[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A STUDY OF SUPERACID SOLUTIONS. I. THE USE OF THE CHLORANIL ELECTRODE IN GLACIAL ACETIC ACID AND THE STRENGTH OF CERTAIN WEAK BASES

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RECEIVED AUGUST 16, 1927 PUBLISHED DECEMBER 10, 1927

It is well known that many substances which show no basic properties in water will nevertheless form salts. Thus the salts of various amides, many oxonium salts and the halochromic salts of unsaturated ketones may be prepared from an equivalent quantity of perchloric or sulfuric acid provided certain non-aqueous media are used. In the presence of water, however, such salts are often completely hydrolyzed. In this and the following paper we investigate certain of the properties of these solutions in which salt formation is exceptionally complete, and we propose to call such solutions "superacid solutions." The work of Brönsted[1] has done much to clarify the problem of the interrelations of acids and bases in different solvents, a problem which forms the general subject of the present series of papers, while the behavior of acids in non-aqueous media has been the subject of investigation by Hantzsch,[2] who has brought to light many important relationships in this field.

We attempted to attack this problem in a quantitative way by investigating the hydrogen-ion activity of various non-aqueous solutions and selected the e.m.f. method as initially the most promising, provided a suitable electrode could be found. If "salt-errors" are to be avoided, an electrode must be used in which the activities of all reacting electrode materials with the exception of the hydrogen ion are the same for all the solvents studied. Such electrodes are the hydrogen electrode, the two *saturated* quinhydrone electrodes of Biilmann[3] and the various saturated electrodes investigated by Conant and Fieser,[4] who studied many substituted quinones. The usefulness of the hydrogen electrode and of certain of the others is limited by the chemical reactivity of their active materials or by the susceptibility of the electrode to the action of "poisons." As a first solvent for investigation we chose acetic acid, because this substance has been repeatedly shown to be suitable for the preparation of salts of very weak bases. In this solvent the most suitable electrode appeared to be that formed by the completely chlorinated quinone (chloranil, tetrachloroquinone) and its hydroquinone. This electrode had already

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[1] Brönsted, THIS JOURNAL, **49**, 2554 (1927) and previous papers.

[2] (a) Hantzsch, *Z. Elektrochem.*, **29**, 221–246 (No. 6, 1923); (b) *Ber.*, **60**, 1933 (1927).

[3] Biilmann, *Bull. soc. chim.*, **41**, 213–286 (1927).

[4] Conant and Fieser, THIS JOURNAL, **45**, 2207 (1923).

been tested in acetic acid solutions in this Laboratory[5] and found to be satisfactory. Its advantages over other saturated electrodes are (1) chemical inertness and (2) low solubility of the electrode materials.

To illustrate the principle of our method, let us consider the following electrochemical cell

$$\begin{array}{c|c|c|c|c} \text{Pt} & \begin{array}{c} C_6Cl_4O_2\ (\text{sat.}) \\ C_6Cl_4(OH)_2\ (\text{sat.}) \\ HX(C') \end{array} & \text{Bridge} & \begin{array}{c} C_6Cl_4O_2\ \text{sat.} \\ C_6Cl_4(OH)_2\ \text{sat.} \\ HX(C'') \end{array} & \text{Pt} \end{array}$$

Both electrodes are strictly reversible. When the cell operates, solid chloranil ($C_6Cl_4O_2$) is converted into hydrochloranil at one electrode and the reverse process occurs to the same extent at the other electrode, according to the following equation

$$C_6Cl_4O_2\ (\text{solid}) + 2H^+ + 2\ominus \rightleftharpoons C_6Cl_4(OH)_2\ (\text{solid}) \tag{1}$$

This is obviously independent of the nature of the solutions in the two halves of the cell. If the bridge adequately eliminates the liquid junction potential, the e.m.f. of the cell (E) is a measure of the free-energy change attending the passage of one mole of hydrogen ion from one solution to the other.

E is thus a measure of the difference in the partial molal free energy of the hydrogen ion in the two solutions or of the difference of the logarithms of the corresponding hydrogen-ion activities, thus

$$E = \frac{\overline{F}' - \overline{F}''}{\mathbf{F}} = \frac{RT}{\mathbf{F}} \ln \left(\frac{a'H^+}{a''H^+}\right) \tag{2}$$

If such a cell is to be used to determine the hydrogen-ion activity of one of the solutions, that of the other must be fixed by reference to some standard state. There are a variety of possible ways of selecting the standard state. It has seemed most desirable to us to choose for each solvent a particular solution of which the electrically measured hydrogen-ion activity is set equal to unity. This we have done for acetic acid as later described (p. 3059). Essentially the same thing has been done for water by assigning the single potential $E = 0$ to the "normal" hydrogen electrode.

