tool in determining the type of chemical bond being ruptured to bring about a specified reaction.

Acid–Base Equilibria in Glacial Acetic Acid[1]

BY THOR L. SMITH AND JOHN H. ELLIOTT

Values of H_0 for dilute solutions (5×10^{-4} to 5×10^{-3} M) of eleven strong acids in acetic acid containing 0.12% water have been measured, using indicators α-naphtholbenzein and o-nitroaniline. The thermodynamic constant, pK_a, for α-naphtholbenzein was found to be 0.53. At equal molarities, strengths of the acids increase in the following order: hydrochloric, methanesulfonic, sulfuric, carboxymethanesulfonic, chloromethanesulfonic, chlorocarboxymethanesulfonic, hydrobromic, perchloric, methanedisulfonic, chloromethanedisulfonic and methanetrisulfonic. H_0 values for anhydrous solutions of four monobasic acids at 5×10^{-3} M were measured also. From the change in H_0 caused by the addition of water, equilibrium constants for the reaction of the acid with water were calculated. Dissociation constants, K_c, of four acids in acetic acid were calculated from the conductance data of Kolthoff and Willman. Dissociation constants for perchloric and hydrochloric acids were found to be approximately 9×10^{-7} and 5×10^{-10}, respectively. Values of ΔpK_c for monobasic acids in anhydrous solutions were calculated from H_0 data and found to be in reasonable agreement with values obtained from the conductance data. The conductance and indicator data demonstrate that equilibria in acetic acid involve, primarily, undissociated species.

Introduction

The acid strengths of several strong acids and a large number of bases in glacial acetic acid have been studied by previous investigators.[2] This solvent has been used for a variety of organic reactions and for a number of analytical methods.[3] Thus, further information on strengths of strong acids, the basic strength of water, and extent of dissociation in this solvent is of considerable practical value.

The strength of an acid may be expressed only by the extent of reaction with some reference base. In water and other basic solvents, the solvent itself can be used as the reference substance. In aprotic or inert solvents like benzene, a reference base must be added so that strengths of various acids may be compared.[4] Thus, no single reference base is employed under these various conditions. Even if a single reference base is used in several solvents, its free energy will vary with the solvent, so that the measurements are not directly comparable.

A convenient and practical method of expressing the tendency of various acidic solutions to transfer a proton to a common reference substance is in terms of the acidity function, H_0, introduced by Hammett and Deyrup.[5,6] H_0 may be obtained by using the equation

$$H_0 = -\log (BH^+)/(B) + pK_a \qquad (1)$$

where (BH^+) and (B) are the concentrations of the acidic and the basic form of an indicator, and K_a is the thermodynamic dissociation constant for the conjugate acid of the indicator; the infinitely dilute aqueous solution is taken as the reference state.

In the present investigation, H_0 for solutions of eleven acids in acetic acid containing 0.12% water has been measured, in most cases at several concentrations (5×10^{-4}, 1×10^{-3}, 5×10^{-3} M) using α-naphtholbenzein and o-nitroaniline as indicators. Some measurements were repeated under anhydrous conditions, and from the increased acidity found, equilibrium constants for the reaction of acids with water were calculated. The dissociation constants of several common strong acids were calculated from the conductance data of Kolthoff and Willman[7] and were found to be 10^{-6} or less. From the acidity and conductance data, it is concluded that most equilibria in acetic acid involve undissociated species.

Experimental

Acids.—Reagent grade perchloric, hydrobromic, sulfuric and hydrochloric acids were used without purification.

Carboxymethanesulfonic Acid.—Barium carboxymethanesulfonate was prepared from chloroacetic acid and sodium sulfite by the method of Stillich.[8] An aqueous suspension of the barium salt was reacted with slightly less than the equivalent amount of sulfuric acid and the barium sulfate precipitate removed by filtration. The filtrate was concentrated under reduced pressure (water aspirator) at a bath temperature of 60–70°. Some crystals of barium carboxymethanesulfonate appeared and were removed by filtration. The filtrate was free of chloride and sulfate ions

(1) Presented before the Division of Physical and Inorganic Chemistry, 122d Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1952.

(2) (a) N. F. Hall, *Chem. Revs.*, **8**, 191 (1931); (b) A. W. Hutchison and G. C. Chandlee, THIS JOURNAL, **53**, 2881 (1931); (c) V. K. La Mer and W. C. Eichelberger, *ibid.*, **54**, 2763 (1932); (d) I. M. Kolthoff and A. Willman, *ibid.*, **56**, 1014 (1934); (e) M. A. Paul and L. P. Hammett, *ibid.*, **58**, 2182 (1936); (f) N. F. Hall and W. F. Spengeman, *ibid.*, **62**, 2487 (1940); (g) N. F. Hall and F. Meyer, *ibid.*, **62**, 2493 (1940); (h) D. S. Noyce and P. Castelfranco, *ibid.*, **73**, 4482 (1951); (i) H. Lemaire and H. J. Lucas, *ibid.*, **73**, 5198 (1951).

