and which would maintain the temperature constant to within 0.1° were found adequate. In the event that equilibrium was not reached before the bath was nearly spent, a fresh bath could be substituted for the depleted one rapidly enough so that the sample tube did not warm.

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Acid–Base Equilibria in Glacial Acetic Acid. V. The Effect of Water on Potentiometric and Indicator End-Points in Acid–Base Titrations in Acetic Acid

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RECEIVED JUNE 14, 1957

The effect of water on acid–base equilibria in acetic acid can be calculated quantitatively for titrations carried out potentiometrically or with indicators. The equations governing the shape of potentiometric titration lines of bases in acetic acid as a function of water concentration have been derived and experimentally verified. These relationships have been used to calculate the change in e.m.f. in the vicinity of, at and after the equivalence point for bases of different concentration and strength. They predict that titration to an equivalence potential, which is independent of concentration of base, will be an accurate procedure. The relationships determining the ratio of acid to basic color of an indicator base over the titration range in water containing acetic acid also have been established and tested and used to predict the color change of *p*-naphtholbenzein (PNB) in a sodium perchlorate solution.

Water is an undesirable contaminant in the titration of bases in acetic acid.[1–6] With increasing water concentration the magnitude of the first derivative in a potentiometric titration of a base and the sharpness of the color change of an indicator in the region of the equivalence point decreases. Furthermore[3] the potentiometric endpoint is found after the equivalence point, and the titration error increases with the water content of the acetic acid. Water is a weak base in acetic acid, and it is possible to calculate quantitatively its effect upon titration curves in acetic acid[7d] and particularly upon the break in potential and the sharpness of the color change of an indicator near the equivalence point, using the various equilibrium constants for acids, bases and salts reported in previous papers.[7a–c]

Water reacts with perchloric acid to form hydronium perchlorate according to equation 1. The equilibrium constant for the reaction as written, $K_f^{H_3OClO_4}$

$$H_2O + HClO_4 \rightleftarrows H_3OClO_4 \qquad (1)$$

is 34.[7b] In order to account quantitatively for the effect of water over the entire region of a titration curve it is necessary to know the over-all dissociation constant of water as a base, K_{H_2O}, and the over-all dissociation constant of hydronium perchlorate, $K_{H_3OClO_4}$. One simple way of determining these constants is to study the change in hydrogen ion concentration of a perchloric acid solution as a function of the water concentration, using a chloranil electrode as the hydrogen ion indicator electrode. Since the acetate ion concentration is negligible in such a solution, we can write

$$[H^+] + [H_3O^+] = [ClO_4^-] \qquad (2a)$$

From the expressions of the various equilibrium constants we find $[ClO_4^-] = K_{HClO_4}C_{HClO_4}/[H^+]$ and $[H_3O^+] = K_{H_2O}C_{H_2O}[H^+]/K_s$. After rearrangement, equation 2a may be written as

$$C_{H_2O} = \frac{K_sK_{HClO_4}}{K_{H_2O}}\frac{C_{HClO_4}}{[H^+]^2} - \frac{K_s}{K_{H_2O}} \qquad (2b)$$

The symbol C refers to the equilibrium concentration of the species indicated by the subscript and $K_s = [H^+][Ac^-]$.[8] From the stoichiometric concentrations of perchloric acid and water added, $(C_{HClO_4})_t$ and $(C_{H_2O})_t$, respectively, and $K_f^{H_3OClO_4}$ it is possible to calculate equilibrium concentrations of water and perchloric acid. Thus, if C_{H_2O} is plotted *versus* $C_{HClO_4}/[H^+]^2$, a straight line of slope $K_sK_{HClO_4}/K_{H_2O}$ and intercept $-K_s/K_{H_2O}$ should result. Such a plot of the experimental results yielded a straight line, and K_{H_2O} was calculated from the intercept using the previously determined value of $K_s = 3.55 \times 10^{-15}$.[7c] $K_{H_3OClO_4}$ could then be calculated from the relationship $K_f^{H_3OClO_4} = K_{HClO_4}K_{H_2O}/K_sK_{H_3OClO_4}$[7a,d] in which the dissociation constant of hydronium perchlorate is the only unknown.

The Effect of Water on *p*H over the Entire Region of an Acid–Base Titration Curve. Solutions of Water and a Pure Base.—The *p*H of a mixture containing water and another base, B, in acetic acid can be calculated by substituting into the electroneutrality rule equation 3a

$$[H^+] + [BH^+] + [H_3O^+] = [Ac^-] \qquad (3a)$$

the expressions $[BH^+] = K_BC_B[H^+]/K_s$, $[H_3O^+] = K_{H_2O}C_{H_2O}[H^+]/K_s$ and $[Ac^-] = K_s/[H^+]$ to yield

$$[H^+]_w = \frac{K_s}{\sqrt{K_s + K_BC_B + K_{H_2O}C_{H_2O}}} \qquad (3b)$$

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[1] J. B. Conant and N. F. Hall, THIS JOURNAL, **49**, 3047 (1927).

[2] (a) J. S. Fritz, *Anal. Chem.*, **22**, 1028 (1950); (b) J. S. Fritz and M. O. Fulda, *ibid.*, **25**, 1837 (1953); (c) J. S. Fritz, *ibid.*, **26**, 1701 (1954).

[3] P. C. Markunas and J. A. Riddick, *ibid.*, **24**, 1837 (1952).

[4] C. W. Pifer and E. G. Wollish, *ibid.*, **24**, 300 (1952).

[5] A. H. Beckett, R. M. Camp and H. W. Martin, *J. Pharm. and Pharmacol.*, **4**, 399 (1952).

