

# CHEMICAL REVIEWS

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## ACIDITY FUNCTIONS FOR STRONGLY BASIC SOLUTIONS

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### I. INTRODUCTION

Strongly basic solutions can be arbitrarily defined as those solutions which ionize acids with an ability equal to or greater than 0.1 *M* aqueous alkali metal hydroxide solutions. Hammett (21) first suggested a suitable acidity function to measure the relative ability of these solutions to ionize weak acids



and the acidity function can be defined as

$$H_- = \text{p}K_a - \log \left( \frac{[\text{HA}]}{[\text{A}^-]} \right) \quad (\text{Eq 2})$$

where  $\text{p}K_a$  is the negative logarithm of the thermodynamic ionization constant of the acid in water and  $[\text{HA}]/[\text{A}^-]$  is the measured ionization ratio of the indicator. The acidity function of the solution is thus equivalent to

$$H_- = -\log (a_{\text{H}^+} f_{\text{A}^-} / f_{\text{HA}}) \quad (\text{Eq 3})$$

where  $a_{\text{H}^+}$  is the hydrogen ion activity in the solution and  $f$  denotes the activity coefficients of the indicator. The function  $H_-$  becomes identical with pH in dilute aqueous solution where the activity of hydrogen ion becomes equal to its concentration and the activity

coefficients of the indicator approach unity (40). Other acidity functions of this kind can be defined according to the charge type of the acid, *i.e.*, the  $H_+$ ,  $H_0$ , or  $H_{2-}$  functions from the ionization of double positively, positively, or negatively charged acids. Most investigations of the  $H_-$  function have been made in strongly basic solutions.

The function  $H_-$  measures the ability of the solution to remove a proton from the acid and enables the strength of weak acids to be measured, kinetic mechanistic studies to be interpreted, and the physicochemical composition of solutions to be investigated.

### II. MEASUREMENT OF ACIDITY FUNCTIONS

#### A. THE $H_-$ FUNCTION

The measurements of  $H_-$  have been made by absorption spectrophotometric estimation of the acid and/or its conjugate anion in the region of room temperature. This method combines high accuracy and precision, and it allows indicator concentrations to be kept low. The measurements can be made down to 200  $\text{m}\mu$  in water or to the lowest practical wavelength for other solvents. To measure the ratio  $[\text{HA}]/[\text{A}^-]$  it is necessary to know the extinction coefficient at a given wavelength of a solution where the indicator

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is partially ionized,  $\epsilon$ , the extinction coefficient of completely un-ionized indicator,  $\epsilon_{\text{HA}}$ , and the extinction coefficient of the completely ionized indicator,  $\epsilon_{\text{A}}$ , at the same wavelength. The ionization ratio can then be found by the relation

$$\frac{[\text{HA}]}{[\text{A}^-]} = \frac{\epsilon_{\text{A}} - \epsilon}{\epsilon - \epsilon_{\text{HA}}} \quad (\text{Eq 4})$$

If the un-ionized acid has a negligible absorption at a selected wavelength, the above relation simplifies. The concentrations must be low enough for the Beer-Lambert law to hold.

Two other important factors must be considered. The completely ionized form may be unattainable in the system under study. This extinction coefficient,  $\epsilon_{\text{A}}$ , in alkoxide solutions may be estimated by the relation (35)

$$(\epsilon - \epsilon_{\text{HA}})^{-1} = (\epsilon_{\text{A}} - \epsilon)^{-1} + [bK_{\text{a}}(\epsilon_{\text{A}} - \epsilon_{\text{HA}})]^{-1} \quad (\text{Eq 5})$$

where  $b$  is the alkoxide concentration and  $K_{\text{a}}$  is the equilibrium constant (see p 128). The concentration of base,  $b$ , must be corrected when that of the acid anion,  $[\text{A}^-]$ , is of comparable size. This appears to give very reasonable results when the size of the extrapolation is not too great (52). A reasonable estimate can be made in the case of anions, whose spectra are not very solvent sensitive, from the extinction coefficient in a similar system (36, 39). The spectra may also be solvent dependent and a shift can be observed for variations in the basicity of the medium. Completely ionized and un-ionized spectra should be observed under as nearly the same conditions as the partially ionized indicator. Most indicators appear to be relatively free from observable solvent dependence, but corrections can be made using the isosbestic point or similar methods (38). Constancy of the position of the isosbestic point is good evidence that the measurements are independent of the solvents.

The measurements should be anchored securely in the dilute aqueous pH region. It has recently been shown that earlier use of *p*-nitrobenzyl cyanide was in error due to its ambiguous ionization (36, 58, 60, 61). Stewart and O'Donnell chose 2,4,6-trinitroaniline to bridge this important region and generated a self-consistent series of indicator  $pK_{\text{a}}$  values which are listed in Table I, together with others derived from their values. The earlier extrapolated  $H_{\text{L}}$  values, using the *p*-nitrobenzyl cyanide indicator, were arbitrary because the complicated spectral changes for this indicator could not be consistently and simply interpreted as a simple ionization. Thus the derived  $pK_{\text{a}}$  values were in very poor agreement. The latter workers have used only indicators which are ionized apparently instantaneously and whose ionization can be completely

TABLE I  
INDICATOR  $pK_{\text{a}}$  VALUES

Substituted diphenylamines (61)	$pK_{\text{a}}$	Substituted anilines (61)	$pK_{\text{a}}$
2,4,6-Trinitro-	10.38	2,4,6-Trinitro-	12.20
2,4,2',4'-Tetranitro-	10.82	6-Bromo-2,4-dinitro-	13.63
2,4,6-Trinitro-4'-amino-	10.82	2,4-Dinitro-	15.00
2,4,4'-Trinitro-	12.35	2,6-Dichloro-4-nitro-	15.55
2,4,3'-Trinitro-	12.65	2,5-Dichloro-4-nitro-	16.05
2,4-Dinitro-	13.84	4-Chloro-2-nitro-	17.22
4,4'-Dinitro-	14.08	2-Nitro-	17.88
2,4-Dinitro-4'-amino-	14.64	4-Nitro-	18.37
4-Nitro-	15.90		
2-Nitro-	17.57		
		Substituted carbazoles (34, 50, 61)	
		3,6-Dinitro-	10.83
		3-Nitro-	14.10
		4-Nitrophenylhydrazones (51)	
2,4-Dinitrophenylhydrazones (51, 52)		4-Nitrophenylhydrazones (51)	
Acetone	12.80	Acetone	14.03
Propanal	12.58	Propanal	13.87
Cyclopentanone	13.03	Cyclopentanone	14.08
Cyclohexanone	12.89	Cyclohexanone	13.68
Benzaldehyde	12.47	Benzaldehyde	13.78
Acetophenone	12.81	Acetophenone	14.39
Benzophenone	13.57	Benzophenone	14.34

reversed and interpreted as a simple Brønsted ionization.

Direct evidence (10) has recently been presented that indicators such as 2,4-dinitroaniline and 2,4-dinitrodiphenylamine ionize (*i.e.*, lose a proton from the amino group) in methanolic dimethyl sulfoxide containing sodium methoxide. Similar evidence for 2,4,6-trinitroaniline in methanolic sodium methoxide show features of the formation of the simple anion and an addition reaction to form a "Meisenheimer" 1:1 complex. Thus, 2,4,6-trinitroaniline should not be used for measurements in alkoxide systems. The excellent correlation of the  $pK_{\text{a}}$  values of the latter indicator (from aqueous buffers) and other substituted anilines with their basicities ( $pK_{\text{BH}^+}$ ) and with the  $pK_{\text{a}}$  values of similarly substituted phenols suggests that all these anilines ionize in the same way (61). It should be *especially* noted that the  $pK_{\text{a}}$  values of 12.31 for 2,4,4'-trinitrodiphenylamine obtained directly by use of aqueous buffers corresponds very closely to the values, 12.33 and 12.31, obtained by the stepwise comparison to 2,4,6-trinitroaniline in partially aqueous systems. This indicator effectively reinforces the bridging from aqueous to partially aqueous and non-aqueous systems. The possibility remains that, in addition to ionizing normally, 2,4,6-trinitroaniline forms a complex (1:1) in aqueous base, *i.e.*, presence of hydroxide (19). The present evidence suggests that this is not likely and will not introduce any significant error.