(3) (a) G. F. Nadeau and L. E. Branchen, *ibid.*, **57**, 1363 (1935); (b) P. C. Markunas and J. A. Riddick, *Anal. Chem.*, **23**, 337 (1951); (c) W. Seaman and Eugene Allen, *ibid.*, **23**, 592 (1951); (d) T. Higuchi and J. Concha, *Science*, **113**, 210 (1951).

(4) M. M. Davis and P. J. Schuhman, *J. Research Natl. Bur. Standards*, **39**, 221 (1947).

(5) L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721, 4239 (1932).

(6) L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, Chapter IX.

(7) I. M. Kolthoff and A. Willman, THIS JOURNAL, **56**, 1007 (1934).

(8) O. Stillich, *J. prakt. Chem.*, **73**, 538 (1906).

but contained a slight trace of barium ion. A potentiometric titration of an aqueous solution of the carboxymethanesulfonic acid gave a curve with two inflection points, a weak one at pH 2.1 and a very sharp one at pH 7.
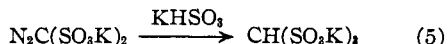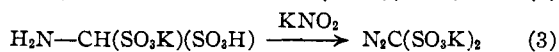
Chlorocarboxymethanesulfonic Acid.—Barium chlorocarboxymethanesulfonate was prepared from chloroacetic acid and sulfur trioxide according to the method of Backer and Burgers.[9] The barium salt was converted into the acid in a manner similar to that used on barium carboxymethanesulfonate. A viscous concentrate of carboxymethanesulfonic acid which was free of chloride and sulfate ions but contained a faint trace of barium ion was obtained.

Methanesulfonic Acid.—"Indoil" methanesulfonic acid, a commercial pilot plant product of the Standard Oil Company of Indiana, which contained 95% methanesulfonic acid, 2% water and 1–3% sulfuric acid, was used after purification. To remove the sulfuric acid, barium hydroxide was added to a dilute solution of "Indoil" and the resulting barium sulfate removed by filtration. The filtrate, which contained some barium ion, was concentrated under reduced pressure. The concentrate was distilled under vacuum, and the fraction that boiled at 115–130° under a pressure of 0.37–0.60 mm. of mercury was collected. This fraction was free of sulfuric acid; it crystallized completely and melted over a range of −8 to 8°.

Methanedisulfonic Acid.—Potassium methanedisulfonate was prepared following the method of Backer.[10] Methylene chloride and an aqueous solution of potassium sulfite were heated in a Monel autoclave for four hours at 155°. When this mixture cooled, potassium methanedisulfonate precipitated which was purified by recrystallization. The recrystallized potassium methanedisulfonate was dissolved in hot water and passed through a column of Amberlite IR-120 ion-exchange resin (Rohm and Haas Co.) which had been heated by passing boiling water through it. The effluent, upon standing, deposited crystals of methanedisulfonic acid. The filtrate was concentrated under reduced pressure on a hot water-bath. When the concentrate was cooled, it crystallized completely. This material was extracted with glacial acetic acid. The resulting solution was titrated with 0.100 N potassium acid phthalate in glacial acetic acid using methyl violet as indicator and was found to contain 0.402 g. methanedisulfonic acid per ml. of solution.

Chloromethanesulfonic Acid.—Sodium chloromethanesulfonate was prepared by heating equal molar amounts of methylene chloride and an aqueous solution of sodium sulfite in a Monel autoclave for four hours at 155°. When the reacted mixture was concentrated and cooled, crystals of sodium methanesulfonate were obtained. The filtrate was acidified with hydrochloric acid and evaporated to dryness. The residue was extracted four times with boiling 2B alcohol. When cooled, the extracts deposited shining plates of sodium chloromethanesulfonate. After recrystallization from alcohol, the compound melted at 261–262.5° and was found to be free of sulfite and sulfate ions but to contain traces of chloride ion. The sodium salt was dissolved in concentrated hydrochloric acid and saturated with gaseous hydrogen chloride while being cooled in an ice-bath. The sodium chloride that precipitated was removed by filtration. The filtrate was concentrated on a hot water-bath until no more distillate was obtained. The residue was free of chloride ion but gave a slight precipitate with aqueous barium chloride solution.

Chloromethanedisulfonic and Methanetrisulfonic Acids.—The potassium salts of these acids were prepared according to the reactions

$$KCN + KHSO_3 \longrightarrow H_2N\!-\!CH(SO_3K)(SO_3H) \qquad (2)$$

$$H_2N\!-\!CH(SO_3K)(SO_3H) \xrightarrow{\text{KNO}_2} N_2C(SO_3K)_2 \qquad (3)$$

$$N_2C(SO_3K)_2 \xrightarrow{\text{HCl}} ClCH(SO_3K)_2 \qquad (4)$$

$$N_2C(SO_3K)_2 \xrightarrow{\text{KHSO}_3} CH(SO_3K)_3 \qquad (5)$$

Monopotassium aminomethanedisulfonate and dipotassium diazomethanedisulfonate were prepared essentially according to the procedures of von Pechmann.[11] Crude, moist potassium diazomethanedisulfonate was converted into

potassium chloromethanedisulfonate and into tripotassium methanetrisulfonate by the procedures of Backer.[12] Potassium chloromethanedisulfonate was dissolved in water and passed through an Amberlite ion-exchange resin (IR-120). There was no chloride or sulfate ion in the effluent. The latter was concentrated under reduced pressure on a boiling water-bath. When cooled, the sample crystallized and was found by titration to be 84% chloromethanedisulfonic acid. Tripotassium methanetrisulfonate was converted into the free acid by a procedure similar to the above.

