JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

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VOLUME 79 JANUARY 15, 1957 NUMBER 1

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Acid–Base Equilibria in Glacial Acetic Acid. IV. Quantitative Interpretation of Acid–Base Titrations in Glacial Acetic Acid

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RECEIVED JULY 19, 1956

Acid–base titrations in anhydrous acetic acid are no longer an empirical subject: it is now possible to calculate quantitatively the characteristics of such titrations carried out either potentiometrically or with indicators. The equations governing the shape of potentiometric titration lines of bases in anhydrous acetic acid have been derived and experimentally verified. These relationships have been used to explain the apparent paradoxes described in the classical studies of Conant, Hall and Werner, to predict the shape of the titration line of urea with perchloric acid, the e.m.f. or pure salt solutions, and the change in e.m.f. in the vicinity of the equivalence point in the titration of sodium acetate with perchloric acid. The relationships determining the ratio of the acid to basic color of an indicator base over the titration range in acetic acid have also been established and used to predict the color of *p*-naphtholbenzein (PNB) in diethylaniline perchlorate and sodium perchlorate solutions. The change in color of PNB on the addition of sodium acetate to a sodium perchlorate solution was found to be in agreement with the calculated values.

Introduction

After the pioneer work of Conant and co-workers[1] on neutralization curves of supposedly strong and weak bases in glacial acetic acid a host of papers has been published on the titration of a large variety of bases and some acids. These papers, in which the end-point was found potentiometrically or visually with an indicator, are all of an empirical nature. After determining the dissociation constants of acids, bases and salts[2] and after the establishment of the acidity scale in glacial acetic acid it is now possible to explain the apparently abnormal shapes of neutralization curves of bases of different strength as observed by Hall,[1a,c,e] to calculate potentiometric titration curves, the equivalence potential and the change of *p*H and potential near the equivalence point. It is also possible to calculate the ratio of acid to basic form of an indicator over the titration range and particularly in the vicinity of the equivalence point, and to present the fundamental equations underlying spectrophotometric titrations.

In the present paper neutralization curves of bases with perchloric acid have been calculated and it is shown that the theoretical values are in excellent agreement with the experimental data. Similar calculations and determinations can be made with other acids, but since perchloric acid is the strongest acid known in acetic acid, it is the only one of practical consequence. Also, the color equilibrium of a suitable indicator has been calculated at and near the equivalence point, and the results compared with experimentally determined data.

Potentiometric Titrations:

Change of Hydrogen Ion Concentration in Titration of a Base with Perchloric Acid

$[H^+]$ of a Solution of a Base B.—In a pure solution of a base B the over-all dissociation is given by eq. 1

$$B + HAc \rightleftharpoons BH^+ + Ac^- \qquad (1)$$

The over-all dissociation constant K_B is

$$K_B = [BH^+][Ac^-]/C_B \qquad (2)$$

in which C_B is the total concentration of undissociated base ($[B] + [BH^+ Ac]$).[2b] For reasons given previously,[2a] concentrations of undissociated species and of ions are assumed to be equal to activities. It is easily derived that in a solution of the base

$$[H^+] = K_s/\sqrt{\{K_B\{(C_B)_t - K_s\}/[H^+]\}} \qquad (3a)$$

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[1] (a) N. F. Hall and J. B. Conant, THIS JOURNAL, **49**, 3047 (1927); (b) J. B. Conant and N. F. Hall, *ibid.*, **49**, 3062 (1927); (c) N. F. Hall and T. H. Werner, *ibid.*, **50**, 2367 (1928); (d) J. B. Conant and T. H. Werner, *ibid.*, **52**, 4436 (1930); (e) N. F. Hall, *ibid.*, **52**, 5115 (1930); (f) N. F. Hall, *Chem. Revs.*, **8**, 191 (1931).

[2] (a) I. M. Kolthoff and S. Bruckenstein, THIS JOURNAL, **78**, 1 (1956); (b) S. Bruckenstein and I. M. Kolthoff, *ibid.*, **78**, 10 (1956); (c) **78**, 2974 (1956).

in which K_s is the autoprotolysis constant of acetic acid while the analytical concentration of the base $(C_B)_t = C_B + [BH^+] = C_B + [Ac^-]$. Since all bases are weak electrolytes in acetic acid, the quadratic eq. 3a usually can be applied in the approximate form

$$[H^+] = K_s/\sqrt{K_B\,(C_B)_t} \tag{3b}$$

The results predicted by eq. 3b accurately account for *p*H data measured in solutions of pure bases in acetic acid. Hall and Werner[1c] found that there is an increase of one *p*H unit for a hundredfold increase in concentration of base. Similar results also have been reported by Higuchi, Danguilan and Cooper[3] and by us.[2c]

$[H^+]$ in Mixtures of B and its Perchlorate $BH^+ClO_4^-$.—For the calculation of hydrogen ion concentration in such mixtures it is necessary to consider not only the dissociation constant of the base B but also that of the salt, eq. 4a, and of perchloric acid, eq. 4b. The over-all dissociation constants of the salt

$$BHClO_4 \rightleftharpoons BH^+ + ClO_4^- \tag{4a}$$

$$HClO_4 \rightleftharpoons H^+ + ClO_4^- \tag{4b}$$

and the acid are $K_{BHClO_4} = [BH^+][ClO_4^-]/C_{BHClO_4}$ and $K_{HClO_4} = [H^+][ClO_4^-]/C_{HClO_4}$, respectively. C refers to the total concentration of undissociated species indicated by the subscript. Equilibria in solutions of $BHClO_4$ are determined by the equilibrium constant $K_f^{BHClO_4}$ of the reaction $B + HClO_4 \rightleftarrows BHClO_4$. The equilibrium constant $K_f^{BHClO_4} = C_{BHClO_4}/C_BC_{HClO_4}$ is a function of K_s, K_B, K_{HClO_4} and K_{BHClO_4}.[2a,3] This relationship is stated in

