ACID-BASE EQUILIBRIA IN NON-AQUEOUS SOLVENTS WITH PARTICULAR REFERENCE TO GLACIAL ACETIC ACID

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Acids and acidity have taken on a new theoretical importance in the last thirty years, because, after the rôle of the hydrogen ion as the common carrier of acid properties had become established, it was discovered that this hydrogen ion or proton, besides being the lightest atomic particle was also *simple* in a way entirely unique among atoms, and *fundamental* in a way shared only with the electron. It is thus possible to say that just as oxidation-reduction reactions are uniquely characterized by electron exchange between molecules, and may be defined by the general equation

$$\text{Red} \rightleftharpoons \text{Ox} + \oplus$$
$$(\text{reductant} \rightleftharpoons \text{oxidant} + \text{electron}),$$

so acid-base or *protolytic* reactions may be defined by the general equation (Goldschmidt, Brönsted)

$$\text{A} \rightleftharpoons \text{B} + \oplus$$
$$(\text{acid} \rightleftharpoons \text{base} + \text{proton}).$$

In actual practice, however, chemical reactions are always more complex than this and the typical "redox" equilibrium involves at least two oxidants and two reductants.

$$\text{Red}_1 + \text{Ox}_2 \rightleftharpoons \text{Red}_2 + \text{Ox}_1$$
$$\text{e.g., } Cu^{+} + Fe^{+++} \rightleftharpoons Fe^{++} + Cu^{++}$$

Similarly, acid-base reactions in general involve such an exchange as

$$A_1 + B_2 \rightleftharpoons A_2 + B_1$$
$$HCl + NH_3 \rightleftharpoons NH_4^{+} + Cl^{-}$$

The example chosen involves us at once in the question of the advantages and disadvantages of the proposed definition. It is seen that to be consistent we must give the name "acid" to all molecules of the A type which release a proton under the conditions of our study, regardless of their charge, and the name "base," or "protophile," to all which accept protons. This results in calling ammonium ion an acid, chloride ion a base (though a very weak one), and in saying that potassium hydroxide is not itself a base although it contains the strong base hydroxyl ion.

Some hostility is naturally aroused in many minds by such a proposal, and it seems fair to say that chemical opinion is divided at the present time on its desirability. On the one hand are those who prefer to retain the customary definition of a base as something that in water gives hydroxyl ions, in spite of the admittedly partial, inadequate, and one-sided character of this formulation. On the other side we have such suggestions as Germann's (15), or Lewis's (41), which would extend the concept of acids to include such things as phosgeno-aluminum chloride $COAl_2Cl_8$, or make "acids" and "bases" synonymous with Sidgwick's (49) "acceptor" and "donor" molecules, respectively.

Brönsted (8), it seems to me, has satisfactorily defended his proposal in the following terms: "If we seek, with these considerations as a background, a more general and more precise definition of acid and base, we recognize that such a definition must in the first place attribute the characteristic acid-base properties to the molecules of acids and bases themselves, (i.e., not to their solutions). Second, it must be a definition which relates the ideas acid and base to each other in a more logical way than has hitherto been the case. It must further give an illuminating explanation of the peculiar character of these substances, and finally we may say that since acids and bases are found so universally in chemical systems, the definition of these substances must be formulated independently of the solvent."

In addition to elegance and logical consistency, one may urge in favor of Brönsted's definition that it has led to new work of importance. This is particularly true in the field of reaction velocity studies, where the recognition of the hydronium and hydroxyl ions, H_3O^+ and OH^-, not as uniquely important substances, but as members of the classes acid and base, has led to the correct evaluation of the rôle of other acids and bases in protolytically catalyzed reactions (6). Thus Brönsted and his students have shown that the velocity of a reaction catalyzed by H^+ ion is a function of the concentrations and acidity constants of all the acid molecules present, and not simply of the hydrogen ion activity of the solution. The same has also been shown to be true of reactions catalyzed by bases.

Recent papers by Kilpatrick (38, 39), Pedersen (45), and Grove (24), may be mentioned among others as examples of the utilization of these ideas.

SOLVENTS

When we consider the rôle of the solvent in acid-base equilibria we recognize that solvents may be roughly classed from this standpoint as predominantly acidic, predominantly basic, amphiprotic, or indifferent. (By taking account of the dielectric constant Brönsted (7) increases these four classes to eight.)

Thus we recognize water as amphiprotic since it is capable of the acid reaction

$$H_2O \rightleftharpoons H^+ + OH^-$$

and the basic reaction

$$H_2O + H^+ \rightleftharpoons H_3O^+,$$

or, what amounts to the same thing, it is self-dissociated to an appreciable extent according to the scheme

$$2H_2O \rightleftharpoons H_3O^+ + OH^-.$$

In this solvent, therefore, all very strong acids are completely decomposed

$$HClO_4 + H_2O \rightleftharpoons H_3O^+ + ClO_4^-,$$

as are all very strong bases

$$OCH_3^- + H_2O \rightleftharpoons OH^- + CH_3OH,$$

while the protogenic and protophilic character of very weak acids and bases is largely masked by the overwhelming prominence of the similar properties of water. A solvent of opposite or *aprotic* character is represented by benzene, which neither gives up nor takes up protons to any considerable extent. *Acid* solvents which have been more or less thoroughly studied are hydrocyanic acid, phenol, and acetic, formic, hydrofluoric and sulfuric acids. Predominantly *basic* solvents are ammonia and the amines.