Solvent.—Acetic acid containing 0.12% water (0.067 M) was used as solvent in the major portion of the acidity measurements. This solvent was prepared by refluxing acetic acid with chromic acid and acetic anhydride.[13] Less acetic anhydride than the amount calculated to react with all of the water in the acetic acid was added. After refluxing for several hours, the acetic acid was distilled. Analysis, using the Karl Fisher method, gave 0.12% water.

Anhydrous acetic acid, used as solvent in some of the acidity work, was prepared by repeated fractional freezings. The acetic acid obtained had a freezing point of 16.6°, a density of $1.0492^{20}{}_4$, and a refractive index of 1.3722^{20}D. Literature values[14] for these properties are 16.6°, $1.04962^{20}{}_4$ and 1.3718^{20}D.

Indicators.—α-Naphtholbenzein and o-nitroaniline were obtained from Eastman Kodak Company and were used without purification.

Solutions of Strong Acids.—Samples of the eleven strong acids described above were titrated with standard aqueous alkali and were found to contain between 35.7 and 98.0% acid. It was assumed that the remaining 2.0 to 64.3% was water. The amount of water introduced in preparing solutions of these acids was small compared with the 0.12% water in the solvent. In the most unfavorable case, $i.e.,$ hydrochloric acid which contained 64.3% water, only 0.03% water was added in preparing a $5 \times 10^{-3}\ M$ solution.

Stock solutions were prepared in 100-ml. volumetric flasks from weighed amounts of the acids and solvent containing 0.12% water. The strengths of the solutions were calculated. As a check, aliquots of the solutions were titrated with a standard solution of sodium acetate in acetic acid, using α-naphtholbenzein as indicator. It was found that in acetic acid all of the acids except methanedisulfonic, chloromethanedisulfonic and methanetrisulfonic function as monobasic acids. Methanedisulfonic and chloromethanedisulfonic, however, function as dibasic acids; the experimentally determined normalities were found to be twice the calculated molarities. Due to the slight solubility of methanetrisulfonic acid, the strength of a stock solution could be obtained only by titration. It is assumed, however, that it is tribasic. The calculated molarities of the stock solutions were found to agree very satisfactorily with the experimentally determined normalities.

The sulfuric acid solution was titrated also with both guanidine and aniline, using α-naphtholbenzein as indicator, and was found to be monobasic.

Anhydrous solutions of perchloric, hydrobromic and hydrochloric acids, and nearly anhydrous solutions of sulfuric, chloromethanedisulfonic, methanedisulfonic and methanetrisulfonic acids were prepared using anhydrous acetic acid as solvent.

Stock solutions of perchloric acid were prepared in two different ways: (1) solid silver perchlorate was dissolved in the solvent and dry hydrogen chloride bubbled through the solution. The silver chloride precipitate was removed by decantation and dry air bubbled through the solution until the latter was free from chloride ion. (2) A known amount of 70.7% perchloric acid was dissolved in the solvent, and the amount of acetic anhydride required to react with the water introduced was added.

The solutions prepared in these two ways were standardized by titration with sodium acetate. Within experimental error, identical values of H_0 (−1.61 and −1.54) were obtained on $5 \times 10^{-3}\ M$ solutions prepared from these two stock solutions.

Anhydrous hydrobromic acid stock solution was prepared by mixing in a volumetric flask a known amount of 35.7%

(9) H. J. Backer and W. G. Burgers, *J. Chem. Soc.*, **127**, 233 (1925).

(10) H. J. Backer, *Rec. trav. chim.*, **48**, 949 (1929).

(11) H. von Pechmann and Ph. Manck, *Ber.*, **28**, 2374 (1895).

(12) H. J. Backer, *Rec. trav. chim.*, **49**, 1107 (1930).

(13) K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, **125**, 960 (1924); **130**, 983 (1927).

(14) A. Weissberger and E. Proskauer, "Organic Solvents" Clarendon Press, Inc., New York, N. Y. 1935, p. 43.

hydrobromic acid with anhydrous acetic acid. The amount of acetic anhydride needed to react with the water was added and the solution diluted to volume. The normality was obtained by titrating with sodium acetate in acetic acid and also with aqueous silver nitrate.

To obtain a stock solution of hydrochloric acid, dry hydrogen chloride was passed into the solvent. The strength of the resulting solution was determined by titration with silver nitrate.