$$K_f^{BHClO_4} = K_{HClO_4}K_B/K_sK_{BHClO_4} \tag{4c}$$

From the rule of electroneutrality, eq. 4d and the expressions

$$[H^+] + [BH^+] = [Ac^-] + [ClO_4^-] \tag{4d}$$

$$[BH^+] = K_BC_B[H^+]/K_s,\ [Ac^-] = K_s/[H^+] \text{ and}$$
$$[ClO_4^-] = K_sK_{BHClO_4}C_{BHClO_4}/K_BC_B[H^+]$$

an explicit expression for hydrogen ion concentration in mixtures of B and $BHClO_4$, eq. 4e

$$[H^+] = \sqrt{\frac{K_s\left\{1 + \dfrac{K_{BHClO_4}C_{BHClO_4}}{K_BC_B}\right\}}{1 + K_BC_B/K_s}} \tag{4e}$$

is obtained. Unless the base is too weak to give a detectable end-point in the titration $K_BC_B/K_s >> 1$, so that the simpler expression, eq. 4f, can be written

$$[H^+] = K_s\,\sqrt{K_{BHClO_4}C_{BHClO_4} + K_BC_B}/K_BC_B \tag{4f}$$

Ordinarily it is sufficiently accurate to neglect the dissociation of the base and of the salt and the solvolysis of the salt with respect to their total concentrations and to assume that C_B and C_{BHClO_4} represent the stoichiometric concentrations. When necessary more exact formulations will be used.

Equation 4f has been verified for mixtures of several bases and their salts[2c] and accounts for the results obtained by Hall and Werner[1c] in the titration of 0.05 *M* guanidine and 0.05 *M* diethylaniline, respectively, with 1 *M* perchloric acid. These two compounds are among the stronger bases in acetic acid and their over-all dissociation constants are both of the order of 10^{-5} and are also of the same order of magnitude as the dissociation constants of their perchlorates. For example, we have found[2c] that for diethylaniline $pK_B = 5.78$ and $pK_{BHClO_4} = 5.79$. Under such conditions we can write eq. 4g instead of eq. 4f in mixtures of the base and its perchlorate in which the sum of the concentration of the base and salt is constant and equal to C.

$$[H^+] = \{K_s/C_B\}\sqrt{C/K_B} \tag{4g}$$

The above conditions were approximately satisfied by Hall and Werner[1c] in their titration of 0.05 *M* guanidine and 0.05 *M* diethylaniline with 1 *M* perchloric acid. The sum of the concentrations of free base and perchlorate changed only 5% up to the end-point and can be neglected for our purposes. The above authors plotted *p*H *versus* log $(1 - X)$, X being the fraction of the base which has been titrated and observed a straight line with a slope of one, similar to that found in aqueous medium for the titration of a *strong* base with a *strong* acid (corrected for volume change). This is quantitatively accounted for by eq. 4g where $[H^+]$ is proportional to $1/(1 - X)$. We now have a quantitative interpretation for the apparently paradoxical fact that the titration lines of guanidine and diethylaniline with perchloric acid in acetic acid are similar in shape to the titration line of a completely dissociated base with a strong acid in water whereas in solution of the pure bases in acetic acid the *p*H change with dilution corresponds quantitatively to the behvaior of a typically weak electrolyte. The *pK* of guanidine and its perchlorate are not known but apparently the same relationships hold as for diethylaniline.

If K_{BHClO_4} is not equal to K_B, the simple expression (4g) does not hold and the plot of *p*H *versus* log $(1 - X)$ does not yield a straight line. For example, Hall and Werner[1c] found this plot did not yield a straight line in the titration of 0.05 *M* sodium acetate with 1 *M* perchloric acid. The reason is that sodium acetate is a weaker electrolyte than sodium perchlorate[2c] ($pK_{NaAc} = 6.68$, $pK_{NaClO_4} = 5.48$).

In aqueous solution the plot of *p*H against log $(1 - X)/X$ yields a straight line with a slope of one in the titration of a weak base with a strong acid. In acetic acid Hall and Werner did not find an acid–base system which satisfied this relation and they ascribed the deviation from a straight line to large activity coefficient effects. Actually it is clear from eq. 4f that no relationship exists between K_B and K_{BHClO_4} which would yield the above relationship.

We may consider here the effect of dilution on the *p*H of a mixture of a base and its salt. In aqueous solution, the hydrogen ion concentration in a buffer mixture of a weak base and its salt with a strong acid as a first approximation is independent of the buffer concentration, depending only on the ratio of the salt to the base. Hall and Werner[2c] found

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(3) T. Higuchi, M. L. Danguilan and A. D. Cooper, *J. Phys. Chem.*, **58**, 1167 (1954).

that a ten-fold dilution of partially titrated bases causes a decrease in *p*H of 0.5 unit in acetic acid. If we let $[\mathrm{H}^+]_V$ equal the hydrogen ion concentration when the total volume is V and the equilibrium concentrations of salt and base are $C_{\mathrm{BHClO_4}}$ and C_{B}, respectively, while when the volume of the buffer is $10V$ and these concentrations are $C_{\mathrm{BHClO_4}}/10$ and $C_{\mathrm{B}}/10$, and the hydrogen ion concentration $[\mathrm{H}^+]_{10V}$, we find from eq. 4f that $[\mathrm{H}^+]_V/[\mathrm{H}^+]_{10V} = 1/\sqrt{10}$. Thus as long as eq. 4f can be written in stoichiometric concentrations rather than equilibrium concentrations, there should be a decrease of 0.5 *p*H unit for each ten-fold dilution. In very dilute solutions, appreciable dissociation of salt and base occurs, and the reaction $\mathrm{B} + \mathrm{HClO_4} \rightleftarrows \mathrm{BHClO_4}$ may no longer be quantitative so that this relationship would be expected to fail. Such a result was also noted by Hall and Werner. Of course it is clear from the above that in an equimolar mixture of B and $\mathrm{BHClO_4}$, $K_{\mathrm{s}}/[\mathrm{H}^+]$ is never equal to K_{B} as is true in water. Several authors have assumed this to be true in acetic acid. From eq. 4f it can be shown that in a solution containing C molar B and $\mathrm{BHClO_4}$

$$\frac{K_{\mathrm{s}}}{[\mathrm{H}^+]} = \sqrt{\frac{K_{\mathrm{B}}{}^2 C}{K_{\mathrm{B}} + K_{\mathrm{BHClO_4}}}}$$

In the neutralization of a very weak base, for which $K_{\mathrm{BHClO_4}} > > K_{\mathrm{b}}$, eq. 4f reduces to eq. 4h. It is evident that a plot of e.m.f. *versus* log $\sqrt{X}/(1 - X)$ should yield a straight line with a slope of 0.0591 volt. We have verified this relationship

$$[\mathrm{H}^+] = \frac{K_{\mathrm{s}}\sqrt{K_{\mathrm{BHClO_4}}C_{\mathrm{BHClO_4}}}}{K_{\mathrm{B}}C_{\mathrm{B}}} \tag{4h}$$

using urea as the weak base.

