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QUANTITATIVE APPLICATION OF THE THEORY OF INDICATORS TO VOLUMETRIC ANALYSIS.

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I. General Considerations.

1. *Purpose of the Article.*—Although the explanation of the behavior of neutralization indicators, originally given by Ostwald,[1] was one of the early triumphs of the Ionic Theory, and although many investigations upon indicators from a physico-chemical standpoint have since been made, yet the quantitative development of the theory of indicators in a systematic form immediately applicable to the problems of volumetric analysis seems not to have been undertaken.[2] It is the purpose of this article to present such a development.

The following discussion, owing to the large number of factors and special cases to be considered, unfortunately involves a somewhat lengthy, though comparatively simple, mathematical treatment. The reader who is interested in the results, rather than the method of derivation, is therefore recommended, after reading Sections 3 and 5 of this Part of the article, to pass directly to the Summary at the end, in which an attempt has been made to present the conclusions fairly completely and connectedly in a form in which they can be directly applied to the problems of volumetric analysis.

2. *The Chemical Nature of Indicators. Equilibrium Relations of the Tautomeric Forms.*—The original explanation of the behavior of indicators suggested by Ostwald was based on the simple hypothesis that the slightly ionized indicator acid or base has a different color from that of its ionized salt, into which it is converted by the addition of alkali or acid. More recent work has, however, shown that this explanation is inadequate in view of the well-known relations between the color and the structure of organic compounds, and in view of the results of the special investigations of Bernthsen, Nietzi and Burckhart, Hantzsch, and others on tautomeric colored substances.[3] It is in all probability true that a neutralization indicator always consists of tautomeric substances[4] of two different structural types possessing different colors, one of which types greatly predominates when the indicator exists as a slightly ionized acid or base, and the other when it exists as a largely ionized salt. Thus, the indicator may consist of a mixture of two tautomeric acids, HIn′ and HIn″, the equilibrium between these two acids being such that the acid HIn′ is present in greatly predominating quantity. Owing to the fact, how-

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[1] *Lehrbuch der allgemeinen Chemie*, 1, 799 (1891). See also his *Wissensch. Grundlagen der anal. Chemie*, 3rd edit., pp. 117–23 (1901).

[2] It should be mentioned, however, that a brief treatment of a part of the problem has already been given by McCoy (*Am. Chem. J.*, 31, 512–6 (1904)), and by Salm (*Z. physik. Chem.*, 57, 497 (1907)).

[3] For a discussion of this matter, see Stieglitz, THIS JOURNAL, 25, 1112–20 (1903).

[4] From the modern standpoint tautomeric substances may be defined as isomeric substances which tend to go over into each other directly in one direction or the other until equilibrium is reached.

ever, that the acid HIn'' has a very much larger ionization-constant, its salt is formed in much larger proportion than that of the other acid when the mixture is neutralized with a base. Hence a change in color takes place in correspondence with the different structural type which predominates in the acid and alkaline solution. It has been shown by Stieglitz[1] that the conditions just stated do not make necessary any substantial modification of the equilibrium relations of indicators, so far as their behavior in titrations is concerned.

Since the limitations just mentioned with reference to the relative concentrations of the different forms are not in all cases necessary, it seems desirable to treat the matter from a somewhat more general standpoint, as follows.

Let us consider an acid indicator composed of two tautomeric substances, HIn' and HIn'', which when neutralized with a base BOH are converted into the corresponding salts BIn' and BIn'', these being largely dissociated into the ions B^+, In'^- and In''^-. In order that an indicator may be satisfactory in the respect that it show a sharp color-change on neutralization, it is evidently essential that the following conditions be fulfilled: (1) One of the structural forms must be colorless and the other colored; or else, the two structural forms must be of distinctly different colors. (2) Either form that may be colored must not exist in appreciable proportion in both acid and alkaline solutions.

In accordance with these general conditions, the three following cases may occur, the convention that the indicator shows in acid solution the color corresponding to the form HIn' being employed in their formulation:

(*a*) The indicator is colorless in acid and colored in alkaline solution. Hence HIn', BIn', and In'^- are colorless; HIn'', BIn'', and In''^- are colored; and $(HIn'')/(HIn')$[2] must be very small.

(*b*) The indicator is colored in acid and colorless in alkaline solution. Hence HIn', BIn', and In'^- are colored, HIn'', BIn'', and In''^- are colorless, and $(In'^-)/(In''^-)$ must be very small.

