[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A STUDY OF SUPERACID SOLUTIONS. III. THE TITRATION AND DILUTION CURVES OF BASES DISSOLVED IN ACETIC ACID[1]

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RECEIVED JUNE 2, 1928 PUBLISHED SEPTEMBER 5, 1928

In the first papers of the present series[2] it was shown that the chloranil electrode, when combined with a suitable salt-bridge and reference electrode, is very well adapted to the study of titrations in glacial acetic acid. Titration curves were there reproduced for a number of bases in 0.2 M concentration. The acid used was sulfuric acid. Here we propose to study the effect of changes in the acid, the concentration and other conditions on the titration curves of bases. The increased precision of the newer measurements permits a more complete study of the form of the titration curves, and also of certain related questions, such as the variation in hydrogen-ion activity when solutions of various bases in acetic acid are diluted.

Effect of the Solvent

The general relationships between acids and bases, while essentially similar in a variety of solvents, may also exhibit significant differences. This has been more or less clearly stated or demonstrated by a number of investigators such as Franklin,[3] Brönsted,[4] Hildebrand,[5] Folin[6] and others. No really precise and comprehensive study of the question appears to have been made, however, and such an investigation is under way in this Laboratory, with the aid of both electrometric and colorimetric methods.

Our preliminary results indicate that certain other solvents may be as superior to acetic acid as the latter is to water, in the titration of certain bases, but that few if any solvents can be found which have all the advantages of acetic acid for a general survey. The first important characteristic of a solvent is the size of the "break" in the titration curve of a given base at a given concentration in that solvent when titrated with a given acid.[6a]

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[1] Part of the material in this paper was presented at the St. Louis Meeting of the American Chemical Society on April 18, 1928.

[2] Hall and Conant, THIS JOURNAL, **49**, 3047 (1927); Conant and Hall *ibid.*, **49**, 3062 (1927).

[3] Franklin, *ibid.*, **46**, 2137–51 (1924).

[4] Brönsted, "The Theory of Strong Electrolytes," *Trans. Faraday Soc.*, April, 1927, pp. 431–2; *Chemical Reviews*, September, 1928 (in press).

[5] Bishop, Kittredge and Hildebrand, THIS JOURNAL, **44**, 135–40 (1922).

[6] Folin and Wentworth, *J. Biol. Chem.*, **7**, 421–6 (1910); Folin and Flanders, THIS JOURNAL, **33**, 1622–6 (1911); *J. Biol. Chem.*, **11**, 257–63 (1912); THIS JOURNAL, **34**, 744–9 (1912).

[6a] See W. M. Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 3d ed., p. 543.

This point is emphasized in Fig. 1, which shows the character of the curves when 99.5% acetic acid, commercial absolute ethyl alcohol, and water are used, respectively, as solvents in the titration of a 0.1 *M* solution of a weak base, acetoxime ($K_B = 6.5 \times 10^{-13}$).[7]

In each case 100 cc. of the 0.1 *M* solution of the base was prepared and titrated with a solution of perchloric acid (approximately 1.0 *M*) in the appropriate solvent, except that in the alcohol titration a 1 *M* solution of perchloric acid in acetic acid was used for the titrating solution. The quinhydrone electrode was employed and the potentials were measured against the saturated calomel half-cell through a glass-stoppered joint, using a quadrant electrometer. The point where $\Delta E/\Delta V$ has a maximum value was taken as the point of complete neutralization in every case. The exact form of the curves is not significant in this particular case, as it may be affected by electrode and liquid junction errors.

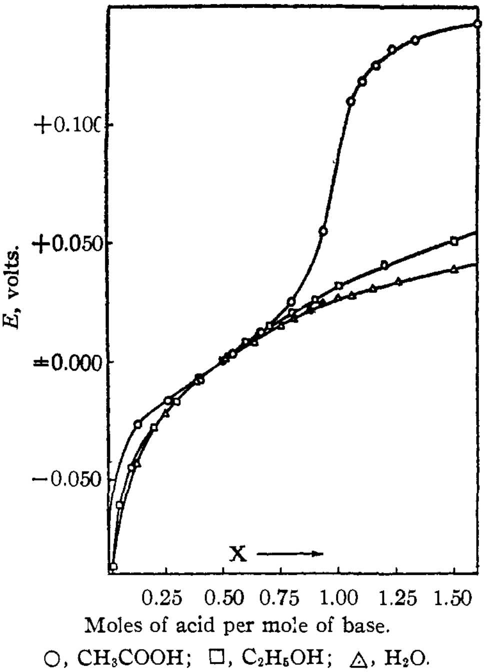

Fig. 1.—Effect of the solvent in the titration of a weak base (acetoxime) with perchloric acid.

The curves have been shifted vertically as a whole by adding a constant to the observed potentials, so as to bring the points of half neutralization into coincidence in the three cases (in order to mask the grosser differences of liquid junction potential). It is plain that this base, which is so weak as to give no break at all in either water or alcohol, gives a break of 0.1 volt when dissolved in acetic acid. This large break is due to the exceptionally high hydrogen-ion activity of solutions of perchloric acid (and some others) in acetic acid (and certain other solvents). Solutions of this sort have been called "superacid."[2]

Aside from this "superacidifying" character, other properties of the solvent are of importance. In particular it must dissolve appreciable quantities of the bases selected for study, and also of the salts of these bases with the titrating acid, if the titration curves are not to be complicated by the appearance of precipitates. In the main, acetic acid meets

[7] Lundén, Landolt-Börnstein, "Tabellen."

this requirement very well, although there are numerous exceptions, as noted in a later paper.

Choice of the Titrating Acid

In the earlier work sulfuric acid was used in all the titrations, although it was remarked that the acidity of equivalent solutions of perchloric acid was apparently higher and although the titration curves showed that the second as well as the first hydrogen of sulfuric acid occasionally entered into reaction (especially with the stronger of the bases). Further, there are certain bases which have insoluble sulfates or acid sulfates but whose perchlorates are soluble. For these reasons it seemed desirable to make a comparative study of the two acids, and as hydrochloric acid also might be supposed to present certain advantages, it was included in the preliminary survey.

This was conducted as follows. Five bases were selected with strengths fairly evenly distributed over the measurable range. Three equal portions of 0.05 *M* solutions of each of these in acetic acid were titrated, respectively, with 1.0 *M* $HClO_4$, 1.0 *M* H_2SO_4 and 1.0 *M* HCl (all in acetic acid), and the curves plotted in the usual way. Fig. 2 gives the results of the titrations.