In the above discussion the equations which govern the slope of the titration lines of bases have been derived in the absence of foreign electrolytes. They cannot be applied when other salts are present. In this connection we may discuss the titration of a very weak base like urea carried out by Conant and Werner[1d] in the presence of 0.2 *M* trimethylammonium perchlorate or 0.2 *M* trimethylammonium *p*-toluenesulfonate as neutral salts for the purpose of "keeping the ionic strength constant during the titration." The expression "neutral salt" needs further qualification (*vide infra*) and must be used with care in acetic acid. As has been stated in a previous publication,[2] concentrations can be written with a good approximation instead of activities in acetic acid and activity effects cannot account for the results obtained by Conant and Werner. Quite generally, complications may be introduced at high electrolyte concentrations because of ion triplet and quadripole formation. However, the results reported by Conant and Werner can be accounted for on the basis of simple equilibria. These authors found that in titrations of various bases in the presence of the 0.2 *M* trimethylammonium salts a plot of *p*H *versus* log $(1 - X)/X$ yielded a straight line of slope one. However, the lines obtained with trimethylammonium perchlorate did not coincide with those obtained with trimethylammonium *p*-toluenesulfonate, the difference amounting to 0.5 *p*H unit in the titration of urea.

We will first consider the titration of a weak base (B) in the presence of a large excess of trimethylammonium perchlorate ($\mathrm{B'HClO_4}$). Since trimethylammonium acetate is undoubtedly one of the stronger bases in acetic acid, there is no tendency for the reaction $\mathrm{B} + \mathrm{B'HClO_4} \rightleftarrows \mathrm{BHClO_4} + \mathrm{B'}$ to proceed appreciably, and we will neglect it. The perchlorate ion concentration throughout the titration is virtually constant and is given by $[\mathrm{ClO_4}^-] = \sqrt{K_{\mathrm{B'HClO_4}}C_{\mathrm{B'HClO_4}}}$ as there is a large excess of $\mathrm{B'HClO_4}$ present. Since $[\mathrm{H}^+] = K_{\mathrm{s}}/[\mathrm{Ac}^-]$, $[\mathrm{Ac}^-] = K_{\mathrm{B}}C_{\mathrm{B}}/[\mathrm{BH}^+]$ and $[\mathrm{BH}^+] = [C_{\mathrm{BHClO_4}}K_{\mathrm{BHClO_4}})/\mathrm{ClO_4}^-]$, eq. 4i describes the variation of hydrogen ion during the titration. As a reasonable approximation $\mathrm{C}_{\mathrm{BHClO_4}}/C_{\mathrm{B}} = X/(1 - X)$, hence according to eq. 4i a plot of *p*H against log $(1 - X)/X$ should yield a straight line of slope one, as was observed experimentally.

$$[\mathrm{H}^+] = \frac{K_{\mathrm{s}}K_{\mathrm{BHClO_4}}C_{\mathrm{BHClO_4}}}{K_{\mathrm{B}}C_{\mathrm{B}}\sqrt{K_{\mathrm{B'HClO_4}}\,C_{\mathrm{B'HClO_4}}}} \tag{4i}$$

In solutions containing trimethylammonium *p*-toluenesulfonate (B'HTs) we must consider the metathesis reaction $\mathrm{HClO_4} + \mathrm{B'HTs} \rightleftarrows \mathrm{HTs} + \mathrm{BH'ClO_4}$ where HTs represents *p*-toluenesulfonic acid. The equilibrium constant for the reaction as written is $K_{\mathrm{BHClO_4}}K_{\mathrm{B'HTs}}/K_{\mathrm{HTs}}K_{\mathrm{B'HClO_4}}$ where $K_{\mathrm{HClO_4}} = 1.35 \times 10^{-5}$ and $K_{\mathrm{HTs}} = 3.8 \times 10^{-9}$.[2c,4] On the basis of unpublished data we estimate that $K_{\mathrm{B'HTs}}/K_{\mathrm{B'HClO_4}}$ is of the order of 0.1. Using this value the equilibrium constant for the above metathesis reaction is approximately 400. Even though we may allow for considerable error in the estimate of $K_{\mathrm{B'HTs}}/K_{\mathrm{B'HClO_4}}$ it is evident that little free perchloric acid can be present during the titration with perchloric acid of 0.05 *M* urea in a 0.2 *M* solution of trimethylammonium *p*-toluenesulfonate (B'HTs). The perchloric acid reacts almost quantitatively with B'HTs with formation of *p*-toluenesulfonic acid and $\mathrm{B'HClO_4}$. Thus, the titration corresponds to that of urea with *p*-toluenesulfonic acid in the presence of a large excess of a sulfonate. This titration is strictly comparable to that of the base with perchloric acid in the presence of an excess of a perchlorate (eq. 4i) and we may write

$$[\mathrm{H}^+] = \frac{K_{\mathrm{s}}K_{\mathrm{BHTs}}C_{\mathrm{BHTs}}}{K_{\mathrm{B}}C_{\mathrm{B}}\sqrt{K_{\mathrm{B'HTs}}C_{\mathrm{B'HTs}}}} \tag{4k}$$

From a comparison of eq. 4i and 4k it follows that the plots of *p*H against $\log(1 - X)/X$ in 0.2 *M* $\mathrm{B'HClO_4}$ and in 0.2 *M* B'HTs will be identical only if $\sqrt{K_{\mathrm{B'HTs}}/K_{\mathrm{B'HClO_4}}} = K_{\mathrm{BHTs}}/K_{\mathrm{BHClO_4}}$. The difference notes for urea, 0.5 unit, agrees well with the value of 0.5 unit calculated using eq. 4i and 4k with the assumption that urea perchlorate is ten times more dissociated than urea *p*-toluenesulfonate.