To increase the reproducibility of our measurements we found it desirable to compare different acetic acid solutions, not directly with each other, but each separately with a standard aqueous reference electrode. In other words, we measured the e.m.f. of cells of the following type

$$\begin{array}{c|c|c|c|c|c} \text{Pt} & \begin{array}{c} C_6Cl_4O_2\ (\text{sat.}) \\ C_6Cl_4(OH)_2\ (\text{sat.}) \\ HX(C') \\ \text{in HAc} \end{array} & \text{Bridge} & \underbrace{\begin{array}{c} \text{KCl} \\ (\text{sat.}) \end{array}}_{\text{in}} & \underbrace{\begin{array}{c} \text{HgCl (sat.)} \\ \text{KCl (sat.)} \end{array}}_{H_2O} & \text{Hg} \end{array}$$

regarding their potentials as positive when the platinum electrode was positive to the mercury.

[5] Conant, Small and Taylor, This Journal, 47, 1959 (1925).

In our work, the siphons of the calomel half cells, which terminated in glass stoppers, usually dipped into a beaker of saturated potassium chloride solution, into which also dipped one end of the special bridge which is later discussed in detail. This was a glass-stoppered U-tube containing a concentrated acetic acid solution of lithium chloride and gelatin. The other end of the bridge dipped into another beaker which contained the solution under investigation (saturated with chloranil and hydrochloranil), the platinum electrodes and an electrically driven stirrer. The e.m.f. of the cell was compensated and measured by means of a potentiometer, with the aid of a quadrant electrometer as null instrument.

The first and most striking of the early results of our work was the large e.m.f. of cells of the type just described when the acetic acid solution contained considerable concentrations of strong acids. For example, a chloranil electrode in a 0.064 *M* solution of sulfuric acid in acetic acid is 0.735 volt more positive than the saturated calomel electrode, when the measurement is made as just described. The corresponding figure for 1 *M* sulfuric acid is +0.756 volt, and for 1 *M* perchloric acid about +0.83 volt. A 1 *M* solution of trichloro-acetic acid gave a potential of only +0.615. These high potentials were reduced in an orderly manner whenever basic substances such as pyridine, urea or sodium acetate were added to the solution, and this fact permitted the *titration* of the various acids with bases, and of the bases with acids. Good titration curves were obtained in numerous instances, as is shown below (Figs. 1 and 3) in the case of bases. *The process of salt formation could thus be studied in as satisfactory a way as in water, by the aid of these titration curves. Indeed it was even possible to titrate such bases as acetamide, benzamide, and acetanilide, which cannot be titrated in water solution.* The titration and relative strengths of acids will be discussed in a later communication.

Apparatus and Materials

Platinum Electrodes.—Two or more electrodes of blank platinum foil or wire were used in each measurement. Foils of a considerable size (10 × 15 mm.) appeared to be most satisfactory. The electrodes were usually cleaned by scrubbing with sand, ignited and allowed to stand in a solution containing the chloranil mixture and some buffer mixture of a not too acid character. After ignition, or prolonged standing in the air, or washing with water, the electrodes often required a considerable time (fifteen to twenty minutes) to attain their equilibrium potentials. If, after use in one solution, they were simply washed in glacial acetic acid and placed in another, their subsequent recovery was much quicker, and if they were merely transferred from one glacial acetic acid mixture containing chloranil to another, the final potential was attained as rapidly as the solution could be completely mixed. This last point was important in titrations, where apparently with sufficiently vigorous stirring there was no lag whatever unless some slow reaction was taking place in the solution.

The criteria by which electrodes were judged were as follows: (1) agreement between many electrodes in the same solution; (2) rapid attainment of final potential; (3) rapid and complete recovery after polarization (in the earlier work with a low resistance circuit); (4) attainment of a particular potential in a particular buffer (in the later work). In general, new electrodes satisfied these criteria very well and often could be used for weeks in solutions of low acidity without exhibiting any indication of poisoning. Agreement of four electrodes within one millivolt was frequently attained and on certain occasions within 0.2 millivolt.

On the other hand, in solutions containing high concentrations of acetic anhydride, perchloric acid, fuming sulfuric acid or even of ordinary sulfuric acid, the agreement between different electrodes was sometimes much less satisfactory, and certain ones exhibited a tendency to give divergent values (generally less positive than the average). After repeated use in such solutions these divergencies sometimes became very large (0.1 to 0.2 volt) so that the electrodes were completely useless. It was remarked that when an electrode gave values say 50 millivolts low in the most acid solutions, it generally gave values about 5 millivolts low in the ordinary solutions. Ignition, scouring and scraping were in some cases effective in restoring the original character to the electrode; at other times the poisoned character persisted. On prolonged standing in the air (several weeks) with subsequent ignition, almost all the poisoned electrodes recovered completely. After it was established that a certain buffer containing urea and sulfuric acid showed a definite potential difference against the saturated calomel half-cell, it was possible to test electrodes by their performances in this mixture, and this was done repeatedly in the later work.

