

2. One of the bases studied (guanidine) is stronger than any other for which a constant has been given.

3. The temperature coefficient of the constant K_w/K_B has been determined for six bases of different strength and found to vary in a regular manner with the base strength.

4. The effect of substituents on the strength of bases has been shown to be strictly comparable to their effects on the strength of acids.

5. Attention is directed for the first time to the effect of two ethyl groups in enhancing base strength.

6. Many other special effects have been exhibited by means of tables and diagrams.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE BUREAU OF MINES, U. S. DEPARTMENT OF COMMERCE]

THEORY OF THE ERROR OF ACID-BASE TITRATION¹

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The origin of the error of acid-base titration lies in the finite sensitivity of the end-point indicator. For a given sensitivity, the magnitude of the titer error increases with decrease in rate of change of P_{H} at the end-point. A weak acid is thus less accurately titrated than a strong one.

Formulation of the titer error permits one to predict the accuracy and limiting conditions of titration without laborious experimental trial and error. Furthermore, by comparison of the actual with the theoretical error, it can be decided whether or not complications that are not considered in the ideal case, such as side reactions, indicator decomposition, adsorption, etc., play a part.

In this paper formulations are presented for the theoretical titer error of the acid-base colorimetric and electrometric titration. For the latter the condition of the appearance of an inflection point and the magnitude of its deviation from the stoichiometric point are given. Owing to the practical utility of the results these are presented in their final form; at the end of the paper derivation is made for a simple case as illustrative of the general method.

Previous Results

McCoy³ expressed the error in titrating a weak acid by a strong base with phenolphthalein as indicator. Noyes⁴ and Tizard and Boeree⁵ have

¹ Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.) Original manuscript received January 30, 1931.

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³ McCoy, *Am. Chem. J.*, **31**, 512 (1904).

⁴ Noyes, *THIS JOURNAL*, **32**, 815 (1910).

⁵ Tizard and Boeree, *J. Chem. Soc.*, **119**, 132 (1921).

deduced particular equations for the error of the color indicator titration of one or two weak acids or bases. Bjerrum⁶ derived an equation that was general but left in an unfinished form. Beyond this, Bjerrum's interpretation of his equation is incorrect; he states that although one ends the titration precisely at the stoichiometric point there will nevertheless be a titer error due to the fact that there can be "no partial compensation of errors." This is contrary to the explicit statement of the equation itself.

Eastman⁷ came to the conclusion that in an electrometric titration the inflection point may deviate from the stoichiometric point or might not appear at all. His numerical result for the condition of the appearance of an inflection point was shown to be erroneous,^{8,9} his other numerical results are also in error as shown below.

The Titer Error.—The percentage titer error E of an acid-base titration is given by equation (1)

$$E = \pm 200 \sqrt{\kappa} \sinh \Delta \quad (1)$$

Δ is the known error of the end-point indicator.

κ , which is a function of the ionization constants and concentrations, is defined by equation (2) in the titration of an acid solution by a strong base, and (2') in the titration of a basic solution by a strong acid.

$$\kappa_A = \frac{1}{(C_{HA,A} + \dots + C_{B,BOH} + \dots)^2} (K_w + C_{HA}K_A + \dots + C_B \frac{K_w}{K_B} + \dots) \\ (1 + C_A \frac{1}{K_A} + \dots + C_{BOH} \frac{K_B}{K_w} + \dots) \quad (2)$$

$$\kappa_B = \frac{1}{(C_{BOH,B} + \dots + C_{A,HA} + \dots)^2} (K_w + C_{BOH}K_B + \dots + C_A \frac{K_w}{K_A} + \dots) \\ (1 + C_B \frac{1}{K_B} + \dots + C_{HA} \frac{K_A}{K_w} + \dots) \quad (2')$$

If the reagent solution is complex and contains not only a strong acid or base but also weak acids, bases, and salts, the second factor in parentheses in equations (2) and (2') is replaced, respectively, by the following

$$K_w + C_{HA}K_A + \dots + C_B \frac{K_w}{K_B} + \dots + \frac{(C_{HA,A} + \dots + C_{B,BOH} + \dots)}{(C_{BOH',B'} + \dots + C_{A',HA'} + \dots)} \\ (C_{BOH',B'} \frac{K_w}{K_B} + \dots + C_{A',HA'}K_A + \dots)$$

$$K_w + C_{BOH}K_B + \dots + C_A \frac{K_w}{K_A} + \dots + \frac{(C_{BOH,B} + \dots + C_{A,HA} + \dots)}{(C_{HA',A'} + \dots + C_{B',BOH'} + \dots)} \\ (C_{HA',A'} \frac{K_w}{K_A} + \dots + C_{B',BOH'}K_B + \dots)$$

In the equations for κ , C stands for concentration at the end-point in moles per liter of a component present at the end-point in the form of

⁶ Bjerrum, *Herz Sammlung*, 21, 1 (1914).

⁷ Eastman, *THIS JOURNAL*, 47, 332 (1925).

⁸ Roller, *ibid.*, 50, 1 (1928).

⁹ Eastman, *ibid.*, 50, 418 (1928).

HA, A, BOH, or B, depending upon the subscript to C . For example, C_{HA} is the molar concentration at the end-point of the component HA; C_A is the molar concentration at the end-point of the weak acid salt component, A, etc. The separate dissociation products of a polybasic acid or base are considered components just as a simple weak acid or base.

