H_0 AND RELATED INDICATOR ACIDITY FUNCTIONS[1]

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CONTENTS

I. INTRODUCTION

The H_0 acidity function is a quantitative measure of acidity conceived originally by Hammett and Deyrup (46). It is derived from ionization equilibria of a particular class of indicators, those behaving in the Brønsted–Lowry sense as uncharged bases,

$$B + H^+ \rightleftharpoons BH^+$$

and is defined (43, 44, 46) by the equation:

$$H_0 \equiv pK_{BH^+} - \log \frac{C_{BH^+}}{C_B} \tag{1}$$

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where C_{BH^+}/C_B is the directly observable concentration ratio of the indicator in its two differently colored forms and K_{BH^+} is the thermodynamic ionization constant of its conjugate acid in terms of molar concentrations, referred to ideal dilute solution in water. Analogous acidity functions derived from ionization equilibria of cationic and anionic bases may be defined as follows (44):

$$B^+ + H^+ \rightleftharpoons BH^{++}; \quad H_+ \equiv pK_{BH^{++}} - \log \frac{C_{BH^{++}}}{C_{B^+}} \tag{1a}$$

$$B^- + H^+ \rightleftharpoons BH; \quad H_- \equiv pK_{BH} - \log \frac{C_{BH}}{C_{B^-}} \tag{1b}$$

etc.

The above definitions are formally equivalent to:

$$H_0 = -\log \frac{a_{H^+} f_B}{f_{BH^+}} \tag{2}$$

$$H_+ = -\log \frac{a_{H^+} f_{B^+}}{f_{BH^{++}}} \tag{2a}$$

$$H_- = -\log \frac{a_{H^+} f_{B^-}}{f_{BH}} \tag{2b}$$

etc., where a_{H^+} denotes hydrogen-ion activity and the f's denote molar-concentration activity coefficients. A convenient function related to H_0 is h_0, defined by the equation $H_0 \equiv -\log h_0$; analogous functions h_+ and h_- may be defined for the other acidities.

The ionic activity and activity coefficient factors in equations 2 enter in the form of ratios or products that are observable in the sense described by Guggenheim (36). If each individual activity coefficient is taken by convention to approach unity at infinite dilution in water so that a_{H^+} under this condition becomes equal to C_{H^+},[2] then each of these acidity functions becomes equal to pH in ideal dilute aqueous solutions. With increasing acid concentration, however, and particularly with transfer to a nonaqueous medium, the various indicator acidity functions deviate from one another and also of course from other measures of acidity. No simple theory exists for calculation of the extent to which various ionic and nonionic solutes will depart from ideal dilute behavior at high electrolyte concentrations, particularly in media of low dielectric constant. Nevertheless we can certainly measure indicator concentration ratios directly and so apply equations such as 1, 1a, or 1b on an empirical basis.

Indicator procedures constitute only one of several possible ways to measure the acidity of solutions. A very simple method is to measure the concentration, C_A, of the acid itself; this is obviously of only limited utility for other than strong acids. Another measure is C_{H^+}, the concentration of hydrogen ion in the

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[2] The symbol H^+ is used, as is customary, to represent hydrogen ions in whatever equilibrium form they may assume in the given medium; e.g., presumably H_3O^+ in dilute aqueous solutions.

given solvent, but the determination and interpretation of this quantity are frequently uncertain. Furthermore, the value of C_{H^+} (or of C_A) is of little use in comparing acidities in different solvents. A different type of measurement is that of the potential of a hydrogen or equivalent electrode in equilibrium with the hydrogen ions of a solution. Such measurements outside the dilute aqueous range involve either a reference electrode with an indeterminate liquid-junction potential or, if a cell without a liquid junction is used, an interrelated contribution to the overall potential from the accompanying anions (3). As would be expected these different methods of measurement will usually lead to different values of the "acidity," and a point of major interest is to compare the values for different situations.

The indicator acidity functions themselves are differentiated from one another on the basis of charge type in recognition of the fact that to a first approximation, at least, this must be a major factor accounting for differences in behavior. Following the lead of Hammett and Deyrup, most investigators of indicator acidity in highly acid solutions have worked with H_0 rather than with other acidity functions. The generality of the H_0 function for aqueous solutions of strong acids has been established by the empirical observation that a series of different indicators of the given charge type, consisting in the main of aromatic amines and oxygen bases, has in fact been found to give a reasonably uniform scale of H_0 values independent of the particular indicator over acid concentrations extending far outside the ideal dilute range. Some degree of uniformity has been established also in certain nonaqueous media. By contrast, few systematic investigations have been reported on indicators of other charge types, and experimental evidence is not yet available as to whether functions such as H_+ or H_- are sufficiently independent of the indicator to be useful outside the dilute aqueous range.

The function H_0 serves specifically as a measure of the tendency for the solution in question to transfer a proton to an uncharged base molecule, increasingly negative values corresponding to higher acidity. The H_0 acidity scale has turned out to be useful for the measurement of base strength of very weak uncharged bases and also for the interpretation of the kinetics of certain classes of acid-catalyzed reactions. As a result there has been an increasing flow of information on various aspects of both this and related acidity functions (85a). The purpose of this review is to assemble the data on such functions and to evaluate their present status. Applications of the H_0 function to kinetic problems will be discussed in a subsequent review.

II. MEASUREMENT OF H_0

The measurement of H_0 falls into two phases, the measurement with a given indicator of C_{BH^+}/C_B and the measurement of pK_{BH^+}.

A. *Measurement of* C_{BH^+}/C_B

An indicator has an acid form and a base form (BH^+ and B, respectively, for the class of indicators here under consideration) with different spectral absorptions. All ordinary indicators show this difference in the visible part of the spectrum, but many other acids and bases which are transparent in the visible undergo a color change in the ultraviolet and hence can be used as indicators.

If $\overset{\lambda}{\epsilon}_B$ represents the extinction coefficient at a given wavelength of a solution containing the indicator practically completely in the basic form, B, and if $\overset{\lambda}{\epsilon}_{BH^+}$ represents the extinction coefficient of a solution in which the indicator is practically completely converted to the acid form, BH^+, then the ratio, C_{BH^+}/C_B, in a solution in which the indicator is partially ionized may be derived from its extinction coefficient, ϵ^λ, at the same wavelength by the equation,

$$\frac{C_{BH^+}}{C_B} = \frac{\overset{\lambda}{\epsilon}_B - \overset{\lambda}{\epsilon}}{\overset{\lambda}{\epsilon} - \overset{\lambda}{\epsilon}_{BH^+}} \tag{3}$$

provided that the concentrations are sufficiently low so that the Beer–Lambert law is applicable and provided of course that one takes into account absorption by the medium itself. Since $\overset{\lambda}{\epsilon}_B$ and $\overset{\lambda}{\epsilon}_{BH^+}$ are necessarily measured in solutions of different composition from the test solution, one must be on guard against a possible shift in spectral absorption by the indicator accompanying changes in the medium not related to its acidity. Hammett and Deyrup noted such shifts with certain indicators in sulfuric acid–water solutions as the concentration of the acid was changed (46). One may minimize these so-called medium effects by taking $\overset{\lambda}{\epsilon}_B$ and $\overset{\lambda}{\epsilon}_{BH^+}$ values in solutions as close as possible to the range of acid concentrations over which significant change in the ionization ratio is actually taking place. Flexser, Hammett, and Dingwall (28) have given a detailed analysis of the problems involved, and Gold and Hawes (32) have discussed further aspects.

Most of the older data on indicators were obtained with optical colorimeters. More recent measurements have been made with photoelectric spectrophotometers. Aside from opening the ultraviolet region to convenient investigation, the spectrophotometer has afforded greater objectivity and precision in the measurements; it is furthermore inherently a more satisfactory instrument in that comparisons may be made under essentially monochromatic conditions in the most favorable part of the spectrum.

Until very recently all the published H_0 data were at room temperature, i.e., within about five degrees of 25°C. An explicit study of the temperature effect is now available for aqueous solutions of sulfuric, hydrochloric, and phosphoric acids (29a). This indicates a small but systematic shift in the relationships between H_0 and acid concentration with changing temperature. In the case of sulfuric acid, for example, the slope of $-H_0$ vs. molar concentration between 1 and 14 M averages about 5 per cent less at 80°C. than at 20°C.; the difference is somewhat greater if the solutions are compared on a weight composition basis, without correction for volume expansion. Even though the change of H_0 itself may be small, it is still highly desirable to control the temperature within a degree or so during precise indicator measurements, since both log C_{BH^+}/C_B and pK_{BH^+} vary separately to considerable extents. The value of pK_{BH^+} for *p*-nitroaniline, for example, is reported to change by -0.20 logarithmic unit between

20°C. and 40°C. Temperature fluctuations during the measurements can therefore certainly lead to errors in C_{BH^+}/C_B values.

B. *Measurement of* pK_{BH^+}

The definition of pK_{BH^+} is

$$pK_{BH^+} = \log \frac{C_{BH^+}}{C_B C_{H^+}} + \log \frac{f_{BH^+}}{f_B f_{H^+}} \tag{4}$$

where the activity coefficients are referred to the value unity for an infinitely dilute solution in water. Noting that the indicator concentration is always exceedingly small, this is equivalent to

$$pK_{BH^+} = \lim_{C_A \to 0} \left[\log \left(\frac{C_{BH^+}}{C_B} \right) - \log C_{H^+} \right] \tag{5}$$

where C_A is the molar concentration of a strong acid, A, in water. For a strong acid, C_{H^+} is calculable by the relation $C_A = C_{H^+} + C_{BH^+}$, assuming that the indicator is introduced in its uncharged form. Hence for an indicator base whose ionization ratio can be directly measured in dilute aqueous solutions of strong acids, one can expect to calculate pK_{BH^+} from the observed values of C_A and the indicator ratio. Empirical evidence shows that the expression in brackets on the righthand side of equation 5, which is equivalent to $pK_{BH^+} + \log (f_{H^+} f_B / f_{BH^+})$, varies linearly with concentration of electrolyte up to at least 2 M concentration (77). Apparently the general effects of interionic attraction on the ionic activity coefficients in equation 4 approximately cancel out over this range. The extrapolation procedure is therefore quite precise for sufficiently strong indicator bases (see figures 2 and 3).

For weaker bases this type of direct determination of pK_{BH^+} is not feasible and a stepwise comparison must be used. With two different indicator bases, B and C, which are studied in the same solution,

$$pK_{CH^+} - pK_{BH^+} = \log \left(\frac{C_{CH^+}}{C_C} \right) - \log \left(\frac{C_{BH^+}}{C_B} \right) - \log \left(\frac{f_C f_{BH^+}}{f_{CH^+} f_B} \right) \tag{6}$$

If the bases B and C are of fairly similar structure, there are, as Hammett (44) points out, both experimental and theoretical reasons for believing that the last term on the right can be neglected for aqueous solutions and presumably for solutions in other solvents of high dielectric constant. Given that the bases B and C have ionization constants sufficiently close together so that both indicator ratios can be measured with good precision in the same medium, the differences in the pK values can be determined by the relation:

$$pK_{CH^+} - pK_{BH^+} = \log \left(\frac{C_{CH^+}}{C_C} \right) - \log \left(\frac{C_{BH^+}}{C_B} \right) \tag{7}$$

A similar procedure will give $pK_{DH^+} - pK_{CH^+}$ for an indicator D whose ionization overlaps that of C, and so on. The absolute values of all the pK's can then

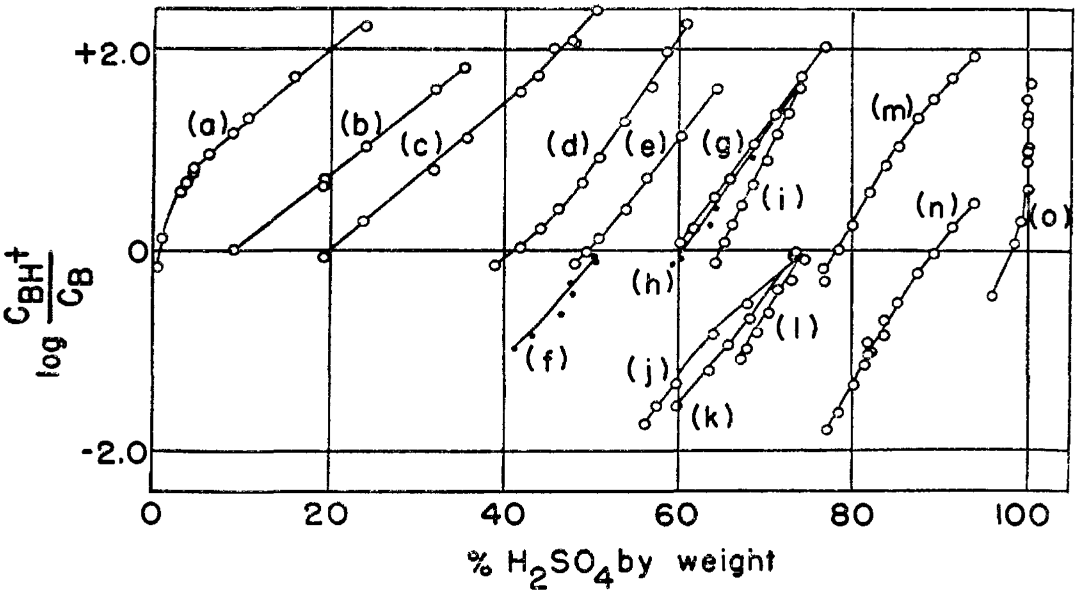

FIG. 1. Logarithm of ionization ratios of indicators in sulfuric acid–water solutions. Indicators: (a) *p*-nitroaniline; (b) *o*-nitroaniline; (c) 4-chloro-2-nitroaniline; (d) *p*-nitrodiphenylamine; (e) 2,4-dichloro-6-nitroaniline; (f) *p*-nitroazobenzene; (g) 2,6-dinitro-4-methylaniline; (h) 2,4-dinitroaniline; (i) *N*,*N*-dimethyl-2,4,6-trinitroaniline; (j) benzalacetophenone; (k) β-benzoylnaphthalene; (l) *p*-benzoylbiphenyl; (m) 6-bromo-2,4-dinitroaniline; (n) anthraquinone; (o) 2,4,6-trinitroaniline (46).

be established if any one of them is determined by direct measurement in dilute aqueous solution.

There are two obvious experimental tests of equation 7 and hence of the validity of this stepwise procedure. One is to see if $\left[\log\left(\frac{C_{CH^+}}{C_C}\right) - \log\left(\frac{C_{BH^+}}{C_B}\right)\right]$ remains constant as the concentration of a particular strong acid in a given solvent is varied. The second test is to see if the value of this difference, and hence of $pK_{CH^+} - pK_{BH^+}$, remains constant in different solvents. Figure 1 is an illustration of the first type of test, taken from the studies of Hammett and Deyrup on aqueous sulfuric acid. It is evident that the plots of log C_{BH^+}/C_B remain parallel for almost all the indicators studied.

The indicator *p*-nitroaniline, (a) of figure 1, is a sufficiently strong base that its pK value can be directly measured by application of equation 5. Sulfuric acid solutions themselves are not suitable for this purpose because of complications in the establishment of C_{H^+} arising from secondary ionization. The strong acids perchloric, hydrochloric, and nitric may, however, be used. Figure 2 gives plots of $\left[\log\frac{C_{BH^+}}{C_B} - \log C_{H^+}\right]$ vs. C_A from spectrophotometric measurements for *p*-nitroaniline in aqueous solutions of hydrochloric acid. The data of Paul (77) extrapolate to a pK value of 0.99 for this indicator; those of Braude (14) extrapolate to 0.98[3]; older colorimetric data (51) (not shown on the figure)

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[3] The authors are unable to account for the difference in slope between the data of Braude and those of Paul (figure 2). Braude introduces two modifications into the procedure for

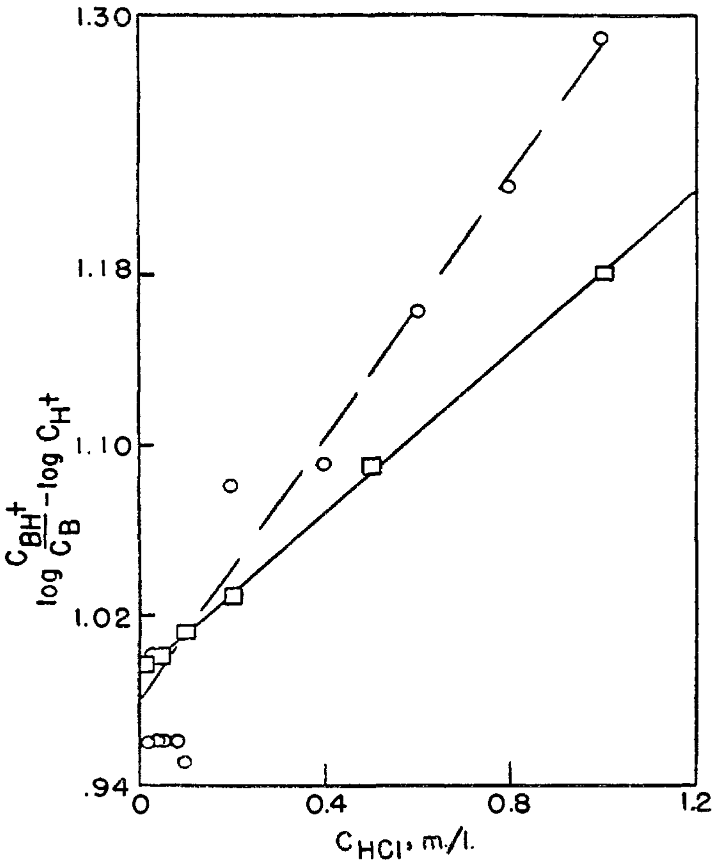

FIG. 2. Plot for determination of pK_{BH^+} for p-nitroaniline in aqueous hydrochloric acid. ○, Braude (14); □, Paul (77).

extrapolate to 1.03. Bell and Bascombe (6) give a value of 1.01 from measurements in approximately 0.01 *M* hydrochloric acid; Hart (54) has very recently obtained the value 0.98 ± 0.005.