Saturation of the Electrode and the Chemical Activity of Chloranil

Theoretically, the peculiar usefulness of the chloranil electrode depends upon the solution being really in equilibrium at all times with both the solid quinone and its hydroquinone. Therefore, although for many practical purposes such as titrations, considerable variation from the equilibrium conditions seemed to introduce no appreciable error, for the final measurements some pains were taken to devise a technique which at least would insure thoroughly comparable conditions in different experiments. It was found that if a large excess of both solid phases was stirred with the solution at the working temperature, the electrodes very quickly took up a potential which was near, but in general not identical with, the equilibrium potential, and the latter was only reached after a considerable time, sometimes as long as thirty to forty minutes. It therefore seemed best to warm the solvent with an excess of the solids. On cooling, both substances readily crystallized providing the supersaturation had been sufficient, and in five to ten minutes after cooling to room temperature, the equilibrium value of the potential was reached. If now to such a solution which is exactly saturated, a certain volume of titrating solution is added, obviously an at least momentary unsaturation will be introduced. With this in view, it was at first our practice previously to saturate the titrating solution also with both solids. Later we abandoned this practice, having convinced ourselves that no measurable error was introduced by so doing provided the relative volume of the solution added was small. This is to be expected if the solutions approach ideality, unless differences in the *solution rate* of the two solids introduce errors.

In order to save material, we ascertained by preliminary experiments how much of each solid was necessary to give a quick crystallization when the solution was vigorously shaken with the solids for about thirty seconds at a temperature not over 50°, and then cooled under the tap to 25°, the working temperature. The amounts added were always 0.8 g. of tetrachloro-hydroquinone and 0.6 g. of tetrachloroquinone per 100 cc. of acetic acid solution. No effect of a three- or four-fold excess over these amounts was observed. Whenever possible, the acetic acid alone was warmed with the solids and the solutes were added later, just before the final cooling was complete. No error was introduced, however, in the majority of cases, when the various buffer solutions were themselves warmed with the chloranil. It was also found that solutions of urea and of sulfuric acid saturated with chloranil could be stored for a considerable time without altering in titer or other properties. Pyridine under such conditions developed a cherry red color, while bases of a more actively reducing character rapidly developed various vivid colors and clearly underwent rapid decomposition. We finally avoided storing any of the substances in contact with chloranil, but instead always saturated the portion to be measured or titrated immediately before use, as just described.

Reference Electrodes

The saturated aqueous calomel half-cell was used as a reference electrode. Several of these were prepared and frequently checked. They always agreed within one millivolt with each other and with similar electrodes prepared by other workers. Their siphons dipped either into a beaker of saturated potassium chloride solution, or for special purposes directly into the solution to be measured. In the latter case the end of the siphon was always stoppered with glass.

Salt Bridge

The liquid used as a salt bridge was a supersaturated solution of lithium chloride in acetic acid, which was prevented from crystallizing by dissolving a small amount of gelatin in the acetic acid. The concentration of the two solutes was varied within wide limits without apparent effect on the performance of the bridge. This solution was enclosed in a glass-stoppered U-tube about 35 cm. long and whose internal diameter was about 4 mm.

Measuring Instruments

At first a simple galvanometer was used as a null point indicator in connection with a Leeds and Northrup Type K potentiometer. Later when the lithium chloride bridge was used the resistance of the system became too great for this apparatus and a quadrant electrometer of the Compton type was substituted for the galvanometer. The needle was charged to a constant potential between 67.5 and 180 volts by a "B" battery. One pair of quadrants was permanently earthed, and the other could be connected either to earth or to the system comprising the potentiometer and the cell to be measured. The polarity of the cell could be reversed at will, while the negative side of the potentiometer was permanently earthed. The high-potential part of the system was very carefully insulated and the entire apparatus protected by an earthed shield. The functioning of the electrometer was very satisfactory and its sensitivity was high (up to 25 mm. of scale per millivolt). (The lamp and scale were about 2.5 meters from the mirror.) Its insensitiveness to abuse in the form of large accidental voltages, and its complete prevention of polarizing currents in the system, are advantageous. It also permitted the use of the clean and convenient but high-resistance ground-glass junctions. Serious difficulty was occasionally encountered in adjusting the electrometer to a high sensitivity. The method described by Compton and Compton[6] was found useful when simple trial and error failed to secure a satisfactory setting. There was also a slow but capricious drift of the zero point, so that a scale with a widely movable zero was a great convenience.

Materials Used

Our principal object was to develop a method of medium accuracy which could be easily applied by others, and to make a rapid exploration of a wide field, rather than

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[6] Compton and Compton, *Phys. Rev.*, **14**, 85 (1919).

to obtain data of high accuracy. We, therefore, whenever possible, used materials of commercial grade, but of definite and reproducible character, instead of subjecting our substances to careful purification.

Acetic Acid.—In all of the work described in this paper, a single grade of glacial acetic acid was used, the P. W. R. analytical reagent. This was supposed to contain "at least 99.5% acetic acid." No attempt was made to free it from water or other impurities. In many preliminary experiments the ordinary "U. S. P. 99.5%" grade purchased in carboys was used and no difference in behavior was detected. In making up the solutions described in the following paper, still another grade of analyzed acid was employed, but no difference in behavior was found.

Tetrachloroquinone (chloranil).—This was the Eastman Kodak Company's "No. 603 MP 283–284°." Recrystallization from acetic acid had no effect on its electrochemical behavior and was generally omitted.

Tetrachlorohydroquinone.—This was prepared from the previous material substantially as described by Conant and Fieser,[4] except that it was not precipitated by alcohol from glacial acetic acid solution. When thoroughly purified it melted very sharply at 236–237°, but certain samples of lower melting point showed identical electromotive behavior.