$C_{HA,A}$, $C_{B,BOH}$, etc., have a slightly different significance. $C_{HA,A}$ stands for the concentration referred to the end-point volume of component HA that has been titrated to its normal salt component, A; ordinarily, with the titration product remaining in solution, $C_{HA,A} = C_A$, where C_A is the concentration of the salt derived from HA. $C_{B,BOH}$ stands for the concentration referred to the end-point volume of component B that has been titrated to component, BOH; ordinarily $C_{B,BOH} = C_{BOH}$, where C_{BOH} is the concentration of base derived from B.

In the form taken by equation (2) or (2') when weak acids, bases and salts are present in the reagent solution, the primed subscripts refer to components contained in the latter solution. For example, $C_{BOH',B'}$ stands for the molar concentration in the reagent solution of component BOH' that in titration goes over to the weak base salt component, B'.

For the simple cases of the titration by a strong base of a weak acid, of a weak acid in the presence of a second acid, of the first H of a dibasic acid, etc., κ reduces substantially to the following, respectively, $\sqrt{\frac{K_w}{C_A K_A}}$,

$$\sqrt{\frac{C_{A_2} K_{A_2}}{C_{A_1} K_{A_1}}}, \sqrt{\frac{K_{A_2}}{K_{A_1}}}, \text{ etc.}$$

Δ in equation (1) for the titer error is defined as follows

$$\Delta = 2.30 \Delta P_H \text{ for the color indicator titration} \quad (3)$$

$$\Delta = 0.158 \Delta \text{ m. v. for the inflection point electrometric titration} \quad (4)$$

$$\Delta = 0.0396 \Delta \text{ m. v. for the absolute electrometric titration} \quad (5)$$

In titrating to the stoichiometric point, ΔP_H in (3) is the error of the color indicator corresponding to its sensitivity. In titrating with an indicator that turns at a P_H different from that at the stoichiometric point, ΔP_H is equal to the deviation in P_H from the stoichiometric point plus the error in P_H (corresponding to its sensitivity) of the indicator.

With an indicator which does not turn at the stoichiometric point, the procedure might also be adopted of correcting the titer for the difference in P_H at which the indicator turns and the P_H at the stoichiometric point. It is not practically desirable to do this, however, because the calculations involved for the titration correction and net titer error are complicated, and because the net titer error, corresponding to the finite sensitivity of the indicator, is greater than that incurred in using an indicator that turns at the stoichiometric point P_H , the qualitative explanation of this fact being that the rate of change of P_H is a maximum in the neighborhood of the stoichiometric point, and the error consequently a minimum.

Δ m. v. in equations (4) and (5) is the error of the e. m. f. measuring instrument. It is seen that the absolute electrometric titration which is made to the e. m. f. at the stoichiometric point is more sensitive than the inflection point titration,¹⁰ and actually four times as sensitive as may be inferred from the work of Hahn.¹¹ This result may be derived as follows. Numerical evaluation of the inflection point is by definition possible with reference only to the second differences of the e. m. f., and not to the e. m. f. itself. A zero value of the second difference determines the value of the e. m. f. at the inflection point. The error of the e. m. f. so determined is the error of the second difference, or four times the error of an e. m. f. measurement itself.

P_H at Stoichiometric Point.—The P_H at the stoichiometric point to which one titrates for optimum accuracy may be calculated from the ionization constants and concentrations. In the titration of an acid solution by a strong base, or of a basic solution by strong acid, P_{HS} is given, respectively, by equations (6) and (6').

$$P_{HS} = -\frac{1}{2} \log \sigma_A \quad (6)$$

$$P_{HS} = -\log K_w + \frac{1}{2} \log \sigma_B \quad (6')$$

σ_A and σ_B in (6) and (6') are defined, respectively, as

$$\sigma_A = \frac{(K_w + C_{HA}K_A + \dots + C_B \frac{K_w}{K_B} + \dots)}{(1 + C_A \frac{1}{K_A} + \dots + C_{BOH} \frac{K_B}{K_w} + \dots)} \quad (7)$$

$$\sigma_B = \frac{(K_w + C_{BOH}K_B + \dots + C_A \frac{K_w}{K_A} + \dots)}{(1 + C_B \frac{1}{K_B} + \dots + C_{HA} \frac{K_A}{K_w} + \dots)} \quad (7')$$

If weak acids, bases and salts are present in the reagent solution, the following expressions are to be added to the numerator on the right-hand side of equations (7) and (7'), respectively

$$\frac{(C_{HA,A} + \dots + C_{B,BOH} + \dots)}{(C_{BOH',B'} + \dots + C_{A',HA'} + \dots)} (C_{BOH',B'} \frac{K_w}{K_B} + \dots + C_{A',HA'} K_A + \dots)$$

$$\frac{(C_{BOH,B} + \dots + C_{A,HA} + \dots)}{(C_{HA',A'} + \dots + C_{B',BOH'} + \dots)} (C_{HA',A'} \frac{K_w}{K_A} + \dots + C_{B',BOH'} K_B + \dots)$$

In the simple cases of titration by a strong base of a weak acid, a weak acid in the presence of a second acid, of the first H of a dibasic acid, etc.,

σ reduces substantially to the following, respectively, $\sqrt{\frac{K_A K_w}{C_A}}$, $\sqrt{\frac{C_{A2}}{C_{A1}} K_{A2} K_{A1}}$, $\sqrt{\frac{K_{A2}}{K_{A1}}}$, etc.

Graphical Expression of Results.—Referring to equation (1) for the titer error, it is seen that if $-\log \kappa$ is plotted against $\log \sinh \Delta$ a series of

¹⁰ Cavanagh, *J. Chem. Soc.*, 2207 (1927); 843, 855 (1928).