(*c*) The indicator has two sharply differentiated colors in acid and alkaline solution. Hence HIn', BIn', and In'^- have one color; HIn'', BIn'', and In''^- have a different color; and both $(HIn'')/(HIn')$ and $(In'^-)/(In''^-)$ must be very small.[3]

Corresponding criteria for a satisfactory color-change can also be readily formulated for the case of a basic indicator existing in alkaline solution in the two structural forms $In'OH$ and $In''OH$, which when

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[1] *Loc. cit.*, p. 1122.

[2] Throughout this article symbols enclosed within parentheses denote the molar concentrations of the substances represented by the symbols.

[3] For evidently, if there were present a considerable proportion of HIn'' in the acid solution, or of In'^- in the alkaline solution, a mixed color corresponding to the superposed colors of the two structural forms would result.

neutralized with an acid HA are converted into the corresponding salts In′A and In″A, these being largely dissociated into the ions In'^+, In''^+, and A^-. It is not, however, necessary to formulate these conditions here.

We may next derive a general expression (as has previously been done by Acree[1]) for the equilibrium-relations of any pair of tautomeric acids and their ions. The three fundamental equilibrium equations are as follows:

$$\frac{(H^+)(In'^-)}{(HIn')} = K_I'; \quad (1) \qquad \frac{(H^+)(In''^-)}{(HIn'')} = K_I''; \qquad (2)$$

and

$$\frac{(HIn'')}{(HIn')} = K_T. \qquad (3)$$

Multiplying (2) by (3), adding (1) to the product, and substituting in the denominator for (HIn′) its value $\frac{(HIn') + (HIn'')}{1 + K_T}$ given by (3), we get:

$$\frac{(H^+)[(In'^-) + (In''^-)]}{(HIn') + (HIn'')} = \frac{K_I' + K_I''K_T}{1 + K_T} = K_{IA}. \qquad (4)$$

If the indicator is a base existing as the two tautomeric substances In′OH and In″OH, having ionization constants K_I' and K_I'' and a tautomer constant K_T defined by equations analogous to (1), (2), and (3), the general expression for the equilibrium between the ionized bases and their ions is:

$$\frac{(OH^-)[(In'^+) + (In''^+)]}{(In'OH) + (In''OH)} = \frac{K_I' + K_I''K_T}{1 + K_T} = K_{IB} \qquad (5)$$

In these expressions a single constant K_{IA} or K_{IB} has been introduced in place of the function of the three constants K_I', K_I'', and K_T. This constant K_{IA} or K_{IB} will throughout this article be called simply the ionization-constant of the indicator acid or base.

The constant so calculated for a pair of tautomeric acids or bases can evidently be substituted for the ionization-constant of an ordinary (non-tautomeric) acid in any derived expression, provided the *sum* of the two ion-concentrations and the *sum* of two acid or base concentrations are the quantities that are known or are to be calculated. Thus the ionization-constant for a pair of tautomeric acids or bases as determined by conductance measurements would be that expressed by equation (4) or (5), since it is the sum of the ion-concentrations that are determined by such measurements. So also the degree of hydrolysis h of the sodium salts of a pair of tautomeric acids would be expressed, like that of the

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[1] *Am. Chem. J.*, 38, 19 (1907).

salt of an ordinary acid, by the familiar equation,[1] $\frac{\gamma_B h^2 C}{\gamma(1-h)} = \frac{K_W}{K_A}$, provided K_A, the ionization-constant of the tautomeric acids, be calculated by an expression of the form of equation (4); for it is the sum of the two forms of the acid that corresponds to the hydrolyzed portion, and it is the sum of the two forms of the salt that corresponds to the unhydrolyzed portion.[2]

Equations (4) and (5) can evidently be used to express the color changes exhibited by indicators or other tautomeric substances when, and only when, the intensity of the color is substantially proportional to the sum of the concentrations of the two tautomeric acids or bases, or to the sum of the concentrations of the two tautomeric ions. It has already been seen, however, that for a satisfactory two-color acid indicator (case *c*) the sum (HIn′) + (HIn″) must be substantially identical with (HIn′) and the sum (In′) + (In''^-) substantially identical with (In''^-). It has also been seen that for a satisfactory one-color acid indicator (case *a* or *b*) either the former or the latter of these two identities must hold true; and it may now be pointed out that the intensity of the color is proportional to the other sum involved, namely to (In'^-) + (In''^-) in case *a*, and to (HIn′) + (HIn″) in case *b*. This follows from the fact that these sums are proportional, in virtue of equations (1), (2), and (3), to (In''^-) and to (HIn′) respectively, which are the substances on which the color alone depends in the two cases. From this it follows, in case *a* for example, that the ratio, of the color intensity of the indicator when partially transformed into its salt, to its color intensity when completely transformed, is equal to the ratio of the sums of the concentrations of the colored and colorless salts in the two cases. Similar conditions prevail in the case of two-color and one-color basic indicators.