[6] A. Anastasi, U. Gallo and L. Novacic, *ibid.*, **7**, 263 (1955).

[7] (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); (d) I. M. Kolthoff and S. Bruckenstein, *ibid.*, **79**, 1 (1957).

[8] The nomenclature used in the present paper is the same as in the preceding papers in this series.

In the present paper we find that $K_{H_2O} = 2.95 \times 10^{-13}$. Thus when K_BC_B is greater than about 10^{-12} and the water concentration is less than about 0.5 *M*, there should be no detectable water effect on the *p*H of the solution of a base.

At concentrations of water greater than 0.5 *M* a decrease in hydrogen ion activity as measured electrometrically has been reported in solutions of bases.[4,5] At such high concentrations of water the properties (dielectric constant) of the solvent change and all equilibrium constants are affected in a complex manner.

Solutions of Water, Base and $BHClO_4$.—In a partially neutralized base solution containing water the rule of electroneutrality is

$$[H^+] + [BH^+] + [H_3O^+] = [Ac^-] + [ClO_4^-] \quad (4a)$$

Solving for the hydrogen ion concentration in terms of C_B, C_{BHClO_4} and C_{H_2O} using the constants K_B, K_{BHClO_4} and K_s, equation 4b is obtained for the hydrogen ion concentration of a mixture of a

$$[H^+]_w = \frac{K_s\sqrt{K_BC_B + K_{BHClO_4}C_{BHClO_4}}}{K_BC_B} \times \sqrt{\frac{K_BC_B}{K_s + K_BC_B + K_{H_2O}C_{H_2O}}} \quad (4b)$$

base and its salt containing an equilibrium concentration of water equal to C_{H_2O}. Denoting $[H^+]_0$, $(C_B)_0$ and $(C_{BHClO_4})_0$ as the equilibrium concentrations of the various species in anhydrous solvent, and $[H^+]_w$, $(C_B)_w$ and $(C_{BHClO_4})_w$ as the equilibrium concentrations of the various species in solvent containing an equilibrium concentration of water, C_{H_2O}, it follows from equation 4b that

$$\frac{[H^+]_w}{[H^+]_0} = \frac{(C_B)_0}{(C_B)_w}\sqrt{\frac{\{K_B(C_B)_w + K_{BHClO_4}(C_{BHClO_4})_w\}\{K_s + K_B(C_B)_0\}}{\{K_B(C_B)_0 + K_{BHClO_4}(C_{BHClO_4})_0\}\{K_s + K_B(C_B)_w + K_{H_2O}C_{H_2O}\}}} \quad (4c)$$

In most practical cases the reaction $BHClO_4 + H_2O \rightleftarrows B + H_3OClO_4$ can be neglected until close to the equivalence point. The larger the value of K_B, the closer the equivalence point can be approached before we must allow for this reaction. Over the region where this approximation holds, $(C_B)_w = (C_B)_0$, $(C_{BHClO_4})_w = (C_{BHClO_4})_0$, and water will have hardly any effect on the *p*H. This has been verified experimentally for sodium acetate–sodium perchlorate mixtures.

When the equivalence point is approached, we must distinguish between the various equilibrium concentrations in anhydrous and water-containing solvent. As a good approximation in this region, in both these solutions, $K_{BHClO_4}C_{BHClO_4}$ is much greater than K_BC_B, K_BC_B is in most practical cases much greater than K_s and $K_{H_2O}C_{H_2O}$, while $(C_{BHClO_4})_w = (C_{BHClO_4})_0$. Thus equation 4c simplifies to

$$\frac{[H^+]_w}{[H^+]_0} = \frac{(C_B)_0}{(C_B)_w} \quad (4d)$$

Neglecting ionic dissociation of the various species in solution, it follows from equations 1 and 4e

$$BHClO_4 \rightleftarrows B + HClO_4 \quad (4e)$$

that

$$(C_B)_w = (C_{HClO_4})_w + C_{H_3OClO_4} + b \quad (4f)$$

where *b* represents the analytical concentration of base. Equation 4f can be written in a more useful form by using $K_f^{H_3OClO_4}$ to obtain an expression for $(C_B)_w$ in terms of $(C_{HClO_4})_w$ and C_{H_2O} as

$$(C_B)_w = (C_{HClO_4})_w\ (1 + K_f^{H_3OClO_4}C_{H_2O}) + b \quad (4g)$$

Combining equation 4g with the expression for $K_f^{BHClO_4}$ yields the quadratic expression

$$(C_B)_w^2 - b(C_B)_w - \frac{(1 + K_f^{H_3OClO_4}C_{H_2O})}{K_f^{BHClO_4}}\ C_{BHClO_4} = 0 \quad (4h)$$

Substituting equation 4h into 4d gives equation 4i which describes the way in which the ratio of hydrogen ion concentrations depends on water content.

$$\frac{[H^+]_w}{[H^+]_0} = \frac{b + \sqrt{b^2 + 4C_{BHClO_4}/K_f^{BHClO_4}}}{b + \sqrt{b^2 + 4(1 + K_f^{H_3OClO_4}C_{H_2O})(C_{BHClO_4}/K_f^{BHClO_4})}} \quad (4i)$$

This expression cannot be simplified further. Qualitatively it shows that the effect of water increases with increasing water content and decreasing values of *b* and of K_B (or $K_f^{BHClO_4}$).