[H⁺] in a Solution of Pure Salt.—The equivalence point in the titration of a base with an acid

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(4) The value of K_{HTs} used here differs from the value reported previously[2c] by about 10%. In a private communication Prof. L. P. Hammett pointed out that the method of purification used by us for *p*-HTs would probably yield the monohydrate of the acid. Analysis by Karl Fischer titration of a sample of the *p*-HTs used earlier showed that it corresponded to the monohydrate, and accordingly we have recalculated K_{HTs} by correcting the concentration of *p*-HTs for the presence of water. *p*-HTs is too weak an acid to react significantly with small amounts of water in acetic acid medium.

corresponds to a solution of the pure salt, and the hydrogen ion concentration of such a solution can be calculated from eq. 4f. For most salts K_BC_B is negligibly small as compared to $K_{BHClO_4}C_{BHClO_4}$ and we may write eq. 5a instead of 4f. If we neglect dissociation of all species in solution

$$[H^+] = \sqrt{\frac{K_s{}^2K_{BHClO_4}C_{BHClO_4}}{K_B{}^2C_B{}^2}} \tag{5a}$$

$C_B = C_{HBIO_4}$ in a pure salt solution. From the definition of the formation constant of the salt, $C_B{}^2 = C_{BHClO_4}/K_f^{BHClO_4} = C_{BHClO_4}K_sK_{BHClO_4}/K_{HClO_4}K_B$. On substituting this expression into eq. 5a, eq. 5b is obtained for the hydrogen ion concentration in a solution of a pure perchlorate.

$$[H^+] = \sqrt{K_sK_{HClO_4}/K_B} \tag{5b}$$

This expression is of the same form as holds for the salt of a weak acid and weak base in water. It allows the calculation of the hydrogen ion concentration of a pure salt solution in acetic acid and predicts that it is independent of the concentration of the salt. Experimental data presented later in this paper are quantitatively in agreement with this relationship. It is of great practical significance since it shows that the equivalence *p*H or equivalence potential is independent of concentration of the titration system and that titration to the equivalence potential should be much more convenient than the conventional method of potentiometric end-point determination. As a matter of fact, titration to the equivalence potential should give more accurate results than the conventional method especially at higher dilutions or when the base is very weak.

$[H^+]$ in Mixtures of Salt with Excess Acid.—After the equivalence point an expression for hydrogen ion concentration involving C_{CHIO_4} and C_{BHClO_4} is the most convenient for calculation purposes. Since $C_B = C_{BHClO_4}/C_{HClO_4}K_f^{BHClO_4} = K_sK_{BHClO_4}C_{BHClO_4}/K_{HClO_4}K_BC_{HClO_4}$ eq. 6a can be obtained from eq. 4e.

$$[H^+] = \sqrt{\frac{K_s + K_{HClO_4}C_{HClO_4}}{1 + \frac{K_{BHClO_4}C_{BHClO_4}}{K_{HClO_4}C_{HClO_4}}}} \tag{6a}$$

Equation 6a holds at all points in the titration, but when enough excess of perchloric acid is present, $K_{HBIO_4}C_{HClO_4}$ is usually greater than K_s, and the simpler expression, eq. 6b, is satisfactory. A similar expression has been verified previously[2c] for hydrochloric acid and some of its salts. Of course, when K_{BHClO_4} is not much smaller than K_{HClO_4}, then eq. 6b simplifies to

$$[H^+] = K_{HClO_4}C_{HClO_4}/\sqrt{K_{HClO_4}C_{HClO_4} + K_{BHClO_4}C_{BHClO_4}} \tag{6b}$$

$$[H^+] = \frac{K_{HClO_4}C_{HClO_4}}{\sqrt{K_{BHClO_4}C_{BHClO_4}}} \tag{6c}$$

in the immediate vicinity of the equivalence point.

Titrations with Indicators

Indicator Color in Mixtures of a Weak Base and its Perchlorate.—We consider the color of an indicator base, I, during the titration of a base with perchloric acid in acetic acid medium. For our purposes the dissociation of $IHClO_4$ into IH^+ and $ClO_4{}^-$ need not be considered because the large excess of $BHClO_4$ suppresses the dissociation of $IHClO_4$ completely. The color of the indicator is then given by the ratio $[IHClO_4]/[I]$ where $[IHClO_4]$ denotes the concentration of the acid and $[I]$ that of the basic form. It has been made clear in a previous paper[2a] that the color of an indicator in acetic acid is not determined by the *p*H of the solution but by the concentration of the free perchloric acid, $C_{HClO_4} = [HClO_4] + [H^+ClO_4{}^-]$, the sum of molecular and ion pair concentrations (eq. 7a), and the formation (ionization) constant of the indicator perchlorate.[5]

$$\frac{[IHClO_4]}{[I]} = K_f^{IHClO_4}C_{HClO_4} \tag{7a}$$

During the course of the titration of B with perchloric acid, C_{HClO_4} is given by eq. 7b

$$C_{HClO_4} = C_{BHClO_4}/C_BK_f^{BHClO_4} \tag{7b}$$

and the color of the indicator by eq. 7c

$$\frac{[IHClO_4]}{[I]} = \frac{K_f^{IHClO_4}C_{BHClO_4}}{K_f^{BHClO_4}C_B} \tag{7c}$$

Equation 7c illustrates the dependence of the color of an indicator in a mixture of a base and its perchlorate on the ratio of concentrations of the salt and base and not on the concentration of each species individually. Thus, as long as we use approximate equations (neglect solvolysis) it is found that the color of an indicator base in a mixture of a base and its perchlorate is not affected by dilution. In a previous section we have seen that upon tenfold dilution of the kind of mixture under consideration the *p*H decreases by 0.5. This is another striking example of the previously noted fact that there is no direct relation between *p*H and the color of an indicator in acetic acid. On the other hand, in a mixture of a perchlorate and perchloric acid the ratio of acid to basic form of an indicator base decreases to one-tenth upon ten-fold dilution while the *p*H increases by 0.5 unit.