Stock solutions of sulfuric, methanetrisulfonic, chloromethanedisulfonic and methanedisulfonic acids were prepared using acids containing 4–20% water. Thus, a 5 × 10^{-3} M solution contained at most 0.02% water, or was 0.01 M in water.

Measurement of H_0.—Stock solutions of α-naphtholbenzein and o-nitroaniline, which were about 1 × 10^{-3} and 9 × 10^{-4} M, respectively, were prepared in acetic acid. From these, several dilutions were made of o-nitroaniline and α-naphtholbenzein; the latter was converted into its colored acid form with a large excess of perchloric acid.

Optical transmissions of the dilutions were measured with a modified Beckman DUR spectrophotometer which used optical cells with a 2.0-cm. light path. The molecular extinction coefficient for the acid form of α-naphtholbenzein was found to be 1.06 × 10^4 at 6400 Å. The basic form of o-nitroaniline was found to have a molecular extinction coefficient of 4.77 × 10^3 at 4000 Å. and 3.90 × 10^3 at 4200 Å. The solutions of α-naphtholbenzein and o-nitroaniline were found to obey Beer's law up to 5 × 10^{-5} and 9 × 10^{-5} M, respectively.

o-Nitroaniline is completely in its colored basic form in acetic acid. This was shown by the sensibly constant value of the optical transmission of the solution when guanidine was added. Also, solutions containing only α-naphtholbenzein and solvent have essentially the same optical transmission at 6400 Å. as pure solvent. Thus, the concentrations of the acid form of α-naphtholbenzein and of the basic form of o-nitroaniline can be calculated directly from optical transmissions.

To measure acidities, solutions were prepared in 100-ml. volumetric flasks by mixing an aliquot of stock indicator solution and a calculated volume of stock acid solution and diluting to volume with solvent. Graduated pipets were used to measure the required volumes of stock acid solutions. Optical transmissions of these solutions were then measured.

The indicator concentrations were kept small compared with the acid concentrations. The ratio of acid to indicator concentration varied in general from 10 to 60. The most

unfavorable situation existed when acid concentrations were 5 × 10^{-4} M and the concentration of α-naphtholbenzein 5 × 10^{-5} M. (The molecular weight of the carbinol form of α-naphtholbenzein was used to calculate concentration.)

Results

Evaluation of pK_a for α-Naphtholbenzein.—Although o-nitroaniline has been used quite extensively to measure H_0[2e,f,g,h,6], α-naphtholbenzein apparently has not been used for this purpose. However, α-naphtholbenzein has been used as an indicator for acid–base titrations in glacial acetic acid.[3a,d] It is not strictly a simple basic indicator,[15] since in aqueous solutions, it shows two color changes, one in basic solution and another in strongly acidic solution. However, in the acetic acid solutions discussed in this paper, it does behave as a simple basic indicator.

Figure 1 shows the ratio (BHX)/(B)(BHX represents the acid form of indicator and B the basic form) for both indicators as a function of molarity of perchloric acid. In very dilute acid solutions, the ratio for α-naphtholbenzein decreases sharply in a manner similar to that for other indicators in dilute acidic solutions.[2,5] In more concentrated solutions, the ratios increase linearly with concentration of perchloric acid. This relation, which has been reported to hold up to 0.14 M,[2i] can occur if the acid is completely dissociated or if the acid and reaction product are slightly dissociated. Evidence for slight dissociation is obtained from freezing point,[16] conductance,[7] and potentiometric titration data.[17]

The indicator ratio for o-nitroaniline parallels that for α-naphtholbenzein, the difference in ordinate being equal to the difference in pK_a of the two indicators. Since pK_a for o-nitroaniline equals -0.17,[2f] pK_a for α-naphtholbenzene is found to be 0.53, in good agreement with the scant data obtained in aqueous solutions.[18]

The indicator ratio for o-nitroaniline in solutions containing both perchloric acid and sodium perchlorate at a total concentration of 0.01 M is also shown in Fig. 1. The salt decreases the ratio slightly if at all.

Values of H_0.—The results of acidity measurements on solutions of eleven acids in solvent 0.067 M in water are given in Table I. Figure 2 shows a plot of H_0 vs. log molarity. Straight lines which are sensibly parallel were obtained. Data obtained on sulfuric acid solutions by Hall and Spengeman[2f] and by Paul and Hammett[2e] are shown also, and are seen to be in agreement with our results.

Data on monobasic acids at 5 × $10^{-3}M$ and all data on polybasic acids were obtained with o-nitroaniline ($pK_a = -0.17$). The concentration of indicator was 8.5 × $10^{-5}M$. Data on monobasic acids at 0.5 × 10^{-3} and 1 × $10^{-3}M$ were obtained with α-naphtholbenzein ($pK_a = 0.53$). The indicator concentrations were 5 × 10^{-5} and 2.5 × $10^{-5}M$, respectively.

Fig. 1.—Variation of indicator ratio with molarity of perchloric acid.

(15) Indicators used to measure H_0 should be simple basic, i.e., capable of accepting only one proton, and must be electrically neutral in the basic form.