Figure 3 shows a similar plot for aqueous solutions of perchloric acid from colorimetric data (46). Included also are data for the weaker bases *o*-nitroaniline and 4-chloro-2-nitroaniline (46), and it is of interest to note that the curves are accurately parallel even though they are no longer linear at the higher acidities. The data of figure 3 for *p*-nitroaniline extrapolate to 0.47; data obtained

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determining the indicator ratio. He takes explicit account of a small optical absorption by the *p*-nitroaniline ion and this seems to be quite reasonable. He also assumes that the wavelength of maximum absorption for the uncharged base shifts with electrolyte concentration and consequently determines C_{BH^+}/C_B from readings at shifting wavelength. This latter procedure may be responsible for the large discrepancy between Braude's H_0 values and those of other investigators for 2 and 3 *M* hydrochloric acid, but it should not significantly influence the data of figure 2. Braude's proposed value of 0.95 for the pK_{BH^+} of *p*-nitroaniline is based exclusively on the observed ionization ratio at hydrochloric acid concentrations of 0.1 *M* and below, on the assumption that in these solutions the activity coefficient ratio in equation 4 is practically equal to unity. The extrapolation procedure suggested in figure 2 seems sounder in principle. See, for example, figure 4 of reference 4, where a similar extrapolation procedure is used.

in nitric acid solutions (51) extrapolate to 1.03. pK_{BH^+} = 0.99 is selected as a best value for *p*-nitroaniline. This value is 0.12 unit more negative than the value of 1.11 previously adopted on a somewhat different basis by Hammett and Paul (51), and 0.41 unit more negative than that of 1.40 originally adopted by Hammett and Deyrup.

Table 1 gives pK_{BH^+} values for a series of uncharged basic indicators in various acid media. Those above *p*-naphtholbenzein (stronger bases) were determined by direct extrapolation as in figures 2 and 3. The others were determined by stepwise comparison, with *p*-nitroaniline as the ultimate reference base. For many of these, cryoscopic studies in 100 per cent sulfuric acid have definitely established that they ionize by adding a single proton (48). One will observe that there is general, if not perfect, agreement among the pK_{BH^+} values obtained in the different media, including the nonaqueous ones, thus providing a

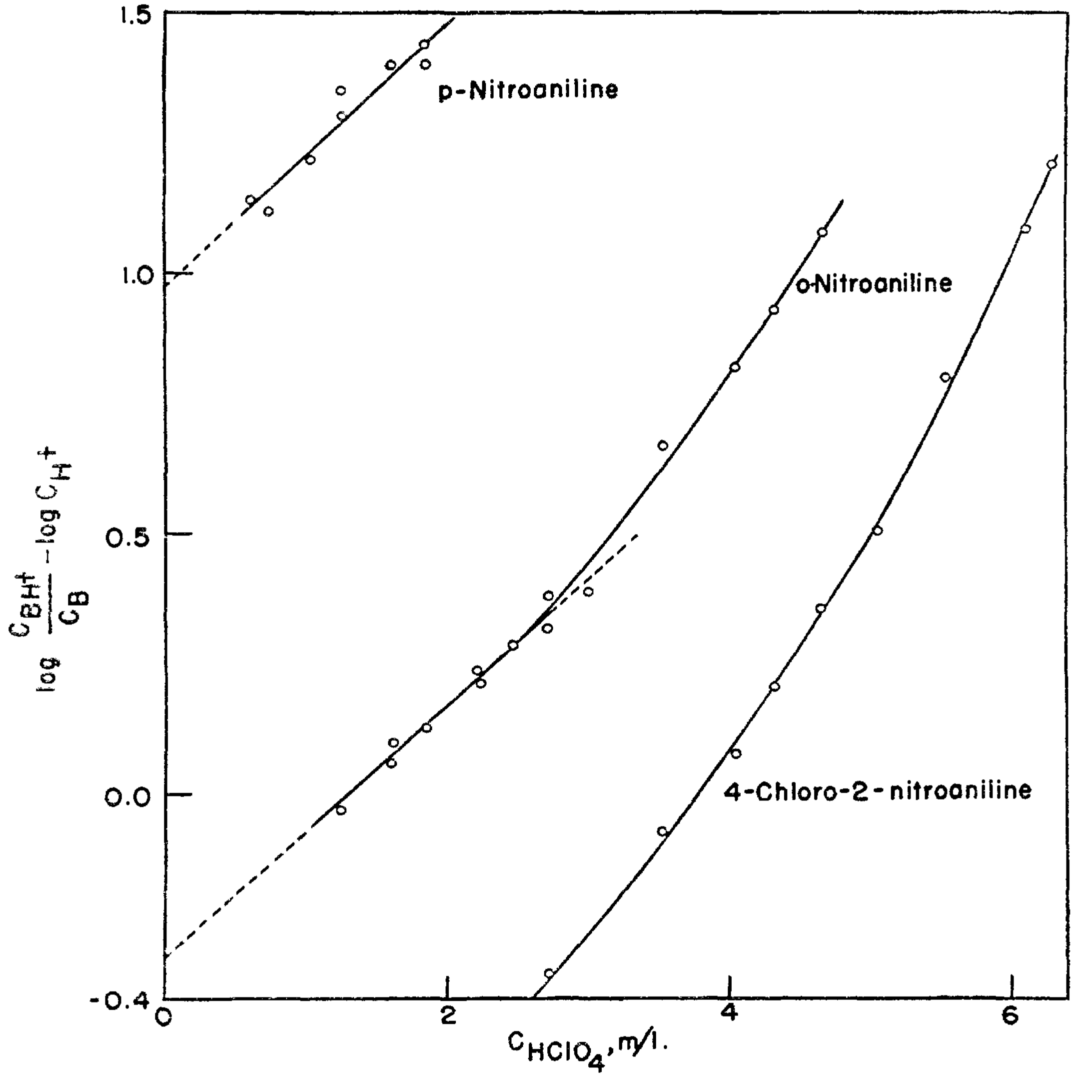

FIG. 3. Ionization of indicators in aqueous perchloric acid (46)

TABLE 1

Indicator constants, pK_{BH^+}, *of very weak bases*

Indicator	Best Value	HCl aq.	HNO_3 aq. (51)	H_2SO_4 aq. (46)	$HClO_4$ aq. (46)	H_3PO_4 aq. (55)	HF aq. (7)	$C_6H_5SO_3H$ in HCOOH (47)	H_2SO_4 in CH_3COOH
By direct extrapolation[a]									
p-Aminoazobenzene	2.77	2.76 (51) 2.78 (6)			2.78 (6)				
m-Nitroaniline	2.50	2.43 (16)[b] 2.50 (6) 2.57 (4)							
2,4-Dichloroaniline	2.00	2.00 (77)							
Benzeneazodiphenylamine	1.42	1.42 (51)							
p-Nitroaniline	0.99	1.03 (51) 0.99 (77) 1.01 (6) 0.98 (54) 0.95[c]	1.03		0.97				
Diphenylamine	0.78	0.78 (77)							
By stepwise comparison (with ultimate reference to *p*-nitroaniline, $pK_{BH^+} = 0.99$)									
p-Naphtholbenzein	0.41[d]								
2,4-Dinitro-*N*,*N*-diethylaniline	0.18[e]								
2,6-Dichloro-4-nitro-*N*,*N*-dimethylaniline	−0.23[e]								
o-Nitroaniline[f]	−0.29	−0.29 (51)	−0.32	−0.25	−0.31	−0.22	−0.27		
4-Chloro-2-nitroaniline[g]	−1.03	−1.03 (51)	−1.09	−0.97	−1.03	−1.01	−1.03	−1.06	−1.03 (78)
4-Chloro-2-nitro-*N*-methylaniline	−1.49[e]								
p-Nitrodiphenylamine	−2.48	−2.47 (9)		−2.50		−2.26		−2.63	
2,4-Dichloro-6-nitroaniline	−3.32			−3.34	−3.30	−3.10		−3.43	−3.79 (41)
p-Nitroazobenzene	−3.47			−3.47	−3.47			−3.41	
2,6-Dinitro-4-methylaniline	−4.44			−4.44					−4.57 (41)
2,4-Dinitroaniline	−4.53			−4.50	−4.55				
N,*N*-Dimethyl-2,4,6-trinitroaniline[h]	−4.81			−4.81					−4.85 (41)
Benzalacetophenone[h]	−5.73			−5.73					
β-Benzoylnaphthalene	−6.04			−6.04					
p-Benzoylbiphenyl	−6.31			−6.31					
6-Bromo-2,4-dinitroaniline	−6.71			−6.71					
Anthraquinone	−8.27			−8.27					
2,4,6-Trinitroaniline	−9.41			−9.41					
p-Nitrotoluene	−10.46			−10.46 (10, 12)					
Nitrobenzene[i]	−11.38			−11.38 (10)					
2,4-Dinitrotoluene	−12.78			−12.78 (12)					

[a] By the method indicated in figures 2 and 3 from data published in the references cited.

[b] Given as 2.52 in reference 98.

[c] Reference 14, as given by the author; see, however, figure 2.

[d] Determined with perchloric acid in glacial acetic acid (93).

[e] Determined with perchloric acid in glacial acetic acid (61).

[f] $pK_{BH^+} = -0.36$ in trichloroacetic acid–water and −0.25 in trifluoroacetic acid–water (83).

[g] $pK_{BH^+} = -1.06$ in trifluoroacetic acid–water (83).

[h] These are probably not satisfactory indicators, judging by the departure of their ionization curves from parallelism with those of other indicators (see figure 1). The indicator *N*,*N*-dimethyl-2,4,6-trinitroaniline shows similar eccentricity in solutions of sulfuric acid in anhydrous acetic acid (reference 41 and figure 10).

[i] pK_{BH^+} values for other substituted nitrobenzenes are given in reference 12.

satisfactory answer to the second form of test mentioned previously. It is noteworthy, for example, that pK_{BH^+} for *o*-nitroaniline given by a direct extrapolation of the perchloric acid data in figure 3 is in good agreement with the values given by stepwise comparison in the other media. The second column of table 1 gives "best" values for pK_{BH^+} based on all the available evidence. Since it is desirable that all H_0 values should be based on the same reference state, one of infinite dilution in water, these "best" pK_{BH^+} values should be used uniformly for all media.

C. Justification and limitations of the H_0 acidity scale

The two experimental tests discussed above for the validity of the determination of pK values are also direct justification of the concept of an H_0 acidity scale. The general parallelism of the plots of figures 1 and 3 strongly suggests that all the indicators are measuring the same property of the solutions, a property which is apparently not a function of the indicator used. This same conclusion is also indicated by application of a more explicit comparison of slopes for adjacent indicators in the manner proposed by Deno, Jaruzelski, and Schriesheim (23). The fact that studies with aqueous solutions of several different strong acids result in almost identical values of pK_{BH^+} for the various indicators (columns 3 to 6 of table 1) shows that the equality

$$\frac{f_{\mathrm{B}}}{f_{\mathrm{BH}^+}} = \frac{f_{\mathrm{C}}}{f_{\mathrm{CH}^+}}$$

holds for pairs of indicators in solutions of quite different character. These points lead to the conclusion that H_0 as defined in equation 2 is independent of the indicator used and in this sense appears to be a property only of the solution being measured.

The indicators of figure 1 and table 1 involve some marked variations in structure. They include amines, azo compounds, ketones, and quinones. At the same time they possess many points of similarity. They are of approximately the same molecular size and are all aromatic compounds. In fact, the large majority are nitroanilines. It is certainly possible and even probable that indicators of markedly different size or type, for example, an aliphatic amine, might not give the same results as does this group. Even within this limited group there are clear examples of individual behavior. Thus in figure 1 curves (i) and (j) are clearly not parallel to their neighbors. Use of the two indicators concerned, *N*,*N*-dimethyl-2,4,6-trinitroaniline and benzalacetophenone, could quite evidently lead to different values of H_0. One may safely predict that similar discrepancies will show up if studies are made of other indicators with widely different size or structure.

As another example of specific behavior, two of the pK_{BH^+} values obtained from studies with aqueous phosphoric acid differ by about 0.2 unit from the values obtained with other aqueous solutions (table 1). This type of behavior is very evident for solutions in nonaqueous and mixed solvents. It is difficult to escape the conclusion that an H_0 acidity function may be experimentally justifiable for one solvent but not for some other. For the particular case of aqueous solutions of strong acids, the data of the previous section constitute ample evidence that an adequately general H_0 function does exist. For other solvents, even aqueous solutions of weak acids, for example, the question of an H_0 function which is reasonably independent of the choice of indicator can only be answered by experiment.

III. VALUES OF H_0 FOR AQUEOUS SOLUTIONS

A. "Strong" acids

Most of the data on the acidity function for aqueous solutions of the more common strong acids go back to the original studies of Hammett, Deyrup, and Paul. These studies were made by colorimetric methods, using the indicators of figure 1. More recently, studies have been made of aqueous solutions of hydrochloric acid (9), of phosphoric acid (55, 81), and of hydrofluoric acid (7), again with some of the indicators of figure 1 but using spectrophotometric measurement of the indicator ratio. All these data have been replotted and tables of "best values" of the acidity function have been prepared. Two different ideas have guided the presentation of the data. One is the belief that, at least for not too concentrated solutions of the strong acids, the most useful concentration unit is moles per liter. The second is the belief that, since pK values are by definition constant (at a constant temperature) and independent of the medium, it is desirable to use a single, consistent set of pK values. Specifically, the "best values" given in table 1 have been used for all calculations of H_0. The result is that the H_0 values in the subsequent tables differ from those of previous tabulations by small but varying amounts. For example, with most of the indicators used for aqueous solutions of sulfuric acid the H_0 values of the authors are more negative than those of Hammett (44) by 0.12 unit. However, with *o*-nitroaniline they are more negative by 0.16 unit and with 4-chloro-2-nitroaniline they are more negative by 0.18 unit. Similar fluctuations enter for other solutions.

Data for aqueous solutions of six common acids are presented in table 2. When available, values of H_0 are given for concentrations of from 0.1 to 10 M. These data will permit construction of graphs for satisfactory interpolation to give intermediate values of H_0. It is difficult to assign meaningful estimates of error in table 2, but it is doubtful whether even relative values of H_0 should ever be considered as known to better than ±0.05 outside of the dilute aqueous range. In some cases the margin of error is considerably greater than this.

Figure 4 gives a plot of H_0 vs. molarity for these acids. The order of acid strength which this plot suggests is consistent with accepted notions. Thus perchloric acid is generally considered to be slightly the strongest of these, followed closely by sulfuric acid, and then by hydrochloric and nitric acids (52, 90). The other two acids, phosphoric and hydrofluoric, give distinctly less acid solutions as judged by the H_0 values. Since in dilute aqueous solution these two acids are known to be measurably weak [$pK_{H_3PO_4} = 1.85$ (80) and $pK_{HF} = 3.17$ (17)], this is the expected result. The molarity scale may be somewhat

TABLE 2

H_0 at selected molarities of aqueous solutions, 25°C.