The  $pK_{\text{a}}$  values are generated by stepwise comparison of the basicities of solutions starting from the pH region.

If an acid HA of known  $pK_a$  and an acid HB of unknown  $pK_a$  ionize in the same solution with ionization ratios that can be measured with reasonable accuracy ( $[HA]/[A^-]$  between 10 and 0.1), then

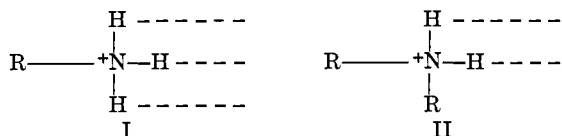
$$pK_a^{HA} - pK_a^{HB} = \log ([HA]/[A^-]) - \log ([HB]/[B^-]) + \log (f_{HA}f_B/f_{HB}f_A) \quad (\text{Eq 6})$$

Hammett has suggested that the activity term can be neglected for acids of similar structure in aqueous solutions (21), and it seems reasonable to expect it to disappear in other solvents of high dielectric.

The absolute test of the meaningful use of the indicators is the near constancy of the derived  $pK_a$  values in different solutions and their ability to give accord in the values found for the basicity of a solution. These criteria seem satisfied. Stewart and O'Donnell (60) find for 4,4'-dinitrodiphenylamine  $pK_a$  values of 14.09, 14.15, and 14.00 for different systems. The  $H_-$  values for the systems shown in Tables II to VIII rarely deviate more than  $\pm 0.2$  unit, except notably in the case of the low dielectric system *t*-pentyl alcohol.

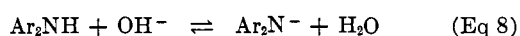
From one source (61)  $pK_a$  values are used in order to minimize the confusion caused by "averaging" methods. The indicators are all substituted aromatic amines to give continuity of acid type. It must be recognized that complete consistency of the indicator measurements must not be expected. The large variation in the solvent systems can be expected to give rise to some specific and general solvation effects if the indicators vary greatly in structure. Manifold overlap of the indicator ionization data should detect deviations of this type. This has been done for the aromatic amine indicators, and good agreement has been found for several solvent systems (61).

In acid solution, the acidity function  $H_0$  had been shown to depend on the type of indicator used (64). In particular, primary and secondary amines follow somewhat different functions because of the differing degree of hydrogen bonding present in the cations I and II.



Even more striking is the deviation observed for olefin bases, which protonate to give carbonium ions since in this case hydrogen bonding by the cation is virtually nonexistent.

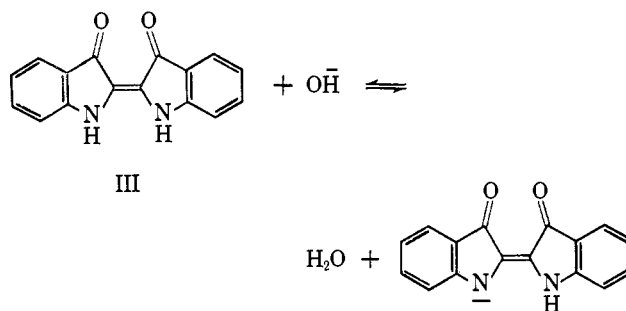
It is probable that effects such as these will be less important for the neutral indicator acids used to establish the  $H_-$  scale in basic solution since the hy-



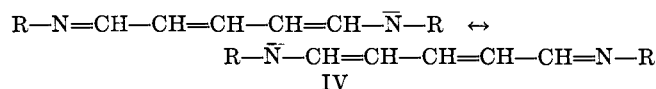
drogens in the anions will not participate in the hydrogen bonding (as shown in Eq 7 and 8). There will be a difference in the degree of hydrogen bonding in the neutral amines,  $\text{ArNH}_2$  and  $\text{Ar}_2\text{NH}$ , but this will be small compared to that found in the cations,  $\text{ArNH}_3^+$  and  $\text{Ar}_2\text{NH}_2^+$ .

A number of different systems have been studied using these indicators: aqueous bases (61), alcoholic alkoxides (17, 23, 27, 28, 34, 36, 42, 45, 51, 52, 55), aqueous and alcoholic dipolar aprotic solvents containing base (7, 59, 61, 62), and aqueous amines (11, 34, 49, 50).

Schwarzenbach and Sulzberger (54) made the first attempt to construct a  $H_-$  acidity scale and used aqueous sodium and potassium hydroxide solutions for the purpose. The strong salting out of the indicator by the concentrated alkali metal hydroxide solution necessitated the presence of an immiscible organic solvent to facilitate measurements of the indicator ionization ratio. Measurements were made from dilute aqueous to saturated solutions. The indicators used successfully were indigo derivatives, whose supposed ionization is shown by III. Other indicators,



particularly substituted glutacondialdehyde dianils, gave results suggesting a more severe increase in basicity. Schwarzenbach attributes this to an anomalous ionization involving addition of hydroxide, while Edward and Wang (14) suggest this is due to differences in hydration. The structure of the derived anion, IV, for the glutacondialdehyde derivative is very different, in that the anion has two nitrogen centers of equal probability for the main charge to reside, and it is reasonable to expect significant differences in acidic behavior.



Recently the acidity function (14) has been re-assessed in aqueous sodium hydroxide (up to 4.5 M concentration) using thioacetamide as the indicator. These studies confirm the acidity scale found in the earlier work. However, both these studies have been made using indicators different from those used in forming the main body of data reviewed herein.

TABLE II  
 H- FUNCTION FOR AQUEOUS SOLUTIONS OF BASES

Base, <i>M</i>	LiOH in water (61)	NaOH in water (54 <sup>a</sup> )	KOH in water <sup>a</sup> (54)	BzMe <sub>2</sub> NOH in water <sup>d</sup> (61)	BzMe <sub>2</sub> NOH in 30 mole % aqueous pyridine (61)	BzMe <sub>2</sub> NOH in 50 mole % aqueous pyridine (61)
1 × 10 <sup>-2</sup>	...	12.01	...	12.02	...	15.73
2 × 10 <sup>-2</sup>	...	12.31	...	12.32	13.89	16.03
5 × 10 <sup>-2</sup>	...	12.71	...	12.72	14.29	16.43
1 × 10 <sup>-1</sup>	...	13.01	...	13.02	14.61	16.73
2 × 10 <sup>-1</sup>	...	13.31	...	13.32	15.06	17.08
5 × 10 <sup>-1</sup>	...	13.71	...	13.75	15.67	17.70
1	13.48	14.16	14.01	14.17	14.26	16.44
1.5	...	...	14.22	...	14.69	17.00
2	13.66	14.52	14.40	14.69	15.27	17.64
2.4	...	...	...	...	16.38	...
3	13.87	14.85	14.66	15.00	...	...
4	14.10	15.08	14.87	15.30	...	...
5	14.33	15.34	...	15.64	...	...
6	...	15.54	...	15.97	...	...
7	...	15.75	...	16.30	...	...
8	...	16.00	(15.78) <sup>c</sup>	16.67	...	...
10	...	16.40	(16.14) <sup>c</sup>	17.45	...	...
12	...	...	(16.70) <sup>c</sup>	...	...	...

<sup>a</sup> Values are those based on the measurements of Schwarzenbach and Sulzberger (54) using a special technique and indicators (see p 121). <sup>b</sup> Values are those based on the ionization of thioacetamide (14). <sup>c</sup> Values in parentheses are those based on the ionization of *p*-nitroaniline (47). <sup>d</sup> Bz is C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>-.

 TABLE III  
 H- FUNCTION FOR ALCOHOLIC ALKALI METAL ALKOXIDE SOLUTIONS

Base concn, <i>M</i>	Alkali metal <sup>a</sup> methoxide in methanol (36, 42, 45, 52)	NaOEt in ethanol (51, 55)	NaO- <i>i</i> -Pr in isopropyl alcohol (23, 27)	NaO- <i>t</i> -Bu or KO- <i>t</i> -Bu in <i>t</i> -butyl alcohol (4, 5)	NaO- <i>t</i> -Pe in <i>t</i> -pentyl alcohol (28)
5 × 10 <sup>-4</sup>	10.36	...	14.65	...	...
1 × 10 <sup>-3</sup>	10.66	12.57	14.95	17.14	16.09
5 × 10 <sup>-3</sup>	11.36	13.27	15.65	17.84	16.79
1 × 10 <sup>-2</sup>	11.66	13.57	15.95	18.14	17.09
5 × 10 <sup>-2</sup>	12.36	14.27	16.65	18.84	17.79
1 × 10 <sup>-1</sup>	12.66	14.57	16.95	19.14	18.09
	LiOMe in methanol	NaOMe in methanol	KOMe in methanol		
2 × 10 <sup>-1</sup>	12.78	12.93	12.91		
4 × 10 <sup>-1</sup>	13.07	13.26	13.33		
6 × 10 <sup>-1</sup>	13.24	13.52	13.67		
1	13.54	13.97	14.25		
1.5	13.89	14.48	14.89		
2	14.20	14.92	15.40		
2.5	14.57	15.31	15.84		
2.7	14.73	...	...		
3.0	...	15.77	16.30		
3.5	...	16.32	16.93		
3.75	...	16.64	...		