¹¹ Hahn, *Z. physik. Chem.*, A146, 363 (1930); Hahn and Weiler, *Z. anal. Chem.*, 70, 417 (1926).

straight lines is obtained corresponding to different values of the percentage titer error, E . If in place of $\log \sinh \Delta$, one substitutes ΔPH and Δ m. v. by equations (2), (3) and (4), the desired graph of the titer error is obtained as shown in Fig. 1.

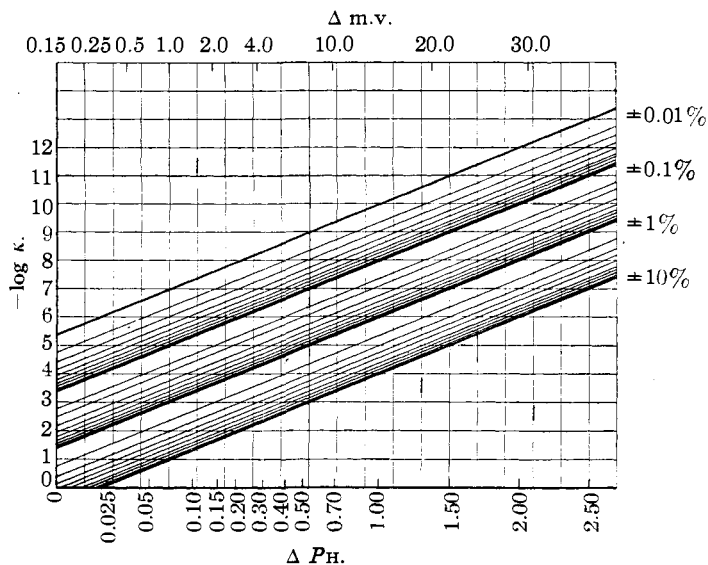


Fig. 1.—Percentage titer error of colorimetric and electro-metric inflection point titration.

To construct this graph a basic line is drawn for a given value of E , say $\pm 0.1\%$, only two plotted points being necessary. These are given in Table I. All other straight lines are drawn parallel to the basic line at a vertical distance from it equal to $2 \log E'/E''$, where E' is equal to $\pm 0.1\%$, and E'' is the percentage error of the line in question.

Table II gives the data necessary to convert the abscissa scale, $\log \sinh \Delta$, to ΔPH for the colorimetric, and to Δ m. v. for the inflection point electrometric titration. Δ m. v. for the absolute electrometric titration has been omitted since this titration is at the present time infrequently used. However, the abscissa scale is for this titration at once obtained by multiplying by four the abscissa values of Δ m. v. for the inflection point titration.

It is convenient also to graph equations (6) or (6') for the PH at the stoichiometric point. A plot of $-\log \sigma_A$ and $-\log \sigma_B$ against PH_S gives two straight lines intersecting at $PH = \frac{1}{2} pK_w$.

Effect of Concentration of the Components.—The concentration of the components enters directly in the expressions given above for the titer error and for the PH at the stoichiometric point. On close examination it is seen that the concentration substantially affects the results only in the case of the unsymmetrical titration, as of a weak acid by a strong base,

but not in the case of the symmetrical titration as of a weak acid by a weak base or of the second H of a dibasic acid by a strong base.

For the unsymmetrical titration the titer error is substantially proportional to the square root of the molar concentration at the end-point. This result is of significance for acidimetry, because it is at times possible to artificially diminish the concentration of components at the end-point, and thus to enhance the accuracy, by precipitation, complex formation, extraction, heat, etc. Empirical application of this principle has been made in a few instances in volumetric practice, as in boiling off carbonic acid, in the formaldehyde titration of amino acids (Sörenson), in the precipitation of CO_3^{2-} as barium carbonate (Winkler titration), etc. The last titration is discussed in detail below.

TABLE I
DATA FOR CONSTRUCTING BASIC LINE ($E = \pm 0.1\%$)

$\log \sinh \Delta$	-0.634	0.024	1.699
$-\log \kappa$	5.334	6.650	10.000

TABLE II
DATA FOR CONVERTING LOG SINH Δ TO ΔpH AND $\Delta \text{m. v.}$

ΔpH	$\log \sinh \Delta$	$\Delta \text{m. v.}$	$\log \sinh \Delta$
0.025	-1.240	0.15	-1.623
.05	-0.939	.25	-1.398
.10	-.635	0.5	-1.102
.20	-.322	1.0	-0.796
.30	-.127	2.0	-.491
.40	.024	4.0	.168
.50	.153	10.0	.370
.70	.381	20	1.080
1.00	.694	30	1.769
1.5	1.196		
2.0	1.700		
2.5	2.195		

TABLE III
MAXIMUM POSSIBLE PERCENTAGE TITER DEVIATION OF THE INFLECTION POINT FROM THE STOICHIOMETRIC POINT

κ	K_A for weak acid $C_A = 0.1$ molar	Maximum possible percentage titer deviation	Percentage titer error for e. m. f. error of ± 0.5 m. v.
10^{-5}	10^{-8}	0.009	0.05
10^{-4}	10^{-9}	.03	.16
$10^{-3.5}$	$10^{-9.5}$.09	.28
10^{-3}	10^{-10}	.3	.50
$10^{-2.5}$	$10^{-10.5}$.9	.89
10^{-2}	10^{-11}	3.0	1.6
$10^{-1.5}$	$10^{-11.5}$	9.5	2.8

Dilution of the reagent solution results in a lower concentration of the components at the end-point, and consequently in an increased titer error for the unsymmetrical titration.

