

[CONTRIBUTION FROM THE LABORATORY OF INORGANIC CHEMISTRY, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

## THE STRENGTH OF ORGANIC BASES IN GLACIAL ACETIC ACID SOLUTION<sup>1</sup>

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Although the earlier papers of this series have frequently dealt with the titration of organic amines in glacial acetic acid, the subject has been treated more or less incidentally, and only scattering selections have been made from the available data. In the present paper are summarized the results of a study of a large number of these compounds, and it has been possible to draw certain conclusions of interest to the general theory of acidity. A clear parallelism has been found between the strengths of these bases in acetic acid and in water, and the results are compared with similar results by other workers in three other solvents.

Table I presents an alphabetical list of the bases successfully studied, and the numerals used to identify them on the diagrams.

TABLE I

LIST OF BASES STUDIED WITH IDENTIFYING NUMERALS

Acetamide	11	Formanilide	3b
Acetanilide	5	Guanidine	52f
Acetoxime	19	N-Methylacetanilide	8
<i>p</i> -Aminodimethylaniline	52b	Methylaniline	37b
Ammonia	52c	Methylethylaniline	52a
Anisalacetophenone	2	Methyl- <i>n</i> -propylaniline	51
<i>m</i> -Anisidine	34	Methyl- <i>o</i> -toluidine	41
<i>o</i> -Anisidine	38	Methyl- <i>p</i> -toluidine	42b
<i>p</i> -Anisidine	35	Methylurea	14
Antipyrine	25	$\alpha$ -Naphthylamine	32
Benzylaniline	36a	<i>o</i> -Nitro-aniline	9
<i>m</i> -Bromo-aniline	27	<i>p</i> -Nitro-aniline	18
<i>o</i> -Bromo-aniline	23	3-Nitro-4-chloro-aniline	21a
<i>p</i> -Bromo-aniline	31	4-Nitro-2,6-dichloro-aniline	1b
<i>m</i> -Chloro-aniline	26	<i>m</i> -Nitrodimethylaniline	22
<i>o</i> -Chloro-aniline	24	<i>p</i> -Nitrodimethylaniline	12
<i>p</i> -Chloro-aniline	30	<i>p</i> -Nitrosodiphenylamine	28
Colchicine	21b	Phenylurea	10
Diacetylmonoxime	3a	$\alpha$ -Picoline	47
Di- <i>n</i> -butylamine	52e	Piperidine	49

<sup>1</sup> This is the fifth of a series of acidity studies to which the present author has contributed. Earlier papers have appeared under the title "Studies in Superacid Solutions" as follows: Hall and Conant, *THIS JOURNAL*, **49**, 3047-3061 (1927) (herein referred to as "I"); Conant and Hall, *ibid.*, **49**, 3062-3070 (1927) (II); Hall and Werner, *ibid.*, **50**, 2367-2386 (1928) (III); and Conant and Werner, *ibid.*, **52**, 4436 (1930) (IV). The principal results of this paper were presented at the Swampscott meeting of the American Chemical Society in September, 1928.

TABLE I (Concluded)

2,4-Dichloro-aniline	20	Propionitrile	1a
2,5-Dichloro-aniline	17	N-Propylacetanilide	7
Diethylamine	50a	Pyridine	45
Diethylaniline	53b	Quinoline	42a
Diethyl- <i>o</i> -toluidine	55	Semicarbazide	29
Diethyl- <i>p</i> -toluidine	54b	<i>m</i> -Toluidine	33
Dimethylamine	46	<i>o</i> -Toluidine	36b
Dimethylaniline	44	<i>p</i> -Toluidine	37a
<i>s</i> -Dimethyldiphenylurea	4	Tribromo-aniline	6
Dimethylpyrone	15	Tri- <i>n</i> -butylamine	52d
Dimethyl- <i>o</i> -toluidine	54a	Triethanolamine	53c
Diphenylamine	16	Triethylamine	54c
Diphenylguanidine	48	Triphenylguanidine	50b
Di- <i>n</i> -propylaniline	53a	Urea	13
Ethylaniline	43		

**Method of Study.**—The bases were all titrated in 0.05 molar solutions with perchloric acid as has been previously described.<sup>2</sup>

The potentials reported are those of cells of a type already pictured<sup>3</sup> and the former convention has been used to define " $P_{\text{H}}^{\text{(HAc)}}$ ." The temperature was  $25 \pm 2^\circ$ . Results are reported in this section of the paper for those bases only whose curves showed no marked abnormality such as is caused by rapid reaction with chloranil, the formation of precipitates, or the formation of hemi-perchlorates.

### Experimental Results

If the titration data are all plotted on a single diagram (Fig. 1),<sup>4</sup> the assemblage of curves has a considerable resemblance, in spite of differences noted below, to such theoretical plots of the curves of unequally strong acids or bases in water as, for example, the one given by Britton.<sup>5</sup>

**Survey of the Titration Curves.**—For convenience in discussion, the bases are divisible into three groups. The first group comprises the weakest bases, as far down as No. 11 (acetamide) and includes those whose curves show no appreciable break. The second or intermediate group extends from *p*-nitrodimethylaniline (12) to *p*-bromo-aniline (31) and includes bases whose curves show both an initial rise and a break at the end of the titration. The remaining (strongest) base curves show no initial rise. The points of division between the groups are of course somewhat arbitrary.