<sup>a</sup> Alkali metal is lithium, sodium, or potassium.

These data were obtained using aromatic amine indicators, and, for the most part, the latter are almost completely insoluble in aqueous sodium or potassium hydroxide.

Rochester (47) has investigated the behavior of *p*-nitroaniline in aqueous sodium hydroxide. The interpretation of the spectral behavior given involves the formation of two species. A simple interpretation, involving the formation of the anion ( $\lambda_{\text{max}}$  433

$\mu$ ) gives values of  $H_-$  for this system in good agreement with values of Schwarzenbach and Sulzberger (see Table II).

The data can be presented in terms of molarity, mole fraction, or volume fraction (*e.g.*, see ref 67). The first two forms seem best suited to the presentation and discussion and both are used herein. In Tables II to VIII the  $H_-$  values are based on the  $pK_a$  values shown in Table I. Where results are presented from

TABLE IV

 $H_-$  FUNCTIONS FOR AQUEOUS ALCOHOLS CONTAINING BASE (0.005 M)<sup>a</sup> (5)

Mole % nonaqueous component	Nonaqueous component				
	Ethanol	Isopropyl alcohol	<i>t</i> -Butyl alcohol	<i>t</i> -Pentyl alcohol	Dioxane
0	11.74	11.74	11.74	11.74	11.74
20	12.40	12.40	13.28	<i>b</i>	12.32
40	13.03	13.20	14.03	<i>b</i>	13.01
60	13.09	13.85	14.75	14.62	<i>b</i>
80	13.16	14.56	15.45	15.23	<i>b</i>
90	...	15.01	16.28	15.68	<i>b</i>
100	13.35	15.71	17.85	16.70	...

<sup>a</sup> Similar results obtained for 0.001 M base, which is NaOR.<sup>b</sup> Immiscible solutions.

TABLE V

 $H_-$  FUNCTION IN AQUEOUS OR METHANOLIC DIPOLAR APROTIC SOLVENTS CONTAINING ADDED BASE

Mole % dipolar aprotic solvent	Aqueous				Methanolic dimethyl sulfoxide containing NaOMe (62)
	Aqueous pyridine containing 0.011 M Me <sub>2</sub> NOH (61)	Aqueous tetra- methylene sulfone containing 0.011 M Me <sub>2</sub> NOH (61)	Aqueous dimethyl sulfoxide containing 0.011 M Me <sub>2</sub> NOH (59, 61)	Aqueous dimethyl sulfoxide containing 0.025 M NaOMe (62)	
0	...	...	...	...	12.23
1	12.27	12.36	...	...	12.32
5	12.60	12.52	12.18	12.63	12.63
10	13.04	12.74	12.94	12.97	12.97
15	13.44	12.97	13.63	13.31	13.31
20	13.75	13.22	14.28	13.67	13.67
25	14.06	13.45	14.86	13.97	13.97
30	14.33	13.72	15.40	14.30	14.30
35	14.56	13.99	15.92	14.56	14.56
40	14.76	14.25	16.41	14.84	14.84
45	14.91	14.55	16.84	15.15	15.15
50	15.05	14.88	17.23	15.43	15.43
55	15.18	15.22	17.60	15.77	15.77
60	15.31	15.56	17.93	16.16	16.16
65	15.40	15.94	18.40	16.47	16.47
70	...	16.37	18.87	16.80	16.80
75	...	16.79	19.3	17.21	17.21
80	...	17.23	19.9	17.64	17.64
85	...	17.70	20.5	18.06	18.06
90	...	18.30	21.3	18.51	18.51
92.5	...	18.76	21.9	18.85	18.85
95	...	19.28	22.5	19.37	19.37

TABLE VI

 $H_-$  FUNCTION FOR AQUEOUS TETRAMETHYLENE SULFONE CONTAINING PHENYLTRIMETHYLAMMONIUM HYDROXIDE (7, 30)

Mole % tetramethylene sulfone	PhMe <sub>3</sub> NOH, M	$H_-$
9.0	0.0121	13.44
9.0	0.0201	13.74
65.2	0.0294	15.24
65.2	0.0541	15.79
78.9	0.0123	16.11
78.9	0.0312	16.48
78.9	0.0430	16.65
78.9	0.0707	17.00
90.5	0.0174	17.34
90.5	0.0232	17.44
90.5	0.0350	17.69
90.5	0.0520	18.09
95.0	0.0032	18.05
95.0	0.0094	18.38
95.0	0.0115	18.89
95.0	0.0165	19.29
95.0	0.0193	19.70

TABLE VII

 $H_-$  FUNCTION FOR AQUEOUS AMINE SOLUTIONS

Mole % nonaqueous component	Hydrazine (11, 50)	Ethylenediamine (49)	2-Aminoethanol (34)
5	...	11.74	11.17
7.5	...	12.44	11.48
10	...	12.97	11.76
12.5	10.87	13.39	12.04
15	11.29	13.77	12.26
17.5	11.68	14.11	...
20	12.05	14.47	12.64
22.5	12.43	14.75	...
25	12.79	15.02	12.89
27.5	13.10	15.27	...
30	13.37	15.50	13.08
35	13.85	...	...
40	14.25	...	13.40
45	14.60	...	...
50	...	...	13.64
75	...	...	14.08
100	(15.5) <sup>a</sup>	(19.0) <sup>a</sup>	14.27

<sup>a</sup> Maximum values estimated in ref 39.

more than one worker (*e.g.*, Table III), little variation is found.

## B. OTHER ACIDITY FUNCTIONS

Other acidity functions have received less attention. The acidity function,  $H_-$ , has also been related to alcohols as the standard state (36, 52). The function can then be designated as, for example,  $H_M$  for methanol as the reference system. The workers who proposed these functions clearly recognized the direct relation between the aqueous  $pK_a$  values of the substituted anilines and the corresponding values obtained in these systems (see p 128). These functions are therefore considered to be, in the main, superfluous.

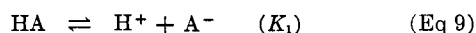
TABLE VIII

 $H_-$  FUNCTION FOR ANHYDROUS 2-AMINOETHANOLS CONTAINING BASE OR ACID

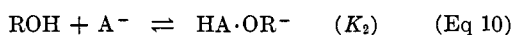
Acid or base, M	2-Aminoethanol		2-Diethyl- aminoethanol containing NaOCH <sub>2</sub> - CH <sub>2</sub> NEt <sub>2</sub> (17)
	Containing NaOCH <sub>2</sub> - CH <sub>2</sub> NH <sub>2</sub> (34)	Containing HOCH <sub>2</sub> - CH <sub>2</sub> NH <sub>2</sub> Cl (26)	
0	14.37	14.37	...
$5 \times 10^{-3}$	14.58	...	14.24
$1 \times 10^{-2}$	14.88	13.99	14.54
$5 \times 10^{-2}$	15.58	13.29	15.24
$1 \times 10^{-1}$	15.88	12.99	15.54
$5 \times 10^{-1}$	16.60	12.29	16.32
1	...	...	16.69

Recently the acidity function,  $H_{2-}$ , has been investigated in strongly basic systems (57). The indicators used in establishing this function are substituted aminobenzoic acids. The ionization studied is the formation of the dianion from the carboxylate mono-anion. The similarity of the acidity function,  $H_{2-}$ , to that of  $H_-$ , in a number of systems, suggests that the activity coefficient ratio  $f_{HA^-}/f_{A^{2-}}$  (indicator HA) is similar to the ratio  $f_{HA^-}/f_{A^{2-}}$  (indicator  $H_2A$ ) in these systems. Thus, these two acidity functions are closely related when the types of equilibria studied are similar. The functions are then largely independent of the charge type of the indicator, when the charge is situated on a different functional group in the indicator to that group where the ionization occurs.