Sensitivity of Color Indicator, and Comparison with Electrometric Measurement.—Tizard and Boeree⁵ and Kolthoff¹² have performed diversified color indicator titrations, the former without and the latter with a comparison solution containing the indicator at P_{H_5} . Applying equation (1) for the titer error to the results obtained by these authors, it is found that the average color indicator error is, when titrating with the unaided eye, $\pm 0.2 P_H$ and when using a comparison solution $\pm 0.1 P_H$. These results are in agreement with previous estimates of $\pm 0.3 P_H$ ^{5,6} and $\pm 0.2 P_H$ ¹³ in titrating with the unaided eye, and of $\pm 0.1 P_H$ ^{6,13} in titrating with a comparison solution.

Assuming that the e. m. f. error is ± 0.5 m. v., and the color indicator error $\pm 0.1 P_H$, it is seen from the equations given above that the absolute electrometric titration is intrinsically about twelve times as sensitive, and the inflection point titration three times as sensitive, as the color indicator titration.

Example.—In the titration by 0.1 *M* strong acid ($K_A = \infty$) of 0.1 *M* sodium hydroxide ($K_B = \infty$) in the presence of 0.1 *M* sodium carbonate ($K_{A_1} = 10^{-6.5}$, $K_{A_2} = 10^{-10.2}$), it is found by calculation from equations (6') and (2') that σ_B and κ_B are equal to $10^{-5.2}$ and $10^{-2.6}$, respectively. From a graphical plot of equation (6') the P_H at the stoichiometric point to which one titrates is found to be 11.5. The value of the titer error is from Fig. 1 for $\kappa_B = 10^{-2.6}$ found to be 4.7% with $\Delta P_H = \pm 0.2$, and 2.2% with $\Delta P_H = \pm 0.1$. The titration is therefore essentially inaccurate as regards the ordinary color indicator titration.

If the concentration at the end-point of the component $C_A = C_{CO_3^{=}}$ is reduced by precipitation with excess barium chloride, the titration (Winkler) becomes quite accurate. From the solubility product of barium chloride the concentration of $CO_3^{=}$ is, in the presence of 0.1 *M* barium chloride, equal to $10^{-7.1}$ mole/liter. σ_B is now $10^{-11.0}$, and P_{H_5} therefore 8.6. κ_B is calculated to be $10^{-8.4}$, and the titer error is therefore less than 0.01% with $\Delta P_H = \pm 0.2$.

This theoretical result of an enhanced titration accuracy obtained by precipitating the component $CO_3^{=}$ with barium chloride has been amply confirmed by experiment.^{14,15,16}

The Electrometric Inflection Point.—A good insight into the nature of the electrometric inflection point is obtained by plotting the rate of change of P_H against quantity of reagent. In such a graph a maximum or minimum corresponds to an inflection point, the meaning of the minimum being that the concave and convex portions of the titration curve are re-

¹² Kolthoff, *Z. anorg. allgem. Chem.*, **115**, 168 (1921).

¹³ Kolthoff and Furman, "Indicators," John Wiley and Sons, New York, 1926.

¹⁴ Küster, *Z. anorg. Chem.*, **13**, 127 (1897).

¹⁵ Poethke and Manicke, *Z. anal. Chem.*, **79**, 241 (1929).

¹⁶ Partridge and Schroeder, *Ind. Eng. Chem., Anal. Ed.*, **4**, 271 (1932).

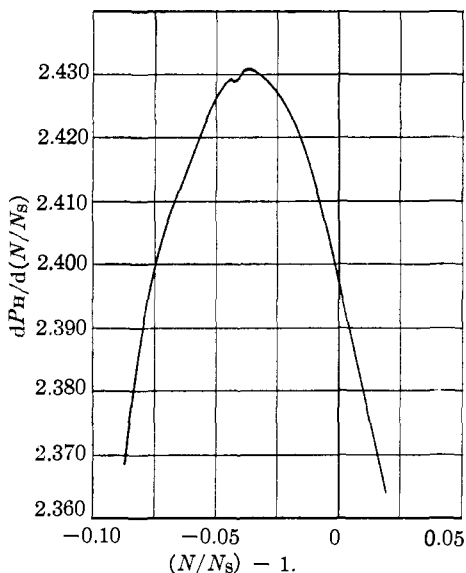


Fig. 2.—Electrometric titration of a weak acid, $K_w/C_A K_A = 10^{-2}$.

there is a prominent maximum corresponding to the ordinary inflection point, with a secondary small maximum and minimum corresponding to secondary trivial inflection points. When the acid is weaker so that $K_w/C_A K_A$ is $10^{-1.5}$, the secondary inflection points are quite pronounced and merge into a broad maximum with the primary inflection point as shown in Fig. 3. For a very weak acid such that $K_w/C_A K_A$ is only 10^{-1} , there are no maxima or minima and therefore no inflection points (Fig. 4).

For the unsymmetrical titration of the first H of a weak acid (Figs. 5 to 8) there is in every case seen to be a maximum or minimum, and therefore an inflection point, precisely at the stoichiometric point. As shown especially in Fig. 7 for $K_{A_1}/K_A = 10^{-1.28}$, there is for this titration also a

versed from their order at the usual inflection point.

By differentiation of an equation similar to equation (11) below, such a plot has been constructed in Figs. 2, 3 and 4 for the unsymmetrical titration of a simple weak acid by a strong base, and in Figs. 5, 6, 7 and 8 for the symmetrical titration of the first H of a dibasic acid by a strong base. In these figures $dP_H/d(N/N_S)$, the rate of change of P_H with fraction of reagent required at the stoichiometric point, has been plotted against $[N/(N_S - 1)]$, the fractional difference between reagent added and titer at the stoichiometric point.