<sup>2</sup> (III) Hall and Werner, *THIS JOURNAL*, **50**, 2367–2386 (1928).

<sup>3</sup> Hall and Werner, *ibid.*, p. 2369 and Fig. 3.

<sup>4</sup> The drawing of the unnumbered curves near the bottom of Fig. 1 is somewhat schematic.

<sup>5</sup> H. T. S. Britton, "Hydrogen Ions," D. Van Nostrand Co., New York, 1929, p. 127, Fig. 36.

**Bases of Intermediate Strength.**—In the second or intermediate group the curves all run substantially parallel throughout most of their course, as required by the elementary theory of titration, but their e.m.f.

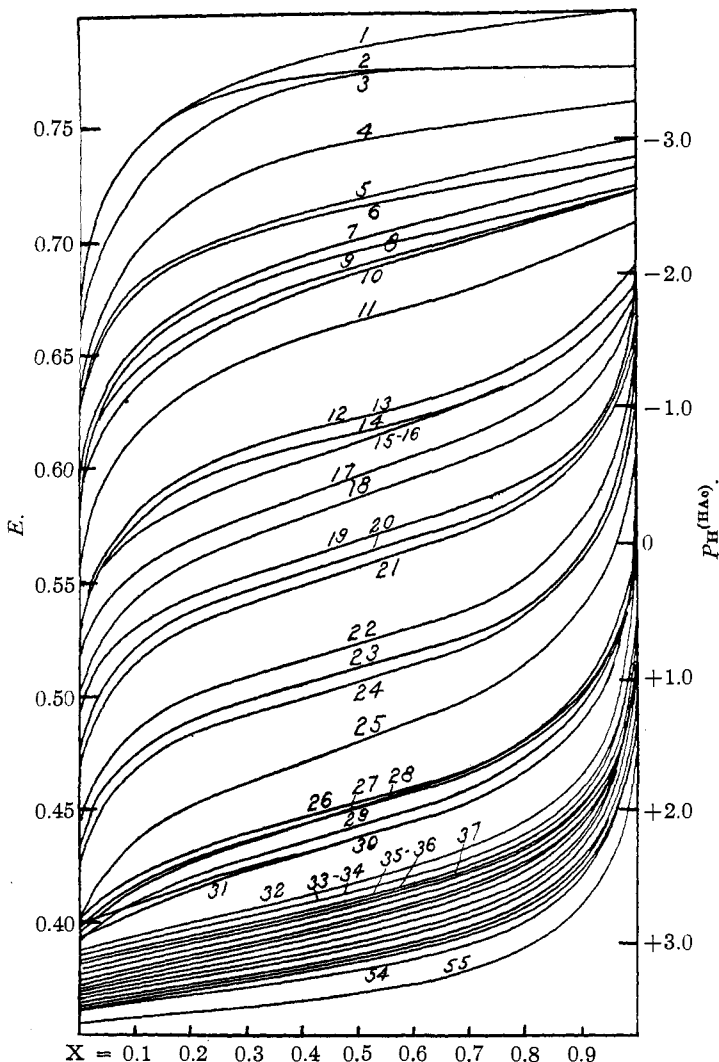


Fig. 1.—Titration curves of 0.05 *M* bases in glacial acetic acid.

values, as pointed out by Hall and Werner (III), are not even approximately a simple function of  $\log R$ , ( $R = x/(1-x)$  ( $x =$  fraction titrated)), so that the curves appear "too flat" when compared with similar curves obtained in water. It is reasonable to ascribe this anomaly to the change in activity coefficients caused by the increase in ionic strength during titration, and

evidence on this point has already been presented by Conant and Werner (IV).

In an attempt to formulate quantitatively the voltage changes during titration, the voltages at round values of  $x$  were read from a large plot of Fig. 1 for the middle group of bases. These voltages were converted into  $P_H^{(HAc)}$  values by the formula  $(0.566 - E)/0.0591 = P_H^{(HAc)}$ . To these observed  $P_H^{(HAc)}$  values were added the values of  $\log R$  for each point and the resulting  $pK'$  values plotted against  $x^{1/2}$ . It then appeared that in every case  $pK'$  was nearly a *linear* function of  $x^{1/2}$ .

As examples, the values of  $pK'$  for the first three bases of the group are given in Table II, together with the corresponding values of  $a + bx^{1/2}$ . The average deviation of the two sets of values is also shown.