(16) W. C. Eichelberger, THIS JOURNAL, **56**, 799 (1934).

(17) N. F. Hall and T. H. Werner, ibid., **50**, 2367 (1928).
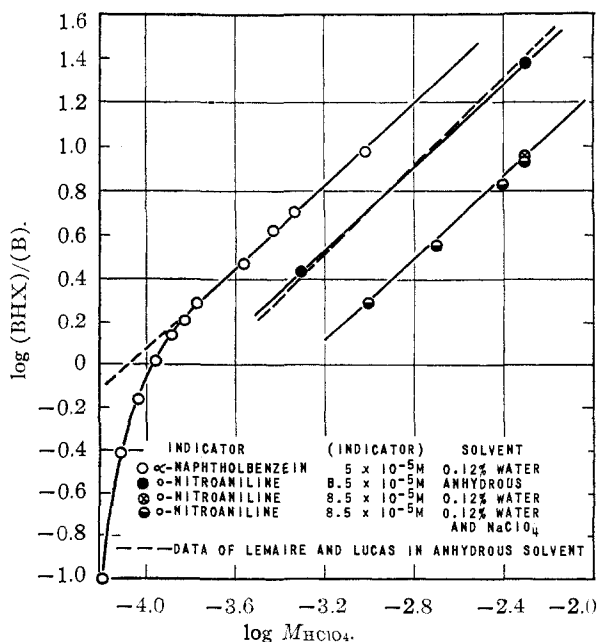
(18) Eastman Kodak Indicator Chart.

TABLE I

H_0 FOR SOLUTIONS OF ACIDS IN ACETIC ACID SOLVENT 0.067 M IN WATER

	Acid concentrations in moles/liter		
Monobasic acids	0.5×10^{-3} M	1×10^{-3} M	5×10^{-3} M
Perchloric	−0.30	−0.44	−1.12
Hydrobromic	....	....	−1.05
Chlorocarboxymethanesulfonic	+0.07	−0.12	−0.94
Chloromethanesulfonic	+ .34	+ .13	− .56
Carboxymethanesulfonic	+ .52	+ .28	− .50
Sulfuric	+ .65	+ .38	− .29
Methanesulfonic	+1.19	+ .90	+ .27
Hydrochloric	+1.33	+1.13	+ .40
Dibasic acids	$0.5 \times 10^{-3} M$	$2.5 \times 10^{-3} M$	$5 \times 10^{-3} M$
Chloromethanedisulfonic	−0.55	−1.18	−1.50
Methanedisulfonic	−0.26	−0.88	−1.33
Tribasic acid	$0.33 \times 10^{-3} M$		$1.67 \times 10^{-3} M$
Methanetrisulfonic	−0.60		−1.29

Degree of Dissociation of Acids in Acetic Acid.—Most acids by themselves or in inert solvents exist as polar molecules. In solvents capable of accepting a proton, the acids react as

$$HX + S \rightleftarrows SHX \rightleftarrows SH^+ + X^- \quad (6)$$
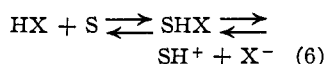
where SHX is an addition complex which may contain either a hydrogen bond or an electrostatic bond[19]; in the latter case, the addition complex is an ion pair, (SH^+X^-).

The extent of reaction of HX with S is determined by their relative acid and base strengths, while the extent of dissociation of the species formed is determined, to a large extent, by the dielectric constant of the solvent. Acetic acid is a very weak base and has a low dielectric constant $(D = 6.13)$.[20] Hence, the extent of its reaction with dissolved acids and the degree of dissociation of the addition complex, as calculated from conductance data, are small.

Kolthoff and Willman[7] have published conductance data for dilute solutions of some strong acids and salts in acetic acid. The logarithms of the equivalent conductivities of perchloric, hydrobromic, sulfuric and hydrochloric acids, and of lithium chloride, are plotted in Fig. 3 against the logarithm of the molarity. The data are fitted to straight lines, drawn parallel with a slope of −0.43.

Typical slightly dissociated electrolytes give similar plots except that the lines have theoretical slopes of −0.50.[21]

To obtain the dissociation constant of perchloric acid, a Fuoss–Kraus plot,[22] shown in Fig. 4, was constructed. The intercept gives a limiting equivalent conductivity, Λ_0, of 44, and the slope along with Λ_0 gives a classical dissociation constant, $K_c = (SH^+)(X^-)/(HX)$, of 9×10^{-7}.