The acidity functions,  $J_-$  and  $J_{2-}$ , have been suggested to relate the addition of base to potential acid, HA (18, 19, 47). The addition of base,  $OR^-$ , to a potential acid, HA, may be assessed in terms of the following hypothetical equilibria.



and



An acidity function,  $J_-$ , can then be defined as

$$J_- = pK_{1,2} + \log ([HA \cdot OR^-]/[HA]) \quad (\text{Eq 11})$$

when  $K_{1,2}$  equals  $K_1K_2$ . This acidity function is thus equivalent to

$$J_- = \log (a_{ROH}/a_{H^+}) + \log (f_{HA}/f_{HA \cdot OR^-}) \quad (\text{Eq 12})$$

A further relation can be postulated if the acidity function,  $H_-$ , is known for the system under study relative to the real equilibria corresponding to Eq 9; then we obtain

$$J_- = H_- + \log a_{ROH} + \log (f_A/f_{HA \cdot OR^-}) \quad (\text{Eq 13})$$

This relation between  $J_-$  and  $H_-$  is then similar to that between  $J_0$  and  $H_0$  (18). No measurements of  $J_-$  for strongly basic systems have yet been made, though suitable systems exist (see p 129). The only application in strongly basic systems (47) of  $J_-$  involves the calculation of this acidity function from  $H_-$  in aqueous sodium hydroxide (54) and known water activities (63), neglecting the activity coefficient ratio term. The variation of  $J_-$  and  $H_-$  in these systems appears to be small.

### III. ACIDITY FUNCTIONS FOR AQUEOUS AND NONAQUEOUS SOLUTIONS

#### A. THE ACIDITY FUNCTIONS

Data are now available for 29 systems. These vary considerably in character. The various solvents are listed in Table IX, with their dielectric and autoprotolysis constants if available.

TABLE IX  
SOLVENTS

Solvent	Dielectric constant $\epsilon$ at 25°		Autoprotolysis constant $pK_H$ , mole <sup>2</sup> l. <sup>-1</sup> at 25°	
	$\epsilon$	Ref	$pK_H$	Ref
Water	78.5	33	14.00	22
Methanol	32.6	33	16.68	12
Ethanol	24.3	33	18.88	53
Isopropyl alcohol	18.3	33	20.80	53
<i>t</i> -Butyl alcohol	10.9 <sup>a</sup>	33	...	
<i>t</i> -Pentyl alcohol	5.8	33	...	
2-Aminoethanol	37.7	43	5.2 <sup>b</sup>	35
2-Diethylaminoethanol	9.1	37	...	
Hydrazine	52.9	33	...	
Ethylenediamine	14.2 <sup>b</sup>	33	...	
Pyridine	12.3	33	...	
Dimethylformamide	36.7	33	18.0 <sup>b</sup>	66
	(26.6)			
Dimethyl sulfoxide	48.9 <sup>b</sup>	65	17.3	29
Tetramethylene sulfone	44.0 <sup>a</sup>	7	...	
Dioxane	2.1	33	...	

<sup>a</sup> At 30°. <sup>b</sup> At 20°.

#### 1. Aqueous Systems

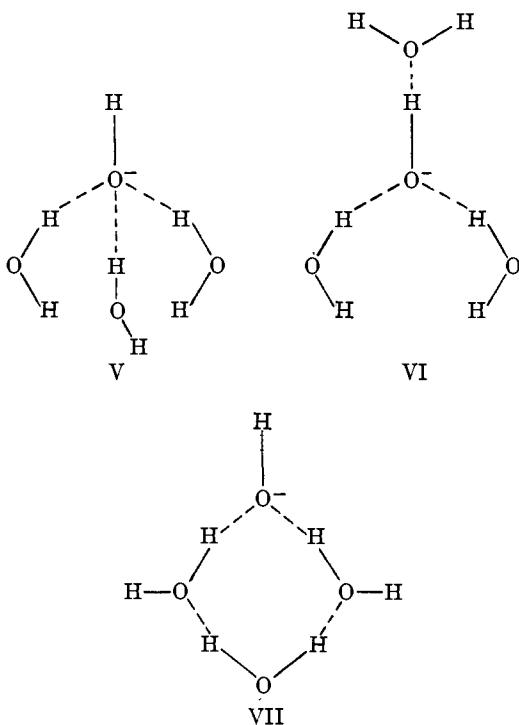
The studies indicate the identity of  $H_-$  with pH in dilute aqueous solution (up to 0.1 *M*). This confirms the firm anchoring of the scale in the pH region. In more concentrated solutions there is a rapid increase in  $H_-$  with base concentration in excess of that expected by the simple expression

$$H_- = pK_w + \log [OH^-] \quad (\text{Eq 14})$$

Unfortunately the results in aqueous potassium and sodium hydroxide have been assessed by different indicator methods to that in standard use. Also the results for lithium hydroxide are less reliable due to the low solubility of the indicators (61). However, it is significant that the order of basicity for the same molarity of aqueous solution,  $LiOH < NaOH < KOH < BzMe_3NOH$ , is the *opposite order* to that of the water content of the very concentrated solutions. Furthermore, there is a very rapid rise in basicity when the water content of the solutions is sharply reduced. It has been suggested that  $OH^-(H_2O)_3$  is the stable species in solution (67) and possible structures V, VI, and VII for this ion are shown (61, 67). Although the constitution of concentrated aqueous alkali is complex, it seems very likely that in the absence of full hydration the activity of the hydroxide is very high (see section IIIB for further details).

#### 2. Alcoholic Systems

Alcoholic solutions have received much attention. For dilute solutions (*e.g.*, 0.1 *M* alkali metal alkoxide in the alcohol) there is an order of basicity rising from methanol ( $H_- = 12.66$ ), ethanol ( $H_- = 14.57$ ), isopropyl alcohol ( $H_- = 16.95$ ), *t*-pentyl alcohol ( $H_- =$



18.09), to *t*-butyl alcohol ( $H_- = 19.14$ ), the basicity of a methanolic solution being comparable to that of an aqueous solution of the same base concentration.

There is a direct relation between  $H_-$  and dilute base concentrations (up to about 0.1 *M* base) such that

$$H_- = B + \log [\text{OR}^-] \quad (\text{Eq 15})$$

where  $B$  is a constant dependent on the nature of the alcohol (5). Values are given in Table X.

TABLE X

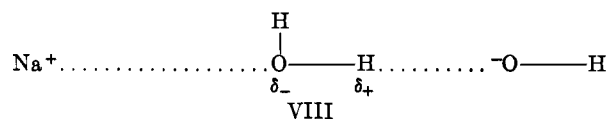
Alcohol	$B$
Methanol	13.66
Ethanol	15.57
Isopropyl alcohol	17.95
<i>t</i> -Butyl alcohol	20.14
<i>t</i> -Pentyl alcohol	19.09
2-Aminoethanol	16.88
2-Diethylaminoethanol	16.54
(Water)	14.00)

The basicity of an alcoholic solution appears to be a function of both the autoprotolysis constant and the proton affinity of the solvent (see p 128).

Measurements have only been made for concentrated solutions of lithium, sodium, and potassium methoxides in methanol. Just as for aqueous solutions the rise in basicity soon becomes more rapid than suggested by Eq 15. The order of this increase for similar, high concentrations of alkoxide seems again dictated by the concentration of methanol in these solutions. Analogous to the hydroxide ion, the stable alkoxide ion would be expected to be hydrated in the

form  $\text{OR}^-(\text{ROH})_3$  if similar to structures V or VII for the hydroxide ion, or  $\text{OR}^-(\text{ROH})_2$  if similar to structure VI. When insufficient solvent exists to fully hydrate the ions, a very sharp rise in the activity of the base is to be expected, and this is observed (36, 42, 52). The much greater deviation from simple behavior, *i.e.*, as shown in Eq 15, in concentrated alcoholic alkoxide solutions is due to the smaller number of moles of alcohol per liter compared to that of water (36). The available solvating species are then more quickly exhausted.