TABLE II  
 $pK'$  AS A FUNCTION OF  $x$

<i>p</i> -Nitrodimethylaniline									
$x$	= 0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
$pK'$ (obs.)	= -1.29	-1.17	-1.09	-1.00	-0.92	-0.87	-0.83	-0.76	-0.64
$-1.58 + 0.917x^{1/2}$	= -1.29	-1.17	-1.08	-1.00	-0.93	-0.87	-0.81	-0.76	-0.71
Average deviation, $\approx 0.01$									
Urea									
$x$	= 0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
$pK'$	= -1.22	-1.12	-1.06	-0.99	-0.91	-0.87	-0.83	-0.76	-0.64
$-1.48 + 0.816x^{1/2}$	= -1.23	-1.13	-1.04	-0.97	-0.91	-0.86	-0.82	-0.76	-0.72
Average deviation, $\approx 0.02$									
Methylurea									
$x$	= 0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
$pK'$	= -1.15	-1.04	-0.98	-0.91	-0.82	-0.77	-0.70	-0.65	-0.52
$-1.45 + 0.896x^{1/2}$	= -1.17	-1.05	-0.96	-0.88	-0.82	-0.76	-0.70	-0.65	-0.60
Average deviation, $\approx 0.02$									

The formulas used for these three bases are fairly representative of all the others in this group—(with the exception of antipyrine, which shows a much steeper curve)—and it seems desirable in order to save space, not to report the results in full. The constants  $a$  and  $b$  are mutually adjustable within narrow limits and their theoretical significance is obscure. If  $pK'$  is plotted against  $\mu^{1/2}$  instead of  $x^{1/2}$  the points approximate slightly *less* closely to a straight line ( $\mu$  is the concentration of the added acid.  $\mu$  and  $x$  are not strictly proportional because of the appreciable volume of the titrant, nor is the relation between the two always the same because of the use of titrants of more than one concentration). Certain systematic trends in the deviations of the experimental points seem to indicate that functions of  $x^{1/2}$  of the type stated are only first approximations to the values of  $pK'$ . The reproducibility of the data is insufficient at present to warrant the use of a more complicated approximation formula. Instead of  $pK' = a + bx^{1/2}$  or  $pK' = a + b'\mu^{1/2}$ , it is conceivable that in this concentration range curves of the form  $pK' = a'' + b''\mu^{1/2} - b''c\mu$  as required by a form

of the Debye-Hückel theory might fit the data. If the dielectric constant of pure acetic acid at 25° is 6.17 as obtained by interpolation in the data of Smyth and Rogers,<sup>6</sup>  $b''$  should have the value +23.0 and  $c$  should be +1.17. The constant  $10^{-8r}$  is the so-called ion radius and should be positive. Equations of this form with these constants do not fit the data. It is probable that due to the presence of water (up to 0.5%) the dielectric constant of the solvent was higher than 6.17, possibly even as high as 10. And it is further possible that it changed during titration under these conditions, so that a theoretical approach along these lines seems unpromising.

**The Strongest Bases.**—When a weak base is dissolved in acetic acid it may be assumed that the reaction of salt formation  $B + \text{HAc} \rightleftharpoons \text{BH}^+\text{Ac}^-$  is very incomplete, while with a strong base it is virtually complete. When a weak base is titrated the reaction  $B + \text{HClO}_4 \rightleftharpoons \text{BH}^+\text{ClO}_4^-$  (or  $B + \text{H}^+(\text{HAc}) \rightleftharpoons \text{BH}^+ + \text{HAc}$ ) removes the free base and alters the concentration ratio of the cation to the free base remaining with resulting changes in the proton activity since

$$P_{\text{H}(\text{HAc})} = pK'(\text{HAc}) - \log \frac{a_{\text{BH}^+}}{a_{\text{B}}}$$

A strong base is already completely converted into salt when the titration starts, and the only effect of the titration is to substitute a perchlorate for an acetate. The increase in proton activity will depend directly on the removal of acetate since  $a_{\text{H}^+} \times a_{\text{Ac}^-} = \text{const.}$  In this latter case the ionic strength does not change during the titration, and the activity coefficients of the ions remain constant as shown by Hall and Werner's analysis of titration curves of the "strong base" type (III).

Between these two extreme cases, in acetic acid as in water, there exists a group of "transition" bases in which both the free base and its acetate may be assumed to exist together in the solution in appreciable quantities at the start of the titration. These should give curves of intermediate form, and such curves are readily observed in Fig. 1. The lowest curve in the diagram (diethyl-*o*-toluidine) is clearly anomalous for unknown reasons; dimethyl-*o*-toluidine (54a) and diethyl-*p*-toluidine (54b) show similar anomalies but to a less extent, and smaller variations are observed for other bases, above and below the "typical" or "average" strong base curve.

**The Weakest Bases.**—As the base strength diminishes, the tendency to react with even so strong an acid as perchloric acid becomes less and finally disappears, so that a point is finally reached where a solution of the base behaves toward the addition of perchloric acid as though the solvent alone were present (Curve 1, bases 1a, 1b). Bases of progressively diminishing strength give curves which should be the transposed mirror images of the transition and strong base curves at the bottom of the diagram. Because of the relative unreliability of the measurements in this highly acid

<sup>6</sup> Smyth and Rogers, *THIS JOURNAL*, 52, 1824-1830 (1930).

region, it has not been very thoroughly studied and secondary influences evidently distort some of the curves obtained.