Hammett (29) has given a highly interesting discussion of the rôle of the properties of the solvent in determining acidity, and has clearly distinguished between the inferences that may legitimately be made from colorimetric work with indicators of various types and from electrometric measurements. Numerous papers of Hantzsch (31, 31a, 31b, 33) should also be cited in this connection, as well as the recent work of Schwarzenbach (48), Fredenhagen (12, 13, 14) and Rabinowitsch (46). Bjerrum's (3, 4) studies of ion-partition coefficients present a novel method of attack on the problem of relative acidities in different solvents.

Aprotic solvents

Let us first consider the phenomena in relatively indifferent or aprotic solvents. Examples of these are the paraffin hydrocarbons, benzene and chloroform. In these solvents the levelling, or degrading, action which water exerts on strong acids and bases is absent, and we may expect the true or intrinsic relative strength of the stronger acids to come to the fore much more clearly than in water.

In benzene, acids and bases may probably be regarded as present as such—though perhaps associated—and not to any great extent as ionized solvates. Brönsted has shown how such solutions may be studied. If two substances are added to benzene such that an equilibrium of the following type is established

$$A_1 + B_2 \rightleftharpoons B_1 + A_2$$

then

$$\frac{C_{\mathrm{A}_2} \times C_{\mathrm{B}_1}}{C_{\mathrm{A}_1} \times C_{\mathrm{B}_2}} = \frac{K_{\mathrm{Ac}_1}}{K_{\mathrm{Ac}_2}} = \frac{K_{\mathrm{A}_1}}{K_{\mathrm{A}_2}}$$

where K_{Ac_1} and K_{Ac_2} are the acidity constants of the two acids concerned and K_{A_1}, K_{A_2} are the corresponding concentration dissociation constants. This follows from the definition of the respective constants:

$$K_{\mathrm{Ac}_1} = a_{\mathrm{H}^+} \frac{C_{\mathrm{B}_1}}{C_{\mathrm{A}_1}} \quad \text{and} \quad K_{\mathrm{A}_1} = C_{\mathrm{H}^+(\mathrm{sol})} \frac{C_{\mathrm{B}_1}}{C_{\mathrm{A}_1}}, \text{etc.}$$

If now one of the substances has at least one colored form—i.e., is an indicator acid or base—the ratio of the concentrations of two of its forms may be determined from the color of the solution, and the strength of a colorless acid may be compared with that of the indicator acid by noting the concentration ratio of, for example, acetic acid to an acetate, which is necessary to produce a given color in the solution.

In this way Brönsted has made a very instructive comparison of the strengths of various uncharged and cation acids with those of a series of indicators in benzene, and arranged these results in a table of relative acid strengths. An inspection of Brönsted's table brings out the following points: for acids of the same charge type the order of strength is nearly the same in benzene as in water; the positively charged acids appear very much stronger in relation to the uncharged, than is the case in water. These results are to be expected from the simple electrostatic theory according to which a separation of unlike charges (ordinary electrolytic dissociation) will occur less readily in a solvent of low dielectric constant, while an equilibrium of the type

$$\mathrm{BH}^+ \rightleftharpoons \mathrm{H}^+ + \mathrm{B}$$

will be relatively unaffected by dielectric constant change. (See also Hammett (29)). In order to bring out more clearly the significance of Brönsted's table, I have amplified his list of acids by writing after their names the values of their negative logarithmic dissociation constants; these are arranged in two columns according to the charge type of the acid concerned.

It is evident that the constants fall into two series, that of the cation acids being displaced in the direction of increasing strength, relative to the uncharged acids. Certain irregularities in the observed order are attributed by Brönsted to the effect of "zwitterion" structure of the "uncharged" forms. The strongest acid investigated by Brönsted was hydrochloric, of which Wynne-Jones (51) estimates the true constant in water to be $10^{7.1}$. (Schreiner (47) gives 10^4–10^6). There is a variety of evidence (16, 18, 31, 33, 34, 35, 47) that hydrobromic and hy-

TABLE 1

Brönsted's acidity series determined colorimetrically in benzene

SUBSTANCE	VALUE OF pK FOR ACID	
	A°	A^+
1. Hydrochloric acid	−7.4	
2. Methyl red	4.9(?)	
3. Dimethyl yellow		3.5
4. Trichloroacetic acid	0.7	
5. Dichloroacetic acid	1.3	
6. Picric acid	0.3	
7. *o*-Nitrobenzoic acid	2.3	
8. Chloroacetic acid	2.9	
9. Salicylic acid	3.0	
10. Bromophenol blue	4.1	
11. β-Dinitrophenol	3.7	
12. *o*-Chlorobenzoic acid	2.9	
13. Neutral red		6.9
14. *m*-Chlorobenzoic acid	3.8	
15. Bromocresol green	4.7	
16. Benzylammonium ion		9.4
17. Formic acid	3.7	
18. Phenylacetic acid	4.3	
19. Benzoic acid	4.2	
20. Acetic acid	4.7	
21. Isoamylammonium ion		10.6
22. Bromocresol purple	6.3	
23. Piperidinium ion		11.1
24. Bromothymol blue	7.0	

driodic acids are stronger still, and that perchloric acid is the strongest of all the common acids, though possibly none of them is *completely* dissociated in water. These great differences in strength are practically obscured in water by the conversion of all the acids of this class into the weaker acid H_3O^+, whose acidity constant is conventionally fixed at 1 by the ordinary definition of proton activity in aqueous solution.