As an illustration some values of the effect of water on the *p*H near the end-point are calculated for three systems which are of practical interest. We assume that the total water content of the solvent is initially 0.1 *M* and that it is unchanged during the titration. Table I lists pH_w and pH_0 values near the end-point in the titration with perchloric acid (no volume change) of 0.1 *M* and 0.01 *M* B with $pK_B = 5.00$ and of 0.1 *M* B with $pK_B = 9.00$. pK_{BHClO_4} is assumed to be 5.00 in all cases. The equations from which the values at and after the equivalence point are calculated are derived in the following section. From the analytical view point it is of interest to note from Table I that the effect of water (0.1 *M*) on the *p*H is negligible up to 99.9% neutralization in the titration of 0.01 *M* or more concentrated solution of a base with a dissociation constant of the order of 10^{-5}. In the titration of a 0.1 *M* solution of very weak base with a *pK* of 9.00 the effect of water is negligible until 95% neutralization. Upon further neutralization the water effect becomes more and more noticeable. However, since the break in potential at the equivalence point is very small, even in the absence of water, it is not necessary to consider the involved equation 4j in any titration of reasonable accuracy in which the end-point is detected by a potential or color change at or near the equivalence point.

Effect of Water on Solutions of Pure $BHClO_4$.—Equation 4i holds generally and is applicable to a pure salt solution where $b = 0$. For such a solution equation 4j can be greatly simplified and we find

$$\frac{[H^+]_w}{[H^+]_0} = \frac{1}{\sqrt{1 + K_f^{H_3OClO_4}C_{H_2O}}} \quad (5a)$$

TABLE I

CALCULATED VALUES OF pH_0 AND pH_w IN VICINITY OF THE EQUIVALENCE POINT IN THE TITRATION OF BASES WITH PERCHLORIC ACID[a]

% Neutral.	$pK_B = 5.00$ 0.1 M Base pH_0	pH_w	$pK_B = 5.00$ 0.01 M Base pH_0	pH_w	$pK_B = 9.00$ 0.1 M Base pH_0	pH_w
90	10.45	10.45	9.94	9.94	6.48	6.48
99	9.45	9.45	8.94	8.94	5.54	5.68
99.9	8.45	8.46	7.95	7.99	5.20	5.49
100	7.16	7.48	7.16	7.48	5.16	5.48
100.1	5.87	6.51	6.38	6.98	5.12	5.47
101	4.88	5.52	5.38	6.03	4.79	5.30
110	3.90	4.54	4.41	5.05	3.90	4.54

[a] These data were calculated, allowing for dissociation of the various species into ions. $pK_{HClO_4} = 4.87$; $pK_{BHClO_4} = 5.00$; $pK_s = 14.45$. Constant volume was assumed. $(C_{H_2O})_t = 0.1\ M$.

It is of interest to note that the dissociation constants of the base, acid and $BHClO_4$ do not enter into equation 5a. The reason is clear, when we consider the expressions for the hydrogen ion concentration in the absence[7c] (equation 5b), and in the presence of water (equation 5c).

From equation 5c it follows that the effect of water on the pH of a salt is

$$[H^+]_0 = \sqrt{K_{HClO_4}K_s/K_B} \qquad (5b)$$

$$[H^+]_w = \sqrt{\frac{K_{HClO_4}/K_s}{K_B(1 + K_f^{H_3OClO_4}C_{H_2O})}} \qquad (5c)$$

independent of the salt concentration. This conclusion is also of practical importance in the potentiometric titration of bases with perchloric acid to the equivalence potential. This potential is independent of the concentration of the salt at the equivalence point both in the absence and presence of water. When using this method of end-point detection it is not even necessary to determine the exact water content of the solvent, if some pure $BHClO_4$ is available. The potential of the indicator electrode in a solution of $BHClO_4$ gives the equivalence potential. When the potential in a solution of $BHClO_4$ is known in pure acetic acid, the water content of the solvent can be calculated roughly from equation 5a. Such a simple determination gives at least the order of magnitude of the water content and allows the conclusion whether the solvent is suitable for a given titration. Some calculated values of pH_w and pH_0 are given in Table I.

Effect of Water in Solutions of $BHClO_4$ and $HClO_4$.—The rule of electroneutrality for a solution of a mixture of water, perchloric acid and a perchlorate can be written

$$[H^+] + [BH^+] + [H_3O^+] = [ClO_4^-]$$

neglecting acetate ion. Using the relationships $[BH^+] = K_{BHClO_4}C_{BHClO_4}/[ClO_4^-]$, $[H_2O^+] = K_{H_3OClO_4}C_{H_3OClO_4}/[ClO_4^-]$ and $[ClO_4^-] = K_{HClO_4}\cdot C_{HClO_4}/[H^+]$, the expression obtained for the hydrogen ion concentration for such a mixture containing an equilibrium concentration of water, C_{H_2O}, is

$$[H^+]_w = \frac{K_{HClO_4}C_{HClO_4}}{\sqrt{K_{HClO_4}C_{HClO_4} + K_{H_3OClO_4}C_{H_3ClO_4} + K_{BHClO_4}C_{BHClO_4}}} \qquad (6b)$$

Since $K_f^{H_3OClO_4} = K_{HClO_4}K_{H_2O}/K_{H_3OClO_4}K_s = [H_3OClO_4]/[H_2O][HClO_4]$, equation 6b can be written as

$$[H^+]_w = \frac{K_{HClO_4}C_{HClO_4}}{\sqrt{K_{HClO_4}C_{HClO_4}\left\{\frac{1 + K_{H_2O}C_{H_2O}}{K_s}\right\} + K_{BHClO_4}C_{BHClO_4}}} \qquad (6c)$$