**Comparison with the Water System.**—The basicity constant of a

$$K_{\text{Bas.}} = \frac{1}{\alpha_{\text{H}^+}} \times \frac{c_{\text{BH}^+}}{c_{\text{B}}}$$

given base dissolved in a protogenic<sup>7</sup> solvent HX depends only on the intrinsic strength of the base and on the activity coefficients  $f_{\text{BH}^+}$  and  $f_{\text{B}}$ . These latter are primarily influenced by the acidity and basicity constants and the dielectric constant of the solvent, but also exhibit individual variations. If these are not too great, it should be possible to establish a pairwise correspondence between the basicity constants of a series of bases in any non-aqueous solvent and in water. In sufficiently dilute solution in

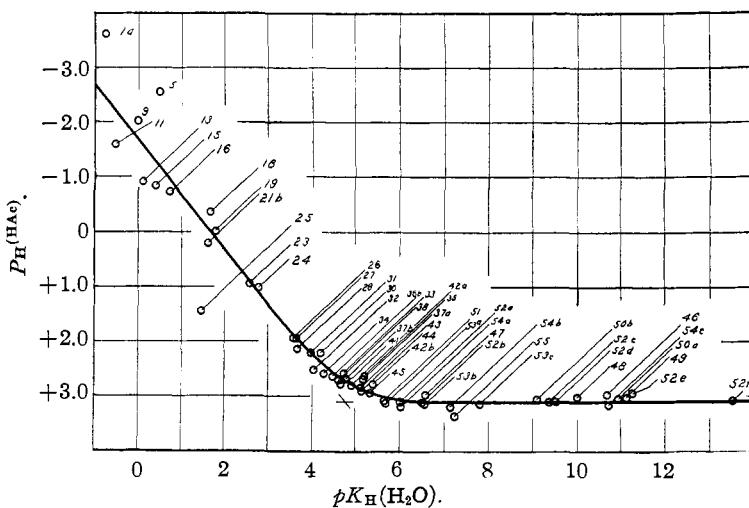


Fig. 2.—Comparative strength of bases in acetic acid and in water.

water  $K_{\text{Bas.}}$  for any base is simply the reciprocal of the ordinary hydrolysis constant (*i. e.*,  $K_{\text{Bas.}} = K_{\text{B}}/K_{\text{W}}$ ). In another solvent  $\log K_{\text{Bas.}} = P_{\text{H}} + \log R$ . In acetic acid  $K_{\text{Bas.}}$  is far from constant when the concentration or the value of  $R$  is varied, so that it is necessary to choose a particular concentration and value of  $R$ , as well as to keep the titrating acid the same in comparing different bases. No satisfactory extrapolation of the values of  $K_{\text{Bas.}}$  to infinite dilution has been possible here. The values to be compared with  $pK_{\text{H}}$  in water are therefore those of  $\log K_{\text{Bas.}}^{(\text{HAc})} = P_{\text{H}}^{(\text{HAc})} + \log R$  at  $R = 1$ , *i. e.*, at the midpoint of titration. This has been done for 52 bases in Fig. 2 for which the necessary data are given in Table V. The abscissa is  $\log K_{\text{Bas.}}^{(\text{H}_2\text{O})} = pK_{\text{H}} = \log K_{\text{B}} + pK_{\text{W}}$ . The ordinate is the value of  $P_{\text{H}}^{(\text{HAc})}$  at the half titration point  $= pK'^{(\text{HAc})} = \log K_{\text{Bas.}}^{(\text{HAc})}$

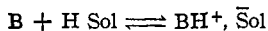
<sup>7</sup> Brønsted, *Z. angew. Chem.*, **43**, 229–233 (1930).

for each base as read from Fig. 1. The line on the diagram needs further explanation.

If bases at a given concentration in water are titrated with a strong acid, the  $P_H$  of the titration midpoints increases with the strength of the base so that it is almost exactly 9 for  $pK_B = 5$ , 10 for  $pK_B = 4$ , etc., etc. However, as  $pK_B$  diminishes, a point is reached, depending on the concentration of the solution, where the increase in  $P_H$  at the midpoint is no longer proportional to the decrease in  $pK_B$ . The  $P_H$  values now approach a certain maximum which is that shown by a completely ionized base half-titrated under the conditions of the experiment. Thus if the total base is 1  $N$ , the  $P_H$  at the midpoint of titration should be 13.7 (neglecting activity coefficients). All bases with  $K_B$  above a certain value will show midpoint  $P_H$ 's experimentally indistinguishable from 13.7. What this limiting value will be depends on the concentration and the precision of measurement. It is clear that in the case of these strongest bases, the equilibrium



is effectively completely displaced to the right even before the titration starts. It is also clear that any solvent capable of releasing a proton to the molecule  $B$  should behave in this respect just like water.



but that the value of  $K_{Bas}$ , at which the maximum  $P_H$  is reached should differ with each solvent.