In Fig. 2 for $K_w/C_A K_A = 10^{-2}$,

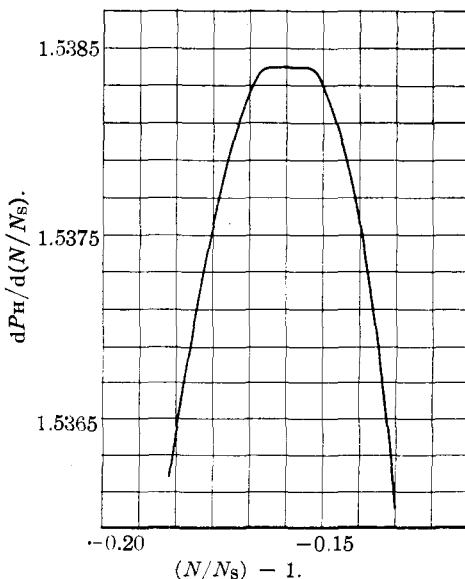


Fig. 3.—Electrometric titration of a weak acid, $K_w/C_A K_A = 10^{-1.5}$.

secondary inflection point but it is generally of quite small significance compared to the secondary inflection points in the unsymmetrical titration of a simple weak acid by a strong base.

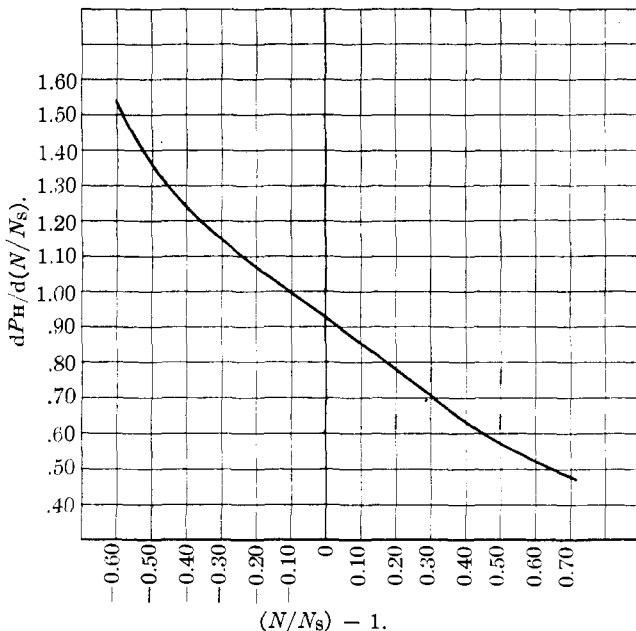


Fig. 4.—Electrometric titration of a weak acid, $K_w/C_A K_A = 10^{-1}$.

Deviation of the Inflection Point from Stoichiometric Point.—By extension of a method of derivation previously employed⁸ the general condition that an inflection point shall appear is given in equations (8) and (8') for the titration of an acid solution and basic solution, respectively.

$$\sqrt{\sigma_A} \left(\frac{1}{K'_A} + \dots + \frac{K'_B}{K_w} + \dots + 0 \right) - \sqrt{\frac{1}{\sigma_A}} \left(K''_A + \dots + \frac{K_w}{K''_B} + \dots + 0 \right) < 10^{-0.71} \quad (8)$$

$$\sqrt{\sigma_B} \left(\frac{1}{K'_B} + \dots + \frac{K'_A}{K_w} + \dots + 0 \right) - \sqrt{\frac{1}{\sigma_B}} \left(K''_B + \dots + \frac{K_w}{K''_A} + \dots + 0 \right) < 10^{-0.71} \quad (8')$$

In these equations K'_A refers to the ionization constant of an acid or weak acid salt that has been titrated at the end-point, and similarly for K'_B . K''_A refers to the ionization constant of an untitrated acid or weak acid salt, and also to a weak acid salt derived from the reagent solution, and similarly for K''_B .

Equation (8) reduces to the condition that an inflection point shall appear in the titration of a simple weak acid by a strong base that was previously derived,⁸ *i. e.*, $K_w/C_A K_A < 10^{-1.42}$. Examination of the general condition given by (8) or (8') shows, in conformity with the graphical analysis, that in the symmetrical titration an inflection point will always

appear, but may not appear in the unsymmetrical titration. The conclusion of Eastman⁷ that an inflection point may not appear in the (symmetrical) titration of a weak acid by a weak base is in the light of these results seen to be incorrect.

The deviation in P_H of the inflection point from the stoichiometric point in the titrations, respectively, of an acid and basic solution is given by equations (9) and (9').

$$P_{H_S} - P_{H_E} = 0.65 \left[\sqrt{\sigma_A} \left(\frac{1}{K'_A} + \dots + \frac{K'_B}{K_w} + \dots + 0 \right) - \frac{1}{\sqrt{\sigma_A}} \left(K'_A + \dots + \frac{K_w}{K'_B} + \dots + 0 \right) \right] \quad (9)$$

$$P_{H_S} - P_{H_E} = 0.65 \left[\sqrt{\sigma_B} \left(\frac{1}{K'_B} + \dots + \frac{K'_A}{K_w} + \dots + 0 \right) - \frac{1}{\sqrt{\sigma_B}} \left(K'_B + \dots + \frac{K_w}{K'_A} + \dots + 0 \right) \right] \quad (9')$$