Acid Concentration	Acid					
	HNO_3	HCl	$HClO_4$	H_2SO_4	H_3PO_4*	HF
moles per liter						
0.1	+0.98	+0.98	—	+0.83	+1.45	—
0.25	+0.55	+0.55	—	+0.44	+1.15	—
0.5	+0.21	+0.20	—	+0.13	+0.97	—
0.75	−0.02	−0.03	−0.04	−0.07	+0.78	—
1.0	−0.18	−0.20	−0.22	−0.26	+0.63	+1.20
1.5	−0.45	−0.47	−0.53	−0.56	+0.41	+1.04
2.0	−0.67	−0.69	−0.78	−0.84	+0.24	+0.91
2.5	−0.85	−0.87	−1.01	−1.12	+0.07	+0.74
3.0	−1.02	−1.05	−1.23	−1.38	−0.08	+0.60
3.5	−1.17	−1.23	−1.47	−1.62	−0.22	+0.49
4.0	−1.32	−1.40	−1.72	−1.85	−0.37	+0.40
4.5	−1.46	−1.58	−1.97	−2.06	−0.53	+0.34
5.0	−1.57	−1.76	−2.23	−2.28	−0.69	+0.28
5.5	−1.69	−1.93	−2.52	−2.51	−0.84	+0.21
6.0	−1.79	−2.12	−2.84	−2.76	−1.04	+0.15
6.5	−1.89	−2.34	−3.22	−3.03	−1.24	+0.08
7.0	−1.99	−2.56	−3.61	−3.32	−1.45	+0.02
7.5		−2.78	−3.98	−3.60	−1.66	−0.04
8.0		−3.00	−4.33	−3.87	−1.85	−0.11
8.5		−3.21	−4.69	−4.14	−2.04	−0.17
9.0		−3.39	−5.05	−4.40	−2.22	−0.24
9.5		−3.54	−5.42	−4.65	−2.40	−0.30
10.0		−3.68	−5.79	−4.89	−2.59	−0.36

* Studies at 19°C.

Added in proof: Values of H_0 have recently been reported for aqueous hydrobromic acid solutions (98a). All data were obtained spectrophotometrically at temperatures between 22°C. and 26°C. Corrected to the same reference basis as tables 1 and 2 the results at rounded molarities are as follows:

C_{HBr}	H_0	C_{HBr}	H_0	C_{HBr}	H_0
moles per liter		*moles per liter*		*moles per liter*	
0.1	0.98	3	−1.11	7	−2.85
0.5	0.20	4	−1.50	8	−3.34
1	−0.20	5	−1.93	9	−3.89
2	−0.71	6	−2.38	10	−4.44

In addition to the indicators of table 1 the investigators used 5-chloro-2-nitroaniline, for which they obtained $pK_{BH^+} = -1.52$ (corrected to the scale of table 1). They report measurements also for aqueous hydrochloric acid; H_0 values for the higher molarities are as follows:

C_{HCl}, moles per liter	6	7	8	9	10	11	12	13
H_0	−2.12	−2.50	−2.86	−3.22	−3.59	−3.99	−4.41	−4.82

These results show a slightly more consistent trend than those listed in table 2 (9).

misleading in the case of hydrofluoric acid, since this substance is supposed to be dimerized to a considerable extent at the higher concentrations (79).

H_0 values are available at higher concentrations than 10 M for hydrofluoric (7),[4] phosphoric (55), and sulfuric acids. Data for the latter are discussed in a later section.

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[4] Values for hydrofluoric acid covering the entire range of aqueous compositions have very recently been reported by Kilpatrick and Hyman (56a), using the aromatic hydro-

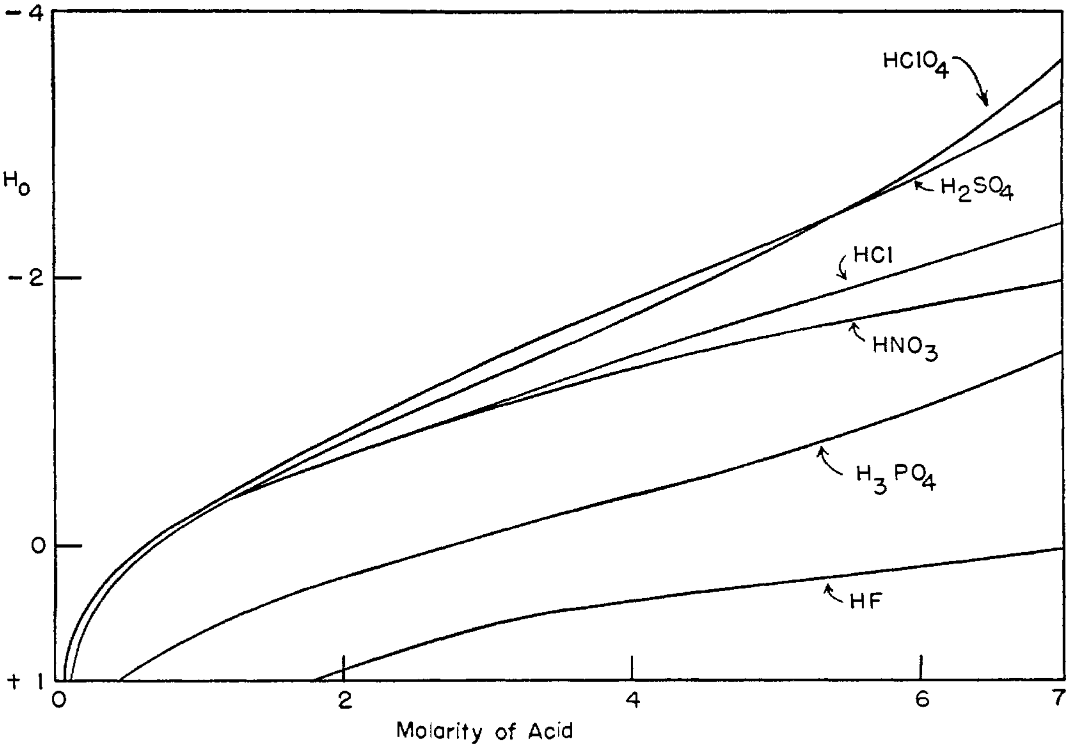

FIG. 4. H_0 for aqueous solutions of acids

For a typical strong monobasic acid such as perchloric, the distinctive feature of H_0 is the rapid increase of $-H_0$ as compared with log C_{H^+} (see figure 5). Although one can quite properly accept H_0 as a measured quantity on a purely empirical basis, it is still instructive to speculate about its detailed makeup. Writing H_0 as

$$-H_0 = \log C_{H^+} + \log f_{H^+}/f_{BH^+} + \log f_B \tag{8}$$

one can ask about the relative importance of the three terms on the righthand side of equation 8. From figure 5 it is apparent that at high molarities log C_{H^+} accounts for only a modest fraction of the total magnitude of $-H_0$. The last term, log f_B, represents the salt effect of the strong acid on the neutral base, B. From general studies of salt effects on nonelectrolytes (64) it is reasonable to conclude that the acids hydrochloric, nitric, sulfuric, and perchloric have little general tendency either to salt in or salt out. One may tentatively conclude that for these acids the term log f_B makes only a small contribution to H_0. Thus a large part of the departure of $-H_0$ from log C_{H^+} must be due to the term log $_{H^+}/f_{BH^+}$. It is at least plausible that this term is large and positive at high acid concentrations, since various studies suggest that the influence of electrolyte concentration on the activity coefficient of a small cation can become very large relative to that on a large cation.

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carbons benzene, mesitylene, and hexamethylbenzene as indicators. The value of H_0 for the anhydrous acid is -9.9.

It is also instructive to note in figure 5 that for perchloric acid the acidity as measured by H_0 increases considerably faster than does $\log a_{\pm}$, where $a_{\pm}$ is the mean ionic activity (85). This is not surprising, since $\log a_{\pm}$ measures the average escaping tendency of both ions, whereas $-H_0$ is more nearly a measure of the escaping tendency of hydrogen ions only.

Kuivila (60) has recently reported that for aqueous solutions of the three acids phosphoric, perchloric, and hydrochloric (but not for sulfuric), there is a linear correlation between $-H_0$ and $\log (a_{HX}/a_{H_2O})$ of the form:

$$-H_0 = \alpha + \beta \log \frac{a_{HX}}{a_{H_2O}}$$

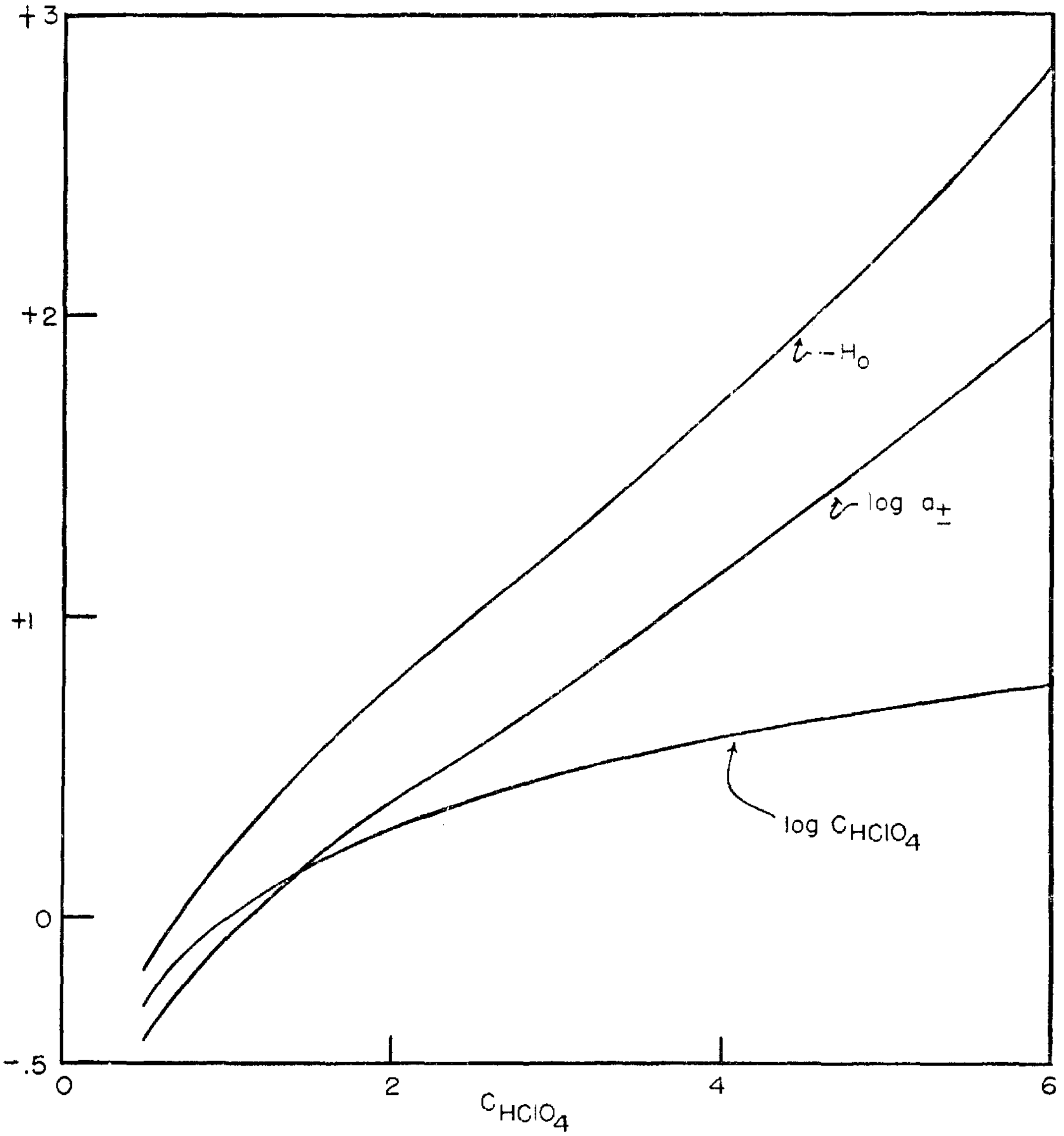

FIG. 5. Comparison of $-H_0$ (46) and $\log a_{\pm}$ (85) with $\log C$ for aqueous perchloric acid

TABLE 3

H_0 for selected percentages of sulfuric acid in water, 25°C.

H_2SO_4	$-H_0$	H_2SO_4	$-H_0$	H_2SO_4	SO_3	$-H_0$
per cent		*per cent*		*per cent*	*per cent*	
10	0.31	80	6.97	100.0	0.00	11.10
15	0.66	85	7.66	100.1	0.44	11.30
20	1.01	90	8.27	100.2	0.89	11.43
25	1.37	95	8.86	100.3	1.33	11.52
30	1.72	96	8.98	100.5	2.22	11.66
35	2.06	97	9.14	100.7	3.11	11.75
40	2.41	98	9.36	101.0	4.44	11.82
45	2.85	99	9.74	101.5	6.66	11.95
50	3.38	99.3	9.89	102.0	8.9	12.06
55	3.91	99.5	10.03	102.5	11.1	12.18
60	4.46	99.7	10.22	103	13.3	12.28
65	5.04	99.8	10.36	104	17.8	12.47
70	5.65	99.9	10.59	105	22.2	12.62
75	6.30	100.0	11.10	106	26.6	12.74
				107	31.1	12.87

Actually, Kuivila made his calculations with a_{HX}, the activity of the solute, only for the case of phosphoric acid, and in this case the data refer specifically to the activity of the undissociated species. With the other three acids the quantity used for a_{HX} was in fact $m\gamma_{\pm}$, which for hydrochloric and perchloric acids is $a_{\pm}$ or $\sqrt{a_{HX}}$ and which for sulfuric acid is $(a_{H_2SO_4}/4)^{1/3}$. In view of these complications it is difficult to ascribe any general significance to the reported correlations.

A quite different sort of correlation with H_0 was noted by Michaelis and Granick (72), who showed that a measurement of the E.M.F. of certain cells involving dyestuffs in aqueous sulfuric acid gave an acidity scale which was reasonably parallel to H_0. The systems are quite complex and no interpretation of the correlation was attempted.

B. Concentrated solutions of sulfuric acid

Values of H_0 were determined by Hammett and Deyrup for water–sulfuric acid mixtures up to and including anhydrous sulfuric acid. These data have recently been extended to "oleum" solutions of as high as 107 per cent sulfuric acid, i.e., 32 weight per cent sulfur trioxide in anhydrous sulfuric acid (10, 12). Figure 6 gives a plot of the sulfuric acid data for the complete concentration range. Table 3 gives selected H_0 values for solutions containing 10 per cent or more of sulfuric acid, with emphasis on solutions of from 99 to 107 per cent sulfuric acid. These latter data are of considerable interest, both because of the very high acidity and because of the continuous nature of the function in going from solutions of water in sulfuric acid to those of sulfur trioxide in sulfuric acid.

Data are also available for the acidity of solutions of potassium sulfate and of barium di(methylsulfate) in various oleum solutions (10). As expected, these salts decrease the acidity of the oleum mixtures.

Lewis and Bigeleisen (62) have reported H_0 data for solutions of sulfur trioxide

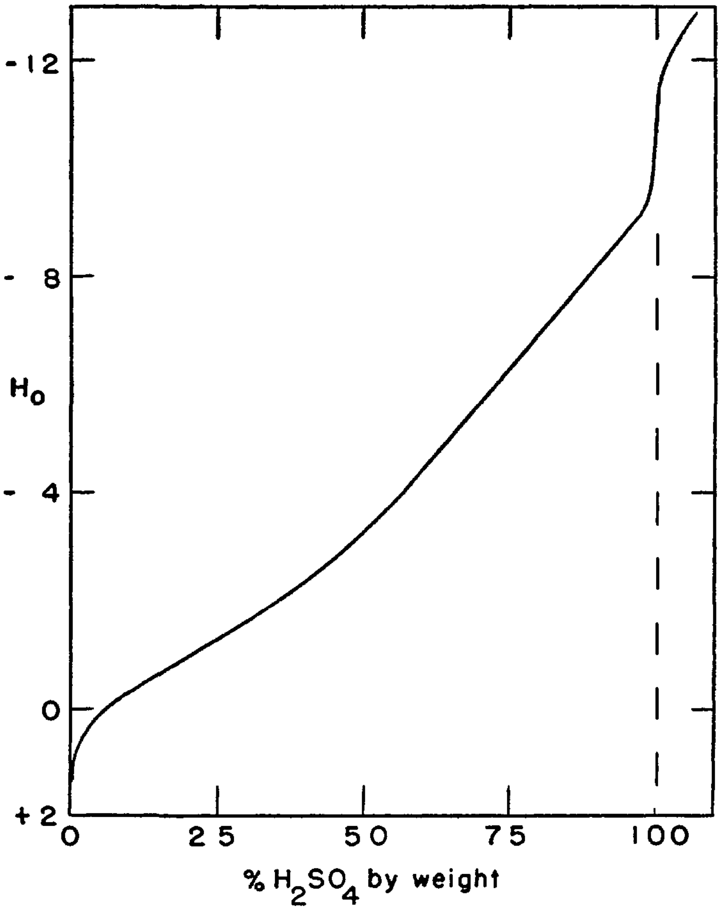

FIG. 6. H_0 for mixtures of sulfuric acid with water and with sulfur trioxide (12, 46)

in anhydrous sulfuric acid. However, the indicator used is not an uncharged base, so it is perhaps not surprising that agreement with the data of Brand is poor. No weight has been given either to the Lewis and Bigeleisen values of H_0 or to the interpolated values of them as tabulated by Coryell and Fix (18). One of the proposals of these investigators (18, 62) is that for fuming sulfuric acid, the value of $-H_0$ increases at the same rate as log p_{SO_3}, where p_{SO_3} is the vapor pressure of sulfur trioxide in the oleum. Actually, a comparison of Brand's $-H_0$ data with values of log p_{SO_3} (13) shows that the proposed parallel behavior does not occur; log p_{SO_3} (at 50°C.) for the range 4 to 30 per cent sulfur trioxide increases distinctly more rapidly than does $-H_0$. This is not really surprising, since there is no particular reason to expect the indicator acidity to be determined solely by the activity of the sulfur trioxide.