We find the numerical value of K_{H_2O}/K_s to be 83. Equation 6c cannot be simplified further. Neglecting ionic dissociation and denoting w as the analytical concentration of water and a as the analytical concentration of perchloric acid, we have the relation

$$C_{HClO_4} + C_{H_3OClO_4} = a + C_B$$

Substituting for $C_{H_3OClO_4}$ from $K_f^{H_3OClO_4}$ gives equation 6d as the explicit expression for the equilibrium concentration of perchloric acid.

$$C_{HClO_4} = \frac{a + C_B}{1 + K_f^{H_3OClO_4}C_{H_2O}} \qquad (6d)$$

Depending on the numerical value of $K_f^{BHClO_4}$ there will be a region just past the end-point where the solvolysis of the salt is appreciable, *i.e.*, C_B is of the same order of magnitude as a, and the quadratic expression obtained by combining equation 6d with $K_f^{BHClO_4}$ yields

$$(1 + K_f^{H_3OClO_4}C_{H_2O})C^2_{HClO_4} - aC_{HClO_4} - C_{BHClO_4}/K_f^{BHClO_4} = 0 \qquad (6e)$$

Equation 6e must be used just after the equivalence point to obtain the equilibrium concentration of perchloric acid. For all practical cases, $C_{H_2O} = w$ in this region, and $[H^+]_w$ is obtained using equations 6e and 6c.

As the analytical concentration of perchloric acid is increased, the contribution of the solvolysis of the perchlorate to the equilibrium concentration of perchloric acid becomes more and more negligible and equation 6f may be used to calculate C_{HClO_4}, provided $a << w$.

$$C_{HClO_4} = \frac{a}{1 + wK_f^{H_3OClO_4}} \qquad (6f)$$

As the analytical concentration of perchloric acid approaches that of water, it is necessary to allow for the decrease in the concentration of water by the formation of hydronium perchlorate. Neglecting ionic dissociation, $w = C_{H_2O} + C_{H_3OClO_4}$ and $a = C_{HClO_4} + C_{H_3OClO_4}$. Thus on substitution of these expressions into $K_f^{H_3OClO_4}$, the quadratic expressions for C_{HClO_4} and C_{H_2O}, equations 6g and 6h are obtained.

$$C_{HClO_4} = \frac{(a - w - 1/K_f^{H_3OClO_4}) + \sqrt{(a + w + 1/K_f^{H_3OClO_4})^2 - 4aw}}{2} \qquad (6g)$$

$$C_{H_2O} = \frac{(w - a - 1/K_f^{H_3OClO_4}) + \sqrt{(a + w + 1/K_f^{H_3OClO_4})^2 - 4aw}}{2} \qquad (6h)$$

Under the specified conditions (negligible solvolysis, $a \sim w$) it is necessary to use equations 6g and 6h in conjunction with equation 6c to obtain $[H^+]_w$. Equation 6c was found to represent accurately the effect of water on the *p*H of sodium perchlorate–perchloric acid mixtures.

Quite generally it may be concluded that the effect of water upon the *p*H in the titration of a base with perchloric acid is negligible until close to the end-point, becomes marked at the equivalence point, and becomes very pronounced with an excess of acid (for a few calculated data see Table I). Pifer and Wollish[4] described titration curves of asterol dihydrochloride with perchloric acid in acetic acid containing different concentrations of water. The results are easily accounted for on the basis of derivations in this section.

Effect of Water on the Color of Indicator over the Entire Region of an Acid–Base Titration. Solutions of B **and** $BHClO_4$.—In a previous section it has been shown that water has little or no effect on the concentration of both $BHClO_4$ and B in their mixtures until very close to the equivalence point. Hence a reasonable concentration of water has no effect on the color of an indicator base in such mixtures. Under these conditions equation 7a is obtained directly from the definitions of $K_f^{BHClO_4}$ and $K_f^{IHClO_4}$.

$$\frac{[I]}{[IHClO_4]} = \frac{[I_b]}{[I_a]} = \frac{1}{R} = \frac{K_f^{BHClO_4}C_B}{K_f^{IHClO_4}C_{BHClO_4}} \qquad (7)$$

However, close to and after the equivalence point there is a pronounced effect since the water will compete with the indicator base for the perchloric acid. The effect of water on the color of the indicator can be calculated quantitatively.

Solution of $BHClO_4$ **with Slight Excess of** B.—If a solution of $BHClO_4$ contains water, a small amount of base, B, of analytical concentration b, and an indicator base, I, of analytical concentration, $(C_I)_t$, we find in a manner analogous to equation 4f

$$(C_B)_w = (C_{HClO_4})_w + C_{H_3OClO_4} + [IHClO_4] + b \qquad (8a)$$

Substituting the expressions, $(C_{HClO_4})_w = R/K_f^{IHClO_4}$ where R is the ratio $[I_a]/[I_b]$, $C_{H_3OClO_4} = K_f^{H_3OClO_4}RC_{H_2O}/K_f^{IHClO_4}$ and $[IHClO_4] = (C_I)_tR/(R + 1)$ into equation 8a and introducing C_{BHClO_4} from equation 7 yields equation 8b.

$$C_{BHClO_4} = \frac{K_f^{BHClO_4}}{K_f^{IHClO_4}} R^2 \left[\frac{1}{K_f^{IHClO_4}} + \frac{K_f^{H_3OClO_4}}{K_f^{IHClO_4}} C_{H_2O} + \frac{(C_I)_t}{R + 1} + \frac{b}{R}\right] \qquad (8b)$$

The range in which expression 8b (instead of 7) must be used increases with increasing water content, decreasing dissociation constant of base, and increasing concentration of indicator. As an example, in the titration of 0.1 *M* sodium acetate with perchloric acid, without volume change, using *p*-naphtholbenzein as indicator ($K_f^{IHClO_4} = 10^{-5}$, $(C_I)_t = 10^{-5}$ *M*) in acetic acid containing 0.2 *M* water, the term b/R is 24 times larger than the sum of all the other terms in the brackets of equation 8b at 99.8% titrated. Hence, equation 7 may still be applied. In the titration of a weaker base, deviations from this simple equation are observed earlier in the titration.