Robinson and Harned (46) have suggested that concentrated solutions (greater than 0.1 *M*) of alkali metal hydroxides contain "solvent-bridged" ion pairs (VIII), and it is of interest that the stable complex, *t*-BuOK·*t*-BuOH, exists and can be vacuum sublimed without decomposition (9).



Their existence will explain the order of activity coefficients, which is  $\text{Li} < \text{Na} < \text{K} < \text{Cs}$ . The smaller ion,  $\text{Li}^+$ , will polarize more strongly the water molecules involved in hydration and increase the tendency toward bridging. It follows that formation of such solvent-bridged ion pairs as the solution becomes more concentrated will prevent the activity of the hydroxyl ion from rising as fast as it otherwise would. Cram and his colleagues (9) have confirmed that the kinetic basicity of solutions containing alkali metal *t*-butoxide in dimethyl sulfoxide is in the order  $\text{Li} < \text{Na} < \text{K}$ . The  $H_-$  results for concentrated alkali metal methoxides in methanol also follow this order (see Table III). It seems very likely that ions similar to VIII also exist in alkoxide solutions. The strongest "solvent-bridged" ion pair will be the lithium salt, and the decreased availability of the alkoxide ion causes these solutions to have a somewhat lower basicity.

The basicity of aqueous alcohols containing added base has been measured (5). In all the aqueous alcohols studied a regular change in basicity is observed. This is quite unlike the previous data for  $H_0$  (40). Qualitatively the situation can be explained as a gradual and continuous change in the *effective* autoprotolysis constant and in the difference in energy of the proton relative to water (see p 128). A quantitative treatment of the alkoxide-hydroxide equilibria similar to that suggested by Caldin and Long (8) gave poor results. It is probably significant that the aqueous dioxane containing sodium hydroxide shows a small but definite increase in basicity compared to aqueous sodium hydroxide. Unfortunately, dioxane has a very limited range of miscibility with aqueous sodium hydroxide which limits the significance of the

results. However dioxane has a very low dielectric constant and is not a strong hydrogen bond acceptor for water, unlike the dipolar aprotic solvents (see below). A "salting-in" effect on the uncharged acid, as suggested for the  $H_0$  function, would have the opposite effect and decrease the basicity.

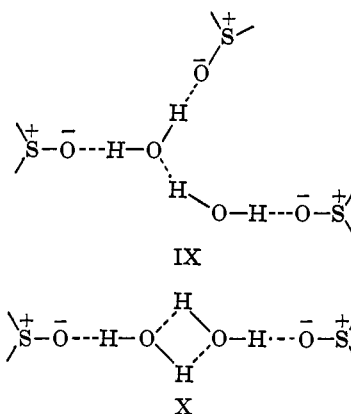
### 3. Aqueous and Alcoholic Dipolar Aprotic Solvents

The results for mixed solvents containing water, a dipolar aprotic solvent, and added base (*e.g.*, a tetraalkylammonium hydroxide) are similar to those found in the aqueous and alcohol systems discussed in the previous section, but the effects are greatly enhanced. A considerable increase in  $H_-$  is observed in all cases as the dipolar aprotic solvent content is raised; the rates of increase are different, however, and are in the order pyridine < tetramethylene sulfone < dimethyl sulfoxide. On the other hand, if the concentration of added strong base is varied and the solvent composition kept the same, it is found that the basicity of the solution increases according to the simple expression

$$H_- = \log ([OH^-]_a/[OH^-]_b) \quad (\text{Eq 16})$$

where  $[OH^-]_a$  and  $[OH^-]_b$  are the concentrations of added base. This applies to each of the three solvent systems, aqueous pyridine, aqueous tetramethylene sulfone, and aqueous dimethyl sulfoxide, *but only* if the water content is not very low; in those cases the increase in basicity is much more rapid than that predicted by the use of Eq 16.

As the water in a dilute solution of tetramethylammonium hydroxide is replaced by dimethyl sulfoxide, the basicity climbs and this is again due to the heightened activity of hydroxide ion. The dimethyl sulfoxide forms hydrogen bonds to water and effectively competes with hydroxide ion in this way. It should be noted that sizeable increases in basicity are found at fairly low concentrations of dimethyl sulfoxide. The hydroxide ion concentration in most of the systems examined has been low (usually 0.01 *M*), and the molarity of water is greatly in excess of that required to form the trihydrate. Thus the  $H_-$  value of a 0.01 *M* tetramethylammonium hydroxide solution in 50 mole % dimethyl sulfoxide and 50 mole % water is 17.2, meaning that this solution is some  $10^4$  times more basic than a purely aqueous solution containing the same quantity of the base. However, the molar ratio of water to hydroxide ion in this system is still high, being about 280. Thus when dimethyl sulfoxide replaces water in an aqueous hydroxide solution, it increases the activity of the  $[OH^-]$  not merely by displacing water but by coordinating with the water that remains, as in structures IX and X (30). Dimethyl sulfoxide is ineffective at complexing with anions, chiefly because it lacks an "active" hydrogen,

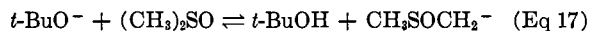


but also because the positive end of its dipole is buried in the molecule (9, 41). The order of the strength of the strong hydrogen-bonded complexes formed between the water and these dipolar aprotic solvents (24) is the same as that shown for the relative rates of increase of  $H_-$ .

This situation is only partly analogous to that found in strongly acid systems. For 8 *M* sulfuric acid the  $H_0$  value of the system is  $-3.87$ , and this reflects a fairly acute shortage of water molecules since the molar ratio of water to protons (2.2) is insufficient to form the ion  $H(H_2O)_4^+$ . The rapid rise in acidity as sulfuric acid replaces water is readily understandable then, since the addition of acid has a double effect. It raises the number of protons and lowers the number of water molecules available for their solvation.

A solution of sodium methoxide in methanolic dimethyl sulfoxide is less basic than a similar sodium hydroxide solution in aqueous dimethyl sulfoxide. This appears to be due both to the more stable structure formed by a water dimethyl sulfoxide solvent and the intrinsically greater basicity of the hydroxide than the methoxide ion (see p 125).

The equilibrium shown below has been shown to exist in alkali metal alkoxide solutions in dimethyl sulfoxide (31).



The equilibrium constant has been found to be  $1.5 \times 10^{-7}$  at  $25^\circ$ , when  $[t\text{-BuOK}]$  is about  $5 \times 10^{-4}$  *M* and, thus, this will only be important for systems of very low alcohol content.

### 4. Amine Solvents

The systems listed in Table VI, aqueous hydrazine, aqueous ethylenediamine, and aqueous 2-aminoethanol, unlike those such as dimethyl sulfoxide, required no added base. This is because the proton has a very high energy of solvation in these amine solvents. Thus, although these systems are quite basic, they are rather ineffective catalysts for the  $H_2$ - $D_2$  exchange reaction (15). The concentration of the hydroxide ion is low in these systems, but the activity is high.



As the water content of aqueous ethylenediamine is decreased, the basicity continues to rise; the basicity of aqueous hydrazine, on the other hand, does not appear to increase greatly after formation of the monohydrate (*i.e.*, 50 mole % water). In the presence of their alkali metal salts, *e.g.*, lithium aminoethyleneamide in ethylenediamine, these amine solvents undoubtedly produce extremely basic systems.

In the presence of its sodium salt, 2-aminoethanol has a behavior similar to that described for alcohols with  $B$  equal to 16.88 (see Eq 15). Similarly, a solution containing 2-aminoethanol hydrochloride,  $\text{RH}_2\text{Cl}$ , can be described by the relation

$$H_- = A - \log [\text{RH}_2^+] \quad (\text{Eq 18})$$

where  $A$  is a constant and  $[\text{RH}_2^+]$  is the concentration of ammonium salt. Similar studies (52) have been made, using 2,2',4,4',6,6'-hexanitrodiphenylamine ( $\text{p}K_a = 2.63$ ) (61) as the indicator, in alcohols containing hydrogen chloride. The values of  $A$  are shown in Table XI. It has pointed out that the autoprotolysis constant,  $\text{p}K_{\text{H}}^{\text{ROH}}$ , may be estimated from those values, as (26; see also p 128)

$$\text{p}K_{\text{H}}^{\text{ROH}} = B - A \quad (\text{Eq 19})$$

These calculated  $\text{p}K_{\text{H}}^{\text{ROH}}$ s are also shown in Table XI. The agreement with the known values is good for 2-aminoethanol alone. The larger differences observed for the alcohols are probably due to the uncertainties in the treatment.