To the German organic chemist, A. Hantzsch, we owe much of our knowledge of the relative strength of the strongest acids, and he has insisted for years on the existence of these differences in relative strength just mentioned. Typical of Hantzsch's investigations are those recently published with Voigt (33) on "the determination of the acidity of undissociated acids." The experiments fall into two parts. In the first the authors prepare the dimethyl yellow salts of the acids studied and dissolve them in a given solvent, diluting with the solvent until the indicator turns color. It is supposed that the dilution at which the color change occurs, and at which presumably the reaction $BH^+ X^- \rightarrow B + HX$ has reached a certain degree of completeness, is an approximate measure of the strength of the acid in the solvent concerned. The relative dilutions necessary in dry chloroform vary from 1 for acetic acid to 95,000 for trichloroacetic acid, while the dissociation constants as ordinarily measured in water show only an eleven thousand fold variation.

Hantzsch attributes this difference to the "levelling down" influence of water on the stronger acids. If the chloroform is moist the strength of the stronger acids appears relatively less, which is in harmony with this view. Hantzsch regards ether as a much less indifferent solvent than chloroform, and one which forms well-defined solvates with the dissolved acids, thus promoting the decomposition of the salt. He finds, in other words, that a much smaller volume of ether than of chloroform is necessary to decompose completely a given quantity of a particular salt. The necessary dilutions vary from 1/17th to 1/80th of the corresponding figures for chloroform. Added water has much less effect on ether than on chloroform.

When the strongest acids are examined it is found that their salts with dimethyl yellow are so stable as to be decomposed only at impracticably large dilutions in dry chloroform, while in both dry and moist ether-chloroform mixtures, and in moist chloroform, the necessary dilutions are measurable and indicate that the strength of the strong acids falls off in the order perchloric, hydrobromic, hydrochloric, nitric, as much similar previous work has shown. The authors then find in the more weakly basic indicator dianisalacetone a suitable substitute for dimethyl yellow in dry chloroform, and find in fact that hydrobromic, hydrochloric, and trichloroacetic acids show diminishing strength in the order named. (Nitric, perchloric and hydriodic acids could not be measured for special chemical reasons.) The study of these three acids was then extended to the solvents benzene, toluene and tetrachloroethane, with the surprising result that in benzene and toluene, hydrochloric acid appeared slightly weaker than trichloroacetic acid. As this result is in direct contradiction to that of Brönsted reported above, one must either suspect some special chemical reaction of this indicator with the acids and solvent concerned, or question the reliability of one or both of the methods as a true measure of relative acid strength. Both Brönsted and Hantzsch clearly recognize the provisional and approximate character of their results, and point out the more obvious uncertainties by which they are affected.

Schwarzenbach (48) has called attention to a phenomenon of "self buffering," which is to be expected in certain concentration ranges when acids are dissolved in aprotic solvents, and also to the fact that in certain of these solutions the molar conductance should decrease with dilution. He believes that both of these effects are shown by his own measurements on ether solutions.

Basic solvents

(*a*) *Ammonia.* The early work of Franklin, Kraus, Cady and others showed that the ammonium salts function as acids in this solvent, that many acids relatively weak in water appear to exhibit a relatively high degree of dissociation in ammonia, and that indicators such as phenolphthalein are affected by the NH_2^-

ion in the same way as by OH^- in water. Quite recently Zintl and Neumayr (52) have determined the E.M.F. of concentration cells with transference, using quinhydrone electrodes, and have obtained values consistent with equations developed by Bjerrum and others.

(*b*) *Organic amines.* Aniline and *p*-toluidine as solvents for acids and bases have been studied by Heinrich Goldschmidt and his coworkers Reinders, Bandke, Salcher, and Bakscht (1, 20, 22, 23), who found that aminolysis of salts was more extensive in *p*-toluidine than in aniline, as would be expected from the relative strength of these bases in water. They also found that the order of apparent strength of acids and bases was the same in these two solvents as in water but that the strongest acids, as mentioned above, show widely different strengths. The ratio of apparent strengths of the strong acids in the two solvents is nearly constant (the velocity constant of the acid-catalyzed reaction is about nine times as great in aniline as in *p*-toluidine), but it falls to about half its value for the weaker *o*-nitrobenzoic acid. When different bases are compared in the two solvents it is found that the salts of the stronger bases are both absolutely and relatively less solvolyzed in aniline than in *p*-toluidine.

The author's E.M.F. measurements in pyridine (unpublished) have also shown that in this solvent the apparent strengths of the strong acids differ widely. This is presumably due to the enormously large salt effects to be expected in solvents of low dielectric constant, and appears to be in harmony with the views of Hammett in the paper previously referred to.

(*c*) *Alcohols.* Goldschmidt and Mathiesen (21), completing and extending earlier studies by Goldschmidt and others (17, 19), report the solvolytic constants for a variety of bases in ethyl and methyl alcohols. These constants are usually smaller in the alcohols than in water and always smaller in methyl than in ethyl alcohol, so that they seem to reach a minimum value in methyl alcohol, a rather surprising result. They also found that the addition of water always reduces the alcoholysis of a salt, and to about the same degree for salts of different acids with the same base. The effect, however, differs in magnitude according to the base employed.