In terms of the percentage titer, the deviation of the inflection point from the stoichiometric point is given, respectively, by equations (10) and (10').

$$100 \frac{(N_S - N_E)}{N_S} = 300 \sqrt{\kappa_A} \left[\sqrt{\sigma_A} \left(\frac{1}{K'_A} + \dots + \frac{K'_B}{K_w} + \dots + 0 \right) - \frac{1}{\sqrt{\sigma_A}} \left(K'_A + \dots + \frac{K_w}{K'_B} + \dots + 0 \right) \right] \quad (10)$$

$$100 \frac{(N_S - N_E)}{N_S} = 300 \sqrt{\kappa_B} \left[\sqrt{\sigma_B} \left(\frac{1}{K'_B} + \dots + \frac{K'_A}{K_w} + \dots + 0 \right) - \frac{1}{\sqrt{\sigma_B}} \left(K'_B + \dots + \frac{K_w}{K'_A} + \dots + 0 \right) \right] \quad (10')$$

Inspection of equations (10) and (10') shows that the percentage titer deviation may be positive or negative depending upon the sign of the expression in brackets, or it may be zero; in other words, the inflection point may precede, follow or coincide with the stoichiometric point.

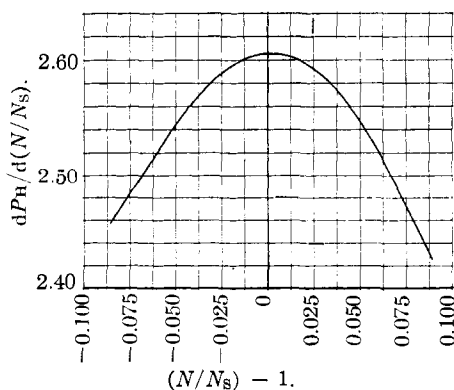


Fig. 5.—Electrometric titration of first H of a dibasic acid, $K_{A_2}/K_{A_1} = 10^{-2}$.

More explicitly it is seen in agreement with the graphical analysis that the inflection point deviates from the stoichiometric point in the unsymmetrical titration, but coincides with the stoichiometric point in the symmetrical titration. The deduction of Eastman⁷ that for the symmetrical titration of a weak acid by a weak base there is a titer deviation of the inflection point from the stoichiometric point is seen

to be erroneous; his estimate of the titer deviation in the unsymmetrical titration by a strong base of a 1 molar weak acid with $K_A = 10^{-12}$ is about ten-fold too low, and his conclusion that the titer deviation for this titration does not vary with concentration of weak acid between 1 and 10^{-3} mole/liter is plainly in error.

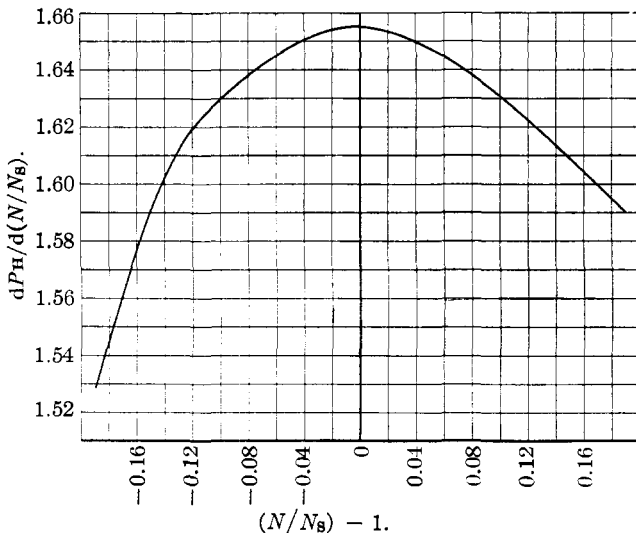


Fig. 6.—Electrometric titration of first H of a dibasic acid, $K_{A_2}/K_{A_1} = 10^{-1.5}$.

Analysis of equations (10) and (10') for the percentage titer deviation of the inflection point from the stoichiometric point shows that the maximum possible percentage titer deviation in any titration is that previously given⁸ for the deviation in the unsymmetrical titration of a simple weak acid by a strong base, namely $100 \frac{N_S - N_E}{N_S} = 300 \frac{K_W}{C_A K_A}$. This maximum possible titer deviation is shown in the third column of Table III for values of κ shown in the first column, while the second column gives the corresponding ionization constant of a 0.1 molar weak acid titrated by a strong base. The last column of Table III gives by equation (1), for an e. m. f. error of ± 0.5 m. v., the percentage titer error of estimating the inflection point.

It is seen from Table III that if $\kappa < 10^{-2.5}$, the percentage titer error of the electrometric titration is, for an e. m. f. error of ± 0.5 m. v., greater than the maximum possible titer deviation of the inflection point from the end-point. Nevertheless, for greatest accuracy the correction for the percentage titer deviation logically should be made, for otherwise it will be added as an error to the percentage titer error resulting from inaccuracy of the e. m. f. measurement.