TABLE XI

Alcohol	$A$	$\text{p}K_{\text{H}}^{\text{ROH}}$	
		Calcd <sup>a</sup>	Lit. <sup>b</sup>
2-Aminoethanol	11.99	4.89	5.2
Methanol	-1.58	15.24	16.68
Ethanol	-1.21	16.78	18.88
Isopropyl alcohol	-0.99	18.94	20.80

<sup>a</sup> From Eq 19. <sup>b</sup> See Table IX.

Although 2-diethylaminoethanol in the presence of conjugate base (the sodium salt) appears to behave normally ( $H_-$  correlation a little poorer than usual; probably due to the low dielectric constant of the medium), the strange behavior of its aqueous mixtures defies understanding at present (37). Only a gradual increase in  $H_-$  with decreasing water content can be predicted, while an apparent fall in basicity occurs after a comparatively low concentration of 2-diethylaminoethanol ( $\sim 85$  mole % water) is reached.

### 5. Other Systems

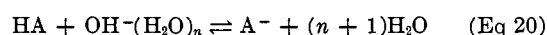
Other systems have been qualitatively investigated and appear promising. Sodium methoxide or isopropoxide in dimethylformamide (16, 66), potassium *t*-butoxide, and the sodium or potassium salt of dimethyl sulfoxide in dimethyl sulfoxide (31, 44, 56) appear to

ionize weak acids with  $\text{p}K_a$  at least as high as 19 in the first case and even greater in the second.

Recent studies of the acidity of weak acids in dimethyl sulfoxide containing the sodium or potassium salt of dimethyl sulfoxide detect specific solvation effects affecting the relative order of acidity of different types of weak acids (31, 56). The latter solvent is unable to effectively solvate anions. This appears to disproportionately affect the alcohols whose anions appear to need hydrogen-bonded solvation, compared to carbon acids, phenols, and anilines.

### B. PHYSICO-CHEMICAL THEORY AND IMPLICATIONS

The  $H_-$  function for aqueous alkali metal hydroxide solution has been rationalized by Yagil and Anbar (67) in a similar manner to Bascombe and Bell's (3) treatment of the  $H_0$  function for concentrated acid solution. The equilibria may be represented as



where  $n$  is the effective hydration number of the hydroxide ion. Assuming the ratio of the activity coefficients in the above equilibria is equal to unity and the hydration of the cation and indicator anion is unimportant, a consideration of the above equilibrium and the relation 2 derived previously, the expression is obtained as

$$H_- = \text{p}K_w + \log ([\text{OH}^-]/[\text{H}_2\text{O}]^{n+1}) \quad (\text{Eq 21})$$

for the molar scale. Similar expressions can be derived for the mole fraction and volume fraction scale. The assumption of the hydration number,  $n$ , as 3 gives the best agreement with the data of Schwarzenbach and Sulzberger, and this fit is good considering the uncertainty in the scale and the inexact nature of the assumptions. The sharp rise in basicity is thus attributed to the fall in the free water concentration. It is suggested that sodium hydroxide exists, in very concentrated solutions, mainly as water-bridged ion pairs (46; see p 125) and that the hydroxide ion exists in solution normally as  $\text{OH}^-(\text{H}_2\text{O})_3$ .

Previously Edward and Wang (14), in a similar treatment, obtained the relation

$$H_- = \text{p}K_w + \log [\text{OH}^-] + \log (f_{\text{HA}}f_{\text{OH}^-}/f_{\text{A}^-}) - (p+1) \log a_w \quad (\text{Eq 22})$$

where  $p$  is the difference in hydration numbers on ionization. As the activity of water becomes unity in dilute solution the equation reduces to Eq 14

$$H_- = \text{p}K_w + \log [\text{OH}^-]$$

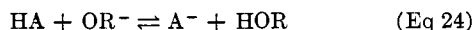
and this has been confirmed for dilute aqueous alkaline solutions. These workers propose that the activity coefficient ratio is a function of the activity of water ( $r \log a_w$ ) so that

$$H_- = \text{p}K_w + \log [\text{OH}^-] + (r-p-1) \log a_w \quad (\text{Eq 23})$$

Over a restricted range of base concentration (up to about 4.5 *M*), this relation gives good agreement with ( $r - p - 1$ ) equal to 3.2.

A similar relation to Eq 21 has been examined for concentrated solutions of sodium methoxide in methanol (36). A satisfactory fit was stated to have been obtained using  $n$  equal to 4. A more reasonable result would have given  $n$  equal to 3 (see p 125), but it seems likely that considering the approximations made the results obtained are in reasonable agreement.

Another approach can be made by an adaptation of the ideas of Grunwald (20) and Izmailov (25). This treatment can only be applied, as yet, to dilute alcoholic alkali metal alkoxide solutions (5). The ionization of an acid in an alcohol may be written as



The negative logarithm of the equilibrium constant  $pK_e^{\text{HA}}$  can be defined as

$$pK_e^{\text{HA}} = \log [\text{OR}^-] + \log ([\text{HA}]/[\text{A}^-]) \quad (\text{Eq 25})$$

The autoprotolysis constant  $K_H^{\text{ROH}}$  is related by

$$pK_H^{\text{ROH}} = -\log [\text{OR}^-] - \log [\text{ROH}_2^+] \quad (\text{Eq 26})$$

From the above relations 25 and 26, together with the earlier considerations (Eq 2 and 3) and assuming the indicator activity coefficient ratio is unity, the following relation is given.

$$pK_a^{\text{HA}} - pK_e^{\text{HA}} - pK_H^{\text{ROH}} = \log [\text{ROH}_2^+] - \log a_{\text{H}^+} \quad (\text{Eq 27})$$

The degenerate activity coefficient,  $\log \gamma^{\text{ROH}}$ , proportional to the difference in chemical energy of solvation of the protons in water and the alcohol<sup>2</sup> (25), is then given by

$$\log \gamma^{\text{ROH}} = \log a_{\text{H}^+} - \log [\text{ROH}_2^+] \quad (\text{Eq 28})$$

or

$$\log \gamma^{\text{ROH}} = pK_e^{\text{HA}} + pK_H^{\text{ROH}} - pK_a^{\text{HA}} \quad (\text{Eq 29})$$

TABLE XII

	$pK_H^{\text{ROH}} + \log \gamma^{\text{ROH}}$	$-\log \gamma^{\text{ROH}}$	
		Calcd	Lit. (25)
Methanol	13.66	3.02	3.1-3.5
Ethanol	15.57	3.31	4.1-4.3
Isopropyl alcohol	17.95	2.85	...
<i>t</i> -Butyl alcohol	20.14	...	...
<i>t</i> -Pentyl alcohol	19.09	...	...
2-Aminoethanol	16.88	-11.68	...
2-Diethylaminoethanol	16.54	...	...

The values so obtained are shown in Table XII and are in reasonable agreement with those calculated by other means (25). The validity of the assumptions, and therefore the derived values, probably becomes less secure as the dielectric falls.

(2) The difference in chemical energy of solvation of the protons in water and the alcohol is equal to  $2.303RT \log \gamma^{\text{ROH}}$  kcal (25).

In the dilute region the acidity of an alcoholic solution is related to that of a similar concentration of base in water by the equation

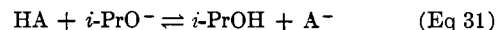
$$H_-(\text{alcohol}) - H_-(\text{water}) = pK_H^{\text{ROH}} - pK_H^{\text{H}_2\text{O}} - \log \gamma^{\text{ROH}} \quad (\text{Eq 30})$$

Thus the relative basicity of the alcoholic alkoxide solution is determined by both the change in the autoprotolysis constant and the difference in the energy of the proton in the alcohol relative to that in water.

#### IV. DETERMINATION OF THE STRENGTH OF WEAK ACIDS

##### A. COMPETITION METHODS

The ionization of aromatic amine indicators has been investigated in isopropyl alcohol containing sodium isopropoxide (23, 27).