One may conclude from Goldschmidt's results that the dissociation constant of a cation acid is usually smaller, but sometimes larger, in ethyl alcohol than in water. The ratio of the two constants varies from 0.06 to 6.0. This is in harmony with the expectation referred to above, that the constant of a cation acid should be substantially unchanged on changing solvents. Goldschmidt also determined the dissociation constants of numerous acids in alcoholic solution by conductivity methods, and found that in general an uncharged acid has a dissociation constant about 10^6 times smaller in alcohol than in water. Larsson (40) recalculated and in part repeated and confirmed Goldschmidt's results, and also made E.M.F. measurements of cells with liquid junctions which he interpreted as confirming the conductivity figures very satisfactorily.

Michaelis and Mizutani (42, 43, 44) studied the E.M.F. of cells consisting of a saturated aqueous calomel electrode and a hydrogen electrode in an aqueous alcoholic solution of a half-neutralized acid or base. Saturated aqueous potassium chloride formed the liquid junction in their cells. They calculated at definite percentage compositions of the water-alcohol mixtures the apparent acidity constants of numerous uncharged and cation acids. In most cases an extrapolation to pure water and pure alcohol was possible. From their results one may infer, neglecting the junction potential, that the acidity constant of an uncharged acid is usually about 10^3 times smaller in ethyl alcohol than in water, while that of a cation acid is about 10^2 times larger.

Since in any solvent

$$K_{\text{A}} = \frac{C_{\text{H}^+(\text{sol})} \times C_{\text{B}}}{C_{\text{A}}} = K_{\text{Ac}} \cdot K_{\text{Bas}(\text{solvent})}$$

Brönsted (6) has been able to calculate from certain of these results combined with others of Bjerrum (5) that K_{Bas} for methanol is about 350 times smaller than for water, while two independent calculations show that ethanol is 330 and 600 times as weak a base as water.

Similar calculations also show that pure methanol is 2.5 times and ethanol 160 times as weak an *acid* as water, but all these figures are affected by numerous uncertainties. In particular, the physical meaning of Brönsted's functions K_{Ac} and K_{Bas} for any substance in a non-aqueous or even a concentrated aqueous medium depends on the possibility of measuring relative hydrogen ion activities, which Taylor (50) and Guggenheim (25) have recently reminded us are fundamentally inaccessible to experimental attack.

Bishop, Kittredge and Hildebrand (2) used the hydrogen electrode for titrations in ethanol and emphasized the effect of the low self-ionization of the solvent on the titration curves.

(*d*) *Ether.* This solvent is distinctly less basic than the alcohols, but more so than the hydrocarbons. In addition to the studies of Hantzsch already referred to, we may mention certain measurements and titrations by Schwarzenbach (48), using hydrogen electrodes.

Acid Solvents

(*a*) *Acetic acid.* If we now turn to glacial acetic acid as a typical acid solvent, we find that acid-base equilibria have been studied in it primarily by means of titration curves.

Conant and Hall (10, 27) found that the stronger inorganic acids and the sulfonic acids, all of which are quite soluble in the medium, could be used as titrants for basic solutions such as those formed by the organic amines or by the acetates of metals. Potentials reproducible within a few millivolts were obtained by the use of a simple cell containing liquid junctions, in which an aqueous calomel electrode served as a reference, and the indicator electrode was a platinum foil in an acetic acid solution of quinhydrone, or better, chloranil and its reduction product. The bridge between the reference electrode and the solution being titrated was a stoppered glass siphon containing a concentrated solution in acetic acid of a salt such as lithium chloride.

Since the extent of solvolysis of a given salt depends on the basic nature of the solvent, it is to be expected that largely unsolvolyzed salts of weaker bases can be formed in acetic acid than in water, as indeed is well-known in organic chemical practice. This point of view was summarized by means of a diagram (figure 1) and discussed in the first papers of this series, which should be consulted for details (27). Later Hall and Werner (28) showed the same thing by a comparison of the titration curves of a weak

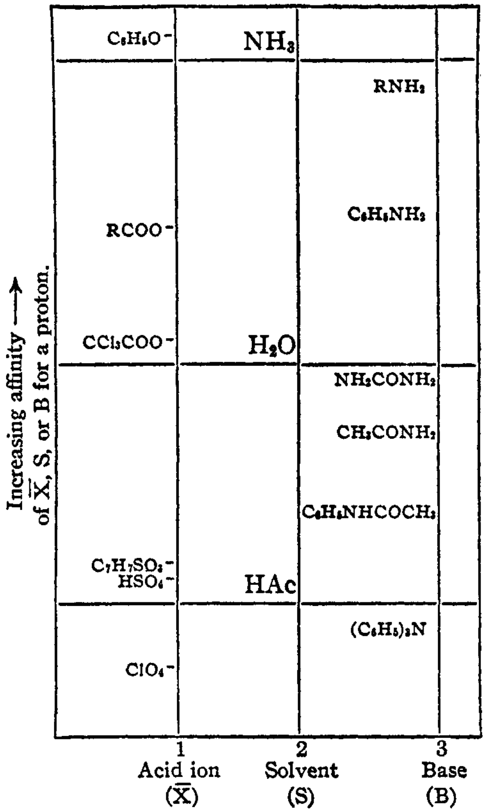


Fig. 1. Diagram Illustrating the Relationship of Acids and Anhydro Bases in a Variety of Solvents

base (acetoxime) in three different solvents (figure 2). It was also found that in this solvent, as Hantzsch had shown to be the case in many others, the relative strengths of the strong acids differ widely, so that the same base will in general give a different titration curve with each acid used. Figure 3 shows the potentials of a chloranil electrode in a solution of acetic acid, either alone or with the addition of various bases, when perchloric, sulfuric, and hydrochloric acids respectively are added to the solution.