Deane (20) has suggested that the value of H_0 for fuming sulfuric acid could be obtained from kinetic data for the decomposition of *o*-benzoylbenzoic acid in this medium. In view of the existence of Brand's indicator studies, this suggestion has not been followed.

The indicator acidity function increases quite smoothly for increasing concentrations of sulfuric acid. Even so, it must be noted that the absolute values of H_0 cannot be considered to be very firmly established beyond about 75 per cent sulfuric acid. The reason is that beyond this there are two places where the overlap in the ranges of the indicators is so poor as to make the pK value of the weaker base somewhat doubtful. As figure 1 shows, a poor overlap occurs between indicators (g) [or (l)] and (m) and again between indicators (n) and (o). It will be very desirable to discover some additional indicators for these acidity regions and use them to establish the acidity scale more certainly.

Brand (10) and also Deno and Taft (25) have attempted to account for the change of H_0 with acid concentration in the region just below 100 per cent sulfuric acid in terms of the ionization reaction:

$$H_2SO_4 + H_2O = H_3O^+ + HSO_4^-$$

The equimolar H_2SO_4:H_2O composition corresponds to 84.5 per cent acid. Brand showed that between 90 and 99.8 per cent acid, H_0 satisfies closely the relationship:

$$H_0 = -8.48 + \log \frac{x_{HSO_4^-}}{x_{H_2SO_4}}$$

where the mole fractions, $x_{HSO_4^-}$ and $x_{H_2SO_4}$, are computed on the basis that the ionization reaction goes to completion (the constant term has been adjusted to the present H_0 scale by addition of -0.12 to the published value). Deno and Taft found that the range of the relationship could be extended down to 83 per cent acid by assuming for the ionization reaction an equilibrium constant of 50. The relationship of H_0 to the water concentration then assumes the form

$$H_0 = -6.78 + \log \frac{x_{H_2O}}{x_{H_3O^+}}$$

Deno and Taft interpret these results on the basis that the activity coefficients involved approach constancy in 83–99.8 per cent sulfuric acid solutions.

Solutions of chlorosulfonic acid in anhydrous sulfuric acid have also recently been investigated with the indicators p-nitrochlorobenzene and 2,4-dinitrotoluene (76b). The value of H_0 decreases steadily with increasing chlorosulfonic acid concentration, 100 per cent HSO_3Cl being more acid than 100 per cent H_2SO_4 by 1.89 logarithmic units. The value obtained for pK_{BH^+} of p-nitrochlorobenzene is -11.70 based on $H_0 = -11.10$ for 100 per cent H_2SO_4 (table 3), while the value for 2,4-dinitrotoluene corrected to the same basis is -12.95; this compares with -12.78 (table 1) derived from measurements with solutions of sulfur trioxide in anhydrous sulfuric acid (12).

C. *Effect of neutral salts on* H_0

Only a few systematic studies have been reported on the influence of added salts on the acidity function; the results are of considerable interest. Harbottle (53) studied a set of perchloric acid–sodium perchlorate solutions all at a total electrolyte concentration of 6 M. Table 4 gives the data corrected to the pK_{BH^+}

TABLE 4

The H_0 acidity function in aqueous perchloric acid–sodium perchlorate solutions

$HClO_4$	Added $NaClO_4$	H_0	$HClO_4$	Added $NaClO_4$	H_0
moles per liter	*moles per liter*		*moles per liter*	*moles per liter*	
6	0	−3.05	2	4	−1.84
5	1	−2.77	1	5	−1.46
4	2	−2.47	0.5	5.5	−1.11
3	3	−2.13	0.3	5.7	−0.85

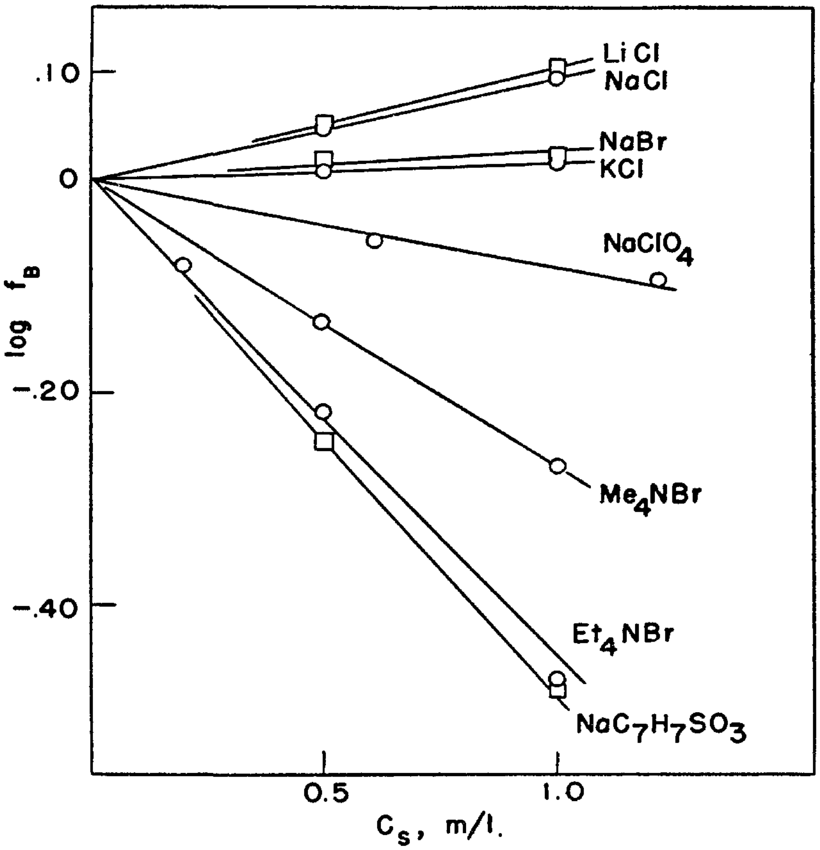

FIG. 7. Salt effects on the activity coefficient of *p*-nitroaniline (59, 65, 77)

values of table 1.[5] The striking point is the very large increase in $-H_0$ caused by the salt. For example, the addition of 5 M sodium perchlorate to 1 M perchloric acid causes $-H_0$ to increase from 0.22 to 1.46. Qualitatively an increase is to be expected according to equation 8, since the added salt should "salt out" the indicator; i.e., log f_B should increase and, as before, the term log (f_{H^+}/f_{BH^+}) should also increase with added electrolyte.

It is well known that the influence of salts on the activity coefficients of non-

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[5] The agreement between Harbottle's H_0 value of −3.05 for 6 M perchloric acid and the "best value" from table 2 of −2.84 is not very satisfactory, considering that the same indicators were used for the two studies.

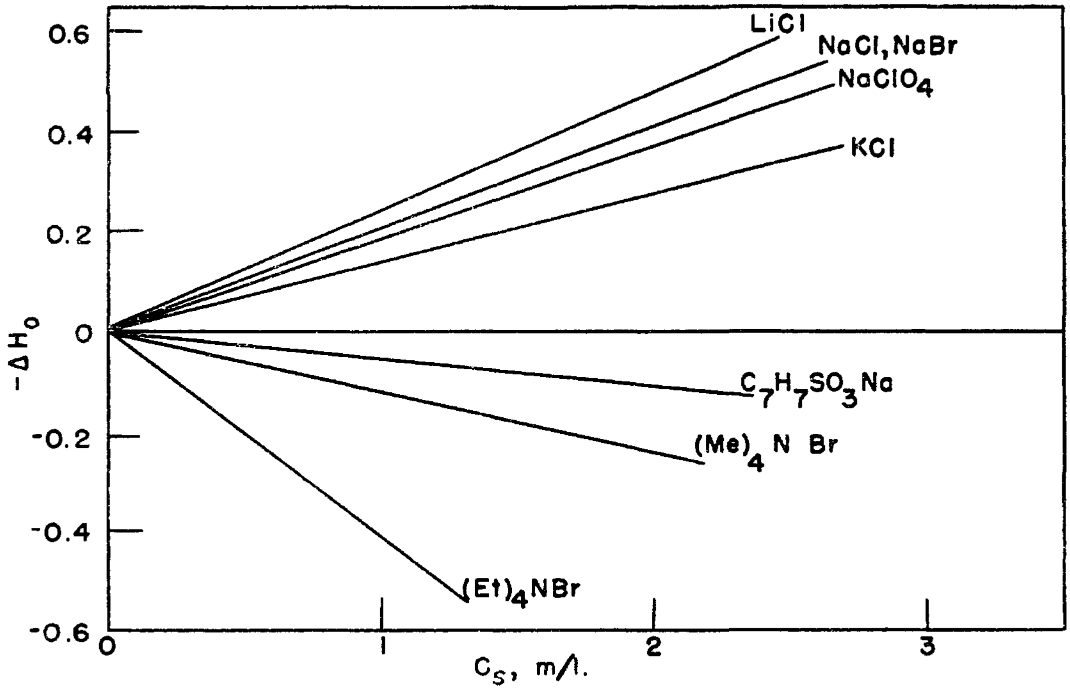

FIG. 8. Salt effects on H_0 of 0.1 *M* hydrochloric acid (65, 77). The indicator is *p*-nitroaniline.

electrolytes depends markedly on the salt (64, 71). Figure 7 shows, for example, how salts affect the activity coefficient of the indicator base *p*-nitroaniline, as determined from solubility measurements (59, 65). One obtains typically a linear relationship between $\log f_B$ and the salt concentration, C_s, and while the particular order observed in figure 7 is more characteristic of nitro compounds than of nonelectrolytes in general (64), the tendency is for the larger ions to salt in (more negative effect on $\log f_B$) as compared with the smaller ions. One would therefore certainly predict that salts would have specific effects on H_0 through the $\log f_B$ term in equation 8 and perhaps through the term $\log (f_{H^+}/f_{BH^+})$ as well.

Paul (77) has reported studies of salt effects on H_0 with several indicators in 0.01, 0.1, and 1 *M* aqueous hydrochloric acid solutions. The results for *p*-nitroaniline in 0.1 *M* hydrochloric acid are summarized in figure 8. One sees that the effects of the various salts are indeed specific and follow much the same order as their effects on $\log f_B$; the conspicuous differences between the salt orders occur in the cases of sodium perchlorate and sodium *p*-toluenesulfonate, both of which have relatively large anions and both of which show a larger relative tendency to salt in the neutral base than would be suggested by their effects on H_0.

Since both the salt effect on $\log f_B$ and the salt effect on H_0 are linear in the salt concentration, C_s, one may profitably compare the slopes of the corresponding $-\Delta H_0$ vs. C_s and $\log f_B$ vs. C_s relationships;

$$-\Delta H_0 = \alpha C_s \tag{9}$$

$$\log f_B = k_B C_s \tag{10}$$

TABLE 5

Comparison of salt effects on $-H_0$ *and on* $\log f_B$ *for the indicator p-nitroaniline in 0.1 M hydrochloric acid*

Salt	Slope, α, Equation 9* (from Figure 8)	Slope, k_B, Equation 10* (from Figure 7)	Difference
NaBr	0.205	0.040	0.17
LiCl	0.245	0.082	0.16
NaCl	0.205	0.072	0.13
KCl	0.145	0.030	0.12
$(CH_3)_4NBr$	−0.12	−0.272	0.15
$(C_2H_5)_4NBr$	−0.41	−0.44	0.03
$C_7H_7SO_3Na$	−0.06	−0.51	0.45
$NaClO_4$	0.180	−0.082	0.26

* The reference solution for $-\Delta H_0$ is 0.1 *M* hydrochloric acid; the reference for $\Delta \log f_B$ is the saturated solution of the indicator in pure water. The difference is not significant for the present purpose.

where in this case

$$\Delta H_0 = (H_0)_{0.1\ M\ \mathrm{HCl} + \mathrm{salt}} - (H_0)_{0.1\ M\ \mathrm{HCl}}$$

and where k_B is the conventional salting-out parameter (64). The comparison is shown in table 5. The last column gives the difference between α and k_B, which according to equation 8 must represent the slope of the hypothetical $\log (f_{H^+}/f_{BH^+})$ vs. C_s relationship at the given acid concentration. One sees that this latter quantity is positive in magnitude for the given indicator and is considerably less dependent on the particular electrolyte than is the effect on H_0 itself. We may reasonably conclude that increasing the acid concentration itself in the absence of added salt will have a similar effect on this term, thus accounting in part at least for the difference between $-H_0$ and $\log C_{H^+}$ at high acid concentrations, as noted in Section III,A.

Paul (77) has also reported that the salt effects on H_0 are dependent on the indicator. Thus the slope, α, of the $-\Delta H_0$ vs. C_s relationship is about 20 per cent greater for diphenylamine than for *p*-nitroaniline. The difference consists almost entirely of an observed difference in the term $\log f_B$. Such specific effects on the different indicators are not observed with the strong acids (sulfuric, perchloric, hydrochloric, nitric). It is likely that their "salt" effects on $\log f_B$ are small in magnitude (64, 65) and therefore show little relative variation from one indicator to another.

Another study of the influence of salts on the acidity function has been reported by Moiseev and Flid (29, 73). They have used the single indicator *p*-nitroaniline and discuss their results in terms of the measured variation in the indicator ratio, C_{BH^+}/C_B. They utilize the equation

$$y = \mathrm{p}K_{BH^+} + \log C_{H^+} + L\mu \tag{11}$$

where y is defined as $\log (C_{BH^+}/C_B)$, μ is the ionic strength due to the added salt (in moles per liter units), and L is the slope of y vs. μ.[6] From the definition of

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[6] An abstract (Chemical Abstracts **49**, 7327 (1955)) erroneously states that in the paper by Moiseev and Flid (73) "an acidity function y is defined as $y = \log C_{H^+} + \mathrm{p}K_a + L\mu$." Actually, y is defined as $\log (C_{BH^+}/C_B)$ and is determined from experiment. The unknown defined by this equation is the parameter L for the salt effects.

H_0 it follows that for 1:1 electrolytes at a constant value of C_{H^+}, the slope L and the slope α of equation 9 should be identical. In one set of experiments Moiseev and Flid utilize a constant acid concentration of 1.075 M hydrochloric acid and determine the effect on y of adding potassium chloride (1.57–2.65 M), calcium chloride (0.517–1.02 M), and magnesium chloride (0.35–1.6 M). These three salts all give a linear plot of y vs. $\Delta\mu$ and lead to the same L value of 0.10. The values of y for solutions of hydrochloric acid itself, with concentrations of from 0.86 to 3.2 M, are also fairly well in agreement with equation 11, using this same value of $L = 0.10$. Put another way, one can approximately treat the departure of $-H_0$ from log C_{H^+} for hydrochloric acid as a salt effect of similar magnitude to that caused by potassium chloride.

These studies with hydrochloric acid are at least roughly in agreement with those of Paul (77). For example, using p-nitroaniline as the indicator, Paul reports for the addition of potassium chloride to solutions of 0.1 M hydrochloric acid a slope of $-\Delta H_0$ vs. C_s of 0.14; with the indicator o-nitroaniline and solutions of 1 M hydrochloric acid containing added potassium chloride the slope is again 0.14. This value is to be compared with Moiseev and Flid's value of $L = 0.10$. Paul also reports (77, Fig. 3) that the "salt effect" of hydrochloric acid itself on values of H_0 (using o-nitroaniline as indicator) is very similar to the salt effects of potassium and sodium chlorides. However, Paul does emphasize the specificity of salt effects, whereas Moiseev and Flid at least implicitly assume an L value which is independent of choice of salt. Presumably this difference of viewpoint results from the fact that Paul deliberately studied salts with widely differing anions and cations and hence found widely different salt effects.

Moiseev and Flid have made similar studies with sulfuric acid, alone and with added salts (both sulfates and nonsulfates). Most sulfates cause a decrease in the observed values of y, obviously because of a lowered acidity due to the reaction $H^+ + SO_4^= = HSO_4^-$. One exception is mercuric sulfate, whose addition causes a marked increase in y. This is interpreted in terms of formation of the complex anion, $Hg(SO_4)_2^=$.