The six families of curves are plotted on the same vertical scale with the same zero. The horizontal scales are the same but the zero is shifted in each case 0.5 unit to the right. The abscissa is the fractional neutralization. The ordinate is the measured potential of a cell such as that sketched in Fig. 3, and constituted as follows

$$\mathrm{Pt}\ \underbrace{\left|\ \begin{array}{l}\mathrm{C_6Cl_4O_2\ (Sat.)}\\ \mathrm{C_6Cl_4(OH)_2\ (Sat.)}\\ \mathrm{Base\ (Cb)}\\ \mathrm{Acid\ (Ca)}\end{array}\ \right|\ \begin{array}{l}\mathrm{LiCl}\\ \mathrm{Cx}\\ \\ \\ \end{array}}_{\text{in HAc}}\ \underbrace{\left|\ \begin{array}{l}\mathrm{KCl}\\ \mathrm{Sat.}\\ \\ \\ \end{array}\ \right|\ \begin{array}{l}\mathrm{KCl\ Sat.}\\ \mathrm{HgCl\ Sat.}\\ \\ \\ \end{array}\ \Bigg|}_{\text{in } \mathrm{H_2O}}\ \mathrm{Hg}$$

The convention

$$(P_H)^{\mathrm{HAc}} = \frac{E - 0.566}{0.0591} \text{ at } 25°$$

(where *E* is the electromotive force of the cell, regarded as positive when the platinum is positive to the mercury) was used as in the earlier papers,[2] to which the reader is referred for experimental details. The following changes may be noted in the technique. The early difficulties with electrode poisoning were almost completely absent, perhaps because the electrodes were always ignited before every new run. We did not warm the solutions to saturate them with chloranil, as we found that stirring for ten minutes at 25° was uniformly effective. The acetic acid used was in all cases the P. W. R. analytical reagent. The perchloric acid was prepared as described below (footnote 9). The hydrochloric acid was prepared by passing the pure gas, dried with sulfuric acid, into acetic

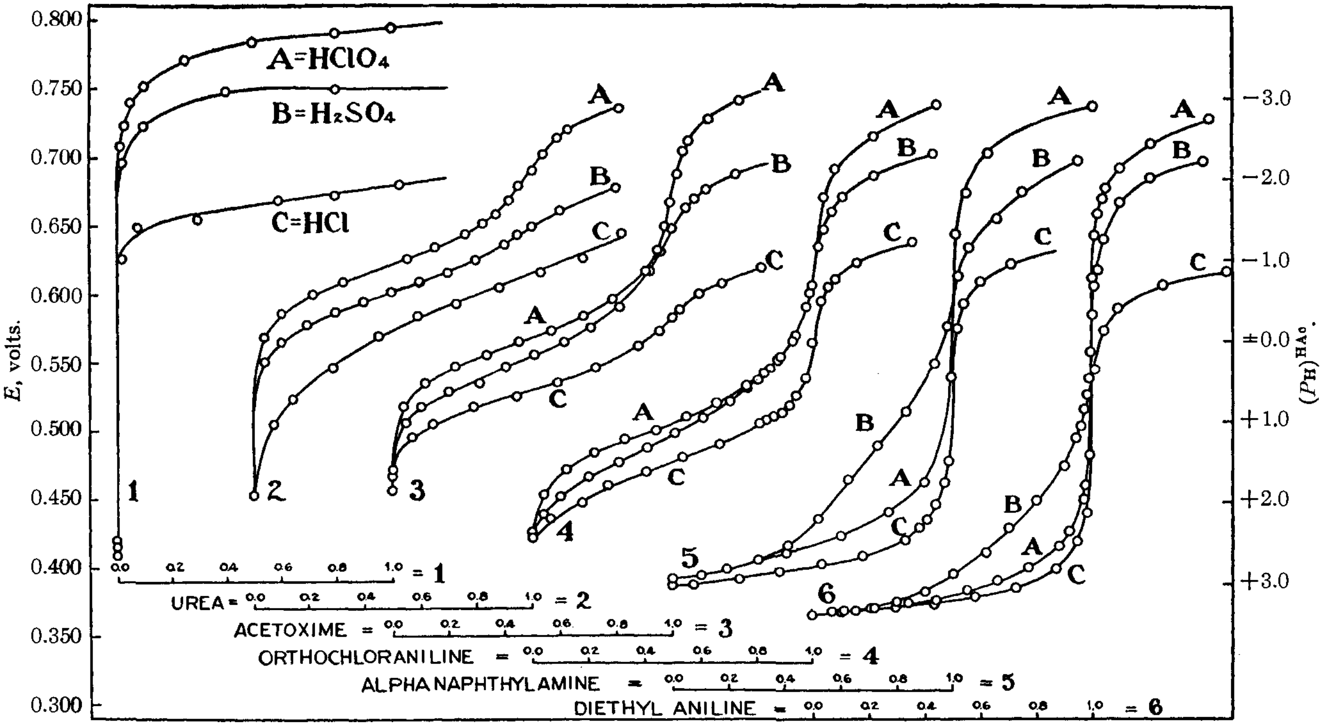

Fig. 2.—Comparison of $HClO_4$, H_2SO_4 and HCl as titrating acids. Abscissas are moles of acid added per mole of base.

acid until the proper concentration was reached or exceeded, and then diluting if necessary. The other materials were of the same nature, as described in the earlier paper.

Beginning in the upper left hand corner of Fig. 2, the first family of curves is not one of titration curves but simply represents the effect of adding the three acids to the pure solvent in amounts corresponding to those used in the other cases (titrations). These curves show clearly that equal concentrations of the three acids are far from being equally "acid." The individual character of strong acids, masked in water by the relatively basic solvent, is here permitted to exhibit itself. It is further apparent that certain bases which would give no break at all with hydrochloric acid could be titrated quite satisfactorily with perchloric acid. The next family of curves (titrations of urea) brings out just this phenomenon. This base is so weak that even in acetic acid it gives no break with hydrochloric acid and only a slight bend with sulfuric acid, while with perchloric acid the break, though slight, is clearly marked. The next two bases, acetoxime and *o*-chloro-aniline, are appreciably stronger, as shown by the increasingly negative potential of their half-neutralization points, and with them first two, and then all three of the acids give a good break.

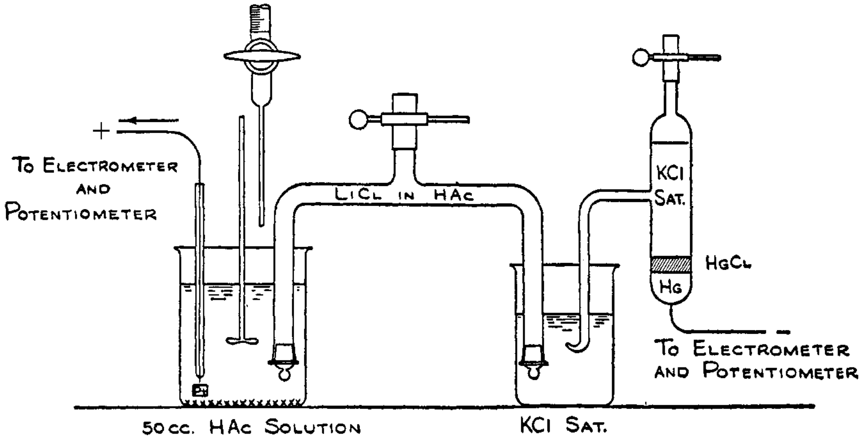

Fig. 3.—Cell for titrations in glacial acetic acid using the chloranil electrode.