Most of the later titrations have been made with perchloric acid because of its strength and because it is monoprotic. Figure 4 shows the curves obtained at 0.05 *M* concentration with some fifty organic amines and oxygen bases. These titration curves with perchloric acid fall into three classes according to base strength, like the titration curves obtained in water, and the "strong base" curves have the same shape as in water solution. The weaker bases, however, give curves that are too flat, presumably because of the change of ionic strength during titration.

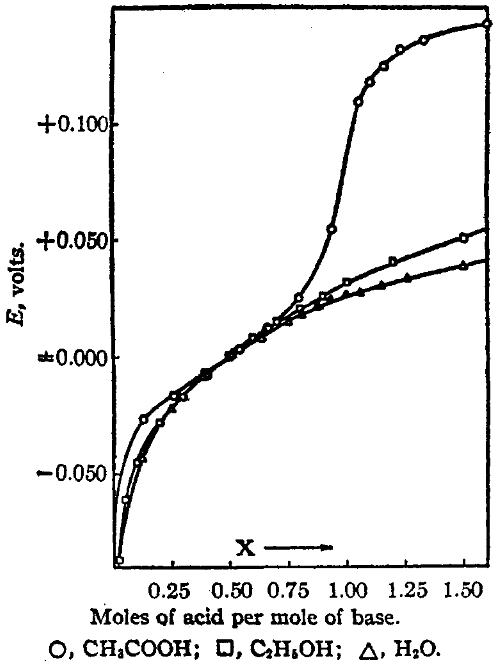


FIG. 2. EFFECT OF THE SOLVENT IN THE TITRATION OF A WEAK BASE (ACETOXIME) WITH PERCHLORIC ACID

Conant and Werner (11) show that, as in many other cases,

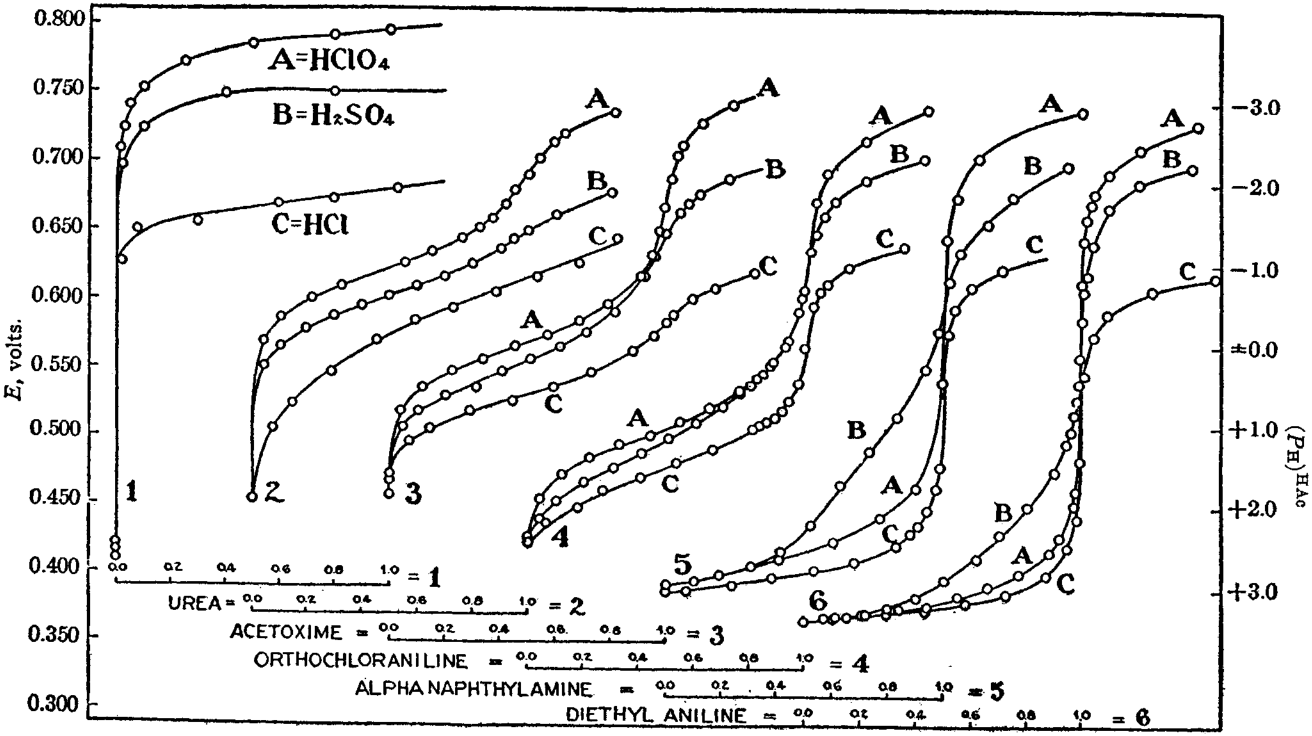


Fig. 3. Comparison of $HClO_4$, H_2SO_4 and HCl as Titrating Acids

Abscissas are moles of acid added per mole of base. The curves in group 1 represent addition of acid to the pure solvent. With the stronger bases (5 and 6) the second hydrogen of H_2SO_4 (B) becomes active. The curves in group 1 begin on the basic side of the neutral point due to accidental contamination with traces of basic material.