If the assumption is made that Λ_0 for the other acids and lithium chloride is 44, dissociation constants can be calculated from values of Λ at a given concentration. Results are given in Table II. Values of ΔpK_c were calculated from the equation

$$\Delta pK_c = pK_c - pK_{HClO_4} = -2 \log \Lambda/\Lambda_{HClO_4} \quad (7)$$

where Λ and Λ_{HClO_4} are the equivalent conductivities of the given substance and perchloric acid, respectively, at 3×10^{-4} M. Values of K_c were calculated from values of ΔpK_c using $K_c = 9 \times 10^{-7}$ for perchloric acid.
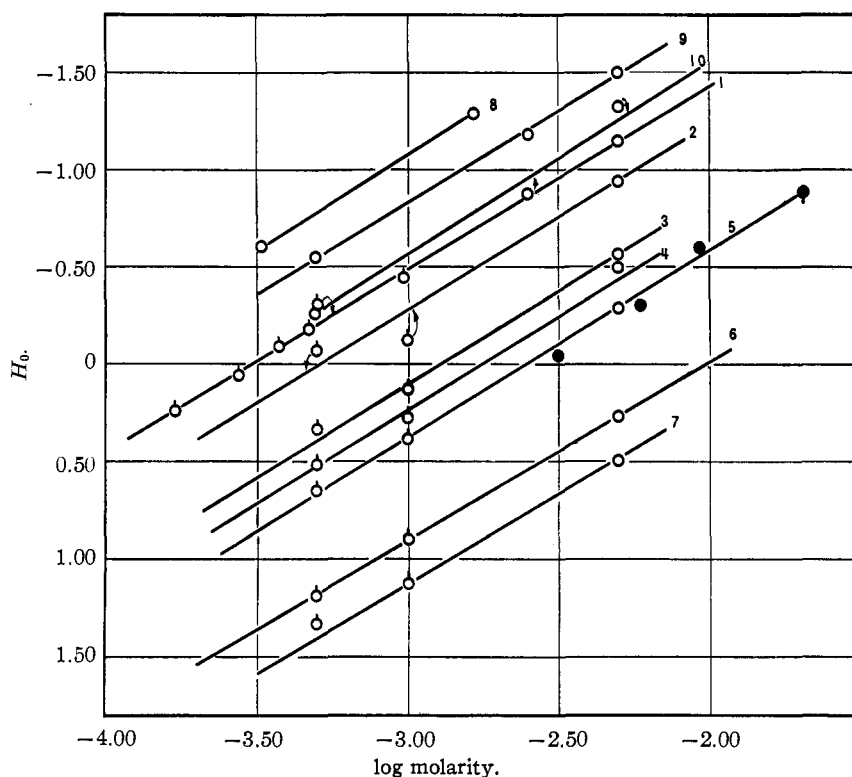

Fig. 2.—H_0 vs. log molarity for ten acids in solvent containing 0.12% water: 1, perchloric; 2, chlorocarboxymethanesulfonic; 3, chloromethanesulfonic; 4, carboxymethanesulfonic; 5, sulfuric; 6, methanesulfonic; 7, hydrochloric; 8, methanetrisulfonic; 9, chloromethanedisulfonic; 10, methanedisulfonic. Indicator used: ◐, α-naphtholbenzein; ○, o-nitroaniline; ●, data of Hall and Spengeman; ◓, data of Paul and Hammett.

The only comparable dissociation constant in the literature is given by Hall and Voge,[23] who estimated from their conductivity studies that the constant for sulfuric acid is approximately 10^{-9}.

Values of K_c for slightly dissociated electrolytes in solvents of low dielectric constant calculated from conductance data are not of high accuracy.

(19) For a discussion of this question and pertinent references, see reference 4.

(20) C. P. Smyth and H. E. Rogers, THIS JOURNAL, **52**, 1824 (1930).

(21) C. A. Kraus, J. Chem. Ed., **12**, 567 (1935).

(22) R. M. Fuoss, THIS JOURNAL, **57**, 488 (1935).

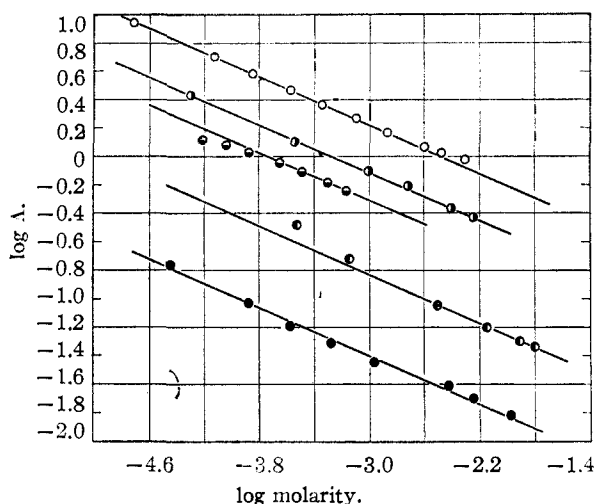(23) N. F. Hall and H. M. Voge, ibid., **55**, 239 (1933).