Equations (4) and (5) may therefore be employed to express the equilibrium relations and color relations of such indicators as are included under cases *a*, *b*, and *c* described above and under the corresponding cases applicable to basic indicators—that is to say, of such indicators as can show a sharp color-change on neutralization. These equations will therefore be made the basis of the considerations presented in the next section; but for greater simplicity, (In^-) will hereafter be written for (In'^-) + (In''^-), (HIn) for (HIn′) + (HIn″), (In^+) for (In'^+) + (In''^+), and (InOH) for (In′OH) + (In″OH), thereby showing also that the indicator behaves as if it were a single acid or base.

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[1] In this equation K_W is the ionization-constant of water, γ_B the ionization of the free NaOH, and C the concentration and γ the ionization of the salt in the solution.

[2] The contrary opinion expressed by Acree (*Am. Chem. J.*, 38, 35 (1907)) and his conclusion that the mass-action law would permit salts of tautomeric acids to exhibit "abnormal hydrolysis," even though equilibrium has been attained, seems to the writer clearly erroneous.

A satisfactory indicator must also fulfil the following conditions:

(*d*) The conversion of one tautomeric form into the other must take place almost instantaneously, for otherwise equilibrium will not be attained under the conditions of the titration.

(*e*) The color-change must be wholly due to the conversion of one tautomeric form into another; and it must moreover be determined only by the hydrogen-ion concentration, and not to an important extent by any other factor that may be involved, such as the presence of neutral salts in the solution.[1]

It is only to indicators which substantially fulfil these conditions that the principles presented in the following pages apply; and it is an important experimental problem to determine to what extent each special indicator conforms to these requirements.

3. *Equilibrium Relations of Indicators with Reference to the End-Point of Titrations.*—The end-point of a titration may be described as the condition attained when such quantities of base BOH and acid HA have been mixed that, as shown by the color-change, a definite fraction α of the indicator acid HIn is transformed into its salt BIn, or a definite fraction α of the salt InA of the indicator base is transformed into the free base InOH, the indicator transformation being for the sake of definiteness considered always to have taken place in the direction from acid to alkaline, in whichever direction the titration may actually have been made. For the ratio of the untransformed to the transformed fraction we then have, when the indicator is an acid,

$$\frac{1-\alpha}{\alpha} = \frac{(\mathrm{HIn})}{(\mathrm{In}^-) + (\mathrm{BIn})} = \frac{(\mathrm{HIn})}{(\mathrm{In}^-)/\gamma}, \qquad (6)$$

where γ represents the ionization of the indicator salt, which can be regarded as equal to the average value for other salts of the same (uni-univalent) type.

The ratio of the untransformed to the transformed fraction, when the indicator is a base, is:

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[1] Thus Michaelis and Rona (*Z. Elektrochem.*, 14, 251 (1908)) have shown that the color of Congo red is greatly influenced by neutral salts, especially by those with bivalent and trivalent metallic elements, owing to coagulation of the particles of the indicator. They also state that the colors of methyl violet and (to a less extent) of methyl orange and phenolphthalein are similarly affected by neutral salts, though it is not shown that the effect is here due to the same cause. Several investigators have shown also that a small proportion of alcohol has a relatively large effect in discharging the color of phenolphthalein (cf. Hillebrand, THIS JOURNAL, 30, 1914 (1908)). The researches of Acree (*Am. Chem. J.*, 39, 528 (1908)) and Wegscheider (*Z. Elektrochem.*, 18, 510 (1908)) upon phenolphthalein have shown, moreover, that the behavior of an indicator may be complicated by its acting as a dibasic acid (thus making possible its existence in any of the six forms H_2In, H_2In', HIn^-, HIn'^-, $In^=$, and $In'^=$).

$$\frac{1-\alpha}{\alpha} = \frac{(\mathrm{In}^+) + (\mathrm{InA})}{(\mathrm{InOH})} = \frac{(\mathrm{In}^+)/\gamma}{(\mathrm{InOH})}. \qquad (7)$$

