molecular substance of some indicator base (dimethylamino-azobenzene, benzalacetophenone, etc.), and IH$^+$ the ion which it forms with acids. Then

$$\frac{a_{H^+}\, a_I}{a_{IH^+}} = K_I \tag{7}$$

Suppose an amount of indicator be added which is insufficient to displace materially the acid solvent equilibrium. Then the salt base ratio of the indicator, which determines the color, is given by

$$\frac{c_{IH^+}}{c_I} = \frac{1}{K_I}\frac{f_I}{f_{IH^+}}\sqrt{K_{HX}\, K_S\, c_a} \tag{8}$$

for weakly ionized solutions, and by

$$\frac{c_{IH^+}}{c_I} = \frac{K_S\, f_{SH^+}\, f_I}{K_I\, f_{IH^+}\, f_S}\, c_a \tag{9}$$

for highly ionized. The same considerations already used concerning the effect of dielectric constant upon the activity coefficients lead to the conclusion *that decrease in dielectric constant will have little effect upon salt formation when ionization is large, and will decrease salt formation when ionization is small. For all except very highly ionized solutions the result of decreased dielectric constant will be a decrease in apparent acidity as measured by a basic indicator.*

We may now explain the conclusions drawn previously from Hantzsch's work. 1. Acids which are highly ionized and strong in water give increased salt formation with indicators in solvents of negligible basicity like chloroform and the hydrocarbons because these solvents are less basic than water. 2. Acids like acetic and formic which are weakly ionized in water give very little salt formation with indicators in these solvents of low dielectric constant because a reaction like $HX + I = IH^+ + X'$ which produces ions from neutral molecules takes place to a smaller extent the smaller the dielectric constant. 3. Acids, except the very strongest, which are presumably highly ionized in both ether and water, give less salt formation with basic indicators in ether than in water because of the low dielectric constant. Ionization is frequently much less in ether than in water, as with HCl, again because the reaction $HCl + S = SH^+ + Cl'$ is displaced toward the left by lowered dielectric constant. Salt formation is, of course, always less in ether than in chloroform or similar solvents of about the same low dielectric constant because of the basicity of the ether.[8]

It will be seen that acidity as measured by a basic indicator does not run parallel to hydrogen-ion activity when there is a change in dielectric constant. It is only necessary to change to an acid indicator to see how unreliable indicator measurements must be for determining relative acidities in different solvents. Thus ordinary glacial acetic acid gives an intermediate shade with dimethylamino-azobenzene. From this one may estimate its P_H on the water scale to be about 3.5. With picric acid it gives a colorless solution, indicating an acidity greater than that of molar aqueous hydrochloric acid, that is a P_H less than 0.[9]

Presumably the true acidity lies between the values indicated by the basic and by the acid indicator. For the color determining ratio acid over salt for an indicator HI (such as picric acid) is given by

$$\frac{c_{HI}}{c_{I'}} = \frac{1}{K_{HI}} \frac{f_{I'}}{f_{HI}} \sqrt{K_{HX}\, K_S\, c_a} \tag{10}$$

for weakly ionized solutions, and by

$$\frac{c_{HI}}{c_{I'}} = \frac{K_S}{K_I} \frac{f_{SH^+}\, f_{I'}}{f_S\, f_{HI}}\, c_a \tag{11}$$

for those highly ionized. The effect is to increase the apparent acidity with decrease in dielectric constant, the change being greater the higher the ionization. A tabulation shows that the effect of decreased dielectric constant upon hydrogen-ion activity lies always between the effect upon apparent acidity by basic indicator and apparent acidity by acid indicator.

[8] If we may drive the analogy between water and ammonia a little farther, the basicity of ether should differ from that of water to about the same extent as that of an aliphatic amine differs from that of ammonia.

[9] It is only with the strongest alkalies that the medium permits, such as sodium acetate, that the picric acid indicator gives a yellow color in acetic acid as solvent.

Ionized system	Basic indicator	Hydrogen-ion activity	Acid indicator
Weakly	Decreased acidity	No effect	Increased acidity
Highly	No effect	Increased acidity	Greatly increased acidity

The best we can say about relative acidities in water and ether and water and acetic acid, then, is that they are approximately the geometric mean of the hydrogen-ion activities estimated by the use of basic and acid indicators.