D. *"Weak" acids*

The acids considered in this section are in fact somewhat stronger than phosphoric and hydrofluoric acids, which were discussed earlier. This is evident from table 6, which compares pK values for all of these acids. The characteristic of the present group, then, is not their weakness as such but the observed lack of dependence of H_0 on concentration which they all exhibit at intermediate concentration ranges. Figure 9 is a plot of the H_0 data and includes the curve for perchloric acid from figure 4 for comparison.

The data for dichloroacetic acid and potassium hydrogen sulfate are those of Bell and Brown (8). The only correction has been to subtract 0.12 from their recorded H_0 values to make them consistent with the pK_{BH^+} values in table 1. The data for trichloro- and trifluoroacetic acids (83) have been recalculated to molar concentrations from the original mole-fraction basis[7] and have been

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[7] Densities for aqueous trichloroacetic acid solutions at 25°C. are given in the *International Critical Tables*, Vol. III, p. 111. Densities for solutions of trifluoroacetic acid

TABLE 6

Ionization constants of weak electrolytes

Acid	pK_a	T	Reference	Acid	pK_a	T	Reference
		°C.				°C.	
CF_3COOH	Strong	25	(56)	$CHCl_2COOH$	0.85	0	(84)
					(1.06)*	25	
CCl_3COOH	0.64	25	(84)	H_3PO_4	2.12	25	(80)
$KHSO_4$	2.00	25	(84)	HF†	3.17	25	(17, 79)

* Estimated.

† Broene and DeVries (17) give $K = 4.0$ for the reaction

$$F^- + HF = HF_2^-$$

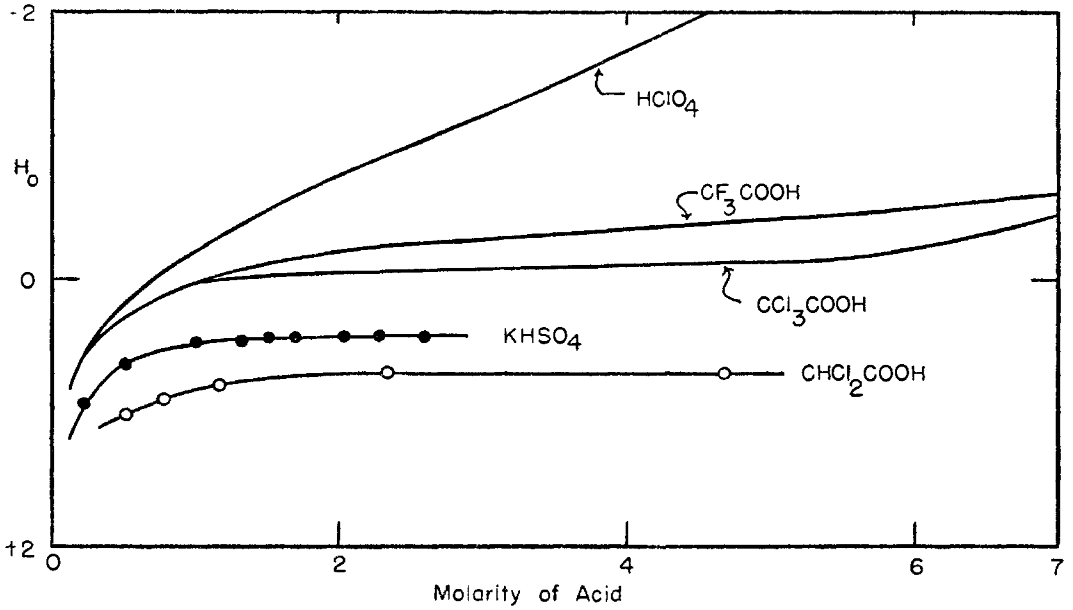

FIG. 9. H_0 for aqueous solutions of weak acids (8, 83)

corrected to be in accord with the pK values of table 1. Besides these weak acids, measurements of H_0 have been obtained for a wide range of aqueous solutions of formic, acetic, chloroacetic, methanesulfonic, and orthophosphorous acids (6).

Hammett and Paul (51) give three H_0 determinations for solutions of trichloroacetic acid. These show a similar lack of dependence of H_0 on concentration but fall about 0.5 unit below the curve of figure 9. This disagreement stands unexplained.

At concentrations of around 0.2 M, the relative acid strengths as judged from figures 4 and 9 for the weak acids are in reasonable accord with the pK values of table 6. The largest H_0 values (lowest acidities) are for the weakest acids, phosphoric and hydrofluoric. The strongest acids, trifluoroacetic acid and trichloroacetic acid, give more acid solutions. Only potassium acid sulfate falls somewhat out of line.

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were estimated by the authors from those of trichloroacetic acid by taking into account the relative densities of the two acids in the liquid state.

The situation at higher concentrations (2 to 6 *M*) is quite different. The $-H_0$ values for phosphoric and hydrofluoric acids increase steadily with concentration (figure 4). In contrast, the acids of figure 9 exhibit broad concentration ranges where the acidity function changes almost not at all. As a result the relative acidities for, say, 6 *M* solutions are no longer even approximately in line with the p*K* values of table 6. A qualitative (and tentative) explanation for these results can be given in terms of the definition of H_0 as written in equation 8. Because of their small size and compact structure it is reasonable that phosphoric and hydrofluoric acids, whether ionized or nonionized, will have little effect on f_B, the activity coefficient of the uncharged indicator base, B. Hence the last term on the righthand side of equation 8 will not change much with concentration, and $-H_0$ will increase with acid concentration owing to an increase in the log C_{H^+} term and probably also to an increase in log (f_{H^+}/f_{BH^+}). The situation for the large acid molecules—dichloroacetic, trichloroacetic, and trifluoroacetic acids—should be quite different. One can expect "salting in" of the base, B, by both the ionized and the nonionized forms of the acid (64, 65, 71).[8] The result will be a decrease in the value of the term log f_B with increasing concentration of acid. The data of figure 9 suggest that this decrease roughly equals the increase in $-H_0$ from the terms log C_{H^+} and log (f_{H^+}/f_{BH^+}), leading to the approximate lack of dependence of H_0 on the concentration. Indirect support for the suggestion that the organic acids themselves will "salt in" the indicator (decrease f_B) and hence lower the indicator acidity is available from the work of Bartlett and McCollum (2), who find that the addition of small amounts of isopropyl alcohol to sulfuric acid–water mixtures causes a marked decrease in $-H_0$, as measured with the indicator 2,4-dinitroaniline.

The implication of this explanation is that for aqueous solutions of weak acids the experimental values of the acidity function may vary considerably for different indicators. This is so because the salting-in contribution, i.e., changes in log f_B, will vary with the nature of B and it is unlikely that changes in log (f_{H^+}/f_{BH^+}) will entirely compensate. In fact, the agreement between results for different indicators is not very good for either trifluoroacetic acid or trichloroacetic acid (83). With the former the data from *o*-nitroaniline are about 0.15 unit above those from *p*-nitroaniline and 4-chloro-2-nitroaniline. With trichloroacetic acid the data for *o*-nitroaniline lie about 0.1 unit below those for *p*-nitroaniline. Similar discrepancies are shown in table 1 for solutions of phosphoric acid. These facts cast doubt on the generality and utility of the H_0 function for such systems and further study is highly desirable.

IV. SOLUTIONS IN NONAQUEOUS AND MIXED SOLVENTS

One of the more important properties of the acidity function is that it can be utilized in nonaqueous solutions and the resulting acidities are automatically referred to the dilute aqueous reference state. However, it is also true that there

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[8] For brevity (and for want of a better term) the phrase "salting in" will be used to denote a decrease in the activity coefficient of an uncharged species, whether this decrease is caused by increased concentration of an electrolyte or of another nonelectrolyte molecule.

are added problems for either nonaqueous or mixed solvents, particularly for solvents with low dielectric constants, and for these cases it is generally necessary to reëxamine the validity of the acidity function concept. This point of view has been emphasized by Grunwald and coworkers (35, 37, 38) and by Bates and Schwarzenbach (5), particularly as a result of studies with ethanol–water mixtures. It will be considered in detail in Section IV,D.

A. Formic acid

H_0 measurements in anhydrous formic acid were reported by Hammett and Deyrup (47) for solutions of benzenesulfonic acid between 0.005 and 0.15 M, for sulfuric acid within the same concentration range, for sodium formate between 0.006 and 0.1 M, and for aniline within the same range. This solvent has a high dielectric constant, 58.5 at 16°C. (70). Sodium formate and aniline behave toward the indicators as completely ionized strong bases; sulfuric acid behaves as a completely ionized monobasic acid, while benzenesulfonic acid at 0.1 M concentration is only slightly weaker. These findings are consistent with potentiometric titration data in formic acid observed by Hammett and Dietz (49). The H_0 values range from -0.22 (corrected to the present $\mathrm{p}K_{\mathrm{BH}^+}$ scale) in 0.10 M sodium formate to -4.04 in 0.15 M benzenesulfonic acid. Self-ionization of the solvent is sufficiently extensive so that its own H_0 could be determined directly by indicator measurements; it has the value $H_0 = -2.21$ (47).

Aside from the generally high level of acidity, the most significant aspect of the results is the agreement of the $\mathrm{p}K_{\mathrm{BH}^+}$ values observed for the various indicators in formic acid with the values observed in aqueous solutions of strong acids (see table 1). This lends conviction to the idea that the different indicators are in fact measuring the same property of the solutions and that H_0 values in this medium are directly referable to values obtained in aqueous solutions.

In dilute solutions of a sufficiently strong acid, A, in a relatively basic solvent, S, one can define $\mathrm{p}K^{\mathrm{S}}_{\mathrm{BH}^+}$ values for the indicators as follows:

$$\mathrm{p}K^{\mathrm{S}}_{\mathrm{BH}^+} = \lim_{C_{\mathrm{A}}\to 0}\left[\log\frac{C_{\mathrm{BH}^+}}{C_{\mathrm{B}}} - \log C_{\mathrm{H}^+}\right]_{\mathrm{in\ S}} \tag{12}$$

where $C_{\mathrm{H}^+} = C_{\mathrm{A}} - C_{\mathrm{BH}^+}$ and C_{A} represents the stoichiometric concentration of A in S. For a given indicator the connection between $\mathrm{p}K^{\mathrm{S}}_{\mathrm{BH}^+}$ and $\mathrm{p}K_{\mathrm{BH}^+}$ (defined as previously for the aqueous reference state) is then as follows:

$$\mathrm{p}K^{\mathrm{S}}_{\mathrm{BH}^+} - \mathrm{p}K_{\mathrm{BH}^+} = \log\frac{f^0_{\mathrm{B}}f^0_{\mathrm{H}^+}}{f^0_{\mathrm{BH}^+}} \tag{13}$$

where the activity coefficients represent the limiting values at infinite dilution in S relative to their values at infinite dilution in water. Application of equation 12 to the data of Hammett and Deyrup for solutions of the strong acids benzenesulfonic and sulfuric in formic acid leads, after allowance for the self-ionization of the solvent, to the empirical conclusion:

$$\mathrm{p}K^{\mathrm{HCOOH}}_{\mathrm{BH}^+} - \mathrm{p}K_{\mathrm{BH}^+} = 5.10$$

That is, $pK^{S}_{BH^+}$ for the conjugate acid of an uncharged base, B, in formic acid solutions may be calculated from the corresponding value of pK_{BH^+} in water simply by adding 5.10. The large magnitude of this number reflects the highly acid character of anhydrous formic acid as a solvent.

Values of H_0 for ether–formic acid mixtures of from zero to 65 per cent ether are reported by Plattner, Heilbronner, and Weber (82). As would be expected, the acidity drops sharply when ether is added to formic acid.

B. Acetic acid

Acetic acid has a much lower dielectric constant than formic acid (6.2 at 25°C. (94) as compared with 58.5). It is not surprising therefore to find that "strong" acids dissolved in this medium do not behave simply as completely ionized solutes; ion-pair association is probably widespread and the concept of hydrogen-ion concentration loses much of its significance. The various acids, in other words, show a much higher degree of specificity than is shown in media of higher dielectric constant or higher basicity. The problem of ion pairs in acetic acid has recently been discussed in some detail by Kolthoff and Bruckenstein (58). These authors have made studies with such indicators as *p*-naphtholbenzein and dimethylaminoazobenzene in anhydrous acetic acid and also in acetic acid containing small amounts of water; they conclude that not only ion pairs but also ion triplets and ion quadruplets must be present. Nevertheless indicator studies may be readily carried out and are capable of yielding useful information.

The most extensive set of H_0 measurements is by Hall and Spengeman (41), who investigated solutions of sulfuric acid in anhydrous acetic acid up to 8 *M* concentration by optical colorimetry. Their results (selected values) are shown in figure 10; results in substantial agreement for sulfuric acid concentrations between 0.002 and 1.6 *M* have been reported by Paul and Hammett (78). Gold and Hawes (32) have also obtained very similar results with the one indicator, 4-chloro-2-nitroaniline, at sulfuric acid concentrations between 0.18 and 0.95 *M*, using a spectrophotometer. In figure 10 "best" values of pK_{BH^+} from table 1 have been used for the indicators. One sees that a reasonably uniform H_0 scale is obtained for the various indicators with the exception of 2,4-dichloro-6-nitroaniline and *N*,*N*-dimethyl-2,4,6-trinitroaniline. The lack of parallelism of the results for the latter with the results for the other indicators is also shown in aqueous sulfuric acid solutions (see figure 1) and presumably reflects a fundamental unsuitability of this indicator. The H_0 values for 2,4-dichloro-6-nitroaniline run parallel with those obtained for the other indicators, but they are displaced by about 0.4 unit in the direction of lower apparent acidity.

One of the noteworthy aspects of the results with acetic acid is the relatively high acidity at given sulfuric acid concentrations as compared with aqueous solutions; a 1 *M* sulfuric acid solution in anhydrous acetic acid, for example, has $H_0 = -3.01$ as compared with $H_0 = -0.26$ in 1 *M* aqueous solution. This high acidity is in qualitative agreement with electrometric "pH" measurements obtained originally by Hall and Conant (39) using the chloranil electrode, although the indicators actually measure a rather different property of the solutions.

If one plots $-H_0$ against log C_A for solutions of sulfuric acid in acetic acid at concentrations below 0.1 *M*, a straight line with unit slope is obtained, corresponding to a limiting value of $H_0 + \log C_A = -2.69$ in infinitely dilute solution. This is the sort of behavior one would expect in ideal dilute solution if sulfuric acid were a strong 1:1 electrolyte. However, if one uses similar data for solutions of perchloric acid in anhydrous acetic acid (61) the limiting value of $H_0 + \log C_A$ is quite different, -4.00. Further studies (93) with a variety of "strong" acids in acetic acid containing a small concentration of dissolved water (0.12 per cent by weight) have shown that, for each, $-H_0$ is linear in log C_A with slopes that are close to unity (see figure 11). The lines, however, are markedly displaced from each other. For example, at $C_A = 10^{-3}$ *M*, the value of $-H_0$ for perchloric acid is 1.6 units greater than that for hydrochloric acid. This behavior suggests that one may be dealing with indicator equilibria involving ion pairs rather than simple solvated H^+ ion. Equation 12 appears therefore to be meaningless when applied to acetic acid. It will be of considerable interest to see if the variations in acidity shown in figure 11 lead to comparable variations in rates of acid-catalyzed reactions for these media.

Measurements of H_0 have also been reported for solutions in anhydrous acetic acid of the basic solutes urea and antipyrine and their buffer mixtures with sulfuric acid (40).