For those concerned with acid–base catalysis it is of interest to consider that in a mixture of a base and its perchlorate the concentration of free perchloric acid remains unchanged with dilution (as

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(5) Rigorously, eq. 7a should be written $C_{IHClO_4}/C_I = K_f^{IHClO_4}\cdot C_{HClO_4}$, but as long as the indicator base is weak, and the indicator salt completely ionized, $C_I = [I]$ and $C_{IHClO_4} = [IHClO_4]$. These conditions are met by *p*-naphtholbenzein, a commonly used indicator in acetic acid medium, and there is no experimental evidence to indicate that the above conditions do not hold equally well for other indicator bases used in titrations in acetic acid. In a previous paper[2a] the constant $K_i^{IHClO_4} = [IHClO_4]/[I][HClO_4]$ was defined, where $[HClO_4]$ represents the concentration of un-ionized perchloric acid in solution. The ratio $K_i^{IHClO_4}/K_f^{IHClO_4} = 1 + K_i^{HClO_4}$, where $K_i^{HClO_4} = [H^+ClO_4{}^-]/[HClO_4]$, $[H^+ClO_4{}^-]$ representing the concentration of the ionized form of perchloric acid in solution, *i.e.*, $C_{HClO_4} = [H^+ClO_4^-] + [HClO_4]$. The distinction between $K_i^{IHClO_4}$ and $K_f^{IHClO_4}$ is of little consequence for a weak acid such as hydrochloric or *p*-toluenesulfonic acid for which K_i^{HX} is much less than one, but is significant for a strong acid such as perchloric acid. Professor Ernest Grunwald of the University of Florida kindly brought to our attention that we did not distinguish between $[HClO_4]$ and C_{HClO_4} when we applied eq. 9 of ref. 2a to perchloric and hydrobromic acid solutions. His criticism is valid and the conclusions drawn from eq. 16d, 17, 17a and 17b of ref. 2a are incorrect. It is not possible to obtain $K_i^{HClO_4}$ from our data since the correct form of eq. 17 is $K_i^{IHX}K_d^{IHX}/K_{i.s.}^{HClO_4}K_{HX} = 1$ (not $1 + K_i^{HClO_4}$).

long as the approximate equations hold), while in a mixture of perchloric acid and a base perchlorate the concentration of free base is unaffected by dilution.

Returning to the color change of an indicator during the titration of a base with perchloric acid we write eq. 7d instead of 7c

$$\frac{[\mathrm{IHClO_4}]}{[\mathrm{I}]} = \frac{K_\mathrm{f}^{\mathrm{IHClO_4}}}{K_\mathrm{f}^{\mathrm{BHClO_4}}} \frac{X}{1 - X} \qquad (7d)$$

An expression of the same form is found in aqueous medium for the titration of a weak base. This expression is of great practical value, both in water and in glacial acetic acid, where the end-point is not found visually, but graphically in a spectrophotometric titration using an indicator with a $K_\mathrm{f}^{\mathrm{IHClO_4}}$ of the same order of magnitude as $K_\mathrm{f}^{\mathrm{BHClT_4}}$.[6]

In connection with the above it is noted that the experimental value of the so-called acidity function H_0 in a mixture of a weak base and its salt is proportional to the negative logarithm of the concentration of free acid but there is no simple relation between H_0 and the hydrogen ion concentration. According to eq. 7d a plot of H_0 *versus* a log $(1 - X)/X$ should give a straight line with a slope of unity. Hall and Meyer[7] determined H_0 in mixtures of sulfuric acid with urea and with antipyrine and found straight line plots with slopes of 1.05 and 0.83, respectively. No correction was made for the solvolysis of the salt.

Indicator Color in a Solution of a Pure Salt.—In a pure solution of a salt, $\mathrm{BHClO_4}$, corresponding to the equivalence point in the titration of B with $\mathrm{HClO_4}$, $C_\mathrm{B} = C_{\mathrm{HClO_4}}$ and $C_{\mathrm{HClO_4}} = \sqrt{C_{\mathrm{BHClO_4}}/ \cdot K_\mathrm{f}^{\mathrm{BHClO_4}}}$. Combining this expression with eq. 7a, eq. 7e is obtained.

$$\frac{[\mathrm{IHClO_4}]}{[\mathrm{I}]} = \frac{K_\mathrm{f}^{\mathrm{IHClO_4}}}{\sqrt{K_\mathrm{f}^{\mathrm{BHClO_4}}}} \sqrt{C_{\mathrm{BHClO_4}}} \qquad (7e)$$

This predicts that the ratio of acid color to base color is proportional to the square root of the concentration of salt present. For example, if for a given indicator $[\mathrm{IHClO_4}]/[\mathrm{I}] = 1$ in a 0.1 *M* salt solution, the ratio decreases to 0.1 in 0.001 *M* salt solution. Thus the color of an indicator at the equivalence point varies with the concentration of the base titrated, while we have seen that the *p*H (potential of electrode) is independent of the salt concentration.

Experimental

The main purpose of the present experimental work was to study the order of agreement between calculated and experimental values of *p*H and of ratios of acid to base color of an indicator in a variety of solutions. In practical analytical work acetic acid with varying small amounts of water is used, which may greatly affect the *p*H and the color of an indicator. The acetic acid used in most of the present work had a water content of 0.01% and in some experiments even this trace of water was removed. In a subsequent paper the effect of water upon potentiometric titrations and titrations with indicators will be calculated and compared with experimentally observed effects.