Perchloric Acid.—The 60 per cent. aqueous solution was added slowly to five times its volume of chilled acetic anhydride reagent and further diluted to the desired volume with acetic acid. The resulting solution was then titrated against a urea, pyridine or sodium acetate solution of known concentration.

Other Materials.—The other acids and bases used were of the best C. P. grade ordinarily obtainable.

Experimental Results

Titration of Bases.—Fig. 1 shows the potentials (E) obtained when small volumes of 2 M sulfuric acid were added to large volumes of solutions of the various bases, at such concentration that they were 0.2 M in total base at the mid-point of neutralization. The temperature was 25 ± 0.5°. The solutions were all prepared and saturated in the same way and the potentials measured against the saturated calomel half-cell, through the lithium chloride bridge, with the quadrant electrometer. The choice of substances was such as to give as wide a range of base strength as possible. Thus acetanilide, at the top of the diagram, is a very weak base indeed. Passing through progressively stronger bases, one notes the appearance of a slight inflection with urea, and this becomes steadily more marked as the strong bases are reached. A double bend is shown by the two strongest bases, *p*-toluidine and pyridine, which is due to the successive action of the two hydrogens of the sulfuric acid molecule. It will be noted that two bases which do not contain nitrogen are included, the two xanthydrols. It was necessary to titrate these in more dilute solution (0.05 M and 0.04 M) on account of their low solubility. The relative position of the curves is reliable to about 0.010 volt at least.

In Fig. 2 the logarithm of R, the ratio of salt to free base, is plotted against the e.m.f. data of Fig. 1. The numbering of the curves is the same in the two figures. "One hundred per cent. neutralized" means 1 mole of sulfuric acid per mole of base. If the curves of Fig. 1 had exactly the theoretical shape, the points for each substance would fall on a straight line in Fig. 2 and the slope of these lines would be

$$\frac{\Delta \log R}{\Delta E} = \frac{1}{.0591}$$

as shown by the lines marked "theoretical slope."[7] Departure from these conditions must be due to changes in the activity coefficients of various molecular species concerned in the equilibria, or to changes in the liquid junction potential. That these departures are no greater, especially in the less acid solutions, is fortunate, and perhaps surprising.

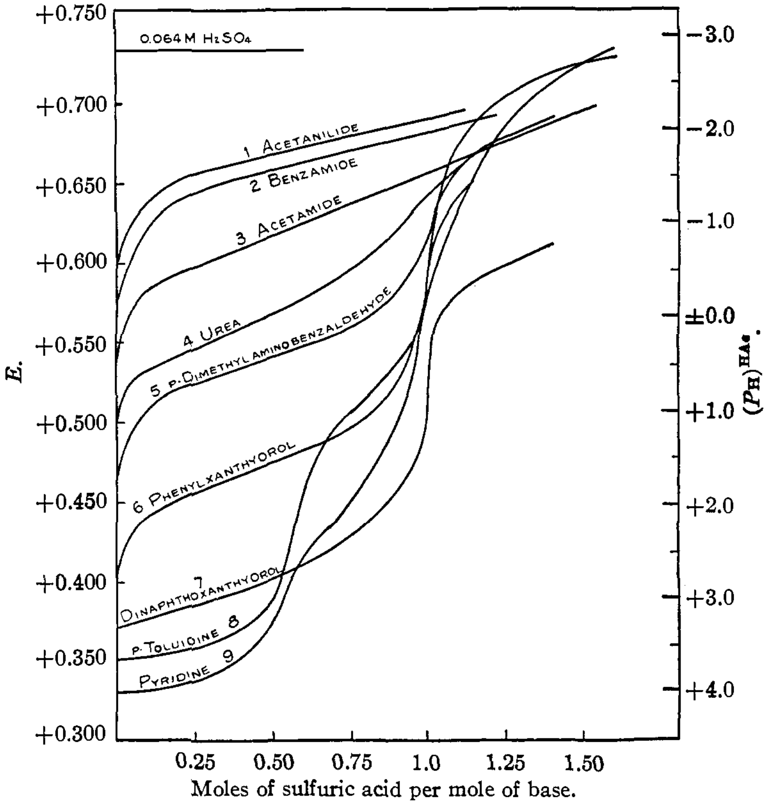

Fig. 1.—Titration curves of bases with sulfuric acid in glacial acetic acid (mono-amines and carbinols).

Polyamines

None of the substances in Fig. 1 adds more than one hydrogen ion per molecule. Fig. 3 shows the titration curves of four polyamines, each of

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[7] For convenience in studying the diagram, percentage neutralizations are shown at the left, as well as the corresponding values of the true ordinate (log R) at the right.

which shows distinctive behavior. These curves were obtained under the same conditions as those of Fig. 1. It will be noted that substance No. 1, Michler's ketone, tetramethyldiaminobenzophenone (4,4′), shows scarcely a trace of inflection until two moles of acid have been added. Hexamethylenetetramine shows a sharp inflection when only one-half mole of acid has been added per mole of base. This must represent the formation of the salt $(RN_4H)_2{}^{+}(SO_4)^{=}$. This point once passed, a heavy white precipitate appears in the solution, which acts as a very efficient buffer, the potential remaining constant while 0.8 mole of acid is being added per mole of base originally present. Then once more a break occurs, steeper this time, corresponding to the complete formation of $(RN_4H_2)^{++}(HSO_4)_2{}^{-}$ or of $(RN_4H_4)^{++++}(SO_4)_2{}^{=}$. The addition of acid was continued until four moles of sulfuric acid were present per mole of base, but no additional inflection was noted.