Pure Solutions of $BHClO_4$.—Since $b = 0$ in this solution, equation 8c follows directly from 8b.

$$C_{BHClO_4} = \frac{K_f^{BHClO_4}}{K_f^{IHClO_4}} R^2 \left[\frac{1}{K_f^{IHClO_4}} + \frac{K_f^{H_3OClO_4}}{K_f^{IHClO_4}} C_{H_2O} + \frac{(C_I)_t}{R + 1}\right] \qquad (8c)$$

This expression has been verified in tenth molar sodium perchlorate using *p*-naphtholbenzein as indicator. For semi-quantitative purposes we make the approximation that the indicator concentration term in the brackets of equation 8c is negligible with respect to the other terms. We then obtain the simple but *approximate* expression, 8d, for the effect of water on the color of an indicator base at the

$$\frac{R_w}{R_0} = \frac{1}{\sqrt{1 + K_f^{H_3OClO_4}C_{H_2O}}} \qquad (8d)$$

equivalence point. From comparison with equation 5a it is seen that the ratio $[I_a]/[I_b]$ changes in the same way with water concentration as the hydrogen ion concentration does.

Solutions of $BHClO_4$ **and** $HClO_4$.—It is possible to derive an expression for a solution containing a perchlorate and a small amount of perchloric acid, analogous to equation 8b but again the expression is involved. A simpler expression is obtained at perchloric acid concentrations where the solvolysis of perchlorate is negligible, again assuming such low indicator concentration that $[IHClO_4]$ may be neglected. Under these conditions equation 8e follows directly from the definitions

$$\frac{R_w}{R_0} = \frac{1}{1 + K_f^{H_3OClO_4}C_{H_2O}} \qquad (8e)$$

of $K_f^{IHClO_4}$ and $K_f^{H_3OClO_4}$. Equation 8e has been verified in sodium perchlorate–perchloric acid mixtures using α-naphtholphthalein as the indicator.

Equation 8e also represents the way in which water affects the color of an indicator base in a pure solution of perchloric acid. The data of Lemaire and Lucas[9] using 4-chloro-2-nitroaniline and 4-chloro-2-nitro-N-methylaniline, Smith and Elliot[10] using *o*-nitroaniline and our work[7b] with *p*-naphtholbenzein substantiate the application of equation 8e to solutions of pure perchloric acid.

Comparing the results obtained for R_w/R_0 with $[H^+]_w/[H^+]_0$ over the entire titration curve it is a fair approximation to say that both quantities are affected in the same manner by the presence of water. This conclusion could also have been reached by assuming that the perchlorate ion concentration changes negligibly on the addition of water. Under these conditions the hydrogen ion concentration is proportional to the equilibrium concentration of perchloric acid, which is in turn proportional to R. Thus, the removal of perchloric acid by reaction with water produces proportional changes in $[H^+]$ and R.

As an illustration Table II gives a few calculated data of the effect of water upon the sharpness of the color change of an indicator in the titration

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(9) H. Lemaire and H. J. Lucas, THIS JOURNAL, **73**, 5198 (1951).

(10) T. L. Smith and J. H. Elliot, *ibid.*, **75**, 3566 (1953).

of 0.1 *M* and 0.01 *M* base, $pK_B = 5.00$, with perchloric acid when the analytical concentration of water is 0.1. The numerical values of $K_f^{IHClO_4}$ were chosen such that $R_0 = 1.00$ at the equivalence point and are given in Table II. The concentration of indicator $(C_I)_T$ is assumed to be negligibly small. In order to keep the indicator error small, it is recommended that the smallest concentration of indicator be used which will still permit a distinct observation of the color.

TABLE II

CALCULATED VALUES OF R_0 AND R_w IN THE VICINITY OF THE EQUIVALENCE POINT IN THE TITRATION OF A STRONG BASE, $pK_B = 5.00$, WITH PERCHLORIC ACID

% Neutralized	0.1 *M* Base[a]		0.01 *M* Base[b]	
	R_0	R_w	R_0	R_w
99.9	0.051	0.050	0.16	0.15
100.0	1.00	0.48	1.00	0.48
100.1	19.3	4.5	6.0	1.5

[a] $K_f^{IKClO_4} = 2.0 \times 10^5$. [b] $K_f^{IHClO_4} = 6.3 \times 10^5$.

When titrating weak bases the effect of water in the solvent may become so large that a visual end-point cannot be detected with desirable accuracy. Especially under these conditions the ingenious method for the detection of the end-point recently proposed by Higuchi[11] is of great practical use. In this method the end-point is found graphically by extrapolation of experimental data obtained in mixtures of $BHClO_4$, B and I for which equation 7 holds. If the initial concentration of the base is such as to require *S* ml. of standard perchloric acid to titrate the base and *X* ml. has been added, $S > X$, we can write equation 9a

$$\frac{[I]}{[IHClO_4]} = \frac{[I_b]}{[I_a]} = \frac{K_f^{BHClO_4}}{K_f^{IHClO_4}} \frac{S - X}{X} \tag{9a}$$

which on rearranging yields

$$\frac{1}{X} = \frac{1}{S} + \frac{1}{S} \frac{K_f^{IHClO_4}}{K_f^{BHClO_4}} \frac{[I_b]}{[I_a]} \tag{9b}$$

Thus, a plot of $1/X$ *versus* $[I_b/I_a]$ has an intercept which is the reciprocal of the number of ml. of acid at the equivalence point. An important characteristic of such a plot, not pointed out in the original work, is that it is relatively insensitive to the presence of small amounts of water in the solvent.