The three curves are also coming closer together as potentials are reached which lie far below those characteristic of the acids alone, but at the same time the sulfuric acid curve (*B*) is rising rather more rapidly over the range from 50 to 95% neutralization, due to a quite different cause. This is clearly apparent in the case of the much stronger base α-naphthylamine (No. 5). Here the break is in all three cases very pronounced—the form of the curves A and C recalls those characteristic of strong bases in water, by comparison with the weak base types 2, 3 and 4, and the sulfuric acid curve, B, has bent sharply upward at the halfway point and lies far above the other two. This is of course due to the fact that the base is now strong enough to react with the second hydrogen of sulfuric acid, and the sulfate thus formed is progressively converted to the acid salt as the neutralization proceeds. An essentially similar state of affairs is shown by Curve 6 (diethylaniline). This base has a K_B in water of about 4×10^{-8},[8] and therefore behaves in this solvent like a strong base (in respect to its titration curve) as will be more explicitly shown below. The break (with perchloric acid) from 50 to 150% neutralization, is about six *P*H units, while with hydrochloric acid it is about two units less.

Only one base (cocaine) has been found whose curve obtained under comparable conditions lies appreciably (as much as 15 millivolts) below that of diethylaniline, while many substances known to be stronger bases, such as diphenylguanidine, triphenylguanidine and triethylamine, have curves practically coincident with the diethylaniline curve. On the other hand, some stronger bases such as eserine, strychnine, ammonia, quinine, quinidine, nicotine, brucine, cinchonine, dimethylamine, diethylamine and piperidine give curves that lie from 5 to 30 millivolts *above* it. It seems probable, in view of all the data at hand, that the curve of diethylaniline represents the limiting value (at this concentration) for a normal base which is "strong" as regards its titration in the solvent and that all bases with curves lying appreciably above this value are definitely not completely "strong," but that minor variations of 15–30 millivolts about this limiting value are to be attributed to unknown chemical influences and not to differences in base strength. The individual behavior of particular bases will form the subject of a later communication.

It is obvious from these diagrams that perchloric acid is far preferable to the other two as far as its purely electrical character is concerned in the titration of bases of all measurable strengths. There are, however, other considerations involved.

A great many of the bases we have studied have rather insoluble perchlorates (pyridine, K, Rb, NH_4, nicotine, brucine, cinchonine, cinchonidine, *p*-amido-acetophenone, arylcarbinols, etc.) or sulfates or acid sulfates (Na, Li, Ca, Sr, Ba, Pb, β-naphthylamine, dianisal acetone, semicarbazide, *p*-bromo-aniline, etc.). We have not tried hydrochloric acid in all of these cases but it seems probable that the chlorides of many of these bases are much more soluble, so that hydrochloric acid might be used in a comparative study of certain (of the stronger) bases which give curves of irregular form when titrated with perchloric or sulfuric acid. On the other hand, the partial pressure of hydrochloric acid from

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[8] Pring, *Trans. Faraday Soc.*, **19**, 705–10 (1923–24); Bourgeaud and Dondelinger, *Bull. soc. chim.*, [4] **37**, 277 (1925).

acetic acid solutions is so large that a 1.0 M solution fumes about as strongly as 16 M hydrochloric acid in water, so that aside from their unpleasantness in use the solutions of this acid are variable in composition, due to the high rate of escape of hydrochloric acid.[9] On the whole it seemed best to use perchloric acid whenever possible, changing to the other acids for particular substances or classes of substances.

The Effect of Concentration

The curves given in the first paper were all obtained at a single concentration (0.2 M), and it was recognized that the observed potentials were in general influenced by concentration changes to a greater degree than is the case in aqueous solutions. We have therefore made a few experiments to determine the nature of this effect. In water the effects of concentration change are as follows. When a strong base such as sodium hydroxide is titrated with a strong acid in a series of concentrations each of which is one-tenth that of the preceding one, the titration curves obtained are all essentially similar and parallel, and are spaced about one P_H unit apart (see Fig. 4A). On the other hand, when a weak base such as ammonia is titrated with a strong acid the titration curves for different concentrations lie very much closer together and presumably almost intersect at the mid-point. In acetic acid as solvent the phenomena are notably different. The curves for a "strong" base are usually quite similar in shape to those determined in water, but the effect of a tenfold dilution is to move the curve only about one-half of a P_H unit instead of a whole one. On the other hand, the effect of dilution is very much greater on a weak base titration curve than it is in water. These relationships are exhibited in Figs. 4 and 5.

Fig. 4A shows calculated curves for the titration of aqueous sodium hydroxide with hydrochloric acid. In drawing these curves the volume has been assumed constant during the titrations and no account has been taken of the change of hydrogen-ion activity coefficient with change in the composition of the solution as the titration proceeds. The activity coefficients of the pure sodium hydroxide solutions were taken from the data of Harned,[10] and the curves are plotted on the assumptions that (*a*) the

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[9] We have found that in making up perchloric acid, by adding an approximately 8 N aqueous solution to the theoretical quantity of chilled acetic anhydride and diluting with acetic acid to 1 M, it is important that there be no excess of acetic anhydride left in the solutions, as otherwise high and irregular potentials are observed. These are due to the action of acetic anhydride on hydrochloranil. A thermal method has proved useful in gaging the exact proportions of acetic anhydride and aqueous perchloric acid to be used. After the two components are mixed in nearly correct proportions, it is found that adding a small amount of one of the components produces a temperature rise. This component is then added until further additions are without thermal effect and the mixture is then diluted with acetic acid to the desired concentration.

[10] Harned, THIS JOURNAL, **47**, 676–689 (1925).

*P*H of 0.0001 *N* NaOH is 10.00, (*b*) the activity coefficients of the two ions of sodium hydroxide are equal at each concentration and (*c*) the activity coefficient of 0.001 *N* NaOH can be calculated from the limiting equation of Debye and Hückel. On the scale of the diagram, the changes in the shape and relative position of the curves introduced by these approximations are negligible.

The curves in the right-hand half of the diagram reproduce the results of actual titrations of solutions of diethylaniline of the concentrations indicated, in glacial acetic acid. The titrating mixture was a solution of perchloric acid in acetic acid. The concentration of this solution was 2.0 *M* in the lowest two curves, 0.2 *M* in the middle curve, 0.02 *M* and 0.002 *M* in the two upper curves. The lowest curve is corrected for the volume change during titration, on the assumption that the measured e.m.f. is 0.018 volt too high when the concentration is halved. Corresponding corrections to the other curves would be negligible and were not applied. The curves show that between 0.02 and 0.002 *M* the $(P\text{H})^{\text{HAc}}$ of the solution changes approximately as the *square root* of the concentration of unneutralized base, while at both higher and lower concentrations the change in $(P\text{H})^{\text{HAc}}$ is greater, approaching that found in water solutions. These rather surprising results suggested the investigations reported below (Figs. 6, 7 and 8).