It follows from this discussion that if  $P_H$  (midpoint) in any protogenic solvent is plotted against  $pK_H$  for a series of bases, the points will lie on a line of slope =  $-1$  over a considerable range. At a certain point, depending on the concentration, this line will begin to bend upward and change with an easily calculable curvature into a horizontal line passing through the limiting  $P_H$  for the concentration in question. Such a line is the one drawn for acetic acid in Fig. 2. In this figure the line is drawn as follows: (a) the slope of the left-hand portion is fixed at  $-1$ . (b) The curvature of the middle part is determined from the simple theory outlined above. (c) The ordinate of the horizontal part is fixed by the average ordinate of the experimental points for the strongest bases. (d) The three parts of the curve thus restricted are then fitted together so as best to reproduce the experimental points. This semi-empirical method of placing the curve evidently results in a satisfactory fit. One may conclude from Fig. 2 that there is a very definite parallelism between the strengths of the bases in the two solvents but that individual minor departures from exact parallelism are the rule rather than the exception. Both of these conclusions are in accord with previous knowledge of acid strength in solvents other than water.

It must not be forgotten, moreover, that the water values used are aver-

aged from the results of numerous investigators, working at different times and places and by different methods. Under such conditions it is rather surprising that the scattering of the individual points is no greater than it is. Among the very weak bases, measurements are reproducible with difficulty both in water and in acetic acid, so that a greater than normal scattering is there to be expected. (The one unmistakable and significant exception is that of antipyrine (25). This base exhibits no unusual titration behavior in water, but in acetic acid it has a titration curve much steeper than any of the others. It seems possible that this irregularity is due to a reaction with chloranil or to a molecular rearrangement of the base.)

It is interesting to note the value of  $pK_H$  at which the bases become "strong" in acetic acid. If the two straight portions of the curve are extended, they intersect at a point which has an abscissa  $pK_H = 4.75$  (approx.). This is almost exactly the figure representing the strength of acetate ion as a base in water. In other words, it appears from these results that the relative base strength of molecules such as those of the chloroanilines, pyridine, etc., and of the acetate ion remains the same when these substances are transferred from water to acetic acid.

In view of the substantial regularities disclosed by Fig. 2, it is reasonably safe to use it in predicting the strength in water of bases for which no measurements are available. Table III lists those bases which have been successfully titrated in acetic acid but whose constants in water are unknown to me. With each base is given its serial number, its midpoint  $pK^{(HAc)}$  value and its predicted  $pK_H$  value in water.

TABLE III  
DATA FOR BASES

No.	Name	$pK^{(HAc)}$ obs.	$pK_H^{(H_2O)}$ predicted
1b	4-Nitro-2,6-dichloro-aniline	-3.69	< -1
2	Anisalacetophenone	-3.50	< -1
3a	Diacetylmonoxime	-3.49	< -1
3b	Formanilide	-3.49	< -1
4	<i>s</i> -Dimethyldiphenylurea	-3.00	< -1
6	Tribromo-aniline	-2.52	-0.8
7	N-Propylacetanilide	-2.27	- .6
8	N-Methylacetanilide	-2.17	- .5
10	Phenylurea	-2.01	- .3
12	<i>p</i> -Nitrodimethylaniline	-0.92	+ .8
14	Methylurea	- .82	+ .9
17	2,5-Dichloro-aniline	- .51	+1.2
20	2,4-Dichloro-aniline	+ .08	+1.8
21a	3-Nitro-4-chloro-aniline	+ .19	+1.9
22	<i>m</i> -Nitrodimethylaniline	+ .73	+2.4
28	<i>p</i> -Nitrodiphenylamine	+1.93	+3.5



Moreover, in the case of certain bases, even though precipitation or other disturbing effects were noted, it is possible from an inspection of the titration curve to predict roughly what the strength in water should be. This has been done for a few additional bases in Table IV.

TABLE IV  
PREDICTED STRENGTH OF CERTAIN BASES IN WATER

	$pK_H$
Acetylphenylhydrazine	+1.3
<i>p</i> -Amino-acetophenone	+2.75
Benzamide	-1
Carbazole	< -1
Dimethylglyoxime	< -1
<i>p</i> -Nitrosodiethylaniline	> +5.5
Pyrrrole	+0.4

From a few titrations with sulfuric acid one may infer that dianisylcarbinol has a  $pK_H < -1$  and hydrobenzamide  $> +5.5$ .

The following bases, the constants of many of which are at least approximately known in water, could not be titrated satisfactorily in acetic acid under the conditions used for the reason indicated.

**Base Insufficiently Soluble.**—Alloxantine, dipiperonalacetone, dianisalacetone, tyrosine.

**Precipitation Occurred.**—Acetone semicarbazone, *o*-aminobenzoic acid, *p*-aminobenzoic acid, 4-aminodiphenyl, asparagine, benzidine, diphenylanisylcarbinol, dipiperonalacetone, ethylenediamine, glycocoll, hexamethylenetetramine, Michler's ketone,  $\beta$ -naphthylamine, *m*-nitro-aniline,  $\alpha$ -nitroguanidine,  $\beta$ -nitroguanidine, *p*-nitrosodimethylaniline, xanthidrol.