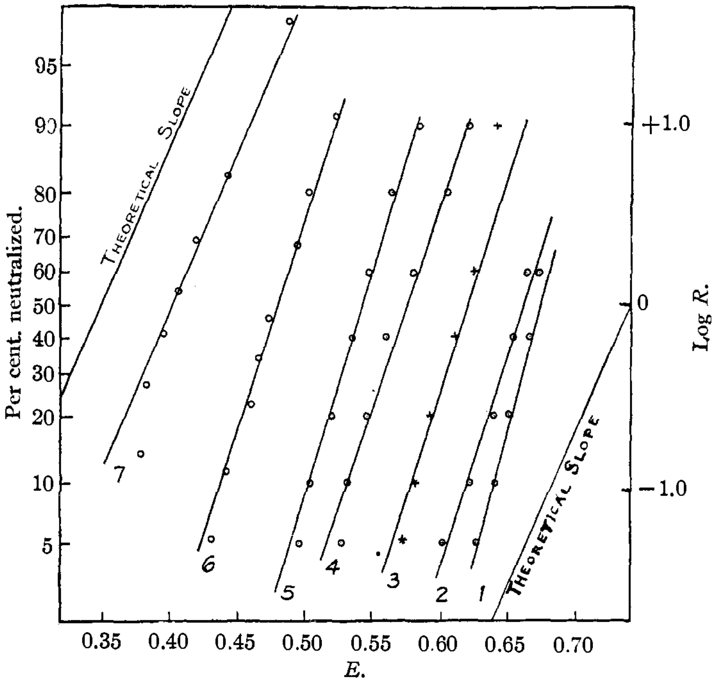

Fig. 2.—Logarithmic titration curves of bases in acetic acid.

No. 3, hydrobenzamide, shows a slight, but distinct, inflection at one mole of acid $[(RN_2H)^{+}(HSO_4)^{-}$ or $(RN_2H_2)^{++}(SO_4)^{=}]$ and a much sharper one at two moles. The substance smelled strongly of benzaldehyde, indicating partial decomposition.

No. 4, *p*-phenylenediamine, formed dark-colored solutions, indicating oxidation by the chloranil, and at least one substance was precipitated in the course of the titration. Nevertheless, it seemed worth while to exhibit its striking curve

The data of Figs. 1, 2 and 3 demonstrate the existence in acetic acid solutions of a system of acids and bases quite similar to the familiar water system, and show that this system may be explored with the aid of the chloranil electrode.

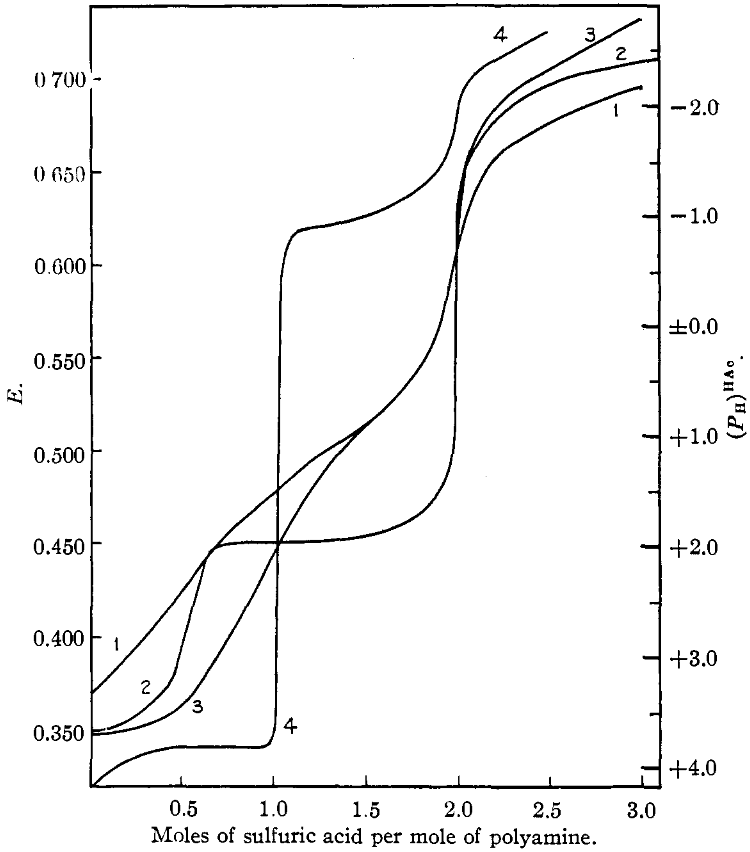

Fig. 3.—Titration curves of polyamines with sulfuric acid in glacial acetic acid. 1. Michler's ketone; 2. hexamethylene tetramine; 3. hydrobenzamide; 4. *p*-phenylenediamine.