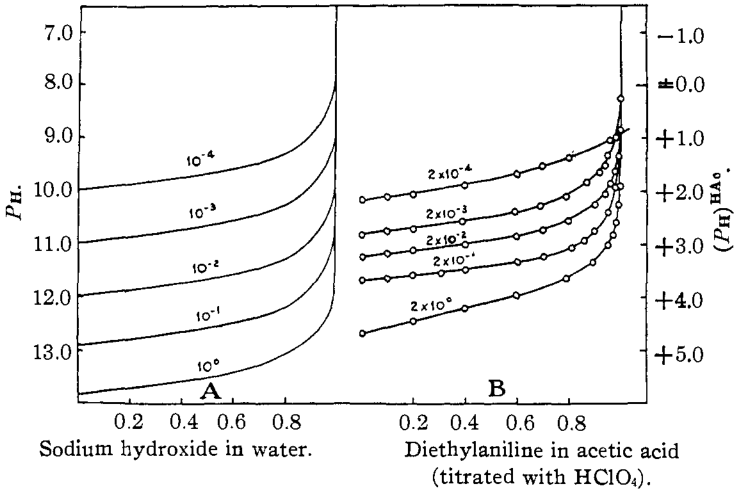
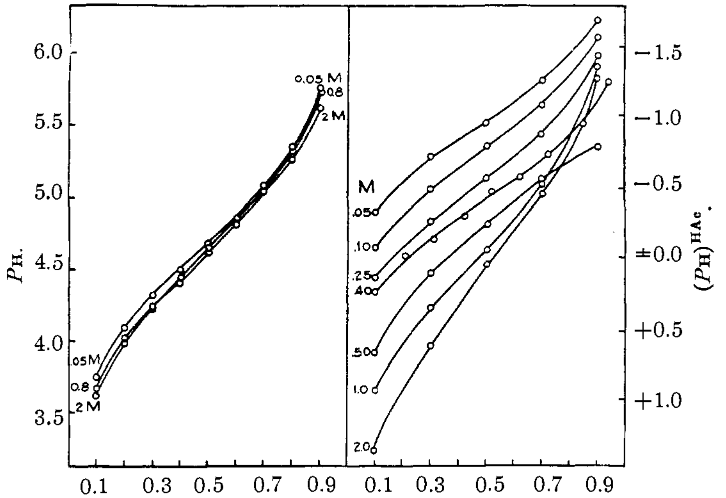


Fig. 4.—Titration curves of "strong" bases. Effect of concentration. Abscissas are moles of acid per mole of base.

In Fig. 5 are reproduced somewhat similar curves for "weak" electrolytes in the two solvents. As we know of no complete data on a weak base in aqueous solution, we decided to use the results of Cohn and his collaborators[11] on acetic acid. These investigators[12] report the values of $-\log \gamma$ for solutions containing varying proportions of acetic acid and sodium acetate at a number of fixed concentrations of total acetate. As $-\log \gamma$ is essentially the measure of the deviation of the actual titration curves from the theoretical curve whose mid-point is at $P_K = 4.73$, it is a simple matter to construct the actual titration curves from their data. This has been done for three concentrations of total acetate: 2 M, 0.8 M and 0.05 M. It is evident that the curves lie close together and do not greatly deviate from the ideal shape.



A. Acetic acid titrated with sodium hydroxide in water.

B. Urea titrated with $HClO_4$ in acetic acid.

Fig. 5.—Effect of concentration change on titration curves of weak electrolytes in water and in acetic acid. Abscissas indicate fractional neutralization.

On the right-hand side of Fig. 5 are found similar curves reproducing our measurements on the titration of urea with perchloric acid in acetic acid solution. Here it is seen that a corresponding concentration change produces an enormously greater effect than in water. Only one of the curves (that for 1.0 M urea) follows closely the theoretical form; the others are either too steep (2 M) or too flat (all others). At the point of 10% titration the change in $(P_H)^{HAc}$ is approximately one unit between 0.5 M and 0.05 M. At 90% titration it is two-thirds of a unit. Between 0.1 M and 1 M the corresponding changes are one unit and one-third of a unit.

Taken in conjunction with Fig. 2, these results show clearly that both the nature of the titrating acid and the concentration used have much

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[11] Cohn, Heyroth and Menkin, THIS JOURNAL, **50**, 696–714 (1928).

[12] Ref. 11, p. 711.

more effect on the P_H of mixtures of a weak base and its salt in acetic acid than is the case in water. The extrapolation involved in computing the dissociation constants of bases will therefore be much greater and more uncertain in the former solvent. Accurate values even of the relative strength of bases will evidently only be obtainable under carefully regulated conditions.

The Form of the Titration Curves

In the course of the earlier work it was noted that the curves there obtained (in the titration of 0.2 *M* bases with sulfuric acid) showed fair approximation to the theoretical form for a weak electrolyte.[13] As can be seen from the present results (Fig. 2 above) sulfuric acid tends to act to some extent as a dibasic acid even with fairly weak bases, and it therefore seemed best to re-examine the question of the exact form of the curves, using perchloric acid, which is free from this particular complication. A concentration was therefore selected (0.05 *M*) at which the peculiarities of individual substances should be less marked than at 0.2 *M*, while the buffer capacity of the solutions should still be adequate and the potentials definite and reproducible. Eight bases were then chosen which did not have insoluble perchlorates and which showed a regular gradation of base strength over the measurable range. These were titrated at the stated concentration with 1 *M* perchloric acid and the resulting potentials are reproduced in Fig. 6. The experimental values have not been corrected for the change in volume during titration because (*a*) the percentage volume change is the same in all the curves, (*b*) it is not yet clear just how great the correction should be in all cases and (*c*) as the volume change is only 5% at 100% neutralization, the correction is probably at most $0.06 \log 1.05 = 0.001$ volt, or within the experimental error.

The strongest of the bases, guanidine, is a diacid base, and was therefore studied in 0.025 *M* concentration. All the others were 0.05 *M*. In preparing the sodium acetate solution, the calculated amount of metallic sodium was quickly weighed out and added to the acetic acid. The top curve, marked "solvent," shows the potentials obtained when pure acetic acid is treated with amounts of the titrating acid corresponding to similar points on the curves below. The measured potentials, except those of the top curve, were steady and closely reproducible on successive trials. However, each curve records the results of a single titration only, except the top one where the potentials are mean values taken from a number of runs, with a mean deviation from the mean of about 0.01 volt. The curves show a clear gradation in character as one goes to progressively weaker bases and the break can be traced as far at least as to urea, even at this low concentration.

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[13] Ref. 2, p. 3053, Fig. 2.

In order to save space, and because the uncertainty of the liquid junction potential throws doubt upon the absolute significance of the numerical results obtained, these will in general be reported only in the form of diagrams. It seems desirable, however, to give a clearer indication of the precision of the numerical values, and accordingly the titration data for some of the stronger bases are reproduced in Table I. These data with others are shown graphically in Figs. 2, 6, 7 and 8.