The equilibrium constants,  $K_e$ , were obtained so that

$$K_e = [\text{A}^-]/[\text{HA}][i\text{-PrO}^-] \quad (\text{Eq 32})$$

These constants are a measure of the relative acidities of the indicators. The  $pK_a$  values of these amines have been measured, and these values appear to be of general validity in a variety of systems (60). The relation between  $pK_e$  and  $pK_a$  is linear, such that for Hine and Hine's results,  $pK_a = 18.31 + pK_e$ , with a mean deviation of  $\pm 0.11$   $pK_a$  unit. Schaal's results give  $17.98 \pm 0.15$ . Edward (13) has recently shown that equilibrium data involving competition between a neutral indicator and a neutral Brønsted base for a molecule of acid can be correlated with  $pK_{\text{BH}^+}$  values. The competition between the neutral acid indicator (HA) and a second neutral acid (HB) for the base ( $i\text{-PrO}^-$ ) has also been measured by the above workers (23, 27). The equilibrium constants,  $K_e'$ , given by

$$K_e' = [\text{B}^-]/[\text{HB}][i\text{-PrO}^-] \quad (\text{Eq 33})$$

have been obtained for certain interesting compounds, for which direct measurements are difficult or impossible. The  $pK_a$  of these compounds can now be estimated using the relation between  $pK_a$  and  $pK_e$  obtained above, and these are given in Table XIII. These values are dependent on the similarity of the  $H_-$  scale applicable to aromatic amines as acids to that applicable to alcohols and other compounds as acids.

##### B. DIRECT METHODS

The application of  $H_-$  acidity scale to the measurement of the acidity of acids other than aromatic amines, by direct spectral measurements, has not been extensively tested.

TABLE XIII

pK <sub>a</sub> VALUES OF SOME ALCOHOLS AND AMIDES <sup>a</sup>			
Compound	pK <sub>a</sub> <sup>b</sup>	Compound	pK <sub>a</sub> <sup>b</sup>
Isopropyl alcohol	19.43	2-Phenoxyethanol	17.27
Ethanol	18.33 (12.7-18)	2-Ethoxyethanol	17.23
Water	18.23 (15.74)	Formamide	17.20
1-Methoxy-2-propanol	18.05	Phenoxyacetamide	17.20
Benzhydrol	17.99	<i>p</i> -Bromobenzamide	17.13
Allyl alcohol	17.88 (15.5)	Ethylene glycol	16.68 (15.5)
Benzyl alcohol	17.73	Benzanilide	16.53
Methanol	17.71 (15.5-16.6)	Methyl lactate	15.99
Acetanilide	17.59	<i>p</i> -Nitrobenzamide	15.85
2-Aminoethanol	17.42	<i>p</i> -Bromobenzanilide	15.73
2-Methoxyethanol	17.41 (14.8)	Formanilide	15.56
Phenylacetanilide	17.31	Diethyl malonate	14.29 <sup>c</sup>

<sup>a</sup> From Hine and Hine's results (23). <sup>b</sup> Values in parentheses are values taken from Arnett's review (2); they are mainly from the studies by Long and Ballinger (32). <sup>c</sup> From Schaal's studies (27).

The recent investigations of the  $H_0$  function show that a number of acidity function scales are applicable. The function applicable is dependent on the nature of the base to be protonated. Thus, a complete  $H_-$  scale relative to carbon acids especially is highly desirable. Such a scale has been recently constructed (6), and the pK<sub>a</sub> values are given in Table XIV. The generality of the derived pK<sub>a</sub> values and the relation of these scales to those obtained using substituted anilines has yet to be widely tested. Two of the carbon acids have previously been studied relative to the established  $H_-$  scale (7, 30), and these values are in good agreement with those obtained directly. It seems quite possible that nitrogen acids (substituted anilines) and carbon acids respond in a similar way to the basic systems studied. Rochester has investigated certain substituted phenols in methanolic sodium methoxide (47a). This scale is not related to the aqueous system by the author. Using the known value of 10.23 for the pK<sub>a</sub> of *p*-*t*-butylphenol (8a), these phenols seem to have a distinctly different response to methanolic methoxide compared to anilines. The acidity function also appears to increase less rapidly in the more concentrated solutions, but the other indicators are unfortunately *o*-*t*-butylphenols which have appreciable steric hindrance to solvation of the anion.

The equilibrium constants of a number of polynitroaromatic hydrocarbons, which cannot, or apparently do not, ionize normally, have been measured (19, 48, 52). These compounds, it would appear, form addition complexes (19, 49), though the equilibria appears

TABLE XIV

CARBON ACID INDICATORS pK <sub>a</sub> VALUES (6)	
Acid	pK <sub>a</sub>
Malonitrile	11.14
9-Cyanofluorene	11.41
Methyl fluorene-9-carboxylate	12.88
4,4',4''-Trinitrotriphenylmethane	14.32
4,4'-Dinitrodiphenylmethane	15.85 <sup>a</sup>
2,4'-Dinitrodiphenylmethane	17.38
3,4'-Dinitrodiphenylmethane	17.62
9-Phenylfluorene	18.59 <sup>a</sup>
Fluorene	21.0

<sup>a</sup> Values obtained by use of  $H_-$  scale (substituted anilines) are 15.82 (4,4'-dinitrodiphenylmethane) and 18.49 (9-phenylfluorene) (7, 30).

to follow the  $H_-$  function in a particular solvent system. In Table XV apparent "pK<sub>a</sub>" values are given, *i.e.*, using  $H_-$  scales as if acid ionizes normally. The similarity of the "pK<sub>a</sub>" values for the substituted toluenes to those of the substituted benzenes confirms the likelihood of the addition mechanisms. The very significant difference in the derived "pK<sub>a</sub>" values in the aqueous solutions to that in the alcoholic solutions reflects the difference in the basicities of these solutions and their "nucleophilic" reactivity (*e.g.*, ref 1).

Assuming that  $J_-$  and  $H_-$  are identical in dilute aqueous hydroxide (up to 0.1 *M*), pK<sub>1,2</sub> values and  $J_-$  for other solvents can be calculated. The assumptions are that the aqueous  $H_-$  values are valid for these equilibria and the activity coefficient ratio (see Eq 13) can be neglected. The latter is probably not completely valid. The results, in Tables XVI and XVII, appear quite reasonable. The pK<sub>1,2</sub> values are in the order expected for the formation of an addition complex. The change in the relative values of the acidity functions for aqueous and alcoholic systems confirms the greater "nucleophilic" character of the alkoxide ions.

## V. SUMMARY

The  $H_-$  acidity function appears to be well established for strongly basic solutions using aromatic amine indicators. The function is governed by the relation

$$H_- = pK_a - \log ([HA]/[A^-])$$

through the indicator's pK<sub>a</sub> value and its ionization ratio [HA]/[A<sup>-</sup>]. The function is securely anchored in the dilute aqueous regions where  $H_-$  and pH become identical.

The basicity of 29 aqueous and nonaqueous solutions has been assessed. The basic solutions have varied characteristics in solvents with dielectric constants in the range 78.5 to 5.8. The relation of the basicities to the solvent and base is adduced and the application of quantitative physicochemical theory is discussed.

TABLE XV  
 APPARENT "pK<sub>a</sub>" VALUES OF POLY-NITROAROMATIC COMPOUNDS

	Aqueous ethylenediamine (49)	Aqueous hydrazine (50)	Aqueous sodium hydroxide (5, 19)	Methanolic alkali metal methoxide (19, 52)	Ethanollic alkali metal ethoxide (52)
1,3,5-Trinitrobenzene	13.53	...	13.57	12.45	12.37
2,4,6-Trinitrotoluene	13.60	13.73	13.69	12.81	12.43
2,4,6-Trinitro- <i>m</i> -xylene	14.98	...	...	13.94	13.87
1,3-Dinitrobenzene	15.70	...	...	...	...
2,4-Dinitrotoluene	15.99	...	...	...	...