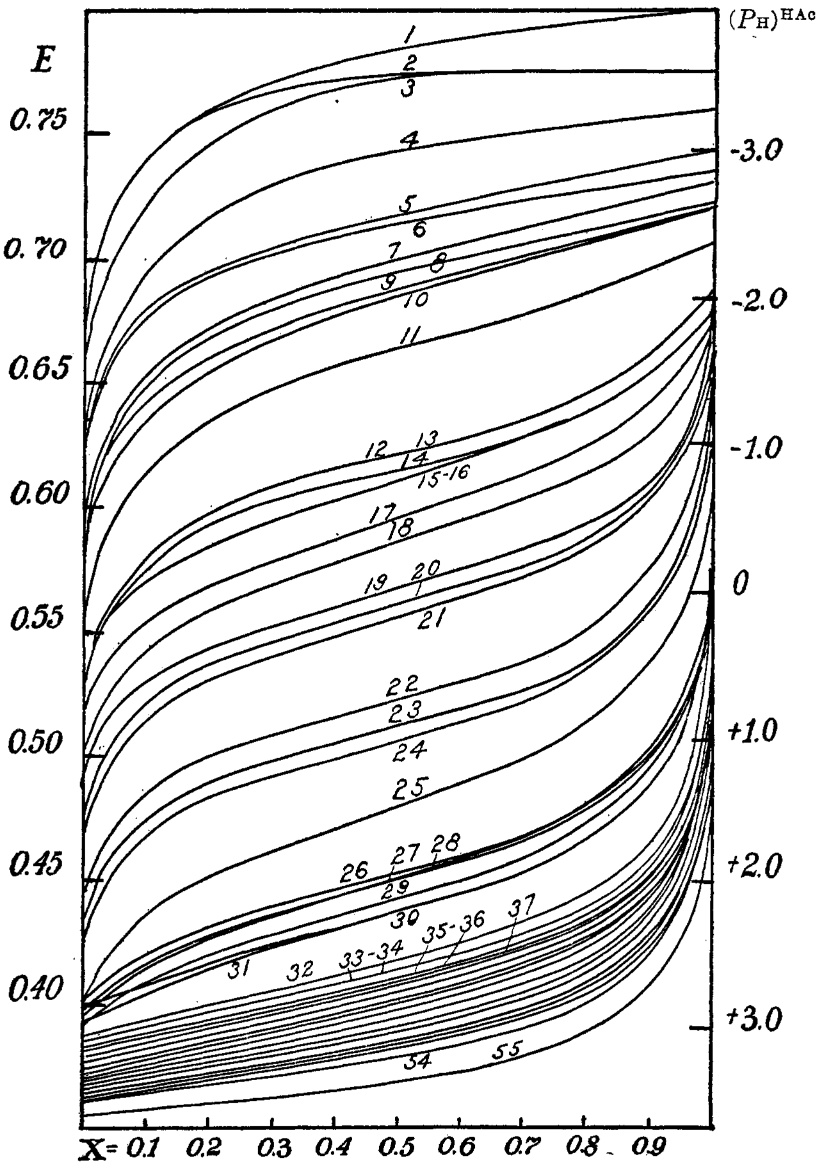


Fig. 4. Titration Curves of 0.05 M Bases in Glacial Acetic Acid

Note the three classes: very weak (1–11); weak (11–31); strong (32–55). No. 55 is anomalously low. No. 11 is exceptionally steep.