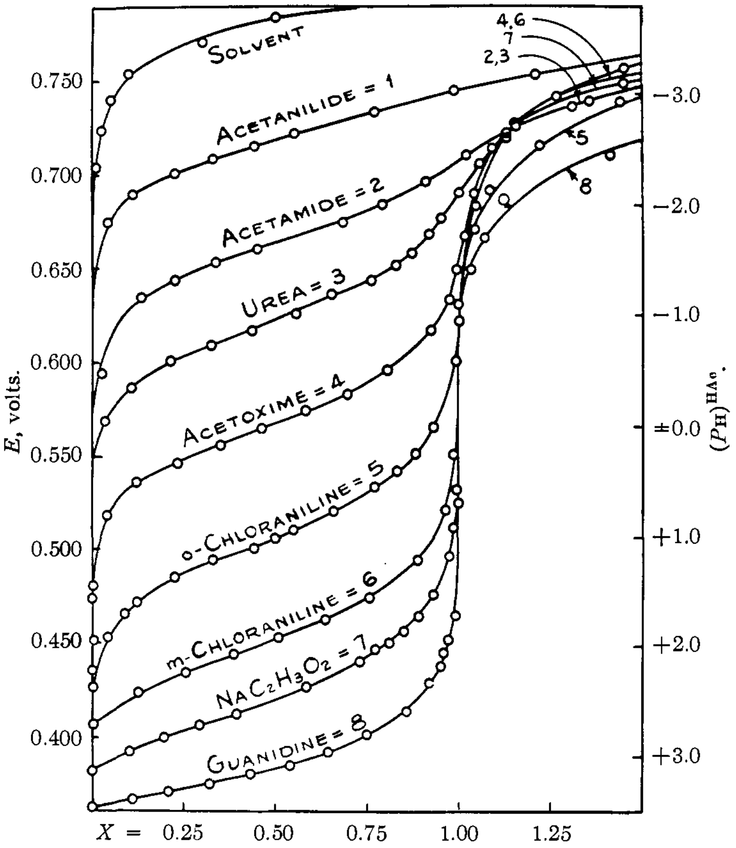

Fig. 6.—Titration of 0.05 N bases in glacial acetic acid with perchloric acid. Abscissas show fraction of base neutralized.

In Table I the first column ($100X$) gives the percentage neutralization. (The point where $\Delta E/\Delta V$ [the change of potential with volume of titrating acid] has a maximum value is taken in every case as the point of complete neutralization.) Col. 2 is the observed e.m.f. of the cell constructed as shown in Fig. 3 and described on p. 2369. The third column gives the negative logarithm of the fractional part of the original base remaining unneutralized. The fourth column is the $(P_H)^{HAc}$ value calculated accord-

Table I

Titration Data

100 X	E, volt	−Log (1 − X)	$(P_H)^{HAc}$	$(P_H)^{HAc}$ −Log (1 − X)
Guanidine				
0	0.362	0	3.45	3.45
10.7	.366	0.05	3.39	3.44
21.4	.370	.10	3.32	3.42
32.1	.374	.17	3.25	3.42
42.8	.379	.24	3.16	3.40
53.6	.384	.33	3.08	3.41
64.2	.391	.45	2.96	3.41
75.0	.400	.60	2.81	3.41
85.7	.413	.84	2.59	3.43
92.2	.428	1.11	2.34	3.45
94.7	.437	1.28	2.18	3.46
96	.444	1.40	2.06	3.46
97.2	.451	1.55	1.95	(3.50)
98.6	.464	1.85	1.79	(3.64)
99.6	.525	2.40	0.70	(3.31)
			Mean 3.43 ±0.02	
Diethylaniline Run No. 1				
0	0.362	0	3.45	3.45
11.0	.365	0.05	3.40	3.45
22.0	.369	.11	3.33	3.44
33.0	.373	.17	3.26	3.43
44.0	.377	.25	3.20	3.45
55.0	.383	.35	3.10	3.45
66.0	.391	.47	2.96	3.43
76.9	.400	.64	2.81	3.45
87.9	.417	.82	2.52	3.34
99.0	.519	1.00	1.79	(2.79)
			Mean 3.43 ± .02	
Diethylaniline Run No. 2				
0	0.366	0	3.38	3.38
11.0	.368	0.05	3.35	3.40
21.9	.370	.11	3.31	3.42
33.8	.374	.17	3.25	3.42
43.9	.376	.25	3.21	3.46
54.9	.383	.35	3.13	3.48
65.8	.390	.47	3.01	3.48
76.8	.400	.63	2.81	3.44
87.8	.415	.91	2.55	3.46
92.2	.427	1.11	2.35	3.46
96.6	.450	1.47	1.96	3.43
97.4	.460	1.58	1.79	3.37
98.8	.482	1.92	1.42	3.34
99.6	.612	2.40	−0.78	(1.62)
			Mean 3.43 ± .03	
Ethylaniline				
0	0.375	0	3.23	3.23
11.1	.380	0.05	3.15	3.20
21.7	.385	.11	3.06	3.17
34.4	.391	.18	2.96	3.14
45.3	.396	.26	2.88	3.14
57.5	.404	.37	2.74	3.11
67.9	.412	.49	2.61	3.10
78.9	.423	.68	2.42	3.10
90.5	.444	1.02	2.06	3.08
95.0	.462	1.30	1.76	3.06
97.3	.477	1.57	1.50	3.07
98.2	.490	1.74	1.28	3.02
99.2	.514	2.10	0.88	2.98
Sodium Acetate				
0	0.382	0	3.12	3.12
9.7	.392	0.04	2.94	2.98
18.9	.399	.09	2.83	2.92
29.0	.406	.15	2.71	2.86
38.6	.412	.21	2.61	2.82
57.5	.426	.37	2.37	2.74
67.5	.435	.49	2.22	2.71
73.0	.440	.57	2.13	2.70
77.2	.446	.64	2.03	2.67
81.2	.450	.73	1.96	2.69
85.0	.456	.82	1.86	2.68
88.9	.464	.95	1.73	2.68
93.0	.476	1.15	1.52	2.67
97.0	.497	1.52	1.17	2.69
98.5	.512	1.82	0.91	2.73
99.4	.532	2.22	.58	2.80

ing to the convention stated on p. 2369. The fifth column gives the sum of the third and fourth. An idea of the precision of the measurements may be obtained from the constancy of this sum for diethylaniline and guanidine—two bases which are "strong" in their titration behavior that is, which act in this respect like sodium hydroxide in water. This is not true of the other bases, which are weaker, and for which the values in the fifth column of Table I show a definite trend. These points will be further discussed on p. 2380.

To test the approximation of the curves of Fig. 6 to theoretical forms, one may employ various types of logarithmic plotting. Thus if X is the fraction of the base neutralized, one may plot e.m.f. against log $X/(1 - X)$. On such a plot the titration curve of a base which obeys the mass law without correction is a straight line having a slope of 59 millivolts for a unit change in the logarithm of the ratio.