**Base Apparently Formed a Hemi-perchlorate.**—Aminoazobenzene, diazo-amidobenzene, dimethylaminoazobenzene.

**Base Reacted with Chloranil.**—Aniline, hydrazine hydrate, methylphenylnitrosamine, *p*-nitrophenylhydrazine, phenylhydrazine, piperine, taurine, thiourea.

**Titration Curve Had an Irregular Form.**—*p*-Phenylenediamine, *o*-phenylenediamine, quinaldine, thiocarbanilide.

**Data Used in Preparing Fig. 2.**—In Table V are given in order the identifying numeral of the base, its name, the  $P_H^{(HAc)}$  of the titration midpoint as read from a large plot of Fig. 1, the preferred value of  $pK_H$  for the base in water at 25° as determined by averaging the values in the next column, the particular values selected from the literature and used in computing the average, and a letter or letters indicating the literature reference from which the value in question was obtained. Figure 2 was drawn with the values in Columns 3 and 4 of Table V as ordinate and abscissa, respectively.

TABLE V  
 STRENGTH OF BASES IN ACETIC ACID AND IN WATER

		$pK'(\text{HAc})$	$pK_{\text{H}}(\text{H}_2\text{O})$			
1a	Propionitrile	-3.65	-0.80	-0.8	W. L.	
5	Acetanilide	-2.59	+ .4	+0.3	Wo.	+0.5 Re.
9	<i>o</i> -Nitro-aniline	-2.03	+ .06	+ .06	Lö.	+ .06 G. I.
11	Acetamide	-1.64	- .48	- .45	W. L.	- .50 E. O.
13	Urea	-0.93	+ .10	+ .10	W. W. L.	+ .13 Z.
				+ .05	Ko.	
15	Dimethylpyrone	- .76	+ .40	+ .30	Wald.	.49 Spr.
16	Diphenylamine	- .74	+ .85	+ .64	Far.	+1.06 Thi.
18	<i>p</i> -Nitro-aniline	- .36	+1.9	2.03	Lö.	1.8 Re.
19	Acetoxime	- .05	+1.75	1.77	Lun.	1.75 Wo.
				1.74	W. L.	
21b	Colchicine	+ .19	+1.65	1.65	KO <sub>2</sub>	
23	<i>o</i> -Bromo-aniline	+ .90	+2.60	2.60	G.	
24	<i>o</i> -Chloro-aniline	+1.00	+2.77	2.77	G.	
25	Antipyrine	+1.45	+1.51	1.66	KO <sub>1</sub>	1.46 Spr.
				1.49	B. G.	1.5 Osb.
				1.42	Re.	
26	<i>m</i> -Chloro-aniline	+1.93	+3.52	3.47	Flür.	3.56 G. K.
27	<i>m</i> -Bromo-aniline	+1.93	+3.51	3.51	Flür.	
29	Semicarbazide	+2.13	+3.66	3.67	Wo.	3.65 Spr.
30	<i>p</i> -Chloro-aniline	+2.20	+4.00	4.07	F. W.	3.93 Flür.
31	<i>p</i> -Bromo-aniline	+2.20	+3.91	3.94	F. W.	3.87 Flür.
32	$\alpha$ -Naphthylamine	+2.54	+3.99	3.92	F. W.	4.04 Spr.
				4.02	H.	
33	<i>m</i> -Toluidine	+2.57	+4.71	4.78	Miz.	4.74 Br. D.
				4.67	Flür.	4.70 Spr.
				4.67	Bred.	
34	<i>m</i> -Anisidine	+2.59	+4.21	4.21	Spr.	
35	<i>p</i> -Anisidine	2.62	5.30	5.30	Spr.	
36b	<i>o</i> -Toluidine	2.65	4.43	4.45	Miz.	4.47 Br. D.
				4.41	Bred.	4.40 Spr.
37a	<i>p</i> -Toluidine	2.67	5.12	5.09	D. S.	5.08 Spr.
				5.20	Br.	5.12 Pring
				5.10	Flür	5.13 H.
				5.20	Lö.	5.07 Br. D.
37b	Methylaniline	2.67	4.78	4.79	Miz.	4.86 Spr.
				4.70	Pring	
38	<i>o</i> -Anisidine	2.69	4.51	4.51	Spr.	
41	Methyl- <i>o</i> -toluidine	2.77	4.60	4.60	Spr.	
42a	Quinoline	2.79	4.87	4.92	Bred.	4.81 H. K.
				4.90	G. S.	4.83 B. G. S.
42b	Methyl- <i>p</i> -toluidine	2.79	5.34	5.34	Spr.	
43	Ethylaniline	2.83	5.14	5.15	Pring	5.13 Spr.
44	Dimethylaniline	2.86	5.10	5.17	B. G. K.	5.10 L. G.
				5.03	Miz.	5.06 Spr.
				5.12	Pring	
45	Pyridine	2.93	5.21	5.05	Miz.	5.26 G. S.
				5.29	Lu.	5.24 B. G. S.
				5.21	H. K.	