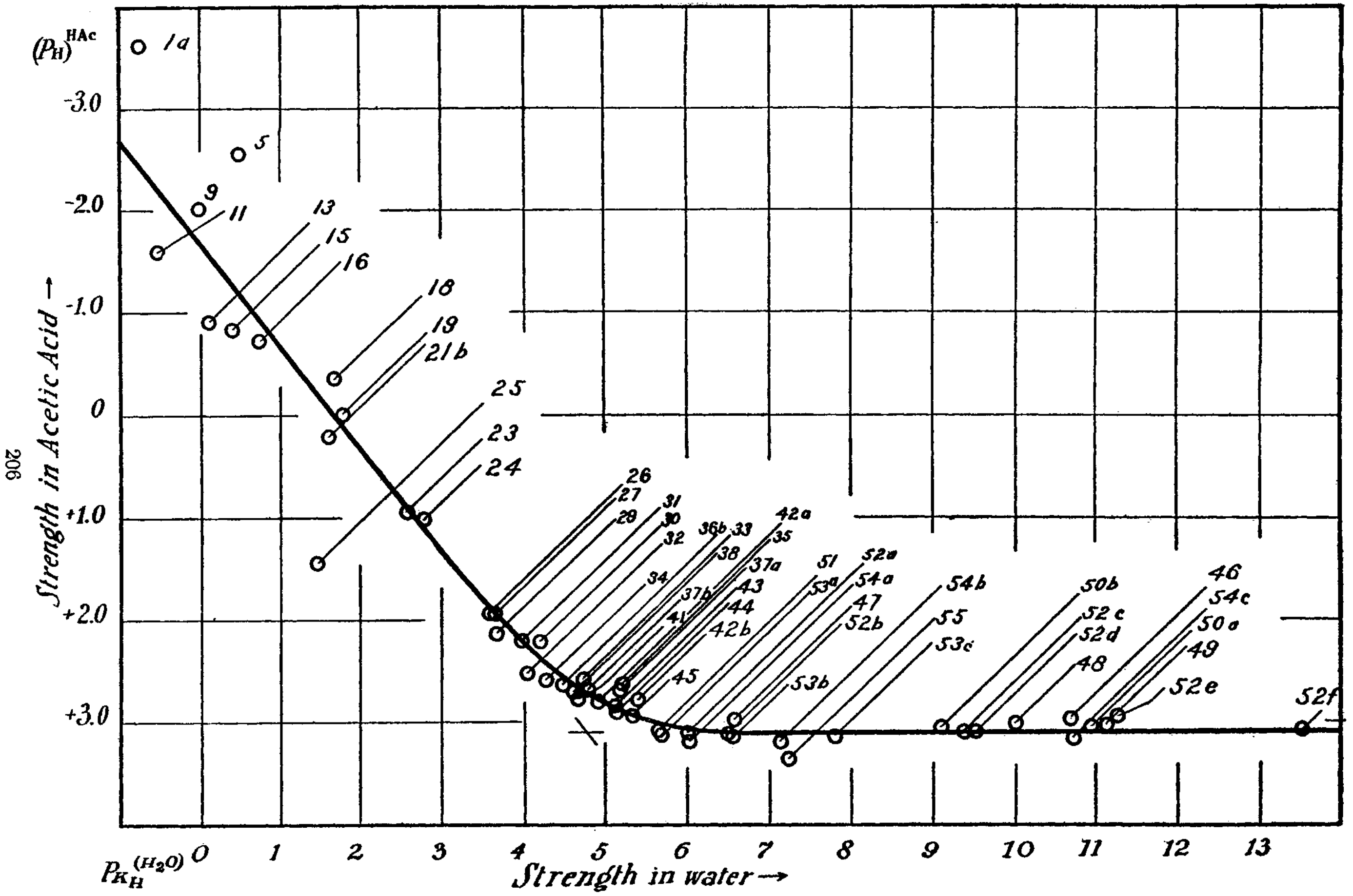
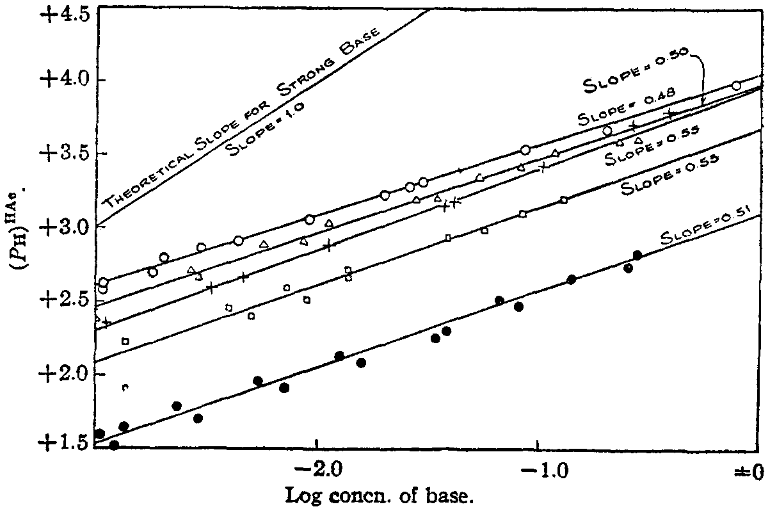


FIG. 5. COMPARATIVE STRENGTH OF BASES IN ACETIC ACID AND IN WATER

these anomalies largely disappear when the ionic strength is maintained nearly constant by a large concentration of added salt.

Similar points on the titration curves of different bases should measure the relative acidity constants of the bases in the solvent, and according to theory these should be nearly proportional to the similar constants in water solution. Because, however, of the strongly acid character of the solvent a much weaker base may be expected to react completely with it than is the case in water, where none of the ordinary amines can be called strong bases.



○, Diethylaniline; +, pyridine; □, sodium acetate; △, guanidine; ●, *o*-chloro-aniline.

FIG. 6. $(P_H)^{HAc}$—DILUTION CURVES OF BASES IN ACETIC ACID

Both of these points are brought out by figure 5, in which the logarithmic strength constants in the two solvents are plotted against each other for fifty bases. It is seen that bases stronger than aniline ($P_{K_H}(H_2O) = 4.75$) are completely strong in acetic acid. (For the names of the bases and other details the reader is referred to a recent paper (26) by the author.) In spite of this complete reaction with the solvent, solutions, even of the strongest bases, do not show conductance or voltage changes on dilution which suggest a high degree of dissociation in the ordinary sense. In fact, the acidities of the solutions change on dilution in just the same way as those of weak bases in water, as though the electrolyte obeyed the dilution law and the activity coefficients of the ions formed remained constant. If the strong base acetates are completely ionized at all concentrations, then the activity coefficient of the acetate ion (not its logarithm) varies as the inverse square root of the salt concentration. These facts are exhibited in figure 6, in which the apparent "pH" of various dilutions of the bases is plotted against the logarithm of the dilution. The points lie on straight lines with a slope of 1/2, as is to be expected for weak protophiles (28).

In a paper which has just come to hand, Isgarischew and Pletenew (37), working at Moscow, have measured the hydrogen electrode potentials of various concentrations of sodium acetate in dry acetic acid. Allowing for the different electrodes used, their values may be compared with those of Hall and Werner, with the result that neither the actual values of the potentials nor the type of their variation with concentration agrees with the earlier measurements. Further investigation of this discrepancy is very desirable. The Russian investigators are led by their results to the surprising conclusion that pure acetic acid is dissociated "in sehr bedeutendem Masse" into hydrogen and acetate ions, a view difficult to reconcile with a specific conductance of 10^{-7} to 10^{-8} (36).