Fig. 3.—Conductivity data of Kolthoff and Willman (lines drawn parallel with slope of −0.43): O, HClO₄; ◑, HBr; ◒, LiCl; ◐, H₂SO₄; ●, HCl.
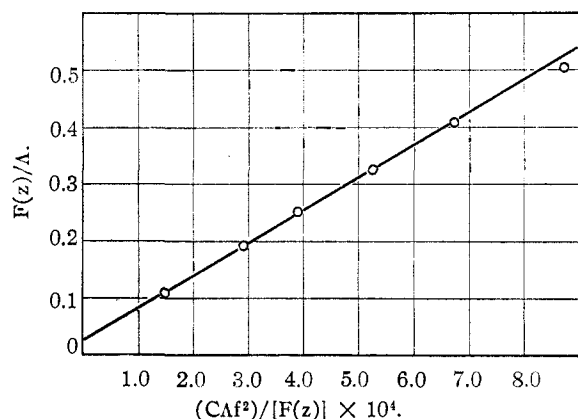

Fig. 4.—Fuoss–Kraus plot of conductivity data of perchloric acid in acetic acid.

However, the values of K_c given in Table II are of the correct order of magnitude.

TABLE II

DISSOCIATION CONSTANTS FOR ACIDS AND LITHIUM CHLORIDE IN ACETIC ACID

Substance	log Λ	$-\log\Lambda/\Lambda_{\text{HClO}_4}$	$\Delta pK_0{}^a$	pK_0	$K_0{}^a$	$\Delta pK_0{}^b$
HClO₄	0.44	0	0	−6.05	9 × 10⁻⁷	0
HBr	.10	.34	0.68	−6.73	1.9 × 10⁻⁷	0.50
LiCl	− .10	.54	1.08	−7.13	7.4 × 10⁻⁸	..
H₂SO₄	− .60	1.04	2.08	−8.13	7.4 × 10⁻⁹	2.36
HCl	−1.18	1.62	3.24	−9.29	5.1 × 10⁻¹⁰	3.98

a Calculated from conductance data of Kolthoff and Willman. *b* Calculated from values of H_0 for solutions in anhydrous solvent.

Values of ΔpK_c may be calculated also from the acidity data obtained using o-nitroaniline in anhydrous solvent. The difference in H_0 for solutions of two acids is given by

$$\Delta H_0 = (H_0)_2 - (H_0)_1 = -\log(a_{\text{H}^+})_2/(a_{\text{H}^+})_1 - \log$$
$$(f_\text{B}/f_{\text{BH}^+})_2/(f_\text{B}/f_{\text{BH}^+})_1 \quad (8)$$

where the subscripts refer to acids one and two. By replacing a_{H^+} with $(SH^+)f_{\text{H}^+}$, equation (8) can

be rewritten with the ratio

$$\frac{(f_{\text{H}^+})_2(f_{\text{BH}^+})_1(f_\text{B})_2}{(f_{\text{H}^+})_1(f_{\text{BH}^+})_2(f_\text{B})_1}$$

in the second term. In dilute solutions, activity coefficients vary with the ionic strength and the ionic strengths of solutions of indicator and different acids at the same concentrations are very low and nearly equal. Also, if $(SH^+)_2$ is larger than $(SH^+)_1$, then $(BH^+)_2$ will be larger than $(BH^+)_1$, and the resultant changes in the activity coefficients in the ratio will tend to cancel each other. Thus the last term in equation (8) is approximately zero. By multiplying both sides by two, the following equation is obtained

$$2\Delta H_0 = -2\log (SH^+)_2/(SH^+)_1 = \Delta pK_0 \quad (9)$$

Values of ΔpK_c calculated from H_0 for solutions of acids in anhydrous solvent are given in Table II. Reasonable agreement is found between these values and those calculated from conductance data.
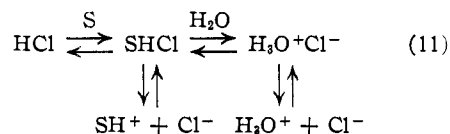
Kolthoff and Willman found that the addition of water to perchloric acid solutions caused only a slight increase in conductivity, while addition of water to solutions of the other acids, and especially to hydrochloric acid solution, caused a marked increase in conductivity. They concluded that perchloric acid is completely ionized, but hydrochloric acid is only slightly ionized. The dissociation constant for perchloric acid given in Table II is thus for the dissociation of the ion pair $SH^+ClO_4^-$.

Upon the addition of water, which is a stronger base than acetic acid, to a perchloric acid solution, the following equilibrium is set up

$$SH^+ClO_4^- + H_2O \rightleftharpoons H_3O^+ClO_4^- \quad (10)$$
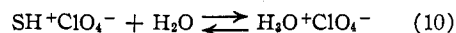
Both ion pairs, i.e., $SH^+ClO_4^-$ and $H_3O^+ClO_4^-$, would be expected to dissociate to approximately the same extent. Thus, the total concentration of ions is changed only slightly by the addition of water, causing only a small change in conductivity.

The addition of water to a hydrochloric acid solution, however, will cause an increase in the number of free ions. The following equilibria may be written

$$HCl \overset{S}{\rightleftharpoons} SHCl \overset{H_2O}{\rightleftharpoons} H_3O^+Cl^- \quad (11)$$
$$\downarrow\uparrow \qquad\qquad \downarrow\uparrow$$
$$SH^+ + Cl^- \quad H_3O^+ + Cl^-$$

In the absence of water, most of the hydrochloric acid will be in the form of un-ionized molecules, and (SHCl) will be small. The addition of water shifts the equilibria: some SHCl is converted into H_3O^+-Cl^- and additional SHCl formed from HCl and S. (The species formed from H_2O and HCl may be more nearly a hydrogen-bond type complex than an ion pair. However, for convenience we shall designate it as $H_3O^+Cl^-$.) The $H_3O^+Cl^-$ dissociates slightly, increasing the number of free ions in solution, which produces greater conductivity.