We may eliminate from each of these equations the concentration-ratio in the last member by combining with it the first or second of the following ionization equations, which correspond to equations (4) and (5) considered in the last section:

$$\frac{(\mathrm{H}^+)(\mathrm{In}^-)}{(\mathrm{HIn})} = K_{\mathrm{IA}}. \qquad (8)$$

$$\frac{(\mathrm{OH}^-)(\mathrm{In}^+)}{(\mathrm{InOH})} = K_{\mathrm{IB}}. \qquad (9)$$

The combination of these equations with (6) and (7) evidently leads to the following results:

$$(\mathrm{H}^+) = \frac{(1-\alpha)K_{\mathrm{IA}}}{\alpha\gamma}; \text{ and} \qquad (10)$$

$$(\mathrm{OH}^-) = \frac{\alpha K_{\mathrm{IB}}}{(1-\alpha)\gamma}. \qquad (11)$$

If in the last equation we substitute for (OH⁻) the value of it given by the mass-action equation expressing the ionization of water,

$$(\mathrm{H}^+)(\mathrm{OH}^-) = K_{\mathrm{W}}, \qquad (12)$$

we get the following expression:

$$(\mathrm{H}^+) = \frac{(1-\alpha)\gamma K_{\mathrm{W}}}{\alpha K_{\mathrm{IB}}} \qquad (13)$$

Equations (10) and (13) are the fundamental equations upon which the theory of indicators is based. They express the principle that in any titration with a given indicator *the end-point* (determined so as to correspond to a definite color-change) *is reached when the hydrogen-ion concentration in the titrated solution attains a definite value*, and that the end-point is determined solely by that concentration. This definite value varies, however, with the ionization-constant of the indicator, and with the proportion of the indicator transformed.[1]

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[1] It follows from this principle that the ionization-constant of an indicator can be determined, as has been done by Friedenthal, Salessky, Fels, and Salm, by adding it to a series of solutions of decreasing hydrogen-ion concentration until the color-change shows that a definite fraction of it has been transformed. Conversely, the unknown hydrogen-ion concentration in any solution (for example, in that of a very weak acid or hydrolyzed salt) can be determined by adding to it a series of indicators of decreasing ionization-constants—a principle previously applied by Salm and others. This principle may be expected, on account of the ease with which the experiments can be made, to have many important technical applications, especially in cases where a small degree of acidity or alkalinity is to be approximately determined. In place of a series of indicators, the use of a single indicator (2,5-dinitrohydroquinone) which shows a series of markedly different colors in solutions varying in hydrogen-ion concentration by powers of 100 from 10^{-2} to 10^{-12} has recently been proposed by Hender-

It is evident from a comparison of equations (10) and (13), since the value of (H^+) determines the end-point, that a basic indicator of ionization-constant K_{IB} behaves exactly as if it were an acid indicator having an ionization-constant K'_{IA} equal to $\gamma^2 K_W/K_{IB}$. Although it is for this reason impossible to determine from its behavior upon titration whether a given indicator is an acid or base, yet for practical purposes all that is essential to know about a basic indicator is the value of the constant, which an acid indicator would have that showed a behavior identical with that of the basic indicator in question.

Mention may finally be made of the fact that the ratios K'_{IA}/γ and K_{IB}/γ that occur in equations (10) and (13) are equal to the ionization-constants that would be calculated if, disregarding the degree of ionization of the indicator salt, the color due to the latter were taken as a measure of the concentration of the indicator ion. That this is so becomes obvious upon dividing both members of equations (8) and (9) by γ. For the ratio K_{IA}/γ and for the ratio $\gamma K_W/K_{IB}$ will hereafter be written simply K_I, and this will be called the *apparent ionization-constant* of the indicator.

4. *Experiments Illustrating the Relation between the Color-Change of Indicators and the Hydrogen-Ion Concentration.*—The fundamental principle of the theory of indicators and the fact that the various indicators change color at different hydrogen-ion concentrations may be illustrated by the following experiments, which are described in a form adapted to lecture demonstration.[1]

Prepare one liter of each of nine solutions, whose hydrogen-ion concentration differs progressively by each power of 10 from 10^{-3} normal to 10^{-11} normal by proceeding as follows:

(H^+) = 10^{-3} to 10^{-5}: Make up for use in preparing these solutions 3 liters of 0.1 normal acetic acid (concentration to be accurate within 5 per cent.) by dissolving 18.0 g. glacial acetic acid in 3000 cc. distilled water.

(H^+) = 10^{-3}: Mix 570 cc. 0.1 normal acetic acid solution with 430 cc. water, yielding a 0.057 normal solution of the acid. For this case:

$(H^+)(Ac^-) = (H^+)^2 = K_A(HAc) = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-2})$; therefore $(H^+) = 10^{-3}$.