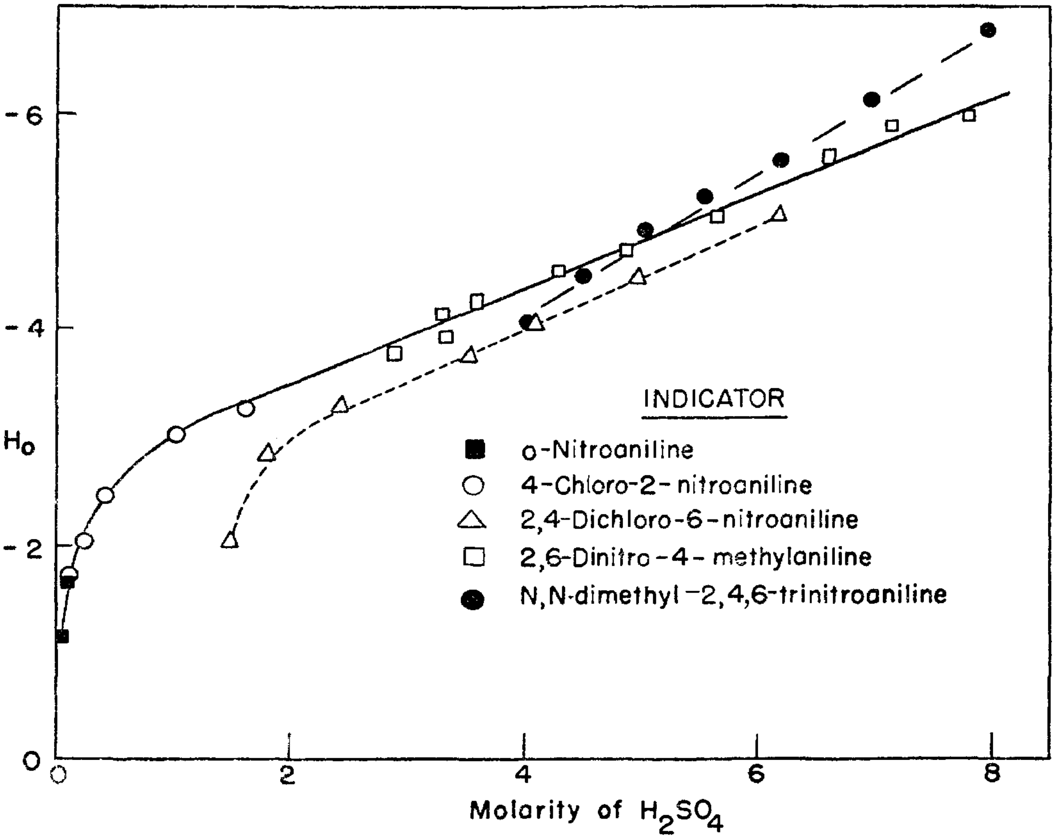

FIG. 10. H_0 for solutions of sulfuric acid in acetic acid (41)

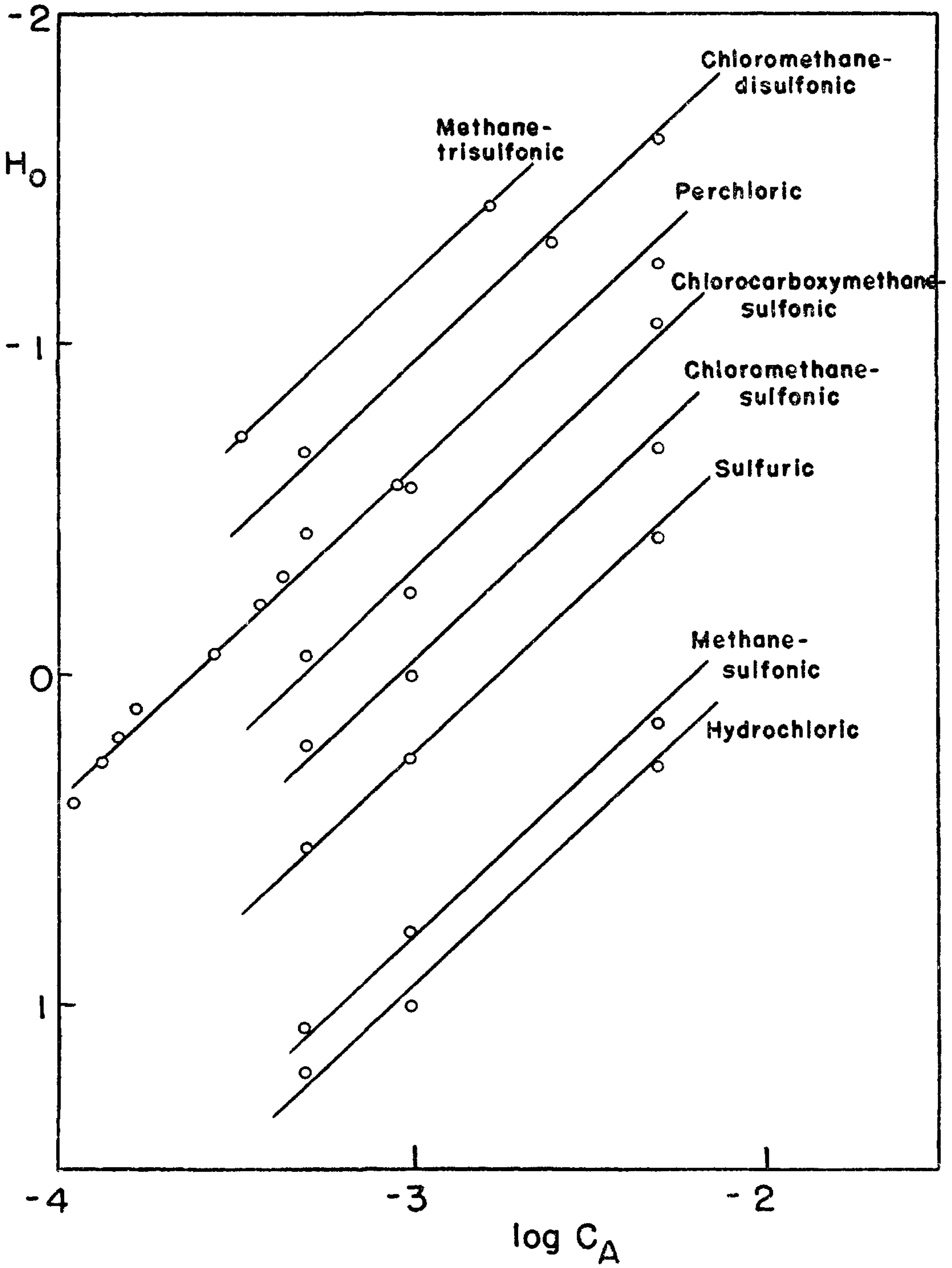

FIG. 11. H_0 for solutions of several acids in acetic acid containing 0.12 per cent water. Straight lines of unit slope have been drawn through the experimental points of Smith and Elliott (93).

The influence of water on H_0 in acetic acid solutions has been investigated for several situations. For solutions which contain a constant concentration of 0.001 *M* perchloric acid, addition of water causes a large decrease in acidity, since H_0 goes from -1.00 to $+1.93$ as the water content increases from 0 to 5

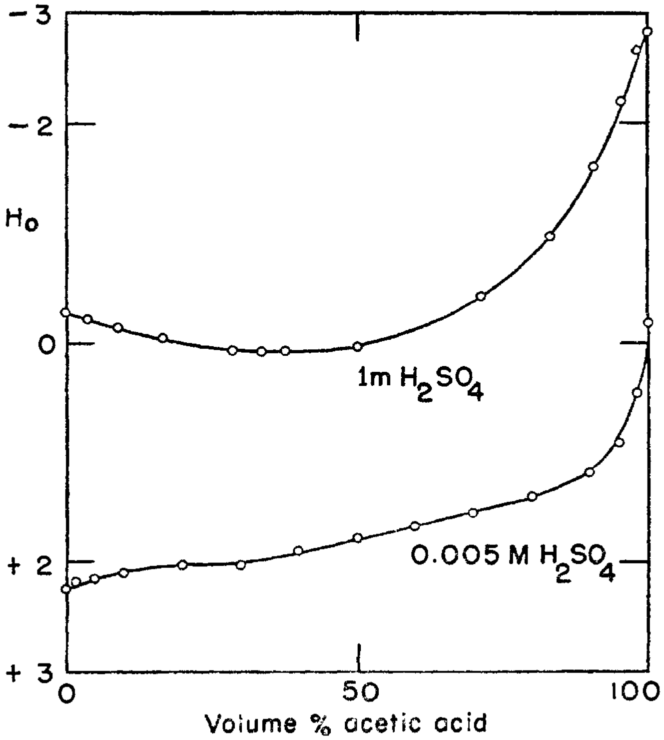

FIG. 12. H_0 for acetic acid–water mixtures containing sulfuric acid (76)

per cent (67). Somewhat similar results are shown for studies of phosphoric acid (concentrations ranging up to 15 per cent) in acetic acid solutions containing up to 6 per cent water (57).[9] Finally, a study is available of both 1 molal and 0.01 normal sulfuric acid in solutions ranging from pure water to pure acetic acid (76). In 0.01 normal sulfuric acid the value of $-H_0$ increases continually from -2.24 to $+0.18$ with increasing acetic acid concentration but in 1 molal sulfuric acid $-H_0$ passes through a shallow minimum at about 38 volume per cent acetic acid (figure 12). This may well be the result of a "salting-in" effect of acetic acid on the neutral indicator molecule, B (as in the case of the substituted acetic acids shown in figure 9). The acidity increases with still higher concentrations of acetic acid because the weaker acid, H_3O^+, is ultimately replaced by the stronger acid, $CH_3COOH_2^+$, while at the same time the decreasing dielectric constant of the medium takes effect (42).

C. Acetic acid–acetic anhydride

Mackenzie and Winter (68) report what they call "apparent H_0 values" for 0.078 *M* perchloric acid in acetic acid–acetic anhydride mixtures of from 20 to 90 volume per cent anhydride. Their conclusion, that the acidity increases with

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[9] *Note added in proof:* Additional data have been reported for perchloric and sulfuric acids at varying concentrations in acetic acid containing up to 15 per cent by weight of water (85b) and for hydrochloric and sulfuric acids in acetic acid containing 10 per cent by volume of water (76a); the indicators used in these various studies were *p*-nitroaniline, *o*-nitroaniline, and 4-chloro-2-nitroaniline.

increasing amounts of the anhydride, seems quite reasonable. However, the listed H_0 values are questionable, since the indicator used, 2,6-dimethoxyquinone, apparently reacts with acids in a quite complicated manner to give eventually a doubly charged acidic form. The acetic acid–acetic anhydride system is an important one, and it will be of interest to repeat this work with a more conventional indicator.

D. Ethanol, acetone, dioxane, and their mixtures with water

These three organic solvents are extensively used both in the pure form and when mixed with water and perhaps as a result have been the subject of several studies on the acidity function. They are all characterized by relatively low dielectric constants: 2.2 for dioxane at 25°C. (63); 24.2 for ethanol at 25°C. (70); 19.1 for acetone at 25°C. (1) (for their mixtures with water see reference 1). As a result, a point of major importance is whether the concept of the acidity function can usefully be applied to these systems.

Solutions of hydrochloric acid in ethanol, acetone, and dioxane have been investigated up to 1 *M* acid concentration by Braude (14), using the single indicator *p*-nitroaniline. Similar though less extensive studies with the same indicator have been reported by Eaborn (26) for hydrochloric acid in dioxane–water mixtures and for hydrochloric and perchloric acids in methanol–water solutions. Mixtures containing varying proportions of water with the three solvents ethanol, acetone, and dioxane have been investigated at 0.1 *M* and 1 *M* concentrations of hydrochloric acid by Braude and Stern (16), using the indicators *p*-nitroaniline and *m*-nitroaniline. All measurements were with a spectrophotometer. Judging by the constancy of $H_0 + \log C_{\mathrm{H}^+}$ in dilute solutions, hydrochloric acid behaves as a strong acid in ethanol and acetone. The calculated $\mathrm{p}K^{\mathrm{S}}_{\mathrm{BH}^+}$ values for *p*-nitroaniline are 1.3 and 1.6 for ethanol and acetone, respectively, compared to 0.99 in water. In dioxane, hydrochloric acid apparently behaves as a weak acid, a result consistent with the much lower dielectric constant. Actually, in view of the marked specificities discussed earlier for solutions of strong acids in acetic acid, it is probably unsafe to conclude that solutions in ethanol and acetone are free from similar specific effects.

According to Braude and Stern (15, 16) the effect of water is similar for all three solvents in that $-H_0$ goes through a minimum with changing water concentration at fixed concentration of the acid (0.1 *M* and 1 *M*). Figure 13 shows the results for 0.1 *M* hydrochloric acid (corrected to a $\mathrm{p}K_{\mathrm{BH}^+}$ value of 0.99 for *p*-nitroaniline). The depth of the minimum is greater in each case than for comparable data in the case of acetic acid (figure 12), but its occurrence probably stems from a similar source. Addition of ethanol, acetone, or dioxane to a water solution of the acid surely tends to decrease the term $\log f_{\mathrm{B}}$ in equation 8, i.e., to "salt in" the neutral base B. Further addition must ultimately increase $\log f_{\mathrm{H}^+}$ as the acid ion, H_3O^+, gives way to the stronger acid, SH^+, conjugate with the organic solvent base, S.[10] An alternate view, presented by Braude and

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[10] In a personal communication Professor Braude states that the H_0 value of about 1.4 shown in figure 13 for pure dioxane is actually for dioxane which contains from 0.2 to 0.3

TABLE 7

$pK^{S}_{BH^+}$ *values at 25°C. for ethanol–water solutions (37)*

Acid Cation	Weight Per Cent Ethanol			
	0.0	35	65	100
Anilinium	4.636	4.161	3.799	5.70
p-Toluidinium	5.098	4.642	4.312	6.24
m-Toluidinium	4.77	4.28	3.87	5.78
o-Toluidinium	4.46	3.96	3.56	5.55
N-Methylanilinium	4.839	4.276	3.636	4.86
N, *N*-Dimethylanilinium	5.01	4.30	3.50	4.37
Ammonium	9.26	8.78	8.45	
Monomethylammonium	10.70	10.11	9.58	
Dimethylammonium	10.58	9.95	9.36	
Trimethylammonium	9.79	9.13	8.36	

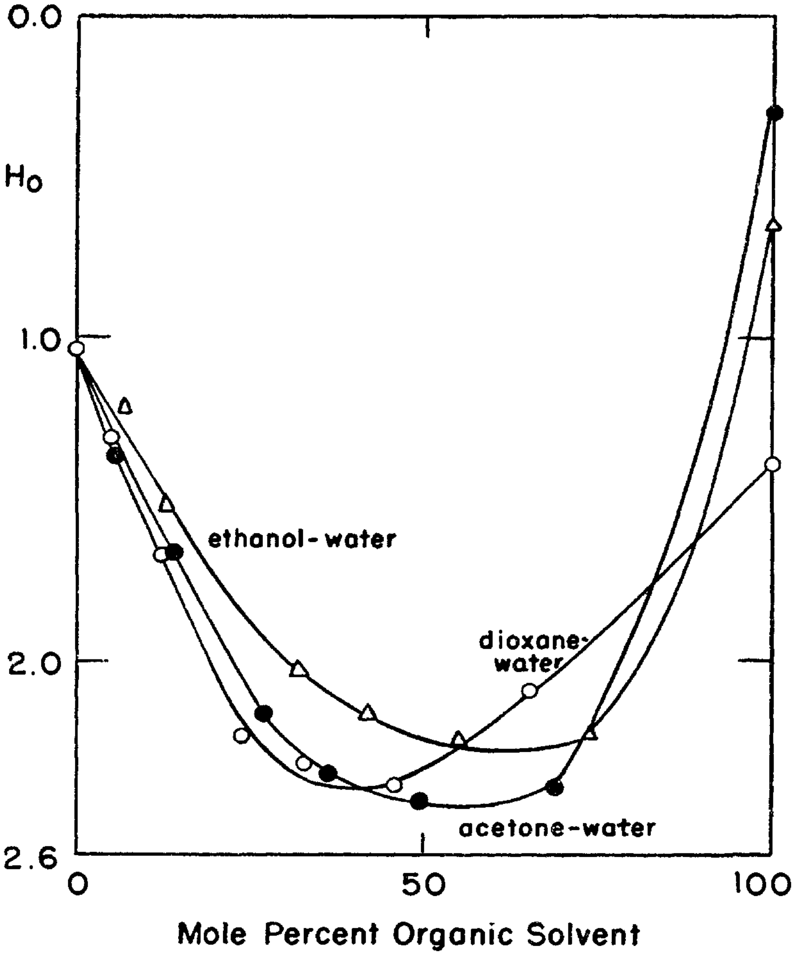

FIG. 13. H_0 in mixed solvents containing 0.1 *M* hydrochloric acid (16)

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per cent water. As these last traces of water are removed the indicator acidity drops sharply to values about like those at the minimum of figure 13. Professor Braude concludes that hydrochloric acid in strictly anhydrous dioxane is probably "not only very incompletely dissociated but also incompletely ionized."

Stern, is that the minima stem from disturbance of the hydrogen-bonded structure of water.

Grunwald, Berkowitz, and Gutbezahl (35, 37, 38) have investigated the ionization of various uncharged acids and bases in ethanol–water mixtures by a differential potentiometric method; a similar study has been made in dioxane–water mixtures by Marshall and Grunwald (69). These investigators find that the acid ionization constants, $\mathrm{p}K^{\mathrm{S}}_{\mathrm{BH}}$ or $\mathrm{p}K^{\mathrm{S}}_{\mathrm{BH^+}}$, respectively, at infinite dilution in the solvent S (including the mixed as well as the pure nonaqueous solvents), are displaced from their values in pure water by varying amounts, as shown in table 7. Thus $\mathrm{p}K_{\mathrm{BH^+}}$ for anilinium ion goes from 4.64 in water at 25°C. to 5.70 in pure ethanol, passing through a minimum of about 3.75 at 80 weight per cent ethanol, while the value for *N*-methylanilinium ion goes from 4.84 to 4.86, with a minimum of 3.42 also at about 80 per cent ethanol. From the differences in behavior exemplified by these two they conclude that the H_0 function does not exist in pure ethanol or in the more concentrated ethanol–water mixtures.