For values of $\kappa > 10^{-2.5}$ the maximum possible titer deviation exceeds the titer error of estimating the inflection point. Because of this fact, and

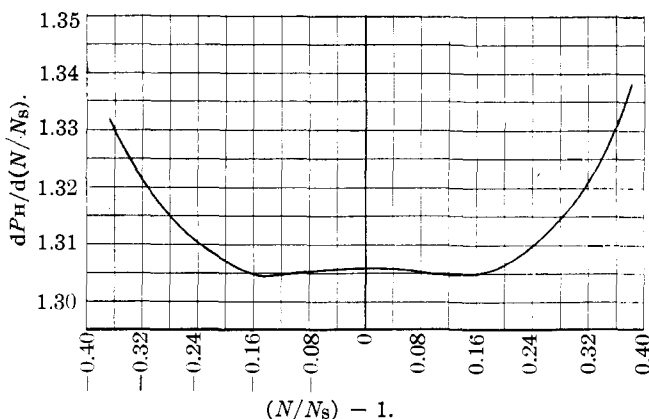


Fig. 7.—Electrometric titration of first H of a dibasic acid,
 $K_{A_2}/K_{A_1} = 10^{-1.28}$.

the fact that the titer error is now greater than 1%, for $\kappa > 10^{-2.5}$ the inflection point titration might advantageously be replaced by the absolute electrometric titration.¹⁷ As already pointed out, the absolute titration

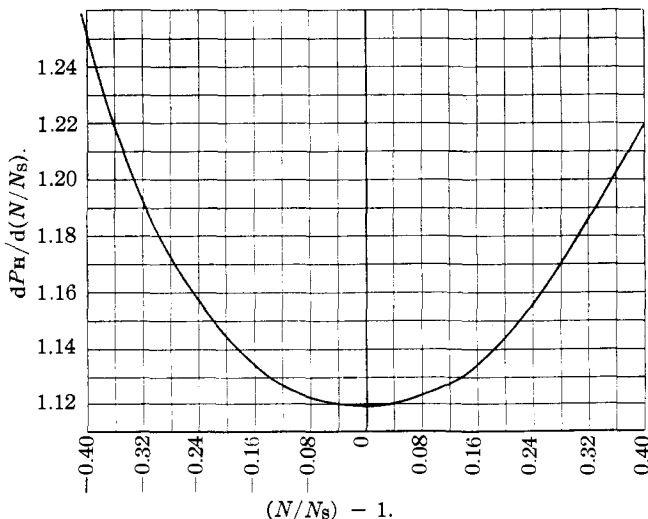


Fig. 8.—Electrometric titration of first H of a dibasic acid,
 $K_{A_2}/K_{A_1} = 10^{-1}$.

which is made to the e. m. f. at the stoichiometric point is inherently four times as sensitive as the inflection point titration.

¹⁷ Cf. Kolthoff, *Rec. trav. chim.*, **47**, 397 (1928); Kolthoff and Furman, "Potentiometric Titrations," John Wiley and Sons, New York, 1931.

Derivation of Equations.—As an example of the method of derivation, the titration of the stronger of two weak acids by a strong base is considered. In the general case, all terms corresponding to different acids and bases are grouped into one or two categories of which the first and second weak acids in the particular example are representative types.

The initial procedure is exactly analogous to that employed in a previous publication,⁸ and results in the following equation connecting the cc. of reagent, N and H .

$$C_{OH'} \frac{N}{V} = C_{HA_1}^0 + C_{HA_2}^0 - (V + N)/V \left(H - \frac{K_w}{H} \right) - \frac{C_{HA_1}^0 H}{K_{A_1} + H} - \frac{C_{HA_2}^0 H}{K_{A_2} + H} \quad (11)$$

$C_{HA_1}^0$ and $C_{HA_2}^0$ are the initial concentrations of the acids in volume V . If concentrated solutions are considered, correction for the ion activities may be made to the ionization constants.

When each acid has been 50% neutralized the H-ion concentration is equal to the K_{A_1} or K_{A_2} as the case may be. Therefore, at the normal salt or stoichiometric point of the first acid, $K_{A_1} > H_S > K_{A_2}$. Expanding then in a binomial series the last two terms on the right-hand side of equation (11) and remembering that at the normal salt or stoichiometric point $C_{OH'} N_S/V = C_{HA_1, A_1}^0 = C_{HA_1}^0$, the P_{H_S} at the stoichiometric point in titrating the first acid is found to be

$$P_{H_S} = -1/2 \log \left(\frac{K_w + C_{HA_2} K_{A_2}}{1 + C_{A_1} 1/K_{A_1}} \right) \quad (12)$$

In (12) the concentrations now refer to the volume at the end-point and C_{A_1} is written for C_{HA_1} since only the salt of HA_1 now exists.

The generalized form of equation (12) is given by equation (6). For the general case the error due to neglect of powers of H_S/K_A or K_A/H_S can be expressed in terms of κ . It is found that for the extreme case of $\kappa = 10^0$, P_{H_S} calculated by equation (6) or (6') is in error at the most by 0.3 P_H . This corresponds to the unsymmetrical titration and the sign may be positive or negative; for the symmetrical titration the error is virtually nil. For $\kappa = 10^{-1}$, the maximum error of the calculated result is 0.04 P_H , and for $\kappa = 10^{-2}$ it is only 0.005 P_H .

To determine the titer error the differential of equation (11) is taken and two of the terms expanded in a binomial series as before. With $dN = \Delta N$, and $dH = \Delta H = \pm (H_E - H_S)$, where H_E is the hydrogen-ion concentration to which one on the average titrates in attempting to titrate to H_S , and taking H as the geometric mean of H_S and H_E (or P_H the arithmetic mean of P_{H_S} and P_{H_E}), the following expression is obtained for the titer error of titrating the first acid

$$\frac{\Delta N}{N_S} = \pm \frac{1}{C_{HA_1, A_1}} \left(1 + \frac{K_w}{H_S H_E} + \frac{C_{A_1}}{K_{A_1}} + C_{HA_2} \frac{K_{A_2}}{H_S H_E} \right) (H_S - H_E) \quad (13)$$

If in equation (13) we substitute for H_S from equation (12), and transform in the reduced equation the factor $(1/H_S + 1/H_E) (H_E - H_S)$ into the

transcendental form by virtue of the definition of the P_H ($= -\log H$), the following simplified form of equation (13) for the titer error is obtained.

$$100 \frac{\Delta N}{N_S} = \pm \frac{200}{C_{HA_1, A_1}} \sqrt{(K_w + C_{HA_2} K_{A_2}) \left(1 + C_{A_1} \frac{1}{K_{A_1}}\right)} \sinh 2.30 (P_{HE} - P_{HS}) \quad (14)$$

The general form of equation (14) is given by equation (1), E being written for $100 \Delta N/N_S$.