(H^+) = 10^{-4}: Dissolve 0.020 formula wt. sodium acetate, equal to 2.7 g. $NaC_2H_3O_2.3H_2O$, in one liter of 0.1 normal acetic acid. In this case:

$$(H^+) = K_A\frac{(HAc)}{(Ac)} = (1.8 \times 10^{-5})\frac{10^{-1}}{0.9 \times 2.0 \times 10^{-2}} = 10^{-4}.$$

(The 0.9 in the denominator represents the ionization of the sodium acetate.)

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son and Forbes (THIS JOURNAL, **32**, 687 (1910)). Attention may in passing also be called to the fact that for the case that $\alpha = {}^1/_2$, that is, that the indicator is half transformed, equations (10) and (13) assume the simple forms:

$$(H^+) = K_{IA}/\gamma \text{ and } (H^+) = \gamma K_W/K_{IB}.$$

[1] To Mr. B. H. St. John, who ably assisted me in working out these experiments, I desire to express my indebtedness.

$(H^+) = 10^{-5}$: Dissolve 0.11 formula wt. sodium acetate, equal to 15.0 g. $NaC_2H_3O_2.3H_2O$, in 500 cc. water, and add 500 cc. 0.1 normal acetic acid. In this case:

$$(H^+) = K_A\frac{(HAc)}{(Ac)} = (1.8 \times 10^{-5})\frac{5 \times 10^{-2}}{0.8 \times 0.11} = 10^{-5}.$$

$(H^+) = 10^{-6}$ to 10^{-11}: Make up 10 liters of a 0.1 formal[1] solution of $Na_2HPO_4.12H_2O$ by dissolving 358 grams of the crystallized salt in this quantity of water. (As the concentration of this solution should be known within about $^1/_2$ per cent., it is well as a control to evaporate a 100 cc. portion of it in a platinum dish and to ignite and weigh the residue of sodium pyrophosphate.) Prepare also a 0.1 normal solution of hydrochloric acid and one of sodium hydroxide (or some other strong base), and determine their concentrations within 0.3–0.5 per cent. By mixing the phosphate solution in appropriate proportion with the acid or base, we may prepare solutions of the desired hydrogen-ion concentration; for the added acid or base converts the hydrophosphate-ion ($HPO_4^=$) almost quantitatively into dihydrophosphate-ion ($H_2PO_4^-$) or into phosphate-ion ($PO_4^{\equiv}$); and the ratio which the concentration of these must bear to that of the hydrophosphate-ion in order to give the desired hydrogen-ion concentration can be readily calculated from the ionization-constants (K_2 and K_3) of the second and third hydrogens of phosphoric acid as determined by Abbott and Bray.[2] We have namely the relations:

$$\frac{(H_2PO_4^-)}{(HPO_4^=)} = \frac{(H^+)}{K_2} = \frac{(H^+)}{2.0 \times 10^{-7}}, \text{ and } \frac{(PO_4^{\equiv})}{(HPO_4^=)} = \frac{K_3}{(H^+)} = \frac{3.6 \times 10^{-13}}{(H^+)}.$$

Substituting the various values of (H^+) we may get the values of the first members of these equations, and from them by a simple transformation the values of the ratios given in the following table:

(H^+)	$\frac{(H_2PO_4^-)}{(H_2PO_4^-) + (HPO_4^=)}$	$\frac{(PO_4^{\equiv})}{(PO_4^{\equiv}) + (HPO_4^=)}$
10^{-6}	0.833 (0.850)	....
10^{-7}	0.333 (0.450)	....
10^{-8}	0.047 (0.050)	....
10^{-9}	0.005 (0.0)	....
10^{-10}	...	0.0036 (0.030)
10^{-11}	...	0.036 (0.140)

(The values within parentheses are those derived by Salm (*Z. physik. Chem.*, **57**, 480 (1907)) by an entirely different method, namely, by determining (H^+) by measuring the electromotive force of hydrogen gas cells containing the phosphate solutions as electrolytes.)

These ratios evidently represent the fraction of the hydrophosphate in the original solution which is to be transformed by the addition of the acid or base. Assuming the latter to have the same formal concentration as the phosphate solution, then the various standards may be made up by mixing the quantities of the solutions shown in the following table:

(H^+).	Na_2HPO_4 solution. cc.	HCl solution. cc.	NaOH solution. cc.
10^{-6}	600	500	..
10^{-7}	700	350	..
10^{-8}	1000	47	..
10^{-9}	1000	5	..
10^{-10}	1000	..	3.6
10^{-11}	1000	..	36

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[1] In accordance with the practice of this laboratory, a solution containing x formula weights of solute per liter is designated an x-formal solution.