TABLE XVI

APPLICATIONS OF THE ACIDITY FUNCTION *J*-

Indicator	pK <sub>1,2</sub>
1,3,5-Trinitrobenzene	13.55
2,4,6-Trinitrotoluene	13.68
2,4,6-Trinitro- <i>m</i> -xylene	14.98

TABLE XVII

*J*-FUNCTION FOR AQUEOUS AND ALCOHOLIC BASE

Base, <i>M</i>	NaOH in water (5, 19)	LiOMe or NaOMe in methanol (19, 52)	NaOEt in ethanol (52)
1 × 10 <sup>-3</sup>	11.00	11.66	13.75
5 × 10 <sup>-3</sup>	11.70	12.36	14.45
1 × 10 <sup>-2</sup>	12.00	12.66	14.75
5 × 10 <sup>-2</sup>	12.70	13.36	15.45
1 × 10 <sup>-1</sup>	13.00	13.66	15.75

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## VI. REFERENCES

- (1) Alet, I. R., and England, B. D., *J. Chem. Soc.*, 5259 (1961).
- (2) Arnett, E. M., "Progress in Physical Organic Chemistry," S. G. Cohen, *et al.*, Ed., Interscience Publishers, New York, N. Y., 1963, p 223.
- (3) Bascombe, K. N., and Bell, R. P., *Discussions Faraday Soc.*, 24, 158 (1957).
- (4) Bethel, D., *J. Chem. Soc.*, 666 (1963).
- (5) Bowden, K., *Can. J. Chem.*, 43, 2624 (1965).
- (6) Bowden, K., and Stewart, R., *Tetrahedron*, 21, 261 (1965).
- (7) Burwell, R. L., and Langford, C. H., *J. Am. Chem. Soc.*, 82, 1503 (1960).
- (8) Caldin, E. F., and Long, G., *J. Chem. Soc.*, 3737 (1954).
- (8a) Cohen, L. A., and Jones, W. M., *J. Am. Chem. Soc.*, 85, 3397 (1963).
- (9) Cram, D. J., Rickborn, B., Kingsbury, C. A., and Haberfield, P., *J. Am. Chem. Soc.*, 83, 3678 (1961).
- (10) Crampton, M. R., and Gold, V., *Proc. Chem. Soc.*, 298 (1964).
- (11) Deno, N. C., *J. Am. Chem. Soc.*, 74, 2039 (1952).
- (12) Dondon, M. L., *J. Chim. Phys.*, 48, 27 (1951).
- (13) Edward, J. T., *Chem. Ind. (London)*, 489 (1963).
- (14) Edward, J. T., and Wang, I. C., *Can. J. Chem.*, 40, 399 (1962).
- (15) Flournory, J. M., and Wilmarth, W. K., *J. Am. Chem. Soc.*, 83, 2257 (1961).
- (16) Fritz, J. S., "Acid-Base Titrations in Non-aqueous Solvents," G. F. Smith Chem. Co., Columbus, Ohio, 1952, p 44.
- (17) Gaboriaud, R., Monnaye, B., and Schaal, R., *Compt. Rend.*, 254, 4027 (1962).
- (18) Gold, V., and Hawes, B. W. V., *J. Chem. Soc.*, 2102 (1951).
- (19) Gold, V., and Rochester, C. H., *J. Chem. Soc.*, 1692, 1697, 1722, 1727 (1964).
- (20) Gutbezahl, B., and Grunwald, E., *J. Am. Chem. Soc.*, 75, 865 (1953).
- (21) Hammett, L. P., "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter IX.
- (22) Harned, H. S., and Robinson, R. A., *Trans. Faraday Soc.*, 36, 973 (1940).
- (23) Hine, J., and Hine, M., *J. Am. Chem. Soc.*, 74, 5266 (1952).
- (24) Holmes, J. R., Kivelson, D., and Drinkard, W. C., *J. Am. Chem. Soc.*, 84, 4677 (1962).
- (25) Izmailov, N. A., *Proc. Acad. Sci. USSR, Phys. Chem. Sect.*, 127, 501 (1959).
- (26) Jacquinet-Vermeesse, C., and Schaal, R., *Compt. Rend.*, 254, 2679 (1961).
- (27) Jacquinet-Vermeesse, C., Schaal, R., and Rumpf, P., *Bull. Soc. Chim. France*, 2030 (1960).
- (28) Jacquinet-Vermeesse, C., Schaal, R., and Souchay, P., *Bull. Soc. Chim. France*, 141 (1960).
- (29) Kolthoff, I. M., and Reddy, T. B., *Inorg. Chem.*, 1, 189 (1962).
- (30) Langford, C. H., Ph.D. Thesis, Northwestern University, 1960.
- (31) Ledwith, A., and McFarlane, N., *Proc. Chem. Soc.*, 108 (1964).
- (32) Long, F. A., and Ballinger, P., "Electrolytes," B. Pesce, Ed., Pergamon Press Ltd., Oxford, 1962, p 152.
- (33) Maryott, A. A., and Smith, E. R., National Bureau of Standards Circular 514, U. S. Government Printing Office, Washington, D. C., 1951.
- (34) Masure, F., and Schaal, R., *Bull. Soc. Chim. France*, 1138, 1141 (1956).
- (35) Masure, F., Schaal, R., and Souchay, P., *Bull. Soc. Chim. France*, 1143 (1956).
- (36) More O'Ferrall, R. A., and Ridd, J. H., *J. Chem. Soc.*, 5030 (1963).
- (37) Mouronval, S., Gaboriaud, R., and Schaal, R., *Compt. Rend.*, 255, 2605 (1962).
- (38) Noyce, D. S., and Jorgenson, M. J., *J. Am. Chem. Soc.*, 83, 2525 (1961).
- (39) O'Donnell, J. P., Ph.D. Thesis, University of British Columbia, 1962.
- (40) Paul, M. A., and Long, F. A., *Chem. Rev.*, 57, 1 (1957).
- (41) Parker, A. J., *Quart. Rev. (London)*, 15, 163 (1962).
- (42) Peure, F., and Schaal, R., *Bull. Soc. Chim. France*, 2636 (1963).
- (43) Pinkston, J. T., and Briscoe, H. T., *J. Phys. Chem.*, 46, 469 (1942).
- (44) Price, G. G., and Whiting, M. C., *Chem. Ind. (London)*, 775 (1963).
- (45) Ridd, J. H., *Chem. Ind. (London)*, 1268 (1957).

- (46) Robinson, R. A., and Harned, H. S., *Chem. Rev.*, **28**, 419 (1941).
- (47) Rochester, C. H., *Trans. Faraday Soc.*, **59**, 2820 (1963).
- (47a) Rochester, C. H., *J. Chem. Soc.*, 676 (1965).
- (48) Schaal, R., *Compt. Rend.*, **239**, 1036 (1954).
- (49) Schaal, R., *J. Chim. Phys.*, **52**, 784, 796 (1955).
- (50) Schaal, R., and Favrier, P., *Bull. Soc. Chim. France*, 2011 (1959).
- (51) Schaal, R., and Gadet, C., *Bull. Soc. Chim. France*, 2154 (1961).
- (52) Schaal, R., and Lambert, G., *J. Chim. Phys.*, **59**, 1151, 1164, 1170 (1962).
- (53) Schaal, R., and Tézé, A., *Bull. Soc. Chim. France*, 1783 (1961).
- (54) Schwarzenbach, G., and Sulzberger, R., *Helv. Chim. Acta*, **27**, 348 (1944).
- (55) Stearns, R. S., and Wheland, G. W., *J. Am. Chem. Soc.*, **69**, 2025 (1947).
- (56) Steiner, E. C., and Gilbert, J. M., *J. Am. Chem. Soc.*, **85**, 3054 (1963).
- (57) Stewart, R., Bowden, K., and Buckley, A., *J. Am. Chem. Soc.*, in press.
- (58) Stewart, R., Bowden, K., and O'Donnell, J. P., *Can. J. Chem.*, **43**, 1225 (1965).
- (59) Stewart, R., and Dolman, D., unpublished results.
- (60) Stewart, R., and O'Donnell, J. P., *J. Am. Chem. Soc.*, **84**, 493 (1962).
- (61) Stewart, R., and O'Donnell, J. P., *Can. J. Chem.*, **42**, 1681, 1694 (1964).
- (62) Stewart, R., O'Donnell, J. P., Cram, D. J., and Rickborn, B., *Tetrahedron*, **18**, 917 (1962).
- (63) Stokes, R. H., *J. Am. Chem. Soc.*, **67**, 1689 (1945).
- (64) Taft, R. W., *J. Am. Chem. Soc.*, **82**, 2965 (1960).
- (65) "Technical Bulletin on Dimethyl Sulfoxide," Crown Zellerbach Corp., Camas, Wash., 1963.
- (66) Tézé, M., and Schaal, R., *Bull. Soc. Chim. France*, 1372 (1962).
- (67) Yagil, G., and Anbar, M., *J. Am. Chem. Soc.*, **85**, 2376 (1963).