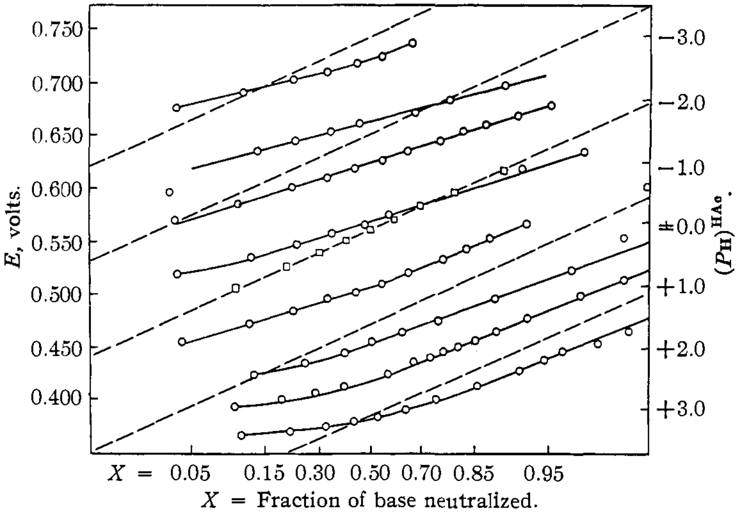

Fig. 7.—Logarithmic titration curves of bases in acetic acid titrated with perchloric acid. True abscissa = log $[X/(1 - X)]$.

In Fig. 7 this type of plotting is applied to the data of Fig. 6. The curves for the different substances lie in the same order and relative position as in that figure. The diagonal broken lines reproduce for comparison the slope which would be shown by bases which obeyed the mass law without correction. For comparison also we have taken the data of Cohn, Heyroth and Menkin[11] for acetic acid in water at the concentration 0.05 M, and arbitrarily placed the mid-point of this curve so that it falls upon the most centrally located broken line. The data at other points are then represented by squares. It is seen that in this case the deviations of the points from the theoretical slope are scarcely appreciable.

In the cases of all the substances dissolved in acetic acid, however, the deviations are considerable. The lines show a curvature which steadily increases with the strength of the base, and in all cases the slope is less than the theoretical.

It is thus evident that none of the bases act when titrated exactly as do weak electrolytes in water. On the other hand, the lowest curves in Fig. 6 are surprisingly similar to those given in water by *strong bases.*

In a further test of this point, a different type of logarithmic plotting may be employed. If the electromotive force is plotted against the logarithm of $1 - X$ (the unneutralized fraction), a curve of the strong base type will be a straight line. Thus in water the titration of sodium hydroxide with hydrochloric acid gives a straight line on such a plot. This is generally attributed to the essentially complete dissociation of NaOH and NaCl, the essentially constant value, within the range, of the activity coefficient of the hydroxyl ion and the fact that $a_{H^+} \times a_{OH^-} =$ Const. $= Kw$.

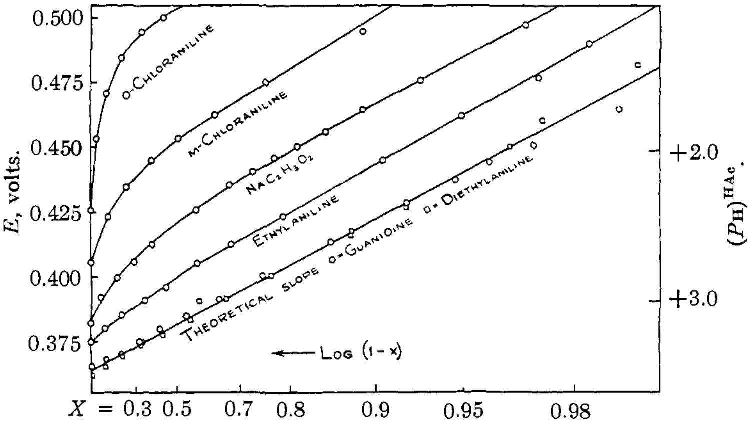

Fig. 8.—Logarithmic titration curves of bases in acetic acid. X = fraction of base neutralized. Abscissa = $-\log(1 - X)$.

If now this method of plotting is applied to the four lowest curves of Fig. 6, and to the titration of ethylaniline and diethylaniline under the same conditions (as shown, for example, in Fig. 2, 6A), Fig. 8 is obtained. Here the lowest line has the theoretical slope (for strong bases) of one PH unit (59 millivolts) per unit change of $\log(1 - X)$, and has been adjusted vertically so as best to fit the points for the two bases diethylaniline and guanidine. The other lines are fitted as well as possible to the experimental points without regard to theory. All these latter exhibit a curvature which rapidly increases as the bases become weaker. This sort of plotting is a sensitive test for "strong base" behavior and shows that diethylaniline and guanidine have titration curves of the strong base type within the experimental error of 2 or 3 millivolts, as may also be seen from the constancy of the values in Col. 5 of Table I.

A possible inference from these results would be that the acetates of diethylaniline and guanidine are completely dissociated, while those of the other bases are incompletely dissociated. However, such a view encounters difficulties when one reflects that the dielectric constant of acetic acid is rather low (possibly about 10 at 25°)[14] and that, therefore, the attraction between univalent ions should be enormously greater than in water, so that there should be in this solvent no electrolytes which are strong in the sense in which this term is used in water; that is, in the sense that their ions at appreciable concentrations act like point charges almost unaffected by the surrounding ion atmosphere.

It seemed desirable, in seeking further light on this question, to abandon titration curves and to study the effect of dilution on solutions of the pure bases. This is, of course, the classical procedure followed by Ostwald and all his successors who have tested the applicability of the dilution law to electrolytic solutions—principally in water. These studies have nearly all been made with the aid of *conductivity* measurements. In non-aqueous solutions the conductivities are frequently very low and the effects of impurities proportionately great, so that significant results are only obtainable by this method at the price of extreme care and effort. There is available, however, another convenient method of following the course of electrolytic dissociation on dilution. If an electrode is available which is responsive to changes in the activity of one of the ions formed by the dissociating substance, and if the activity coefficient of this ion can be estimated at the various concentrations employed, dissociation can be studied by e.m.f. measurements as satisfactorily as by conductivity. Apparently this method has been surprisingly little used. On account of its many advantages, we decided to use the chloranil electrode in studying the form of the dilution curves of bases.

The Form of the Dilution Curves of Bases

If the hydrogen-ion activities of solutions of a base in water are measured over a large concentration range, and a plot is made of e.m.f. (or P_{H}) against the logarithm of the normal concentration of the base, the points for each substance should lie very nearly on a straight line with a slope of one (P_{H}) if the base is completely dissociated, while if its dissociation obeys the law of concentration effect, the slope should always be less than one, and there should be a considerable range where the points lie on a line with a slope of $^1/_2$.[15]

Fig. 9 shows theoretical curves for bases of varying strength in a solvent having an ion activity product of 10^{-14} (water at 25°). In drawing the

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[14] Landolt, Börnstein, "Tabellen," 5th ed., p. 1037, Suppl. 557.