[2] THIS JOURNAL, **31**, 760 (1909).

(The accuracy of the first of these standards is evidently especially sensitive to errors in the relative concentrations of the hydrophosphate and acid solutions, since so large a proportion of the former is converted into dihydrophosphate.)

Arrange 27 lecture jars or large lecture test tubes in three rows of nine, preferably upon a wooden stand covered with white cloth or paper and made in the form of three long narrow steps, so that each row will be visible above or below the other rows. Place 200 cc. of the $(H^+) = 10^{-3}$ solution in each of the jars at the left end of the three rows, 200 cc. of the $(H^+) = 10^{-4}$ solution in the three jars next to these, and so on till all the jars are charged with the nine standard solutions. Place cards with large figures —3, —4, —5, etc., pasted or marked upon them above each set of three jars.

Prepare in small 100 cc. bottles about 100 cc. of the following indicator solutions:

(*a*) 0.5 per cent. solution of thymolphthalein (TP) in alcohol.
(*b*) 0.5 per cent. solution of phenolphthalein (PP) in alcohol.
(*c*) 0.5 per cent. solution of rosolic acid (RA) in 50 per cent. alcohol.
(*d*) 0.1 per cent. solution of methyl red[1] (MR) in water.
(*e*) extract of cochineal (Coc) commonly employed in volumetric analysis.
(*f*) 0.1 per cent. solution of methyl orange (MO) in water.

Place in each of these indicator solutions a straight tube about 15 cm. long and 8 mm. in bore slightly constricted at its lower end.

When the demonstration is to be made, add by means of the straight tubes, capped temporarily with the finger, about 2 cc. of the appropriate indicator solutions to the various jars in the manner shown in the following table, where the letters represent the indicators to be added:

10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}
...	MR	MR	MR*	MR	TP	TP	TP	TP*
Coc	Coc	Coc*	Coc	...	PP	PP*	PP	PP
MO	MO*	MO	RA	RA*	RA	RA	...	...

The stars in the above table show the point at which the transition-color of the indicator is most marked.

5. *Discussion of the Indicator-Function.*—In the following discussion we will for the sake of brevity substitute for the cumbrous expressions for (H^+) given in equations (10) and (13) a single letter k. That is, we will put:

$$k = \frac{(1-\alpha)K_{IA}}{\alpha\,\gamma} = \frac{(1-\alpha)\gamma K_W}{\alpha K_{IB}} = \frac{1-\alpha}{\alpha} K_I. \qquad (14)$$

It is evident that k is a quantity that depends on the apparent ionization-constant of the indicator and on the proportion of it transformed in the titration. For brevity it will throughout this article be designated the *indicator-function.*[2]

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[1] A new, apparently very satisfactory indicator recently described by Rupp and Loose (*Ber.*, 41, 3905 (1908)) and readily prepared according to their directions. See also *C. A.*, 3, 523 (1909).

[2] In consequence of some complication, such, for example, as would arise if the indicator were a dibasic acid or if neutral salts influenced its ionization relations or its tautomeric equilibrium, the hydrogen-ion concentration may be some other function of the fraction transformed than that expressed by equations (10) and (13). In that case the true functional relation $(H^+) = f(\alpha)$ might be determined by experiment; and

The function k plays a most important part throughout the following considerations; and it will be seen later that when the titration is sensitive to errors, its accuracy is determined by the closeness with which a definite value of k can be realized. It is therefore well to consider in advance the practical conditions regulating the values of the two factors α and K_I which determine k and their bearing on the quantity of indicator that should be employed. It is evident that theoretically any desired value of k could be secured with any indicator of any ionization-constant K_I by giving α, the fraction of it transformed at the end-point, an appropriate value. To secure accuracy, however, α must be given (1) such a value that the eye can best recognize a small percentage change in its value, and (2) such a value that k will not be unnecessarily sensitive to the unavoidable error in so determining the end-point as to give the desired value of α.