With Bramann (9), Conant has investigated the catalysis in acetic acid solution of the acetylation of β-naphthol. The logarithm of the velocity constant is shown to decrease linearly with increasing apparent pH of the medium, until a minimum is reached, after which further increase in pH causes a linear increase in the logarithm of the rate constant. This result can be interpreted simply, following the lines of the similar studies of Brönsted in water solution. It appears that the rate depends on the concentration and strength of all the acids and bases present, and that the reaction is catalyzed both by acids and by bases, such as acetate ion.

Acetic acid is thus again shown to be, as Professor Davidson's paper in this symposium has made clear, a solvent worthy of study from many points of view.

(*b*) *Formic acid.* In a very interesting paper which has just appeared, Hammett and Dietz (30) report titrations of sodium formate and other basic substances in anhydrous formic acid. Quinhydrone electrodes were used, and the titrating agent was benzene sulfonic acid. Curves of the theoretical form for strong electrolytes were obtained, and it was possible to calculate the ion product constant of the solvent for different values of the salt concentration. A high and constant ionic strength was maintained during the titrations. Such weak bases as triphenylcarbinol, benzalacetophenone and urea appeared to be completely dissociated in formic acid, while ether and water showed hardly any basic properties.

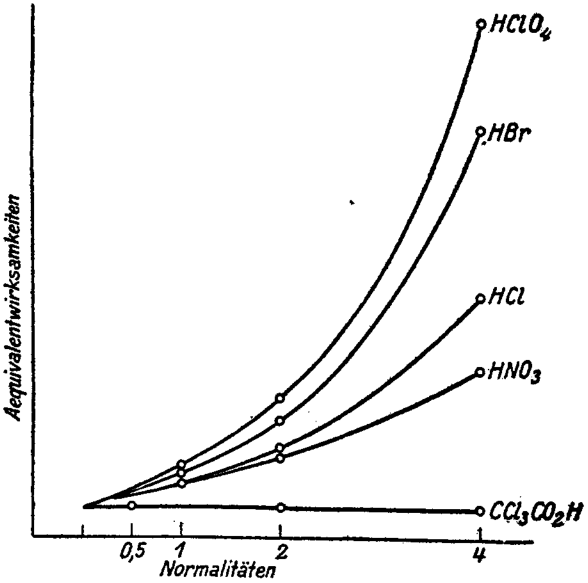


FIG. 7. THE CHANGE WITH CONCENTRATION OF THE EFFECT PER EQUIVALENT OF ADDED ACID ON THE VELOCITY OF INVERSION OF SUCROSE

This figure is taken from an article by Hantzsch and Weissberger: Z. physik. Chem. **125**, 251–63 (1927).

If we now return for a moment to the general rôle of the solvent in these reactions, and to the behavior of the strongest acids in various solvents, we may note that even in water itself, if the solution is sufficiently concentrated, the individual behavior of the strong acids comes out very clearly. This has been shown by Hantzsch and Weissberger (34) in studies of the rate of inversion of cane sugar, and is exhibited in figure 7, where the relative increase in the velocity of inversion per equivalent of acid present is plotted against the normality of the solution. It is seen that the relative effect of an equivalent of the acid increases rapidly with the intrinsic strength as inferred from the work in non-aqueous solvents. Studies of the activities of hydrochloric acid, sulfuric acid, etc. in concentrated aqueous solutions should also be mentioned in this connection.

Pure liquid acids themselves represent limiting cases of concentrated acid solutions. Such liquids show specific conductances ranging from 10^{-2} (for sulfuric acid) to 10^{-13} for isovaleric and caprylic acids (36). This conductance is presumably to be attributed to a self-ionization of the type $2HX \rightleftharpoons H_2X^+ + X^-$, and its magnitude must depend (aside from mobility corrections) on the product of the acidity and basicity constants of the liquid (6). Hence it is possible to infer that the basicity of hydrofluoric acid is greater, compared to its higher homologs, than would be expected from its relative acid strength in water. The stability of the fluoracidium salts of Hantzsch (32) supports this view. Many other interesting results may be expected from a combination of conductivity and E.M.F. methods of studying the acids.

In conclusion we may ask to what extent it is possible to reduce to a quantitative basis of comparison the data already accumulated and later to be secured on the variations of acid strength from solvent to solvent. If it were possible to establish a significant scale of relative acidities, so that one could say in an unequivocal manner that a certain solution in one solvent was more or less acid than a solution in another, whatever the acids present in either, the whole question would be reduced to a highly desirable order and simplicity. Such an outcome was apparently envisaged by Brönsted in his proposal of the acidity constant as a general measure of acid strength and in his reference to a scale of "absolute (hydrogen ion) activity" (reference 6, page 292), although he speaks of the fact that "high and difficultly accessible boundary potentials will most likely obscure the results" (reference 6, page 351). If, however, the argument of Taylor and Guggenheim referred to above is accepted, and "the electric potential difference between two points is a conception without any physical significance unless the two points are in the same media," the notion of absolute acidity, as distinct from the relative activities of some particular acid in two different solutions, must be relegated to the limbo of seductive but meaningless fictions.

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