TABLE V (Concluded)  
 $pK'(\text{HAc})$      $pK_{\text{H}}(\text{H}_2\text{O})$ 

46	Dimethylamine	2.96	10.71	10.69 Miz.	10.73 H. S.
				10.70 I. C. T.	10.70 Br. S.
47	$\alpha$ -Picoline	2.98	6.5	6.65 G. S.	6.43 C. W.
48	Diphenylguanidine	3.01	10.0	10.0 Kr.	10.0 Spr.
				10.0 H.	
49	Piperidine	3.03	11.09	11.10 Bred.	11.08 H. S.
50a	Diethylamine	3.05	10.95	11.00 Bred.	10.90 Spr.
50b	Triphenylguanidine	3.05	9.1	8.9 Kr.	9.3 Bar.
51	Methyl- <i>n</i> -propylaniline	3.08	5.62	5.62 Spr.	
52a	Methylethylaniline	3.10	5.99	5.99 Spr.	
52b	<i>p</i> -Aminodimethylaniline	3.11	6.48	6.59 H.	6.37 Mc.C.
52c	Ammonia	3.10	9.27	9.32 Lund.	9.25 Miz.
				9.31 N. K. S.	
52d	Tri- <i>n</i> -butylamine	3.10	9.85	9.85 Spr.	
52e	Di- <i>n</i> -butylamine	3.10	11.18	11.18 Spr.	
52f	Guanidine	3.10	13.5	13.5 Spr.	
53a	Di- <i>n</i> -propylaniline	3.13	5.60	5.60 Spr.	
53b	Diethylaniline	3.15	6.52	6.64 Pring	6.36 L. G.
				6.55 Spr.	
53c	Triethanolamine	3.15	7.78	7.78 Spr.	
54a	Dimethyl- <i>o</i> -toluidine	3.20	5.92	5.87 Spr.	5.96 L. G.
54b	Diethyl- <i>p</i> -toluidine	3.20	7.09	7.09 Spr.	7.09 Spr.
54c	Triethylamine	3.18	10.74	10.72 Br.	10.75 H.
55	Diethyl- <i>o</i> -toluidine	3.36	7.16	7.16 Spr.	

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## NOTES ON TABLE V

It was necessary to make a complete resurvey of the literature in preparing Table V. In this the well-known compilation of Scudder<sup>8</sup> was of great assistance as were the various large tables of physico-chemical data. All these sources must be used with caution for the following reason. Although most determinations of base strength in water are made by a hydrolytic method which leads directly to the calculation of  $K_H$  instead of  $K_B$ , the data are all converted to values of  $K_B$  in the tables *with the use of a great variety of values for  $K_w$* , so that it is nearly always necessary to go to the original paper in order to find out which value of  $K_w$  was used in the particular computation under review. The advantages of the  $pK_H$  values used in this paper over the values of  $K_B$  are obvious. Moreover, as the bases must be compared at a single temperature (here 25°), many of the data in the literature which apply to some other neighboring temperature are useless unless a suitable temperature correction can be applied to them. Mr. Sprinkle in this Laboratory has determined the temperature coefficient of  $pK_H$  for a number of bases of different strengths, and found the coefficient to increase with the base strength from about  $\Delta pK_H/\Delta t = 0.01$  at  $pK_H = 4$  to about  $\Delta pK_H/\Delta t = 0.02$  at  $pK_H = 11$ . This work will shortly be published in connection with new determinations of the strength of a variety of bases in water. The coefficients found by Mr. Sprinkle have been used in correcting to 25° those data in the literature which were obtained at temperatures from 15 to 40°, where a determination on a given base at 25° by the same author was lacking.

The values cited do not represent a complete list of the values published up to the present time. The determinations of Veley, aside from being made at low temperatures and by unreliable colorimetric methods, are so discordant with other work as to appear valueless and have not been included. They may be found in Scudder, and in Landolt-Börnstein. The work of Bourgeaud and Dondelinger,<sup>9</sup> while in many cases it agrees with that of others, has been justly criticized by various authors<sup>10</sup> as fundamentally unreliable, and includes a number of values so fantastically incorrect as to make it seem advisable not to include any of it in the averages. The values of Farmer and Warth have also

<sup>8</sup> Scudder, "The Conductivity and Ionization Constants of Organic Compounds," D. Van Nostrand Co., New York, 1914.

<sup>9</sup> Bourgeaud and Dondelinger, *Bull. soc. chim.*, **43**, 37, 277 (1925).

<sup>10</sup> See, for example, Carothers, *THIS JOURNAL*, **49**, 2908-2914 (1927).

been criticized by Flürscheim and are mostly distinctly too low (*i. e.*,  $pK_H$  is too low). They have been omitted except in a few cases.