This existence test is actually quite drastic, more so than has been considered necessary for the establishment of the H_0 scale in aqueous solutions of strong acids. As one examines the data of Grunwald and coworkers in detail, one notes for example that the simple aromatic amines aniline and the three toluidines are in fact in quite good agreement with changing medium, while divergence from them is most conspicuous on the part of the aliphatic amines and *N*-substituted aromatic amines. The *N*,*N*-substituted amine (i) in figure 1, however, has been found to diverge from the other indicators even in sulfuric acid–water solutions without destroying the validity and usefulness of the H_0 acidity scale in this medium. It is quite possible that a useful H_0 scale can still be constructed even for pure ethanol by the selection of a suitable set of indicators.

Grunwald and coworkers emphasize the importance of testing for the consistency of indicator acidity measurements by the use of several different indicators with overlapping ranges. Outside the dilute aqueous range, indicator studies based on but a single indicator may well involve an unknown contribution on the part of the particular indicator, even when it is of a specified charge type. One therefore has no right to assume that an uncharged base necessarily gives universal H_0 values in mixed and nonaqueous solvents. On the other hand, one may well be able to show on empirical grounds that over a significantly wide range of structural variations in the indicators, an H_0 scale may be established

TABLE 8

H_0 values for water–dioxane mixtures

$c_{\mathrm{HClO_4}}$	H_0 60% Dioxane	H_0 40% Dioxane	H_0 Water	$c_{\mathrm{HClO_4}}$	H_0 60% Dioxane	H_0 40% Dioxane	H_0 Water
moles per liter				*moles per liter*			
0.25	+1.90	+1.43	+0.52	2.5	−0.70	−0.66	−1.01
0.5	+1.40	+1.00	+0.18	3.0	−1.10	−0.99	−1.23
1.0	+0.75	+0.42	−0.22	3.5	−1.48	−1.33	−1.47
1.5	+0.22	+0.03	−0.53	4.0	−1.84	−1.67	−1.72
2.0	−0.26	−0.33	−0.78				

for a given medium within a reasonable degree of consistency, even though individual bases may be found that do not conform exactly with this scale.

Indicator measurements have recently been obtained by Bunton, Vernon, and coworkers (17a) for solutions of perchloric acid in dioxane–water mixtures containing respectively 60 per cent and 40 per cent dioxane by volume. The indicators were *p*-nitroaniline, *o*-nitroaniline, and 4-chloro-2-nitroaniline; the acid concentrations were between 0.2 and 4.5 *M*. Table 8 lists H_0 values calculated by using indicator pK_{BH^+} values from table 1, together with comparison values for aqueous solutions. For both mixed solvents the H_0 values fall nicely on continuous curves. On this basis it appears that a useful H_0 function exists for these solutions. It is of interest to note that at low concentrations of perchloric acid the aqueous solutions show a considerably higher indicator acidity but that for the 4 *M* solutions this difference has essentially disappeared. For both mixed solvents $-H_0$ increases considerably faster than log C_{H^+} even at 0.5 *M* acid concentration, i.e., at a concentration where the value of $-H_0$ is only about -1.0. This separation of the two acidity measures at such low acidities may be of considerable advantage for applications to reaction kinetics.

A comparison of these data with those of Braude (14) for solutions of hydrochloric acid in the same solvents suggests that for 0.1 *M* solutions the indicator acidities for perchloric and hydrochloric acids are closely similar. For 1 *M* solutions, however, hydrochloric acid shows a considerably lower indicator acidity; the H_0 values for 1 *M* hydrochloric acid in 60 per cent and 40 per cent dioxane are, respectively, 1.28 and 0.93.

Indicator acidities have also been reported by Kreevoy (58a) for solutions of perchloric acid in "50 per cent by volume" dioxane–water with 4-chloro-2-nitroaniline as the indicator. The data are in general agreement with those of table 8, but a precise comparison cannot be made since the procedures for preparing the solutions are different. Bunton and his associates maintained the stated volume proportion of dioxane and water for all solutions; Kreevoy mixed equal volumes of dioxane and of an aqueous perchloric acid solution.

The same three indicators have been applied to solutions of methanesulfonic acid in anhydrous methanol (17a). For this system the apparent H_0 value depends markedly on choice of indicator and as a consequence a useful acidity function scale is not available. In view of the discussion in Section III,D, it is quite likely that this failure is a result of the choice of acid solute rather than of the solvent. The large anion of methanesulfonic acid will probably lead to extensive salting in of the indicators, and the extent of this will be expected to vary with the indicator. In spite of this difficulty, H_0 values from the three indicators for dilute solutions of the acid are in rough agreement and lead to an approximate value of $H_0 = 0.1$ for 0.25 *M* methanesulfonic acid in methanol. The implication is that methanol is a decidedly more acid solvent than any of those in table 8.

Bates and Schwarzenbach (5) have reported an interesting comparison of acidity measures for ethanol–water mixtures with particular emphasis on the acidity functions H_0 and H_-. They have employed three different solutions: a mixture of 0.002 *m* hydrochloric acid and 0.008 *m* sodium chloride; an acidic buffer with 0.02 *m* acetic acid, 0.01 *m* sodium acetate, and 0.005 *m* sodium chloride; a basic buffer with 0.002 *m* triethanolamine and 0.004 *m* triethanolamine hydrochloride. They have measured the following acidities: H_0 using aromatic amine indicators; H_- using nitrophenols and also dimedon as indicators; conventional pH using a cell with a liquid junction and calomel reference electrode; the acidity pw⊕, defined as

$$\text{pw}\oplus = \frac{F(E^{A} - E_0^{W})}{2.3RT} + \log C_{\text{Cl}^-}$$

where E^{A} is the potential of the cell

$$\text{Pt, H}_2 \mid \text{test solution} \mid \text{AgCl(s), Ag(s)}$$

and E_0^{W} is the standard potential for the same cell in water, i.e., for an aqueous hydrochloric acid solution of unit activity. This last acidity is equivalent to $-\log a_{\text{H}^+}f_{\text{Cl}^-}$. Data for the hydrochloric acid–sodium chloride solutions are given in figure 14. The H_0 values are from measurements with the indicator *m*-nitroaniline (using $\text{p}K_{\text{BH}^+} = 2.57$); the H_- values are from the use of 4-chloro-2,6-dinitrophenol ($\text{p}K_{\text{BH}} = 2.97$). The point of major interest is the different behavior of the various functions. The H_0 function shows a minimum in acidity at an intermediate ethanol concentration, very similar to that of figure 13. The functions H_- and pH(conv) both show slight minima. They give similar values of the acidity over most of the range but lead to quite different acidities for pure ethanol. The function pw⊕ shows a steadily increasing acidity.

The different behavior of the various acidity scales is, of course, the expected result, since both the methods of measurement and the quantities involved are

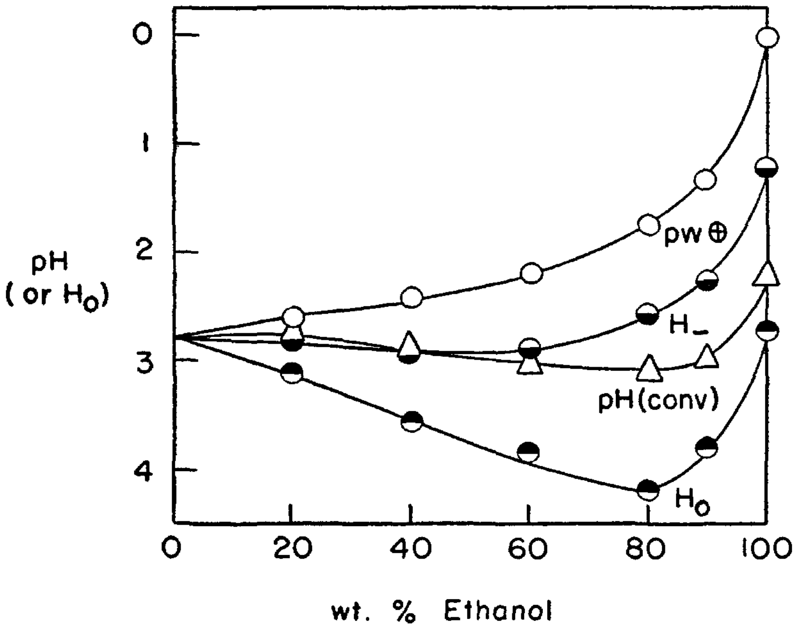


FIG. 14. Various acidity functions in ethanol–water mixtures containing 0.002 *m* hydrochloric acid and 0.008 *m* sodium chloride (5).

quite different. The data very nicely point up the fact that there is no single, uniquely good measure of acidity. There are a variety of them, and any preference depends on such things as ease of measurement and ultimate application. As an example, H_0 is an obvious function to apply to the kinetics of an acid-catalyzed reaction of an uncharged molecule, whereas equally obviously H_- might apply to the kinetics of an acid-catalyzed reaction of a negatively charged ion.

Bates and Schwarzenbach conclude from their studies that the "acidity function" is not useful for solutions of low dielectric constant. This conclusion seems somewhat premature, since for no one of the solutions is H_0 measured with more than one indicator. It is true that the H_0 and H_- acidity functions show different trends with changing ethanol concentration (see figure 14), but there is actually no reason to expect these functions to show similar behavior.

E. Nitromethane

Solutions of sulfuric, hydrochloric, and methanesulfonic acids in nitromethane were investigated by Smith and Hammett (92). They studied also buffer mixtures of sulfuric acid with pyridine. The values of ΔpK for several of the indicators of figure 1 were determined in nitromethane solutions and were found to be in close agreement with the values obtained in aqueous solutions of strong acids.

Between 0.005 and 0.03 *M* concentration $-H_0$ for the sulfuric acid solutions increases linearly with $\log C_A$ but with a slope of 1.76. The $-H_0$ value for a 0.01 *M* solution of sulfuric acid is about 3.2, indicating much higher acidity than at a similar concentration in water. For hydrochloric acid, $-H_0$ between 0.02 and 0.15 *M* concentration likewise increases linearly with $\log C_A$, at the same slope of 1.76, but the $-H_0$ values at equal concentrations are displaced about 4.1 units below those for sulfuric acid. The buffer solutions also showed behavior very different from that of aqueous solutions; with a fixed ratio of acid to base, for example, $-H_0$ was found to increase linearly with the logarithm of the total buffer concentration, the slope of the relationship having the same order of magnitude as that found between $-H_0$ and $\log C_A$ for the unbuffered acids.

Nitromethane has a rather high dielectric constant, 35 at 25°C. (95), but it apparently has very little capacity for ion solvation; in this latter respect it differs from the oxygen-base solvents such as water, ethanol, acetone, etc. One is therefore dealing with solutions in which ion association is prevalent, not as a consequence of uncommonly strong interionic attraction but rather as a consequence of low solvation energy. There is little experience in terms of which to interpret the behavior of such solutions. The indicators at any rate appear to be measuring a real property of the solutions, and further study of this medium is desirable.

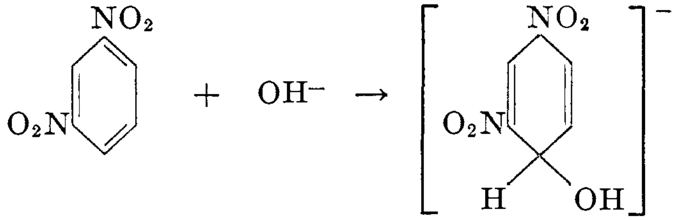
V. RELATED ACIDITY FUNCTIONS

A. H_+ and H_- functions

It was noted in the introduction that other acidity functions closely related to H_0 can be defined according to the charge type of the indicator base. A few studies have been made with H_+ and H_-, but neither has had as extensive development as has H_0. In fact there have not yet been enough studies with varying indicators to be certain that useful H_+ and H_- acidity functions can be developed.

Schwarzenbach and Sulzberger (91) determined H_- acidities at 20°C. for aqueous solutions of sodium and potassium hydroxide ranging from 0.1 M to saturated. The indicators were various glutacondialdehyde derivatives, for example, indigo. They were used as solutions in inert media rather than being added directly to the aqueous alkali solutions. A somewhat similar study was made by Deno (21) for aqueous hydrazine solutions ranging from 5 to 60 per cent by weight. The indicators were such compounds as 3,6-dinitrodiphenylamine and 4,4′,4″-trinitrotriphenylmethane. The list includes none of those used by Schwarzenbach and Sulzberger, so that no direct comparison of the two scales can be made. Deno's data cover the range from $H_- = 11.2$ at 5 per cent hydrazine (11.2 is the pH of this solution) to $H_- = 15.9$ at 60 per cent hydrazine. There is no firm evidence that the H_- function for this system is independent of choice of indicator but the system is *a priori* a favorable one, since hydrazine has a notably high dielectric constant of 51.7 at 25°C. (97).

A very similar study has been reported for the system water–ethylenediamine (86). The indicators include such compounds as 3-nitrocarbazole and 2,4-dinitroaniline. The resulting acidity function is stated to cover the range $H_- = 13$ for 15 weight per cent ethylenediamine to $H_- = 18$ for 70 per cent ethylenediamine. However, the H_- values for the high end of the scale are very doubtful, since the data result from the use of *m*-dinitrobenzene as the indicator and it seems quite unlikely that this molecule will lose a proton in 70 per cent aqueous ethylenediamine. A more probable source of a color change for this molecule in basic solution is some such reaction as



Schaal (86) used three of the same indicators that were used by Deno: *p*-nitrobenzyl cyanide, 3,6-dinitrocarbazole, and 3-nitrocarbazole. For the former Schaal reports a pK_{BH} value of 13.45, which is very close to the value of 13.43 reported by Deno and also close to the value of 13.4 obtained from studies in aqueous alkali (96). With 3,6-dinitrocarbazole, which was studied in fairly dilute solutions of ethylenediamine, Schaal reports p$K_{BH} = 13.10$, in good agreement with Deno's value of 13.07. However, with 3-nitrocarbazole Schaal reports p$K_{BH} = 15.10$, whereas Deno gives the value 14.16. This large discrepancy casts considerable doubt on the assumption that these H_- scales are independent of the indicator used and makes it imperative that this be tested by studies with other indicators.

The system water–ethanolamine has also very recently been investigated with some of the same indicators (70a). The value of H_- is reported to increase continuously from 12.05 for 5 per cent ethanolamine to 15.35 for 100 per cent ethanolamine.

Two fairly explicit comparisons have been made of the H_- and H_0 scales. One is included in the study by Bates and Schwarzenbach (5) which was discussed in a previous section (see figure 14). Comparisons were made of H_- and H_0 for three kinds of solutions, hydrochloric acid–sodium chloride, a triethanolamine buffer, and an acetate buffer. Each comparison was for solvent mixtures varying from pure water to pure ethanol. For the first two kinds of solutions the measurements involved only a single amine indicator for H_0 and a single phenol indicator for H_-. In both cases the trends of H_0 and H_- with increasing concentration of alcohol were quite different. For the acetate buffer, H_- as measured with 2,4-dinitrophenol was very similar to H_0 as measured with *p*-chloroaniline. However, a second set of H_- measurements was made with dimedon as the indicator and the results were very different from those for the nitrophenol. In this case at least the H_- function for ethanol–water mixtures is strongly dependent on choice of indicator. It is quite possible that for a solution which contains a weak acid or base the same would be true for H_0.

Another comparison of H_0 and H_- is that of Randles and Tedder (83), who studied aqueous solutions of trifluoroacetic acid and trichloroacetic acid, using as indicators the uncharged bases *o*- and *p*-nitroaniline and the negatively charged picrate ion. The pK_{BH} for the latter of -0.08 (on a scale where pK_{BH^+} for *p*-nitroaniline is 0.99) was chosen so that the H_0 and H_- scales coincided in the dilute region. Above a concentration of about 1.5 *M* for both trifluoroacetic and trichloroacetic acid the H_0 and H_- scales diverge and at concentrations of about 6 *M* the H_- scales indicate acidities of from 0.5 to 1 unit above those for the H_0 scales. Incidentally, the direction of this divergence as well as of that noted by Bates and Schwarzenbach (5) is nicely consistent with the "salting-in" discussion of Section III,D, since salting in of the uncharged form of the indicator will cause a decrease in the H_0 acidity but an increase in the H_- acidity.

At least one set of measurements has been made of H_+, that of Brand, Horning, and Thornley (12) for solutions of sulfur trioxide in sulfuric acid. The indicator was *m*-nitroanilinium ion. For this case H_+ was found to parallel H_0, and from approximate calculations the investigators conclude that for these sulfuric acid solutions the H_+ scale is about 0.3 unit more negative than H_0.