Effect of Water and Alcohol on the Potentials

It seemed interesting to determine the effect on the potentials of our solutions of adding small amounts of water or alcohol. The results of such an inquiry are summarized in Fig. 4. The abscissas are percentages of water or alcohol; the left-hand scale of ordinates, potentials measured in the usual way. The measurements were obtained as follows. (1) (Top curve). An acetic acid solution 0.2 *M* in perchloric acid, half neutralized with urea (and containing some acetic anhydride), was prepared and saturated with chloranil mixture. It was 0.802 volt more positive than the calomel electrode. Small amounts of absolute alcohol were then added until the total alcohol content of the solution reached 70% by volume. The potential had now fallen to +0.525 volt. The other solutions studied were 0.2 *M* sulfuric acid half neutralized with urea and 0.2 *M* urea half-neutralized with sulfuric acid. To each of these three, water and alcohol were separately added. The effect of water was much the greater, particularly at the beginning of the curve. The exact course of the curves is doubtless affected by changing liquid junction potentials. These data show clearly that a variation in the water content of the acetic acid of the order of one per cent. is not serious in the urea solutions but becomes very important as the highest acidities are reached. A few scattered experiments indicated that the addition even of small amounts

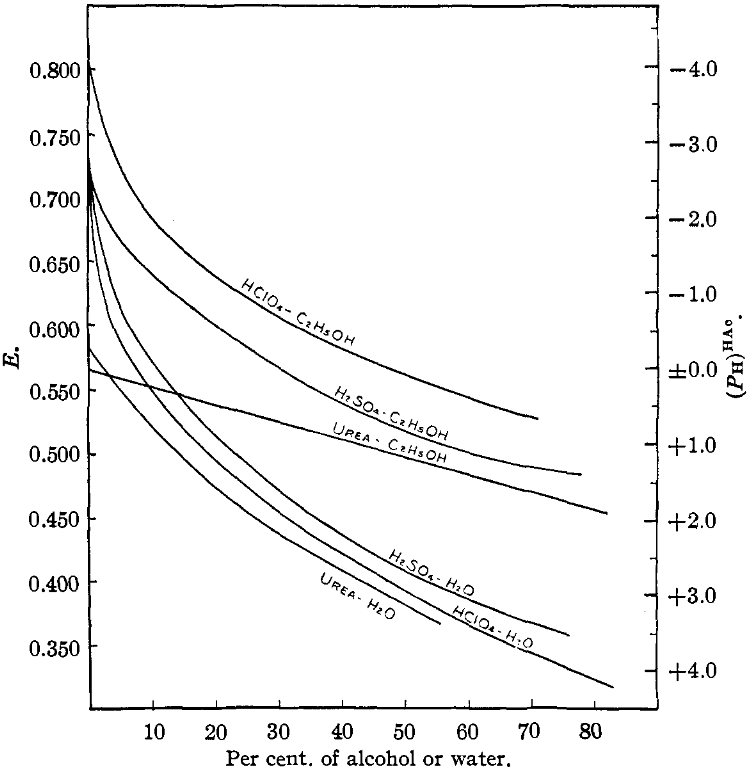

Fig. 4.—Effect of alcohol and water on potentials of buffer mixtures in glacial acetic acid. The first formula or name on each curve gives the principal solute, which is in each case half neutralized with urea (or sulfuric acid), and at an initial concentration of 0.2 *M*.

of acetic anhydride produced a slight but significant increase in the potentials, particularly in the most acid solutions.

Effect of Concentration and of Various Ions

In order to limit as far as possible the number of variables in our preliminary work, we made our final comparisons all at the same concentration and with no other anions present than those furnished by sulfuric acid. The concentration chosen, largely for convenience and to secure good buffer capacity, was 0.2 *M*. A few preliminary tests indicated that between 0.1 *M* and 0.4 *M* the effect of change of concentration was slight. At concentrations below 0.1 *M* rather large variations were encountered. We have reserved for a later paper the question whether these are due to activity changes incident to changes in the ionic strength of the solutions or to changes in the liquid junction potentials. Preliminary calculations support the former view.

In general, when a base was titrated with perchloric acid rather than with sulfuric, the corresponding potentials were slightly higher. The presence of acetic anhydride in the perchloric acid solutions, coupled with the extreme water-sensitivity of their potentials, makes it difficult to be certain whether this effect is really due to a difference in anion or to a difference in the effective water content of the solutions. This point also will form the subject of later work.

Discussion of Results

The Magnitude of the Potentials and the Use of the Lithium Chloride Bridge

The high values of the potentials, especially in the most acid solutions (see p. 3049), raise the question of the extent to which they are affected by the unknown liquid junction potentials in the cell. It also remains to justify the use of the lithium chloride bridge in all our final measurements. A salt bridge in measurements of this kind may be said to have three functions.

(1). To promote the reproducibility of the measurements.

(2). To neutralize the effect of varying liquid junction potential between the different acetic acid solutions.