The error in E due to neglect of powers of H_S/K_A or K_A/H_S is in general quite small and may be estimated in terms of κ . It is found that E calculated by equation (1) is always greater than the exact value; for the extreme case of $\kappa = 10^0$ the calculated titer error is at the most four times as great as the exact value, for $\kappa = 10^{-1}$ it is at the most 1.25, and for $\kappa = 10^{-2}$ it is at the most only 1.02 times as great as the exact value.

If an indicator is chosen that turns not at P_{HS} but at P_{HE} , equation (14), while expressing the error in terms of the P_H deviation, may also be considered as a titer correction. The net titer error, due to the finite sensitivity of the indicator, is obtained by a derivation analogous to that above and is

$$100 \frac{\Delta N}{N_S} = \pm 400 \frac{1}{C_{HA, A_1}} \sqrt{(K_w + C_{HA_2} K_{A_2}) \left(1 + C_{A_1} \frac{1}{K_{A_1}}\right)} \cosh 2.30 \left(P_{HS} - P_{HE} + \frac{\Delta P_H}{2}\right) \sinh 1.15 \Delta P_H \quad (15)$$

Examination of equation (15) shows that the net titer error is greater than the error incurred in titrating with an indicator that turns at the stoichiometric point.

Summary

The theoretical titer error of the colorimetric and electrometric acid-base titration has been formulated analytically and graphically. The titer error is a simple function of the known error of the color indicator or e. m. f. measuring instrument, and of the concentrations and ionization constants.

For the unsymmetrical titration the error is proportional to the square root of the concentration of the product at the end-point, so that the accuracy of the titration may be enhanced by artificially diminishing the end-point concentration. This procedure has been empirically applied to a few titrations.

The nature of the electrometric inflection point is examined and discussed with reference to the symmetrical and unsymmetrical acid-base titration. For the symmetrical titration the primary inflection point will always appear, and coincides precisely with the stoichiometric point. For the unsymmetrical titration the inflection point may not appear, and does not coincide with the stoichiometric point. The percentage titer deviation may be as high as 11% as for instance in the unsymmetrical titration of a

weak acid by a strong base. The titer deviation is compared with the titer error due to inaccuracy of e. m. f. measurement.

The absolute titration since it is inherently four times as sensitive as the inflection point titration might advantageously replace the latter when the titer error is above about 1%.

NEW BRUNSWICK, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY THE IODINE-IODIDE COUPLE. II AND III. THE RATE OF OXIDATION IN NEUTRAL, AND IN ACID, SOLUTION OF HYDROGEN PEROXIDE BY IODINE

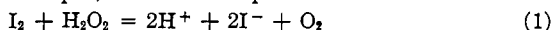
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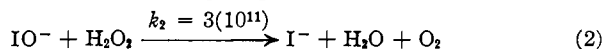
PUBLISHED SEPTEMBER 5, 1932

II. THE RATE OF OXIDATION, IN NEUTRAL SOLUTION, OF HYDROGEN PEROXIDE BY IODINE

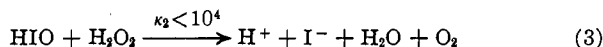
In certain investigations of the catalytic decomposition of hydrogen peroxide by the iodine-iodide couple,¹ it has been postulated that the reaction



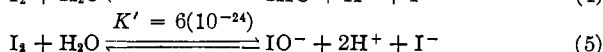
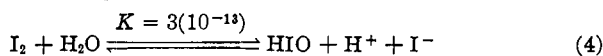
proceeds through the rate-determining steps



and



The concentrations of hypiodite ion and of hypiodous acid are governed at the steady state by the equilibria



Whether or not the hydrolysis equilibrium of iodine (Reaction 4 or 5) is maintained as the steady state is approached through the progress of Reaction 1 has been questioned by Abel.^{1a,2}

¹ (a) Abel, *Z. physik. Chem.*, **136**, 16 (1928); (b) Liebhafsky, *THIS JOURNAL*, **54**, 1792 (1932). References to earlier work may be found in Ref. 1a. Ref. 1b is the first paper of this series and will be referred to as I. The values of k_2 , κ_2 , and k_1 are taken from I, where references will also be found for the values of K , K' and $(I_2)(I^-)/I_3^-$ given above. ($k_2 = 3(10^{11})$ is an average value deduced from I, Table Ib, Expts. 155-151 incl.; for these experiments the buffer solutions were identical in composition with those employed in the present investigation.) Numerical values of all constants are for 25°. As in other communications, \longrightarrow denotes that the reaction may be rate-determining and () means "concentration of" in moles/liter.

² Cf. also (a) Liebhafsky, *Z. physik. Chem.*, **155**, 289 (1931); (b) *THIS JOURNAL*, **53**, 2074 (1931); (c) *J. Phys. Chem.*, **35**, 1648 (1931).