Experimental

The preparation of the various reagents with the exception of α-naphtholphthalein and the experimental techniques used have been described in previous papers in this series.[7a–d] An Eastman Kodak Co. sample of α-naphtholphthalein was purified by filtering a suspension in acetone, evaporating the filtrate to dryness and drying the residue *in vacuo* at 60°.

All e.m.f. measurements were made at 25.0° with the chloranil (saturated tetrachloroquinone-saturated tetrachlorohydroquinone) electrode as the hydrogen ion indicator electrode and the modified acetic acid–calomel electrode as reference electrode. The *p*H of the various acetic acid solutions was calculated using the expression $pH = (0.9095 - E)/0.0591$,[7c] where *E* is the e.m.f. of chloranil electrode–calomel electrode cell. The chloranil electrode potential has the same algebraic sign as *E*.

Experimental Results and Discussion

Determination of K_{H_2O} and $K_{H_3OClO_4}$.—The *p*H of a tenth molar perchloric acid solution containing varying concentrations of water was determined and the results are listed in Table III. The anhydrous solution was prepared by adding a slight excess of acetic anhydride to the solution containing 0.043 *M* water and permitting several hours to elapse before measuring the e.m.f. It was found that the apparent *p*H tended to decrease slowly with time even though all the water had been removed. Rapid stirring of the cell contents increased the apparent *p*H to 2.95, but on standing it decreased again. Stirring the solution again raised the *p*H to 2.95. We attribute this effect to an acid-catalyzed reaction between acetic anhydride and tetrachlorohydroquinone to produce an electrochemically inactive product. Stirring the solution resaturates the supernatant liquid with chloranil and re-establishes the equilibrium conditions for the chloranil electrode. A spectrophotometric experiment showed that there is a slow reaction between tetrachlorohydroquinone and acetic anhydride in 0.1 *M* perchloric acid proceeding in at least two successive steps.

TABLE III

EFFECT OF WATER ON THE *p*H OF 0.106 *M* PERCHLORIC ACID

$(C_{H_2O})_t$, *M*	*E*, v.[a]	C_{H_2O},[b] *M*	C_{HClO_4},[b] *M*	pH_{exp}	pH_{calcd}
0.000	0.7350	0.000	0.106	2.95	2.92
.043	.7180	.0121	.0752	3.24	3.16
.155	.6950	.078	.0290	3.63	3.67
.256	.6786	.167	.0152	3.91	3.97

[a] Obtained using the saturated chloranil electrode. [b] Equilibrium concentrations calculated using equations 6g and 6h.

When the data in Table III are plotted according to equation 2b the straight line in Fig. 1 is obtained. Using the value $pK_s = 14.45$, we find from the slope and intercept of this plot, $pK_{HClO_4} = 4.82$ and $pK_{H_2O} = 12.53$. Since $K_f^{H_3OClO_4} = K_{HClO_4}K_{H_2O}/K_sK_{H_3OClO_4}$, we obtain $K_{H_3OClO_4} = 3.3 \times 10^{-5}$, using the known values of the other constants. The value of pK_{HClO_4} obtained in this experiment differs negligibly from our previous value of 4.87[7c] and we shall continue to use the old value in our calculations.

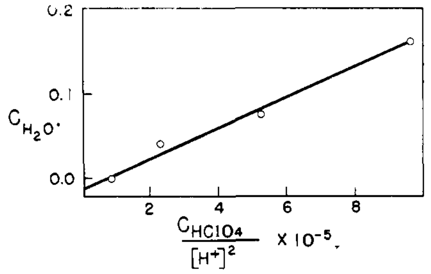

Fig. 1.—Determination of K_{H_2O} according to equation 2b; intercept = −0.012; slope = 1.82×10^{-7}.

The column labeled pH_{exp} in Table III represents the experimental value while the column labeled pH_{calcd} lists the values calculated with the aid of

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[11] T. Higuchi, C. Rehm and C. Barnstein, *Anal. Chem.*, **28**, 1506 (1956).

equation 6b with C_{BHClO_4} set equal to zero. The agreement between the experimental and calculated hydrogen ion concentrations is satisfactory.

In the second paper in this series[7b] a value of $pK_{H_2O} = 10.08$ was derived from a spectrophotometric investigation of solutions of *p,p'*-dimethylaminoazobenzene (DMAAB) in water-containing solvent. Starting with the rule of electroneutrality, $[IH^+] + [H_2O^+] = [Ac^-]$ and substituting into this from K_{H_2O}, $K_i^I = [IH^+Ac^-]/[I]$ and $K_d^I = [IH^+][Ac^-]/[IH^+Ac^-]$, we obtained the expression

$$\frac{[I]}{[IH^+]^2} = \frac{K_{H_2O}C_{H_2O}}{[K_i^IK_d^I]^2}\frac{1}{[I]} + \frac{1}{K_i^IK_d^I} \qquad (10a)$$