The second of these conditions, which can be treated very simply in a mathematical way, may be first considered. By differentiating equation (14), and dividing the result by the original equation, we get:

$$\frac{dk}{k} = \frac{dK_I}{K_I} - \frac{d\alpha}{\alpha(1 - \alpha)}$$

This equation shows that any small fractional error in α (represented by $d\alpha/\alpha$) causes a fractional error in k (represented by dk/k) which is $1/(1-\alpha)$ times as large as that in α. The quantity $1/(1-\alpha)$, however, evidently approaches a minimum value of unity as α approaches zero. Yet, it is to be noted that $1/(1-\alpha)$ does not change very greatly until α assumes a fairly large value; thus for $\alpha = 25\%$, $1/(1 - \alpha)$ becomes only 1.33; so that any value of α up to say 25 per cent. is nearly as good as a much smaller value, so far as this effect is concerned. The conclusion to be drawn is, therefore, that α should always be given a fairly small value, which may, however, if other conditions require it, be made as large as 25 per cent.

If the indicator is being transformed in the other direction, by the addition of an acid rather than a base, and the color-change being observed is that corresponding to the form of the indicator whose proportion is represented by $(1 - \alpha)$, it also is true that the fraction of it *so* transformed must be relatively small. For the last term of the preceding equation can be written $+ \frac{1}{\alpha} \frac{d(1-\alpha)}{1-\alpha}$, from which it is evident that the multiplying factor $1/\alpha$ approaches a minimum value of unity as α approaches unity.

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if k were then understood to signify the value of that function in any given case, all the formulas derived in the following sections of this article would still be valid; for in the derivation of them k merely represents the value which (H^+) has at the end-point of the titration.

The other condition—that relating to the sensitiveness of the eye to the color-change—may be first considered for the case of one-color indicators, such as phenolphthalein, paranitrophenol, or cyanine, which are colorless in acid and colored in alkaline solution. Evidently in this case the definite depth of color, to a change in which the eye is most sensitive, may be attained by varying either the total concentration of the indicator (ΣIn) or the fraction (α) of it transformed, for the depth of color is proportional to the product $\alpha(\Sigma \text{In})$. Therefore by adding different quantities of indicator we can often vary α within fairly wide limits without sacrificing sensitiveness, and thereby attain even with a single indicator of constant K_{I} a fairly large variation in the value of k. Thus when the indicator is sufficiently soluble, it might well be practicable to vary α from 0.1 per cent. to 25 per cent.[1] which would correspond to a variation of k from 1000 K_{I} to $3K_{\text{I}}$. A minimum value for α is, however, often determined by the fact that the solubility of the indicator in water is not sufficient to allow the necessary depth of color to be secured without increasing α beyond that minimum value.[2] Thus, if I represents the value of the concentration α (ΣIn) of the transformed part of the indicator which gives the proper intensity of color, and if S is the solubility of the indicator (that is, the value of the concentration (ΣIn) in the saturated solution), the relation $\alpha > I/S$, and therefore also the relation $k < \frac{S - I}{I} K_{\text{I}}$, must evidently hold true.

In the case of a one-color indicator, the relation between depth of color, concentration of indicator, and fraction transformed can be experimentally determined by placing a measured quantity (1 to 5 cc.) of its solution in a graduate, adding 5 to 10 cc. of 0.1 normal alkali solution (whereby the indicator will be completely transformed) and enough water to make the volume 100 cc., and then diluting measured fractional

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[1] The upper value of α here mentioned is so chosen as to accord with the considerations of the preceding paragraphs. The lower value, though not necessarily the limit in all cases, could hardly ever be much further reduced without adding an extraordinary amount of the indicator.

For example, experiments that have been made with p-nitrophenol in the way described in the next paragraph show that, if 10 cc. of its saturated solution in water were added to 100 cc. of water, a depth of color sufficient to constitute a satisfactory end-point would be obtained by transforming 0.1 per cent. of the indicator into its salt.

[2] For example, experiments made with phenolphthalein have shown that when the solution to be titrated is saturated with it, about 4 per cent. of it must be transformed into its salt to give such a depth of color as would serve as a satisfactory end-point. This minimum value of α corresponds to a maximum value of k equal to 24 K_{I}. In the case of thymolphthalein, on the other hand, it was found that in an aqueous solution saturated with it a suitable color is obtained only when about $^1/_3$ of the indicator is transformed into its salt.

portions (say 10 cc. and 1 cc.) of this solution to 100 cc. The resulting color corresponds to that which the quantity of indicator taken at the start gives to 100 cc. liquid when the fraction of it transformed equals the fraction ($^1/_{10}$ and $^1/_{100}$) of the solution that was diluted. In this way the quantity of indicator that must be added to secure any desired fractional transformation and at the same time the desired depth of color can readily be determined.