(3). To eliminate if possible the potential at the junctions between the saturated aqueous potassium chloride and the various acetic acid solutions, or at least to promote its constancy.

(1). When two acetic acid solutions were directly joined through a porous cup or a ground-glass stopper, it was found that their difference of potential generally, but not always, had the same value within 0.005 volt. When these solutions were then each separately measured against a third solution, the difference of the potentials thus obtained often varied from the "direct" value by ±.015 volt or more. A number of solutions were tried as "reference electrodes" but in no case was the system of potentials measured against a wide variety of other solutions completely self-consistent. As it seemed that part of the difficulty might lie in the non-reproducibility of the various acetic acid chloranil half-cells, we next prepared a number of (aqueous) saturated calomel half-cells, whose siphons were stoppered rather tightly at the end with glass stoppers.

These stoppered ends, which thus formed potassium chloride bridges of a fairly reproducible type, were allowed to dip directly into the various acetic acid solutions and the measurements thus all referred to the saturated calomel half-cell. Under these conditions, reproducible values (within .005 volt) were nearly always obtained *except in the more acid solutions*, where gross discrepancies of the order of .04 volt made their appearance.

It now occurred to us to interpose, between the highly acid solutions and the saturated aqueous potassium chloride, another acetic acid solution, substantially "neutral" (in the acetic acid system), and containing a high concentration of some electrolyte. Lithium chloride seemed to be the best salt for our purpose.

In order to increase the available concentration range, we prepared supersaturated solutions which we prevented from crystallizing with the aid of gelatin. These solutions were enclosed in a U-tube with well ground stoppers, and the ends of this tube dipped, respectively, into the acetic acid solutions and into saturated potassium chloride connected with the calomel electrode.

With this experimental arrangement the reproducibility of all the measurements, even in the more acid solutions, appeared satisfactory for our purpose. The discrepancies were rarely as great as 0.005 volt.

(2). The self-consistency of the measurements made with the aid of the lithium chloride bridge, and the approximation of the lines of Fig. 2 to the theoretical slope, seem to indicate that there are no errors due to liquid junction potentials between the different acetic acid solutions, of a much higher order of magnitude than the extreme variation of the individual measurements (0.005 volt).

(3). The question of the magnitude of the junction potential between the saturated potassium chloride solution of the calomel electrode and the various acetic acid solutions through the lithium chloride bridge is much more uncertain. A small amount of evidence, as yet of a very uncertain character, leads us to believe that this potential is of the order of 0.15 volt, and of such sign as to increase the apparent e.m.f. of the cells. In preliminary work of this character the *magnitude* of such a potential is of much less importance than its *constancy*. The reproducibility and self-consistency of all our measurements in acetic acid seem to be evidence that the junction potential is effectively constant.

As they stand, our e.m.f. measurements give a direct measure of the hydrogen-ion activity of the acetic acid solutions, relatively to each other. As it is customary, however, in dealing with aqueous solutions, to think of hydrogen-ion activity in terms of "P_{H} units" (1 P_{H} unit = .0591 volt at 25°) instead of in volts, it has seemed desirable to employ a similar unit in discussing our results in glacial acetic acid. We have, therefore, adopted the symbol $(P_{\mathrm{H}})^{\mathrm{HAc}}$ as a convenient designation for our purpose.

We are then confronted with the necessity of selecting a zero for the scale thus constituted. If it could be assumed that the liquid junction potential between water and acetic acid solutions was *eliminated* by the bridge in our measurements, it would be rational to choose as zero a potential of +0.418 volt against the calomel electrode, as this is the normal potential of the chloranil electrode when so measured in aqueous solution.[4] Since we have no assurance that our liquid junction potential is negligible, we have arbitrarily taken the zero of our scale to correspond to a potential of 0.566 volt.[8] This means merely that we have decided to call unity, for our present purposes, the hydrogen-ion activity of a solution in which the chloranil electrode has the stated potential (+0.566 volt) measured as above described.

The measured potentials (E) and the $(P_{\mathrm{H}})^{\mathrm{HAc}}$ values are thus related as follows

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

We have inserted in our diagrams as alternative ordinates the $(P_{\mathrm{H}})^{\mathrm{HAc}}$ values as thus defined. It will be noted that many of these values are negative, because of the high acidity of some of our solutions. In terms of the new unit, the acidities of the solutions mentioned on p. 3049 are as follows

TABLE I

ACIDITIES OF SOLUTIONS

Solution	E (volts)	$(P_{\mathrm{H}})^{\mathrm{HAc}}$
1.0 M Cl_3CCO_2H	+0.615	−0.83
1.0 M H_2SO_4	+0.756	−3.23
1.0 M $HClO_4$	+0.83	−4.4

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[8] It is our hope that the zero point of this arbitrary scale will be shown eventually to be very near the zero point of the P_{H} scale in water. The two chief reasons which have led us to adopt tentatively this particular standard are as follows. (1) It seems probable that the strength of anhydro bases should be approximately the same in different solvents, and this is the case for urea, dimethylpyrone and acetamide in acetic acid and water as we have defined the $(P_{\mathrm{H}})^{\mathrm{HAc}}$ scale (see Table II). (2) The solvent (acetic acid) half neutralized with a relatively strong base such as pyridine might be expected to have a hydrogen-ion activity of the same order of magnitude as the pK_A of acetic acid dissolved in water. The $(P_{\mathrm{H}})^{\mathrm{HAc}}$ of an equimolar mixture of pyridine and pyridine acetate is about +4.4 as compared to the value +4.7 given for the pK_A of acetic acid in water.