A plot of $[I]/[IH^+]^2$ *versus* $1/[I]$ yielded a slope and intercept which permitted the calculation of K_{H_2O} and $K_i^IK_d^I$. We have repeated this experiment several times with different batches of solvent containing varying amounts of water, and found that the numerical value of the intercept remained unchanged, but that the slope of this plot varied. No constant value of K_{H_2O} could be obtained. We attribute the previous erroneous result to the presence of traces of a strong base, probably ammonia, in the solvent used in the older experiments. With a trace of ammonia as the basic impurity, the rule of electroneutrality yields $[IH^+] + [H_3O^+] + [NH_4^+] = [Ac^-]$, and by means similar to that used to derive equation 9a we obtain

$$\frac{[I]}{[IH^+]^2} = \frac{[K_{H_2O}C_{H_2O} + K_{NH_3}C_{NH_3}]}{[K_i^IK_d^I]^2}\frac{1}{[I]} + \frac{1}{K_i^IK_d^I} \qquad (10b)$$

Clearly, the presence of a basic impurity will not alter the intercept, but it will change the slope. Using the electrometric procedures described in the third paper of this series[7c] it was found that $pK_{NH_3} = 6.40$, so that a concentration of ammonia on the order of $1\text{–}2 \times 10^{-6}$ *M* could account for the values of the slopes reported previously. This trace of ammonia is far too small to alter any of the other results and does not change the value we have reported for the over-all dissociation constant of DMAAB.

Effect of Water on the *p*H of Solutions of a Pure Base.—Table IV gives the *p*H in the presence of water in 0.125 *M* sodium acetate solutions in acetic acid. The data of $pH_{calcd.}$ were calculated from equation 3b, using $pK_{NaAc} = 6.68$. As expected water has no significant effect, although there is a distinct trend toward slightly higher *p*H values when the water concentration becomes greater than 0.5 *M*. The latter effect is undoubtedly caused by the change in the nature of the solvent and may result from a different rate of change of the various equilibrium constants with increasing dielectric constant, a change in E^0 of the chloranil electrode, and/or a change in the liquid junction potential.

TABLE IV

EFFECT OF WATER ON THE *p*H OF A SOLUTION OF 0.125 *M* SODIUM ACETATE

Concn. of water, *M*	pH_{exp}	pH_{calcd}
0.010	10.62	10.66
.28	10.63	10.66
.56	10.65	10.66
1.1	10.69	10.66

Effect of Water on the *p*H of a Mixture of B and BHClO₄.—As stated in the discussion of equation 4b the *p*H of a mixture of 0.0760 *M* sodium acetate and 0.0431 *M* sodium perchlorate ($pK_{NaClO_4} = 5.48$) should also be independent of water concentration and be given by the same expression as in the anhydrous solvent. The results in Table V are in agreement with this postulate. Again, the tendency toward higher *p*H values is observed at higher water concentrations.

TABLE V

EFFECT OF WATER ON THE *p*H OF A MIXTURE 0.0760 *M* IN SODIUM ACETATE AND 0.0431 *M* IN NaClO₄

Concn. of water, *M*	pH_{exp}	$pH_{calcd.}$
0.01	10.02	10.05
.28	10.05	10.05
.56	10.11	10.05

Effect of Water on the *p*H of Pure BHClO₄ Solutions.—Table VI illustrates that equation 5a accounts quantitatively for the difference in *p*H in anhydrous and water-containing solutions of pure sodium perchlorate.

TABLE VI

EFFECT OF WATER ON *p*H OF 0.109 *M* SODIUM PERCHLORATE SOLUTION

(Initial water concn. = 0.026 *M* (H cell technique)[7d]

Total water concn.	$(pH_w - pH_{0026.})_{exp}$	$(pH_w - pH_{0.026})_{calcd}$
0.0260	0.00	0.00
.0399	.05	.05
.0536	.09	.10
.0816	.15	.15
.1094	.20	.20
.193	.27	.29

$\Delta pH = 0.5 \log(1 + K_f^{H_3O^+ClO_4^-}C_{H_2O})/(1 + K_f^{H_3O^+ClO_4^-} \times 0.026)$

Effect of Water on the *p*H of a Mixture of BHClO₄ and HClO₄.—Finally, in Table VII we compare the experimental and calculated *p*H values for, respectively, solutions containing 0.1 *M* sodium perchlorate and 0.1 and 0.05 *M* perchloric acid in the presence of different concentrations of water. Excellent agreement was found between the experimental *p*H values and the values calculated using equation 6c.

Effect of Water on $[I_a]/[I_b]$ in a Solution of Base and BHClO₄.—We have found that in a solution of anhydrous acetic acid containing 0.079 *M* urea, 0.059 *M* urea perchlorate and 5×10^{-6} *M* PNB, $[I_a]/[I_b]$ is unaffected by adding water up to concentrations of 0.3 *M*. This result is in agreement with our conclusion in the theoretical section.

Effect of Water on $[I_a]/[I_b]$ in Pure BHClO₄ Solutions.—The effect of water on the color of an

TABLE VII

EFFECT OF WATER ON THE pH OF MIXTURES OF SODIUM PERCHLORATE AND PERCHLORIC ACID

$(C_{HClO_4})_t$, M	$(C_{NaClO_4})_t$, M	$(C_{H_2O})_t$, M	$p\mathrm{H}_{exp}$	$p\mathrm{H}_{calcd}$
0.0462	0.104	0.0948	3.84	3.83
.0462	.104	.164	4.04	4.07
.0462	.104	.234	4.25	4.23
.0462	.104	.373	4.51	4.45
.0462	.104	.527	4.63	4.60
.0989	.0889	.0560	3.31	3.29
.0989	.0889	.0815	3.42	3.42
.0989	.0889	.109	3.53	3.53
.0989	.0889	.138	3.63	3.66
.0989	.0889	.165	3.73	3.76