[15] For a strong base, $a_{\mathrm{H}^+} = \frac{Kw}{C_{\mathrm{B}}}$, $\therefore\ P_{\mathrm{H}} = Pw + \log C_{\mathrm{B}}$, $\frac{\partial P_{\mathrm{H}}}{\partial \log C_{\mathrm{B}}} = 1$. For a weak base $K_{\mathrm{B}} = \frac{a_{\mathrm{BH}^+} \times a_{\mathrm{OH}^-}}{a_{\mathrm{B}}}$, $a_{\mathrm{BH}^+} \cong a_{\mathrm{OH}^-}$, $a_{\mathrm{B}} \cong C_{\mathrm{B}}$ and $a_{\mathrm{H}^+} = \frac{Kw}{a_{\mathrm{OH}^-}}$. $\therefore\ \frac{Kw^2}{a^2_{\mathrm{H}^+}} \times \frac{1}{C_{\mathrm{B}}} = K_{\mathrm{B}}$, $2P_w - 2P_{\mathrm{H}} + \log C_{\mathrm{B}} = P_{\mathrm{B}}$ and $\frac{\partial P_{\mathrm{H}}}{\partial \log C_{\mathrm{B}}} = {}^1/_2$.

curves account has been taken both of the dissociation of the solvent where that is appreciable and of the cases where the concentration of the undissociated base is not substantially equal to that of the total base. It is seen that the strong base curve has a unit slope while there is a range where each weak base curve has a slope of $^1/_2$. We could find no complete set of data to compare with these curves and, indeed, it would be difficult if not impossible to make the necessary measurements at the lower concentrations. A few measurements on a single strong base (NaOH) and a single weak base (NH_3) are reported by Michaelis[16] (for 18°) and these have been included. It is obvious that their behavior is typical of the classes to which they respectively belong.

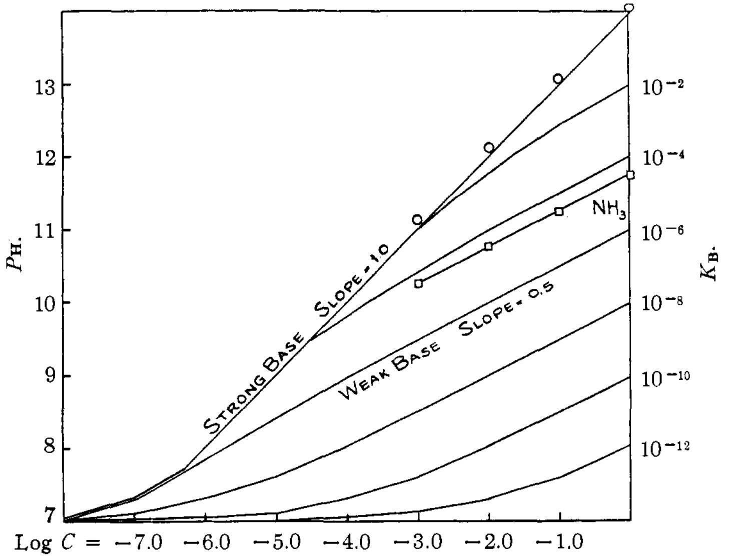

Fig. 9.—Pн-Dilution curves of bases in H_2O. Theoretical curves drawn for t = 25°. Data from Michaelis at t = 18°. ○ = NaOH; □ = NH_3.

In applying this method to acetic acid solutions, we proceeded as follows: a rather concentrated solution of the base was first prepared (2 or 3 M) and from this two or three other solutions, each of which was one-tenth as concentrated as its predecessor. Fifty cc. of pure acetic acid was then measured out and its $(P_H)^{HAc}$ determined in the usual way. Then measured volumes of the most dilute solutions of the base (up to a volume of 5 cc.) were run into the acetic acid, and the new $(P_H)^{HAc}$ values determined. After 5 cc. had been added, the procedure was repeated with more concentrated solutions of the base. In this way the concentration

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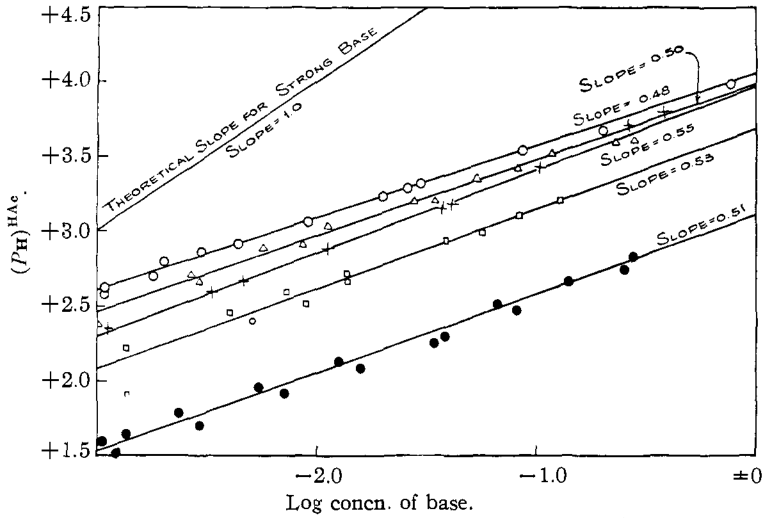
[16] Michaelis, "Hydrogen-Ion Concentration," Williams and Wilkins Co., Baltimore, Md., **1926**, p. 24.

at each stage could be computed with sufficient accuracy on the assumption that the volumes were additive and it was therefore possible to plot $(P_{\mathrm{H}})^{\mathrm{HAc}}$ against the logarithm of the concentration. Fig. 10 is such a plot for two thoroughly "strong"[17] bases (diethylaniline and guanidine) and three that are appreciably "weaker" (pyridine, sodium acetate and *o*-chloro-aniline). The potentials are less reproducible in these dilute solutions of pure bases than in the case of the titrations; nevertheless, most of the points fall on a straight line between concentrations of 1 *N* and 0.001 *N*, and these lines have very nearly the theoretical slope (for a weak base) of 0.5. At lower concentrations the measurements are not reproducible but seem to indicate an increase in the slope, as would be expected. At higher concentrations good measurements are very easy to make but their interpretation is obscure due to the individual peculiarities of concentrated solutions (see Fig. 11) and possibly to deviations of the volumes from additivity. A few measurements on still weaker bases indicated that their points fell on lines parallel to and below those given in Fig. 10. These data seem to constitute a convincing demonstration that in acetic acid bases which behave during titration like strong bases are nevertheless actually quite regular in their conformity to the requirements of the law of concentration effect, and are not to be regarded as completely dissociated in the sense in which this term is used of aqueous electrolytes.



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

Fig. 10.—$(P_{\mathrm{H}})^{\mathrm{HAc}}$-Dilution curves of bases in acetic acid.