Relative Strength of Bases

As a matter of interest we now present a list of numbers (Table II) intended to represent as closely as possible the relative strength of all the bases we have been able to titrate accurately, in the absence of complications such as the appearance of precipitates. This list includes not only most of the bases of Figs. 1 and 3, but also several others for which the measurements, for lack of space, are not reported in detail. In this table we designate by $(pK_A)^{HAc}$ the $(P_H)^{HAc}$ value of a 0.2 M solution of each base half neutralized with sulfuric acid. These $(pK_A)^{HAc}$ values should be more or less closely related to the negative logarithms of the hydrolysis constants of strong-acid salts of the base in water solution.

$$pK_H^{H_2O} = -\log K_H^{H_2O},\ K_H^{H_2O} = \frac{10^{-14}}{K_B^{H_2O}}$$

where $K_B^{H_2O}$ is the ordinary dissociation constant of the base. Where they are known, values of $pK_H^{H_2O}$ at 25° are given for comparison.

Most of the water values are taken from Landolt-Börnstein's "Tabellen." The figures for *p*-toluidine and triethylamine are from unpublished measurements by one of us. The essential identity of behavior in acetic acid shown

TABLE II

RELATIVE STRENGTH OF BASES IN ACETIC ACID SOLUTION

Substance	$(pK_A)^{HAc}$	$(pK_H)^{H_2O}$
Triphenylcarbinol Triphenylamine 2,4-Dinitroaniline	Too weak to measure	Too weak to measure
Acetanilide	−1.75	Too weak to measure
N-*p*-methylbenzyl formamide N-*p*-methylbenzyl acetamide N-*p*-methylbenzyl butyramide	about −1.65	Too weak to measure
Benzamide	−1.60	Too weak to measure
Acetamide	−0.9	−0.5
Urea	−0.05	+0.18
Dimethylpyrone	about 0.0	+0.3
Diphenylamine		?
p-Nitro-aniline		+2.0 (?)
p-Dimethylaminobenzaldehyde	+0.4	?
Michler's ketone (2nd stage)	+1.0	?
Hydrobenzamide (2nd stage)	+1.0	?
Phenylxanthydrol	+1.5	?
Michler's ketone (1st stage)	+2.5	?
Dinaphthoxanthydrol	+2.65	?
"Nitron"	strong	?
p-Toluidine	strong	+5.11
Pyridine	strong	+5.36
Triethylamine	strong	+10.75

NOTE: In the case of the methyl benzyl amides, the measured values have been increased by 0.1 unit to allow for differences in the concentration of their solutions from the standard concentration.

by urea and *p*-nitro-aniline leads us to believe that a redetermination of the constant of the latter substance in water is desirable.

It is necessary to add that while the picture of relative base strength thus presented is undoubtedly correct in its main outlines, the possibility remains that the zero of our scale is improperly placed by as much as one or two units and that the "constants" we have given would be modified in the presence of water, acetic anhydride or other substances, or by changes in concentration.

It is perhaps entertaining at this point to pursue somewhat further the implications of our choice of zero for the acetic acid scale. If, as we hope, we have estimated the junction potential between acetic acid and aqueous solutions with approximate correctness, then our $(P_{\text{H}})^{\text{HAc}}$ values become approximate measures of the hydrogen-ion activity of the various solutions referred to the water standard. The hydrogen-ion activities (or activity coefficients, since we are dealing with unit concentrations) of the three solutions listed in Table I, are then respectively 6.7, 700, and 25,000. That such high activities are possible, even in water solutions, is indicated by the work of Lewis and Randall[9] on concentrated HCl solutions. Their most acid solution (16 molal hydrochloric acid) showed a mean ionic activity coefficient of 43.2, or a mean ionic activity of 691, which compares favorably with the values for our (much less concentrated) solutions in acetic acid. The "P_{H} value" of such a solution is —2.84 on the assumption that the two individual ion activities are equal. The true value is doubtless still more negative. We feel that our work indicates that the proximate cause of superacidity in a solution is an abnormally high value of the hydrogen-ion activity. An hypothesis to account for this phenomenon is tentatively proposed in the following paper.

We take pleasure in expressing our thanks to Mr. Edwin B. Damon, who kindly gave us the benefit of his experience with quadrant electrometers.

Summary

1. A method has been developed in which the chloranil electrode is used to measure hydrogen-ion activities in glacial acetic acid solutions.

2. The reliability and significance of such measurements are discussed.

3. Titration curves are given for several bases in this solvent and their significance noted.

4. The bases studied are arranged in order of increasing strength and characterized by a set of constants allied to the hydrolysis constants of their salts in water solution.

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[9] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p. 336.