Methods and Reagents.—Potentiometric measurements with the chloranil electrode as *p*H electrode and the modified calomel electrode as reference electrode were performed as previously described.[2c] In some solutions it required at least 24 hours before the chloranil electrode had attained its equilibrium potential. Measurements involving the glass-calomel electrode system were performed using a Beckman Model H-2 *p*H meter and the electrodes supplied with this instrument. The glass electrode measurements were carried out for orientation purposes and commercial C.P. glacial acetic acid was used without further purification. These experimental data were not used for any exact calculations. The spectrophotometric technique and all reagents used were described in previous papers.[2a,b,5c]

***p*H of Acetic Acid.**—Considering the high resistance and the poor buffer capacity of the pure solvents the measurements were not as reproducible as those obtained in well-buffered or more conducting solutions. Using three separate batches of solvent the following values of the e.m.f. were measured: 0.474, 0.464, and 0.480 volt. The *p*H may be calculated from eq. 8 in which 0.9095 represents the standard potential of the chloranil electrode with respect to the acetic acid

$$p\mathrm{H} = (0.9095 - E)/0.0591 \qquad (8)$$

calomel electrode.[2c] The average value $p\mathrm{H} = 7.4 \pm 0.1$ is in gratifying agreement with the value of 7.2 calculated from the *pK* of acetic acid, 14.45.[2c] In fact, this close agreement is probably fortuitous.

Neutralization Curve of Urea in Anhydrous Acetic Acid.—Fifteen ml. of 0.0547 *M* urea was titrated with 0.9643 *M* perchloric acid using a chloranil indicator electrode. The reference electrode was a platinum wire sealed into the buret which delivered the perchloric acid previously saturated with chloranil and tetrachlorohydroquinone. From the neutralization curve, K_B, of urea and eq. 3b and 4f the dissociation constant of urea perchlorate is found to be approximately 10^{-5}. This is 10^5 times larger than K_B of urea and eq. 4h should hold. A plot of e.m.f. *versus* log $\sqrt{X}/(1 - X)$ is shown in Fig. 1 and the observed slope is 0.064 v. as compared to the predicted value of 0.0591 v. at 25°.

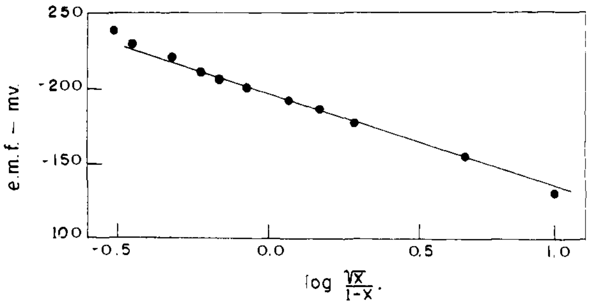

Fig. 1.—Test of eq. 4h. The titration of 0.0547 *M* urea with 0.964 *M* perchloric acid.

***p*H of a Salt Solution.**—Equation 5b states that the *p*H of a solution of a pure perchlorate should be independent of the concentration of the salt. It can be extended to any salt since none of the assumptions involved in the derivation are restricted to perchloric acid. Preliminary experiments were performed in commercial glacial acetic acid containing 0.2% water using the glass–calomel electrode system, and the results obtained with ten salts are shown in Table I. The data verify the independence of *p*H upon concentration, but cannot be interpreted quantitatively because of the uncertainties introduced by the use of the glass electrode and water in the commercial glacial acetic acid. For this reason e.m.f. but not *p*H values are reported in Table I. In Table II the results with the chloranil–calomel electrode cell are given for four salts in acetic acid containing 0.01% water. The data in the column headed $p\mathrm{H}_{\mathrm{exp}}$ were calculated by averaging the e.m.f. data of the preceding column and using this average e.m.f. in eq. 8. The data in the column headed $p\mathrm{H}_{\mathrm{calcd}}$ were calculated from eq. 5b using values of the dissociation constant reported previously.[2c] The *p*H values found are practically independent of dilution in the concentration range used and, realizing the poor

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buffer capacity of the solutions, no serious discrepancies are apparent between observed and calculated *p*H values.

Table I

Effect of Dilution upon the Apparent *p*H of Some Salt Solutions in Commercial Glacial Acetic Acid

		E.m.f. (v.) in	
Salt	Satd. soln.	1/10 satd. soln.	1/100 satd. soln.
$NaClO_4$	0.599	0.599	0.599
KCl	.538	.536	.535
NaCl	.540	.541	.531
LiCl[a]	.569	.560	.557
KBr	.548	.560	.550
NaBr	.568	.570	.563
LiBr[a]	.590	.600	.590
KNO_3	.472	.478	.480
$NaNO_3$	.487	.488	.490
$LiNO_3$	.510	.509	.507

[a] Initial molarity = 1.0.

Table II

*p*H of Pure Salt Solutions in Acetic Acid at 25°

Salt	Molar concn.	E.m.f., v.	pH_{exp}	pH_{calcd}
Sodium perchlorate	0.0582	0.5370		
	.0923	.5405		
	.1300	.5390		
	.213	.5380	6.27	6.32
Diethylanilinium perchlorate	0.0201	0.5310		
	.0409	.5300		
	.0559	.5290		
	.0918	.5325	6.41	6.77
2,5-Dichloroanilinium perchlorate	0.0068	0.6050		
	.0125	.6055		
	.0253	.6075		
	.0519	.6055	5.13	4.94
Sodium *p*-toluenesulfonate	0.00802	0.4210		
	.0192	.4250		
	.0481	.4240		
	.054	.4210	8.07	8.10

_p_H Near the Equivalence Point in the Titration of Sodium Acetate with Perchloric Acid.—The shapes of the neutralization curves with perchloric acid of sodium acetate and diethylaniline were obtained with the chloranil electrode. The data agreed with those of Hall and Werner[10] and therefore are not reported here. As stated in the theoretical section the shapes of these curves were found to be identical with those constructed from calculated data using eq. 4f.