B. The J_0 acidity function for secondary base indicators

A distinctly different acidity function was proposed by Westheimer and Kharasch (99) and has been further developed by several other investigators. This function is designed to provide an acidity scale for secondary bases, those that react (i.e., "ionize") according to the equation:

$$ROH + H^+ \rightarrow R^+ + H_2O$$

where R^+ is a carbonium ion. The initial studies were with the indicator 4,4′,4″-trinitrotriphenylcarbinol in 80–95 per cent aqueous sulfuric acid. That compounds of this type actually react with acids in the manner indicated has been established by cryoscopic studies in 100 per cent sulfuric acid (75). The usefulness of the new acidity function was early evident from the fact that the behavior of this indicator closely paralleled the rate of nitration of nitrobenzene and other compounds, whereas the H_0 acidity function did not (66, 99).

By analogy to H_0, an obvious way to define the new acidity function (for uncharged secondary bases) is by means of the equation:[11]

$$J_0 \equiv -\mathrm{p}K_{\mathrm{ROH}} - \log \frac{C_{\mathrm{R}^+}}{C_{\mathrm{ROH}}} \tag{14}$$

where K_{ROH} represents an equilibrium constant for the above reaction. An equation of this form has in fact been suggested by all of the recent investigators. It is formally equivalent to:

$$J_0 = -\log \frac{a_{\mathrm{H}^+} f_{\mathrm{ROH}}}{a_{\mathrm{H_2O}} f_{\mathrm{R}^+}} \tag{15}$$

where activity coefficients refer to molar-concentration units and approach unity at infinite dilution in water, but (as is conventional) $a_{\mathrm{H_2O}}$ refers to mole-fraction units and itself reduces to unity for pure water. When so defined, J_0 (like H_0) approaches pH in dilute aqueous solutions.

As with the acidity functions previously described, the important problems are to determine the generality of the function and to obtain usable values of it. Lowen, Murray, and Williams (66, 74), who made the first extensive measurements with indicators, showed that such a function probably existed for solutions of from 65 to 90 per cent sulfuric acid in water in that the slopes of the ionization curves, log $(C_{\mathrm{R}^+}/C_{\mathrm{ROH}})$ vs. acid concentration, were essentially parallel for the several indicators tested. They also noted that their data sufficed to give a relative acidity scale over this range but not an absolute one.

All but one of the indicators used by Lowen, Murray, and Williams were in fact ionic carbinols (arylammonium derivatives) bearing two or three positive charge units. The exception was 4,4′,4″-trinitrotriphenylcarbinol, the same indicator used by Westheimer and Kharasch. The observation that the slope of the ionization curve for this indicator was very close to the slopes for the charged carbinols suggests that at least for concentrated solutions of sulfuric acid the charged carbinols are satisfactory J_0 indicators.

A relationship between J_0 and H_0 may be derived by substituting equation 2 in equation 15:

$$J_0 = H_0 + \log a_{\mathrm{H_2O}} - \log \frac{f_{\mathrm{BH}^+} f_{\mathrm{ROH}}}{f_{\mathrm{B}} f_{\mathrm{R}^+}} \tag{16}$$

Gold and Hawes (32) suggested that absolute values of J_0 could be obtained

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[11] Of the symbols (H_{R}, J_0, and C_0) so far suggested by various investigators for this acidity function, the authors have adopted J_0 simply because of serious reservations about the practicality of the other two. H_{R} is too similar to the H functions of Hammett and coworkers; C_0 involves a symbol which is commonly used for concentration and which in any case has been overworked.

from those of H_0 by the approximation

$$J'_0 = H_0 + \log a_{H_2O}$$

i.e., by assuming that the last term in equation 16 might cancel out. Further indicator studies by Williams and Bevan (100) have shown, however, that this approximation is unsatisfactory at the lower acid concentrations, although it does appear to be useful for relative J_0 values in solutions containing more than 75 per cent sulfuric acid. Gold (30, 31) has recently proposed other more satisfactory approximations for the J_0 function.

Brand and Horning (11) have suggested that a J acidity function for fuming sulfuric acid (analogous to J_0 for water–sulfuric acid) can be determined from the relation $J = H_0 - \log p_{SO_3}$, where p_{SO_3} is the partial pressure of sulfur trioxide over the solvent. These authors use this to tabulate relative J values for sulfuric acid containing from 5 to 41 per cent of sulfur trioxide. There is as yet no evidence that this quantity is at all closely related to J_0, and it will be of considerable interest to investigate this medium with appropriate indicators.

The most extensive experimental study of secondary base indicators and of the generality of the J_0 acidity function has been made by Deno, Jaruzelski, and Schriesheim (22, 23, 24). These investigators determined pK_{ROH} values for a series of eighteen indicators by the overlapping-range technique discussed previously for H_0 indicators. The resulting values extend from $pK_{ROH} = -0.82$ (for 4,4′,4″-trimethoxytriphenylcarbinol) to $+17.38$ (for 2,4,6-trimethylbenzyl alcohol). These suffice to establish the J_0 scale for sulfuric acid–water mixtures of from 1 to 92 per cent acid. Since above about 82 per cent acid the last term in equation 16 appears to have a constant (though not zero) value determinable by comparison of J_0 with H_0, this equation may be used to extend the J_0 scale up to 98 per cent sulfuric acid from known values of H_0 and a_{H_2O}. Deno and coworkers showed that in analogy to figure 1, the slopes of the log (C_{R^+}/C_{ROH}) vs. acid concentration curves for adjacent indicators were very similar, suggesting that the J_0 function so defined is reasonably independent of the choice of indicator. This was confirmed by studies with ten additional aryl methanols.

Actually a minor difficulty appears to remain. Deno and coworkers made studies with the indicator 4,4′,4″-trinitrotriphenylcarbinol and report a slope, d log $(C_{R^+}/C_{ROH})/d(\% \ H_2SO_4)$, which is considerably smaller than that given

TABLE 9

The J_0 acidity function for sulfuric acid–water at 25°C. (23)

H_2SO_4	J_0	H_2SO_4	J_0	H_2SO_4	J_0	H_2SO_4	J_0
per cent		*per cent*		*per cent*		*per cent*	
0.5	1.25	15	−1.32	40	−4.80	70	−11.52
1.0	0.92	20	−1.92	45	−5.65	80	−14.12
2.0	0.62	25	−2.55	50	−6.60	90	−16.72
5.0	−0.07	30	−3.22	56	−7.90	95	−18.08
10	−0.72	35	−4.00	60	−8.92	98	−19.64

by the data both of Lowen, Murray, and Williams and of Westheimer and Kharasch for the same indicator in the same range of sulfuric acid concentrations. This may be due to slight variations in temperature or in indicator concentration, although the three studies appear to be quite similar on both counts.

Table 9 presents selected values of J_0 from the work of Deno, Jaruzelski, and Schriesheim (labeled C_0 in table 1 of reference 23). The striking feature is the rapid increase in acidity as measured by J_0 compared even with that measured by H_0. For example, $-H_0$ for sulfuric acid–water mixtures increases by 3.75 units between 60 and 90 per cent sulfuric acid, while $-J_0$ increases by 7.80 units over the same interval. Further studies on the generality of this function will be helpful, but since several investigators have already found correlations between J_0 and the rates of certain acid-catalyzed reactions, there is every reason to believe that this acidity function will be highly useful.

VI. MEASUREMENT OF STRENGTHS OF VERY WEAK BASES

A major field of application of the H_0 and other acidity functions is the study of equilibria involving acids and bases at high acidities, such as are encountered in the measurement of base strengths, solubilities, and distribution coefficients of very weak bases. Thus the establishment of an H_0 acidity scale in effect calibrates the medium for determining the $\mathrm{p}K_{\mathrm{BH}^+}$ of other weak uncharged bases comparable in molecular size and structure to the indicator bases used to establish the scale. The extremely high acidities measurable on the H_0 scale without encountering serious experimental or theoretical difficulties admit significant measurements on extremely weak bases. The fact that many aromatic bases on ionization undergo color changes in the ultraviolet, if not in the visible portion of the spectrum, has been particularly helpful in the application of H_0 to this type of measurement.

Flexser, Hammett, and Dingwall (28) have developed specific methods for calculating values of $\mathrm{p}K_{\mathrm{BH}^+}$ for weak bases from spectrophotometric measurements, particularly in concentrated aqueous sulfuric acid solutions. In principle the procedure is simple. The ratio of concentrations of ionized and uncharged forms is related to the extinction coefficients at a given wavelength by the equation:

$$\frac{C_{\mathrm{BH}^+}}{C_{\mathrm{B}}} = \frac{\epsilon_{\mathrm{B}} - \epsilon}{\epsilon - \epsilon_{\mathrm{BH}^+}}$$

where ϵ_{B}, ϵ_{BH^+}, and ϵ are the extinction coefficients of the uncharged base, the conjugate acid, and the test solution, respectively. Then, knowing H_0 for the test solution:

$$\mathrm{p}K_{\mathrm{BH}^+} = H_0 + \log \frac{\epsilon_{\mathrm{B}} - \epsilon}{\epsilon - \epsilon_{\mathrm{BH}^+}} \qquad (17)$$

The difficulty is that ϵ_{B} and ϵ_{BH^+} are not precisely known because of their dependence on the medium.

Two specific methods were proposed for minimizing the effects of the medium and obtaining accurate pK values. One was to solve equation 17 by least squares for several wavelengths so chosen that either the ϵ_B or the ϵ_{BH^+} absorption curve was flat to minimize medium effects on its determination; that is, the extinction coefficient of the conjugate form was treated as an unknown together with pK_{BH^+}. The other method utilized the assumption that medium effects involve mainly lateral spectral shifts and that a true isobestic point could be found for absorption curves close to the 50 per cent ionization region; the medium effect could then be minimized by shifting all other curves laterally until they intersected at the common isobestic point, thus permitting the determination of corrected values of ϵ_B and ϵ_{BH^+}. Davis and Geissman (19) have recently reported another quite simple procedure for minimizing medium effects; a graphical method is used to determine the point of 50 per cent ionization and hence the point at which p$K_{BH^+} = H_0$.

For a colorless base or for one that undergoes only a slight spectral change with ionization, one may determine pK_{BH^+} by observing its effect on H_0 as measured by an indicator also present in the test solution. By this means the base strengths of some relatively weak bases have been measured in solutions of benzenesulfonic acid in anhydrous formic acid (47) and in solutions of perchloric acid in anhydrous acetic acid (61).

Table 10 gives pK_{BH^+} values for selected weak bases whose strengths have been determined by their ionization in solutions of known H_0. In such determina-

TABLE 10

Strengths, pK_{BH^+}, *of selected weak bases from ionization at approximately 25°C. in solutions of known* H_0

Values referred to p$K_{BH^+} = 0.99$ for *p*-nitroaniline

Base	pK_{BH^+}	References
Benzoic acid	−7.38	(28, 50)
Phenylacetic acid	−7.71	(28)
Acetophenone	−6.15	(28)
p-Methylacetophenone	−5.47	(27)
p-Bromoacetophenone	−6.52	(27)
Propiophenone	−6.40	(101)
n-Butyrophenone	−6.33	(101)
Isobutyrophenone	−6.84	(101)
Flavone	−1.3	(19)
2′,4′,6′-Trimethylflavone	−2.17	(19)
2,4,6-Trimethylbenzaldehyde	−4.7	(89)
2,4,6-Triethylbenzaldehyde	−5.0	(89)
2,4,6-Triisopropylbenzaldehyde	−5.2	(89)
2,4,6-Trimethylacetophenone	−7.9	(88)
2,4,6-Trimethylbenzoic acid	−7.4	(87)
p-Nitrophenol	−9.18	(33)
p-Fluoronitrobenzene	−11.62	(12)
p-Chloronitrobenzene	−11.68	(12)
m-Chloronitrobenzene	−12.27	(12)
m-Nitrotoluene	−10.96	(12)
Acetonitrile	−4.3	(61)
Propionitrile	−4.31	(47)
Dioxane	−4.4	(61)
Urea	+0.4	(61)
Acetamide	+0.25	(34)
Acetylglycine	−2.04	(34)
Acetic acid	−6.2	(34)

tions it is essential that equation 7, on which the validity of the H_0 function depends, be satisfied. One may always test this condition by observing how closely the ionization curve for the base remains parallel with changing acidity to those of the standard indicators. However, for solutions in solvents of low dielectric constant this condition may not be sufficient, as is evident from the observed displacement in figure 10 of the curve for 2,4-dichloro-6-nitroaniline in anhydrous acetic acid. The possibility of this type of difficulty casts doubt on the validity of pK values reported from measurements in such solvents.

Hammett and Chapman (45) have investigated the solubilities of benzoic acid and other very weak oxonium bases in sulfuric acid–water mixtures. These compounds show a striking increase in solubility as the sulfuric acid concentration is increased beyond 60 per cent by weight. Although conversion to the soluble conjugate acid is doubtless an important contributing factor, these investigators showed that it is not the only one responsible. Solubility equilibrium involves specifically the activity coefficient, f_B, which with increasing concentration of dissolved B (and BH^+) is by no means a function simply of the acidity of the medium. A similar consideration applies to the distribution of a weak base between an acid and a nonionizing medium, as in the study of substituted azulene bases by Plattner, Heilbronner, and Weber (81). In studies of this kind involving a second phase, independent knowledge of H_0 and of pK_{BH^+} may prove to be a valuable asset, but acid–base equilibrium in the one phase is itself not determinative.

A rather different kind of application of H_0 indicators is to the determination of the acid strength of solid surfaces. Walling (98b) has proposed that if an adsorbed indicator can go from the uncharged basic form to the acid form in the usual way by accepting a proton from the surface, then observation of the colors respectively assumed by a series of adsorbed indicators permits one to assign to the surface an H_0 value identical in significance with that defined by equation 2, all activities and activity coefficients referring to constituents in the adsorbed layer. The generality of this application of the H_0 scale may be tested by the consistency of the results obtained with different indicators. If, on the other hand, the surface functions as a Lewis acid, then the apparent H_0 value will have a rather different meaning, for the indicator equilibria will then be specific to the particular acid or electron acceptor active in the surface. Using indicators adsorbed from solutions in isoöctane (98b) and in benzene (9a), surface acidities have been determined for a number of common chemical solids (including titanium dioxide, cuprous chloride, silver chloride, tungstic acid) and also for several surface-active catalysts (silica gel, alumina, clay catalysts). Some of these turn out to have astonishingly high acidities. A synthetic silica–alumina cracking catalyst, for example, will convert adsorbed anthraquinone ($pK_{BH^+} = -8.27$) to its yellow acid form (9a).

VII. SUMMARY

The acidity function H_0 is defined by the equation

$$H_0 = pK_{BH^+} - \log (C_{BH^+}/C_B)$$

which is equivalent to

$$H_0 = -\log (a_{H^+}f_B/f_{BH^+})$$

It is determined by measurement of the indicator ratio C_{BH^+}/C_B for an uncharged indicator base B and of the thermodynamic ionization constant K_{BH^+} for its conjugate acid. The reference state is water, and H_0 is designed to become equal to pH and hence to $-\log C_{H^+}$ for dilute aqueous solutions.

The H_0 function is well established for aqueous solutions. Values of the function are tabulated for aqueous solutions of the mineral acids up to 10 *M* concentration (7 *M* for nitric acid) and for sulfuric acid–water mixtures to 107 per cent sulfuric acid (31 per cent sulfur trioxide in sulfuric acid). The H_0 values are calculated using "best values" of pK_{BH^+} for the indicators, referred to $pK_{BH^+} = 0.99$ for *p*-nitroaniline. Some studies have been made of the effect of neutral salts on the magnitude of H_0, and it is found that the results depend both on the specific salt and on the indicator used. A few studies are available on H_0 values for aqueous solutions of weak acids, but it is not yet known whether the H_0 scale for this type of solution is adequately independent of the choice of indicator.

Values of H_0 can be determined for solutions in mixed and in nonaqueous solvents. For any new solvent it is important to establish whether an H_0 function of some generality actually exists. Data are available for solutions of acids in such solvents as formic acid, acetic acid, ethanol, dioxane, acetone, and mixtures of the last four with water, but in almost every case it would be helpful to make studies with additional indicators to ascertain the generality of the H_0 function.

Studies have been made on the related acidity function H_- (where the indicator bases carry unit negative charge) with such solvents as aqueous alkali and aqueous hydrazine. Some comparisons are available of H_- and H_0, as well as of H_0 and H_+. A rather different type of acidity function called J_0 has been defined for the ionization of secondary bases

$$ROH + H^+ = R^+ + H_2O$$

and values of J_0 are available for mixtures of sulfuric acid and water.

The establishment of indicator acidity scales permits the measurement of p*K* values for bases of the same type as the indicator. The procedure is simple in principle, although slightly complicated by effects of the medium. A number of p*K* values for very weak uncharged bases are available from applications of the H_0 function. Similar but less extensive studies have been made with the H_- and J_0 functions.

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