On the other hand, the change in acidity of an acid solution upon the addition of water is determined by the relative basicities of water, the anion of the acid and the solvent. As the chloride ion is a stronger base than the perchlorate ion, the ex-

TABLE III

H_0 IN ANHYDROUS SOLVENT AND SOLVENT $0.067M$ IN WATER. ACIDITY CONSTANTS FOR $H_3O^+X^-$

[(BHX)/(B)]$_0$ and $H_0°$ are in anhydrous solvent.   [(BHX)/(B)]$_w$ and H_0 are in solvent 0.067 M in water.   (Indicator) = 8.5×10^{-5} M.

Acid	$\frac{(BHX)}{(B)}_0$	$\frac{(BHX)}{(B)}_w$	$H_0°$	H_0	$\frac{[HX]}{\times 10^3 M}$	$K_c^B \times 10^3$	$K_c^{H_2O}$
Perchloric	25.8	9.0	−1.58	−1.12	5.0	0.194	0.036
Hydrobromic	14.5	7.5	−1.33	−1.05	5.0	0.345	0.071
Sulfuric	1.70	1.33	−0.40	−0.29	5.0	2.94	0.240
Hydrochloric	0.27	0.27	+0.40	+0.40	5.0	18.6	>2
Methanetrisulfonic	23.3	13.2	−1.54	−1.29	1.67		
Chloromethanedisulfonic	29.3	21.4	−1.64	−1.50	5.0		
Methanedisulfonic	20.3	14.4	−1.48	−1.33	5.0		
Methanedisulfonic	10.3	5.16	−1.18	−0.88	2.5		

tent of reaction of water with SHCl will be less than with SH$^+$ClO$_4^-$; as the species formed by the reaction of water with SHCl and SH$^+$ClO$_4^-$ are too weak as acids to react with the indicator, water will decrease the acidity of a perchloric acid solution more than that of a hydrochloric acid solution. Quantitative data to illustrate this are presented below.

Basic Strength of Water in Glacial Acetic Acid.— In a solution that contains a small amount of water in addition to acid, HX, and indicator base, B, the following equilibria are established

$$B + HX \rightleftharpoons BHX \qquad (12)$$

$$H_2O + HX \rightleftharpoons H_3O^+X^- \qquad (13)$$
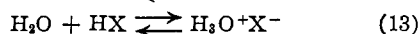
As discussed in the above section, acids and salts are not appreciably dissociated in acetic acid. Thus, ion pairs or association complexes containing hydrogen bonds will be present in large amounts. Acidity constants for BHX and H$_3$O$^+$X$^-$ may be defined as

$$K_c^B = (B)(HX)/(BHX) \qquad (14)$$

$$K_c^{H_2O} = (H_2O)(HX)/(H_3O^+X^-) \qquad (15)$$

where parentheses denote concentrations.

Values of H_0 for 5×10^{-3} M solutions of several acids in anhydrous solvent were measured, and the results along with K_c^B and $K_c^{H_2O}$ are given in Table III. K_c^B was calculated from the indicator ratio and the concentration of acid in anhydrous solvent, using equation (14). Then, $K_c^{H_2O}$ was calculated from K_c^B and the indicator ratio in solutions 0.067 M in water, using the equation

$$K_c^{H_2O} = \frac{(H_2O)[(BHX)/(B)]_w K_c^B}{(HX)_0 - [(BHX)/(B)]_w K_c^B} \qquad (16)$$

where (HX)$_0$ is the total initial acid concentration, and [(BHX)/(B)]$_w$ the indicator ratio found in acid solution 0.067 M in water.

It is seen in Table III and from equation (16) that $K_c^{H_2O}$ depends on the strength of the acid present. Values of $K_c^{H_2O}$ for the polybasic acids were not calculated from equation (16), as such values would have little significance.

With hydrochloric acid, it was necessary to make the solution more than 0.5 M in water before a change in indicator ratio could be detected. Such behavior is as expected, since the weaker the acid, the less it will react with water; consequently, the smaller the effect of water on the indicator ratio.

Lemaire and Lucas[21] have measured the basic strengths of some weak bases in acetic acid by the above method using perchloric acid and indicator. They report $K_c^{H_2O}$ as 0.032, in good agreement with our value of 0.036. However, they assumed in making their calculations of the thermodynamic constants of the bases that perchloric acid is completely dissociated. This assumption is not valid in view of the preceding data. However, if it is assumed that the dissociation constants of SH$^+$-ClO$_4^-$ and B$_1$H$^+$ClO$_4^-$ (B$_1$ is the base being studied) are equal, it can be shown that their calculated thermodynamic constants are correct.