No data are found in the literature of the change of *p*H in anhydrous acetic acid just before and after the equivalence point. Such data are not only of theoretical but are also of practical importance as they provide quantitative information on the magnitude of the break in potential at the end-point. In Table III experimental values of the difference in e.m.f. between 0.1 *M* sodium perchlorate solution and the same solution with slight amounts of free perchloric acid or sodium acetate are compared with the calculated figures. Increments of 0.500 *M* sodium acetate or 0.964 *M* perchloric acid were added to 20.00 ml. of 0.100 *M* sodium perchlorate. The complete absence of water was assured by adding 0.05 mole of acetic anhydride per liter of 0.1 *M* sodium perchlorate solution and heating for 12 hours at 105° in a sealed flask. The concentration of acetic anhydride was in fourfold excess based on the water content of the untreated acid. In order to minimize liquid junction potentials and errors which might arise from contamination of the solution from the standard half-cell, an H type cell was used which consisted of two compartments joined by a ten-cm. fine sintered glass disc. Both compartments were filled with 0.1 *M* sodium perchlorate previously saturated with chloranil and tetrachlorohydroquinone and increments of either perchloric acid or sodium acetate solution were added from microburet to one of the compartments. The data obtained with the cell.

Table III

Change of E.m.f. between 0.8% before and 0.8% after the Equivalence Point in Titration of Sodium Acetate with Perchloric Acid

Concentration of sodium perchlorate = 0.100 *M*

	E.m.f. in mv.	
$HClO_4$, $M \times 10^4$	Obsd.[a]	Calcd.
8.00	97.5, 96.0	94.1
4.00	80.0	76.6
2.00	59.5	59.1
1.00	41.5, 44.0	42.1
NaAc, $M \times 10^4$		
1.00	−42.0, −44.0	−41.6
2.00	−62.0	−58.6
4.00	−79.5, −78.5	−76.2
8.00	−91.5	−94.0

[a] All data are rounded to the nearest 0.5 mv., and represent individual experiments.

$$\mathrm{Pt}\left|\begin{array}{l}\mathrm{C_6Cl_4O_2(satd.)}\\ \mathrm{C_6Cl_4(OH)_2(satd.)}\end{array}\right. \qquad \mathrm{NaClO_4}\ (0.1\ M)$$

$$\left|\begin{array}{l}\mathrm{HClO_4\ (or\ NaAc)}\ (C,\ M),\ \mathrm{C_6Cl_4O_2(satd.)}\\ \mathrm{NaClO_4}(0.1\ M)\quad \mathrm{C_6Cl_4(OH)_2(satd.)}\end{array}\right|\mathrm{Pt}$$

are given in Table III. The calculated e.m.f. values reported in the last column of this table were obtained by using either eq. 4e or 6a and the following constants: $pK_{NaAc} = 6.68$, $pK_{HClO_4} = 4.87$, $pK_{NaClO_4} = 5.48$ and $pK_s = 14.45$.[2c] In these equations C_{NaAc}, C_{HClO_4} and C_{NaClO_4} represent the actual equilibrium concentrations of these species in solution. Calculations were made by successive approximations by initially neglecting dissociation of the various species, but taking into account solvolysis, getting an estimate of the various ionic concentrations and correcting the stoichiometric concentrations appropriately to get an estimate of these equilibrium concentrations. This process was repeated until the hydrogen ion concentration remained constant within 1%. The agreement between experimental and calculated values in Table III is excellent.

It is evident from Table III that the titration of 0.1 *M* sodium acetate to the equivalence potential easily can be made with an accuracy of 0.02% if the end-point potential does not differ more than 10 mv. from the equivalence potential.

Color of an Indicator Base in a Salt Solution at and near the Equivalence Point.—In order that as stringent a test as possible be applied to examine the equations giving the dependence of the color of an indicator base upon the composition of the solution the ratio of acid to basic form of *p*-naphtholbenzein (PNB) was determined spectrophotometrically in the very poorly buffered solutions of diethylanilinium and sodium perchlorate and in the latter solution with traces of sodium acetate. Both these salt solutions are extremely slightly solvolyzed, the logarithm of the formation constant, $K_f^{BHClO_4}$, as calculated using eq. 4c and the constants reported in a previous paper[2c] having the value of 8.38 and 9.58 for sodium and diethylanilinium perchlorate, respectively. These solutions are extremely sensitive to minute traces of acids or bases (especially water) since they are virtually completely unbuffered. The experimental problem is comparable to that of determining the *p*H of a solution of sodium chloride or ammonium chloride with indicators in aqueous solution. For these reasons the over-all reproducibility of an experiment is considerably less than the spectrophotometric limit of approximately 2% in determining ratio $R = [IHClO_4]/[I]$ for *p*-naphtholbenzein. For example, in a 0.108 *M* solution of sodium perchlorate in acetic acid containing 0.01% water, values obtained for *R* in three separate experiments were 1.77, 1.34 and 2.35 with an average value of *R* of 1.8 ± 0.3. However, this uncertainty of 20% in the mean value of *R* is not unreasonable in view of the extreme sensitivity of the system to traces of impurities (including water).

In our discussion of the dependence of *R* upon salt and base concentration the simplifying assumption was made that the amount of perchloric acid reacting with the indicator is negligibly small. In the poorly buffered solutions under consideration this is not precisely true and the amount of perchloric acid reacting with the indicator must be taken into account. Defining p according to eq. 9a and b as the molarity of the base added to the pure salt solution, eq. 9b follows.

$$p = C_{\mathrm{BHClO_4}} + C_{\mathrm{B}} = C_{\mathrm{B}}\,(C_{\mathrm{BHClO_4}}/C_{\mathrm{B}} + 1) \quad (9a)$$

$$C_{\mathrm{B}} = b + C_{\mathrm{HClO_4}} + [\mathrm{IHClO_4}] \quad (9b)$$

Eliminating C_{B} by combining eq. 9a and 9b and substituting into the result $C_{\mathrm{HClO_4}} = R/K_{\mathrm{f}}^{\mathrm{IHClO_4}}$ and $C_{\mathrm{BHClO_4}}/C_{\mathrm{B}}$ as obtained from eq. 7c yields eq. 9c. Since $[\mathrm{IHClO_4}] = (C_{\mathrm{I}})_{\mathrm{t}}R/(R + 1)$