The work of Myrbäck is peculiar in that every one of his values of  $pK_H$  is lower than the most probable value by an amount varying from 0.07 to 0.51  $P_H$  units (average 0.25). The use of a string soaked in *concentrated hydrochloric acid* as a salt bridge from his saturated calomel electrode to the weakly acid solution he was measuring, as well as a temperature drop of  $7^\circ$  along his salt bridge, may have contributed to these discrepancies. His reasons for preferring his own results are not convincing, and I have used them only when other reliable values were lacking.

During the correction of the proof it was found that certain data of Kuhn and Wassermann<sup>10a</sup> had been overlooked in preparing Table V and Fig. 2. The additional values are: for 9, *o*-nitro-aniline,  $-0.3$ , making  $pK_H(H_2O) = -0.06$ ; for 18, *p*-nitro-aniline,  $+1.0$ , making  $pK_H(H_2O) = +1.6$ . The effect of both of these changes would be to bring the corresponding points in Fig. 2 closer to the line, and this would be true to a still greater extent if the values of Farmer and Warth for these bases ( $-0.32$  and  $+1.02$ ) were also included. The revised values would then be  $-0.13$  and  $-1.4$ .

**Acid Strength in Other Non-aqueous Solvents.**—Results somewhat similar to those in the present paper have been reported by other authors for other solvents as follows. Michaelis and Mizutani<sup>11</sup> and Mizutani<sup>12</sup> have shown that in various methanol-water and ethanol-water mixtures the acidity constants of numerous uncharged acids on the one hand and cation acids on the other exhibit roughly equal changes within each class for a given change in composition of the solvent. Goldschmidt and Mathiesen<sup>13</sup> by aminolytic measurements have shown much the same thing in regard to dissociation constants of the two types of acids in absolute methanol, absolute ethanol and certain aqueous mixtures. Brönsted,<sup>14</sup> by a colorimetric method, has determined the relative acidity constants of numerous indicators and uncolored acids in benzene. Acids of the same type are evidently nearly equally affected by transfer from water to benzene, while the strength of cation acids is relatively greatly increased by this transfer.

**Materials.**—Practically all the bases studied were purchased from the Eastman Kodak Company. A few were obtained from laboratory stock at the Harvard Chemical Laboratory and in this Laboratory and these were specially prepared or purified before use. In most, but not all, cases the Eastman liquids were redistilled and characterized by their boiling points, and the melting points of the solids were determined. Where necessary, special purification processes were used. I am indebted to Professor Tenney L. Davis for certain urea derivatives, and to Dr. Wallace H. Carothers for a number of amines and amides. The other materials were prepared and used as described in the earlier papers.

<sup>10a</sup> Kuhn and Wassermann, *Helv. Chim. Acta*, **11**, 3 (1928).

<sup>11</sup> Michaelis and Mizutani, *Z. physik. Chem.*, **116**, 135-159 (1925).

<sup>12</sup> Mizutani, *ibid.*, **118**, 318-326; 327-341 (1925).

<sup>13</sup> Goldschmidt and Mathiesen, *ibid.*, **119**, 439-473 (1926).

<sup>14</sup> Brönsted, *Ber.*, **61**, 2049-2063 (1928).

**Acknowledgment.**—I should like to express my thanks to Messrs. Tyrrell H. Werner, Marshall R. Sprinkle and Victor A. Reinders for assistance in making many of the measurements and for the communication of certain data (to be published later) on the strength of bases in water.

It is further a great pleasure to acknowledge the aid received from a grant from the Milton Fund of Harvard University covering the purchase of many of the bases studied.

### Summary

1. A large number of organic bases have been titrated with perchloric acid in glacial acetic acid solution.

2. It is shown that the relative strengths of the bases in acetic acid and in water are nearly proportional and that it is possible to determine by titration in acetic acid the "water" strength of certain bases which cannot be studied in water.

3. A large part of the published data on the strength of bases in water has been critically resurveyed and the values "corrected" to 25° where necessary in accordance with new determinations of the temperature coefficient of  $pK_H$  for bases of different strengths.

MADISON, WISCONSIN

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE AGRICULTURAL COLLEGE]

## A STUDY OF THE DENSITY, SURFACE TENSION AND ADSORPTION IN THE WATER-AMMONIA SYSTEM AT 20°<sup>1</sup>

BY H. H. KING, J. LOWE HALL AND GLEN C. WARE

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In view of the fact that liquid ammonia behaves as an ionizing medium for electrolytes it was thought that the determination of its behavior as a polar liquid toward adsorbed substances containing polar groups would be of interest. As a preliminary step this investigation is concerned with the surface tension of water-ammonia mixtures as compared with the theoretical values for ideal mixtures obtained by Whatmough's rule.<sup>2</sup> The resemblance of these two liquids as a solvent can be thus quite satisfactorily indicated. Incidentally some indication of the extent to which ammonia is associated in the liquid state may be observed.

Surface tension in liquid ammonia has been investigated by Berthoud<sup>3</sup> but the range of his work was not extensive. Rice<sup>4</sup> recently has made

<sup>1</sup> Contribution No. 155, Department of Chemistry.

<sup>2</sup> W. H. Whatmough, *Z. physik. Chem.*, **39**, 129 (1901).

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