It is evident that the electromotive force method constitutes a powerful

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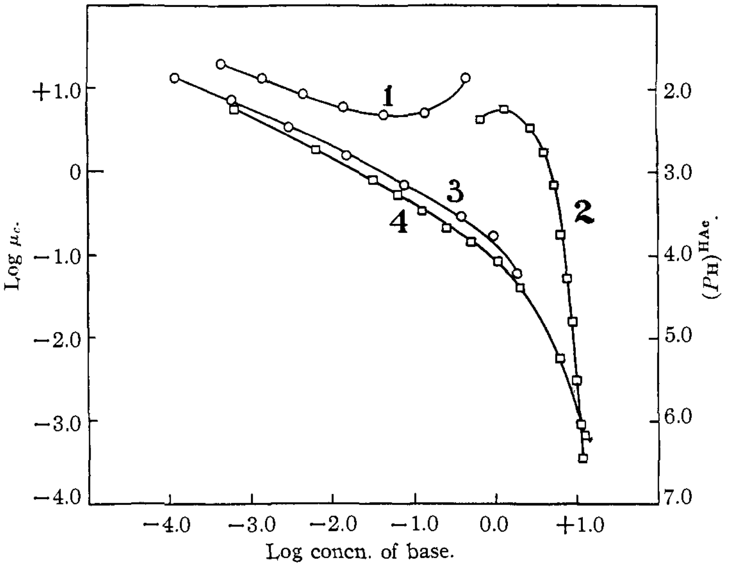
[17] As regards their titration curves.

tool for investigating the effect of concentration on the properties of solutions in non-aqueous solvents. This problem has been the subject of very numerous studies by the conductivity method but the results have been so complex and difficult to interpret that the interest of many investigators in this field has perhaps somewhat cooled in recent years. It is not too much to hope that this interest may be revived as the value of the electromotive force method becomes more widely appreciated. Thus it may be found that certain anomalies in the conductivity results, which make a considerable demand on auxiliary hypotheses such as those of association, solvation, etc., may not appear at all in the electromotive force measurements. A diagram (Fig. 11) will illustrate this idea. The molar conductances of solutions of potassium acetate and of pyridine in acetic acid have been determined over a considerable concentration range by Völmer[18] and by Patten.[19] When their values of μ_c are plotted against the concentration, both curves are anomalous, that for potassium acetate showing a minimum and that for pyridine a maximum value of the molar conductance. In Fig. 11 is given such a plot of their results except that *logarithms* of the molar conductance (μ_c) and of the concentration are



1, Potassium acetate—log μ_c; 2, pyridine—log μ_c; 3, potassium acetate—$(P_H)^{HAc}$; 4, pyridine—$(P_H)^{HAc}$.

Fig. 11.—Comparison of effect of dilution on conductivity (Curves 1 and 2) and on hydrogen-ion activity (Curves 3 and 4) of bases dissolved in acetic acid.

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[18] B. Völmer, *Z. physik. Chem.*, **29**, 187 (1899).

[19] H. E. Patten, *J. Phys. Chem.*, **6**, 554–600 (1902).

used as ordinates and abscissas, respectively (Curves 1 and 2). On the same diagram and with the same abscissa are plotted our values of log $a_{\mathrm{H}^+} = -(P_{\mathrm{H}})^{\mathrm{HAc}}$ (right-hand ordinate) for the same substances over a much greater concentration range. The resulting curves (3 and 4) show no evidence whatever of the anomalies mentioned but steadily fall as the concentration of the base increases and are, of course, straight lines with a slope of $-1/2$ over a large part of the range, as stated above.

It is evident therefore that the form of the conductance functions is complicated in comparison to that of the activity functions, as a result of secondary effects of uncertain nature. Similar anomalies are shown by the conductance functions of sulfuric and hydrochloric acids in the same solvent, and again our (unpublished) activity data give no indication of their existence.

The Liquid Junction Potential

The significance of the results hitherto reported depends in large measure on the (assumed) constancy of the liquid junction potential when the concentration and composition of the solutions are varied, though not directly on the absolute value of this potential. Thus it might be supposed that the failure of the curves of Fig. 7 to approach more closely the theoretical form was due to systematic variations in the junction potential. It is perhaps impossible entirely to exclude this possibility. Nevertheless we feel that the following are strong arguments in favor of the essential constancy of this potential in all our measurements.

(1) The agreement of the individual points with the theory is so good in the case of the data of Table I and the lowest curve of Fig. 8 that there can hardly be any appreciable liquid junction error involved, yet these data cover much the same range of acid–base ratio and of acidity as the curves of Fig. 7.

(2) The similar consistency of the *dilution* curves of Fig. 10 seems to show that *concentration* changes from 1.0 N to 0.001 N are practically without effect on the liquid junction. We therefore feel that the effective constancy of this potential throughout all our measurements, while not definitely proved, is rendered very probable.

The following aspects of the data reported demand further elucidation: (1) the abnormally small effect of dilution on the "strong" base curves (Fig. 4B); (2) the abnormally large effect of dilution on the "weak" base curves (Fig. 5B); (3) the failure of the weak base curves to conform to the theory (Fig. 7); (4) the fact that bases which are clearly "weak" (Fig. 10) should nevertheless behave like "strong" bases when titrated (Fig. 8).

Among the factors which may be suggested as responsible for these anomalies are the following: (1) the low value of the dielectric constant of the solvent with the correspondingly large effect of interionic attractions on the activity coefficients of the ions, so that interionic association is always considerable; (2) large differences in the extent of solvation of the various ionic and molecular species present in the solutions. Thus it seems probable that association with the solvent is very complete in the case of the stronger bases but very incomplete in the pure solutions of the weaker bases.

In the absence of independent information concerning the colligative properties of such solutions as we have studied, it seems undesirable at present to elaborate further mechanical hypotheses to account for their observed peculiarities.

Summary

Diagrams and tables are given which show the effect of the following influences on the shape of the titration curves of bases dissolved in acetic acid: the nature of the titrating acid, the concentration and the strength of the base. It is shown that the weaker bases give anomalous titration curves while the curves of bases which act like strong bases in water conform to the theory of such titrations. The effect of dilution on the hydrogen-ion activity of solutions of bases is studied by the electromotive force method, and it is shown that even the "strongest" bases are truly weak electrolytes in this solvent. It is shown that these results practically demonstrate the effective constancy of the liquid junction potential between saturated aqueous potassium chloride and the various acetic acid solutions used. The value of the electromotive force method in studying the effect of dilution on dissociation is emphasized in the discussion.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE STATE UNIVERSITY OF IOWA AND THE EPPLEY LABORATORY]

A LEAD-MERCUROUS IODIDE VOLTAIC CELL

BY WARREN C. VOSBURGH

RECEIVED JUNE 4, 1928 PUBLISHED SEPTEMBER 5, 1928

The results of measurements of voltaic cells with mercurous iodide electrodes are not very concordant. Gerke[1] has calculated the electromotive force of the cell

$$\mathrm{Hg} \mid \mathrm{Hg_2I_2} + \mathrm{HI}\ (a = 1) \mid \mathrm{HI}\ (a = 1) \mid \mathrm{H_2(Pt)} \qquad (1)$$

from the results of Bugarsky[2] and from the results of Oeholm,[3] obtaining the values 0.0432 v. and 0.0414 v. at 25°, respectively. Cohen and Bruins[4]

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[1] Gerke, *Chem. Reviews*, **1**, 385 (1925).

[2] Bugarsky, *Z. anorg. Chem.*, **14**, 145 (1897).

[3] Oeholm, *Acta Soc. Scientarum Fennicae*, **41**, 1 (1913); *C. A.*, **7**, 2718 (1913).

[4] (a) Cohen and Bruins, *Z. physik. Chem.*, **93**, 53 (1918); (b) see also, Yoshida, *J. Chem. Soc. Japan*, **48**, 435 (1927).