The superacid solutions of Hall and Conant are probably even more acid than their own figures indicate. Their tentative choice of a scale of P_H in acetic acid amounts to the same thing as the assumption that two solutions in which a basic indicator gives identical colors have the same hydrogen-ion activity regardless of the solvent. They assume that two solutions with the same ratio of concentrations of an anhydro base and the salt which it forms by addition of hydrogen ion should have the same hydrogen-ion activity. From the equation $a_{H^+} = K\ (c_{BH^+}/c_B)\ (f_{BH^+}/f_B)$ it will be seen that of two solutions with a given ratio of salt to base c_{BH^+}/c_B the solution in the solvent with lower dielectric constant has the greater hydrogen-ion activity.

If the true P_H relative to aqueous solutions is two to three units less than the values given by Hall and Conant, it is unnecessary to assume such abnormal values for the diffusion potential in their salt bridge,[10]

It is true that salt formation, a concrete, measurable thing, is more important than a concept like activity, which is not susceptible to direct measurement; but it remains extremely important to call the thing we measure salt formation and not hydrogen-ion activity if it is salt formation and if it is not parallel to activity.

If we were to confine our interest in acidity to aqueous solutions the subject matter of the present article would be of little value. It is only when comparing acidities in different solvents that the basicity and dielectric constant of the solvent need be considered. Probably the greatest reason for an interest in acidity outside of the bounds of aqueous solutions is the great importance of catalysis by acids and bases in organic reactions. This becomes particularly important since the appearance of Meerwein's[11] evidence that zinc chloride and aluminum ethylate have acidic properties and that their catalytic properties are probably closely related to their acidity.

According to Hantzsch there is a close and far-reaching parallelism between salt formation with basic indicators and the rate of decomposition of diazoacetic ester, a reaction which has been a classical one for the study of acidity in aqueous media. The reaction is not an ideal one for the purpose of studying acidity in different media, for the product of the

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[10] I am indebted to Professor H. A. Fales for pointing out that a diffusion potential of 0.15 volt is much greater than any previously known or suspected.

[11] Meerwein, *Ann.*, **455**, 227 (1927)

decomposition may be different with different acids and different solvents. Nevertheless it is possible, as Hantzsch supposes, that the reaction velocity depends in any case upon salt formation by addition of hydrogen ion to the ester, and that the final steps of the reaction, leading to the different possible products, do not affect the velocity. This would account for the observed parallelism of reaction velocity and indicator acidity.

It should be of great importance to investigate other, less ambiguous reactions to see if this parallelism can be generalized.

Summary

A generalized theory of acidity is proposed and given mathematical expression. In this the effect of the basicity and of the dielectric constant of the solvent are both considered.

The predictions of the theory are in agreement with the available evidence on acidity in non-aqueous solutions, notably with the work of Hantzsch and with that of Hall and Conant.

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A BALLISTIC GALVANOMETER METHOD OF POTENTIOMETRIC MEASUREMENT FOR HIGH RESISTANCE CELLS

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Introduction

A recent publication by Jones and Kaplan[1] contains a description of a method of potentiometric measurement for high resistance cells which uses a condenser and ballistic galvanometer as a null point indicator. A deflection method for high resistance cells which used the condenser and ballistic galvanometer was used in this Laboratory by Beans and Oakes.[2] Since then we have developed a more exact method[3] which is in many respects similar to that of Jones and Kaplan but differs in that it is a semi-deflection method. We have experimentally demonstrated that our method may be used successfully with cell resistances as high as 50 megohms. The cells which Jones and Kaplan used had internal resistances no higher than 1.6 megohms. At higher resistances the null point method, while still possible, becomes very cumbersome due to the time required to charge the condenser sufficiently to cause a noticeable throw upon discharge. Our method overcomes this difficulty, at the same time retaining an accuracy of 0.1 to 0.5 millivolt.

[1] Jones and Kaplan, THIS JOURNAL, **50,** 1845 (1928).

[2] Beans and Oakes, *ibid.*, **42,** 2116 (1920).

[3] Walden, *Dissertation,* Columbia, **1924.**