TABLE VIII

EFFECT OF WATER ON THE COLOR OF PNB IN 0.104 M SODIUM PERCHLORATE

$C_{PNB} = 2.96 \times 10^{-5}$ M

Total water concn.	$[IHClO_4]/[I]_{exp}$	$[IHClO_4]/[I]_{calcd.}$ for K^{NaClO_4} = 2.40×10^8	2.6×10^{8a}
0.0315	1.03	1.10	1.04
.0500	.94	1.02	.93
.0685	.89	.93	.89
.106	.78	.82	.78
.180	.67	.69	.66
.328	.54	.54	.52

[a] The value of $K_f^{NaClO_4}$ as calculated from our earlier data is 2.40×10^8. However, as the last column shows using a value of 2.6×10^8 gives much better agreement with experiment. The uncertainty in the formation constant of sodium perchlorate is large enough to justify the use of the higher value.

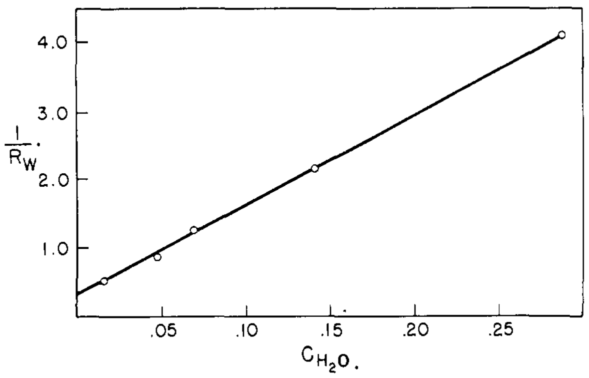

Fig. 2.—Effect of water on R of α-naphtholphthalein in a mixture 0.029 M in perchloric acid and 0.10 M in sodium perchlorate; slope = 13.2; intercept = 0.33.

acetic acid solution containing 2.96×10^{-5} M PNB and 0.104 M $NaClO_4$ is given in Table VIII. Using equation 8c, we have found excellent agreement between calculated and experimental data.

Effect of Water on $[I_a]/[I_b]$ in a Solution of $BHClO_4$ and $HClO_4$.—Using α-naphtholphthalein as the indicator, the effect of water on an acetic acid solution 0.029 M in perchloric acid and 0.10 M in sodium perchlorate was determined. It follows directly from equation 8c that a plot of $1/R_w$ *versus* C_{H_2O} should be a straight line of slope $K_f^{H_3OClO_4}/R_0$ and intercept $1/R_0$. Such a plot is given by Fig. 2 and yields a value of $K_f^{H_3OClO_4}$ equal to 39, in satisfactory agreement with our earlier value of 34.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

The Disproportionation and Combination Reactions of Butyl Free Radicals[1]

BY JOHN W. KRAUS AND JACK G. CALVERT

RECEIVED JUNE 28, 1957

The vapor phase photolyses of di-*t*-butyl, di-iso-butyl, and di-*sec*-butyl ketones are made in full mercury arc light. The rates of formation of the products are determined in experiments at several temperatures, light intensities and ketone concentrations. Product analyses are made by mass spectrometry and vapor partition chromatography. The data suggest the importance of the primary processes: $[(CH_3)_3C]_2CO + h\nu \rightarrow (CH_3)_3C + COC(CH_3)_3$; $[(CH_3)_2CHCH_2]_2CO + h\nu \rightarrow (CH_3)_2CHCH_2 + (CH_3)_2CHCH_2CO$, $[(CH_3)_2CHCH_2]_2CO + h\nu \rightarrow C_3H_6 + CH_3COCH_2CH(CH_3)_2$; $[C_2H_5CH(CH_3)]_2CO + h\nu \rightarrow C_2H_5CHCH_3 + C_2H_5CH(CH_3)CO$, $[C_2H_5CH(CH_3)]_2CO + h\nu \rightarrow C_2H_4 + C_2H_5COCH(CH_3)C_2H_5$. The ratios of the rate constants for the disproportionation reaction, $2C_4H_9 \rightarrow C_4H_8 + C_4H_{10}$ (1), and the combination reaction, $2C_4H_9 \rightarrow C_8H_{18}$ (2), are derived for the different butyl radicals. At temperatures near 100° the ratios of k_1/k_2 are: t-C_4H_9, 4.59; iso-C_4H_9, 0.418; *sec*-C_4H_9, 2.27. If the values for k_2 for the different butyl radicals are near equal then the dominant factor which determines the rate constants for (1) is the number of abstractable hydrogen atoms which can be removed from the radical to form a stable olefin product. Presumably this number is directly related to the probability of formation of the transition state involved in reaction 1, C_4H_8–H–C_4H_9.

Several studies have been made of the disproportionation reaction 1 and the combination reaction 2

$$2R \longrightarrow RH + (R\text{–}H), \text{ olefin} \quad (1)$$

$$2R \longrightarrow R\text{–}R \quad (2)$$

for the ethyl, n-propyl and isopropyl free radicals. A correlation has been noted between the structure of the radical and the relative rates of the reactions 1 and 2.[2–11] Averages of the best published estimates of k_1/k_2 at 25° for the various radicals are:

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(1) Presented in part before the Division of Physical and Inorganic Chemistry, 131st Meeting of the American Chemical Society, Miami, Florida, April, 1957. Taken from the thesis of J. W. Kraus submitted in partial fulfillment of the requirements for the Ph.D. degree, The Ohio State University, 1957.

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