$$p = \left[\frac{K_{\mathrm{f}}^{\mathrm{BHClO_4}}}{K_{\mathrm{f}}^{\mathrm{IHClO_4}}}R + 1\right]\left[b + \frac{R}{K_{\mathrm{f}}^{\mathrm{IHClO_4}}} + [\mathrm{IHClO_4}]\right] \quad (9c)$$

the quadratic expression is R, eq. 9d results. In the immediate vicinity of the equivalence point $K_{\mathrm{f}}^{\mathrm{BHClO_4}}/K_{\mathrm{f}}^{\mathrm{IHClO_4}}$ R is much larger than one, allowing eq. 9d to be simplified to eq. 9e which becomes eq. 9f in a pure salt solution

$$p = \left[\frac{K_{\mathrm{f}}^{\mathrm{BHClO_4}}}{K_{\mathrm{f}}^{\mathrm{IHClO_4}}}R + 1\right]\left[b + \frac{R}{K_{\mathrm{f}}^{\mathrm{IHClO_4}}} + \frac{(C_{\mathrm{I}})_{\mathrm{t}}\,R}{R + 1}\right] \quad (9d)$$

$$p = R^2\,\frac{K_{\mathrm{f}}^{\mathrm{BHClO_4}}}{K_{\mathrm{f}}^{\mathrm{IHClO_4}}}\left[\frac{b}{R} + \frac{1}{K_{\mathrm{f}}^{\mathrm{IHClO_4}}} + \frac{(C_{\mathrm{I}})_{\mathrm{t}}}{R + 1}\right] \quad (9e)$$

$$p = R^2\,\frac{K_{\mathrm{f}}^{\mathrm{BHClO_4}}}{K_{\mathrm{f}}^{\mathrm{IHClO_4}}}\left[\frac{1}{K_{\mathrm{f}}^{\mathrm{IHClO_4}}} + \frac{(C_{\mathrm{I}})_{\mathrm{t}}}{R + 1}\right] \quad (9f)$$

The last result is identical to eq. 7e when $1/K_{\mathrm{f}}^{\mathrm{IHClO_4}} \gg (C_{\mathrm{I}})_{\mathrm{t}}/(R + 1)$.

The experimental results obtained using 3.78×10^{-6} M PNB with sodium perchlorate (0.013 to 0.11 M) and diethylanilinium perchlorate (0.023 to 0.18 M) in the absence of free base are given in Table IV. The calculated values of R listed in this table were obtained using eq. 9f, $\log K_{\mathrm{f}}^{\mathrm{IHClO_4}} = 5.00$,[2a] $\log K_{\mathrm{f}}^{\mathrm{NaClO_4}} = 8.38$ and $\log K_{\mathrm{f}}^{\mathrm{BHClO_4}} = 9.78$ where B represents diethylaniline. The value 9.78 was used for the logarithm of the formation constant (K_{f}) of diethylanilinium perchlorate instead of 9.58 as calculated with eq. 4c because it gave better agreement with experiment. This procedure is justified since the uncertainty in the calculated value, 9.58, is sufficiently large to include the value 9.78. The experimental results agree satisfactorily with the calculated values.

TABLE IV

RATIO OF ACID TO BASE FORMS OF p-NAPHTHOLBENZEIN IN SOLUTIONS OF DIETHYLANILINIUM AND SODIUM PERCHLORATE

Cation	Perchlorate, M	Acetate, $M \times 10^5$	$[\mathrm{IHClO_4}]/[\mathrm{I}]$ Obsd.	Calcd.
Sodium	0.0132	0.00	0.46	0.67
	.0272	.00	.71	.98
	.0537	.00	1.1	1.4
	.108	.00	1.8[a]	2.0
	.108	2.20	1.3	1.2
	.108	4.40	0.94	0.83
	.108	8.80	.60	.48
	.108	17.6	.35	.25
	.108	34.9	.19	.13
Diethylanilinium	0.0226	0.00	0.15	0.17
	.0444	.00	.23	.24
	.0902	.00	.39	.34
	.173	.00	.61	.48

[a] Average of 3 experiments.

The effect of sodium acetate (2.2 to 34.9 × 10^{-5} M) on 0.108 M sodium perchlorate solution is also shown in Table IV. The calculated values of R were obtained using eq. 9e and the agreement between experiment and predicted values is satisfactory. The data in Table IV indicate that in the titration of 0.1 M sodium acetate with perchloric acid (no volume change) the ratio of the acid to basic form of PNB changes from 0.5 at 0.1% before to 1.8 at the equivalence point. This is a reasonably sharp color change, but of several orders of magnitude smaller than is observed in the titration of a strong 0.1 M base with a strong acid in water.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE REFINING TECHNICAL AND RESEARCH DIVISIONS, HUMBLE OIL AND REFINING COMPANY]

Polarography of Metallic Monolayers

BY M. M. NICHOLSON

RECEIVED AUGUST 6, 1956

The current due to electrolytic dissolution of a thin film in a linear voltage scanning process depends on the changing activity of the solid phase. Starting with Fick's second law of diffusion and an unabridged form of the Nernst equation, a system is derived for calculating the polarographic dissolution curve of a fractional metallic monolayer. Comparison is made with the behavior of a bulk metal deposit. Agreement with experimental data is good for silver, fair for lead and poor for copper, on a platinum electrode. The principles developed here should be useful in analytical applications of film polarography and in the study of electrodeposition phenomena.

The electrochemistry of fractional monolayers has been a subject of interest for many years but is not very well developed. Herzfeld[1] first pointed out that the Nernst equation in its classical form cannot be applied in such cases because it fails to consider variations in the activity of the solid phase. The complexity of surface phenomena which influence electrochemical behavior in the monolayer region is evident in discussions by Haissinsky[2,3] and in a recent review by Rogers.[4] Both of these authors have studied the problem by electrodeposition of radioactive elements from extremely dilute solutions. Although the role of active spots sometimes appears to predominate,[5] it is possible in other instances to interpret results in terms of a relatively uniform deposit, using modifications of the Nernst equation.[6]

The anodic dissolution of a metal film is examined here on the hypothesis of a statistically uniform surface layer, in which the activity is proportional to the fraction of the electrode covered. Experimentally, the dissolution current of an elec-

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