In the case of two-color indicators, such as methyl orange, dimethylaminoazobenzene, methyl red, cochineal, and rosolic acid, the fraction transformed can not be similarly varied without a great sacrifice of sensitiveness; for, owing to the fact that the indicator has a color in the untransformed state, the fraction transformed must have a considerable value in order that its own color may be visible. What the best fraction to have transformed is, depends on the character and intensity of the two colors which the indicator exhibits; but ordinarily it is probably between 5 and 20 per cent.[1] The value of k practically attainable with a two-color indicator which is being transformed by passing from the acid to alkaline condition and which has an ionization-constant K_I is therefore ordinarily in the neighborhood of 10 K_I. On the other hand, if the color-change be determined in passing from the alkaline to the acid condition, and if say 9 per cent. of the indicator be transformed in this direction at the end-point (in which case $1 - \alpha = 0.09$ and $\alpha = 0.91$), the value of k becomes $^1/_{10}K_I$.

While a two-color indicator does not possess the same graded adaptability that a one-color indicator possesses, yet it will be seen from the illustration just given that the color-changes at both limits of its transformation may be utilized, provided the eye is sufficiently sensitive to both these changes.

In the case of a two-color indicator, the relation between color-change and fraction transformed can be experimentally studied by preparing a solution of the indicator of any appropriate concentration, dividing this into two parts, adding a small quantity of hydrochloric acid to one part and of sodium hydroxide to the other so as to transform it completely in one direction or the other, then superposing in suitable tubes or beakers a layer of one of these solutions above a layer of the other, and looking through the two layers. The relative thickness of the two layers, or the concentration of the one or the other solution, may then be varied, and the colors compared.

Summing up these considerations we may therefore say that we can

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[1] Experiments made by me with methyl orange have shown that a satisfactory change of color in the direction from yellow to orange is secured when from 5–20 per cent. (depending on the concentration) is transformed, but that in the direction from pink to orange from 20–30 per cent. must be transformed.

in general secure, in the case of one-color indicators (by using a suitably adjusted quantity of the indicator), and in the case of two-color indicators (by titrating in the one direction or the other), values of the indicator-function k which are given by the following expressions, in which K_{I} is the apparent ionization-constant of the indicator:

$$k > 3K_{\mathrm{I}} \text{ and } < \frac{S - I}{I} K_{\mathrm{I}} \text{ for one-color indicators of limited solubility } S. \quad (15a)$$

$$k > 3K_{\mathrm{I}} \text{ and } < 1000\,K_{\mathrm{I}}, \text{ for one-color indicators of sufficient solubility.} \quad (15b)$$

$$k = \text{approx. } 10\,K_{\mathrm{I}} \text{ or } = \text{approx. } {}^{1}/_{10}\,K_{\mathrm{I}}, \text{ for two-color indicators.} \quad (16)$$

It is to be understood, however, that these are only rough general estimates. It is therefore desirable to emphasize the importance of supplementing in any investigation of specific indicators the determination of their ionization-constants by an experimental study of the absolute concentration (I) which the colored form of the indicator must have in order to give a satisfactory color-intensity, of its solubility in water, and of the limits between which it is practicable to vary the fraction of it transformed. Only in this way will an exact application of the theory of indicators to volumetric analysis be made possible.

6. *Concentration of the Indicator.*—Besides these limitations in regard to the fraction of the indicator transformed, there is for an entirely different reason a maximum limit placed on the total normal concentration (ΣIn) of the indicator. Namely, it is evident that the concentration of the indicator salt in the solution titrated to the end-point must in general be negligibly small in comparison with the molal concentration (C) of the salt produced by the neutralization of the base BOH and the acid HA; since otherwise an appreciable excess of the base BOH, if the indicator is an acid, or of the acid HA if the indicator is a base, will be used up in combining with the indicator. Since the fraction of the indicator existing as its salt is α if the indicator is an acid, and is $1 - \alpha$ if the indicator is a base, this condition in regard to the concentration of the indicator may be expressed as follows, if we represent by ρ the maximum fractional error that is considered permissible in the titration:

$$(\Sigma\mathrm{In}) < \frac{\rho C}{\alpha} \text{ for an acid indicator.} \quad (17)$$

$$(\Sigma\mathrm{In}) < \frac{\rho C}{1 - \alpha} \text{ for a basic indicator.} \quad (18)$$

By these expressions the maximum quantity of indicator that may be added to a given volume of solution in any titration without introducing a fractional error greater than ρ may readily be calculated.[1]

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[1] Thus if an accuracy of 0.1 per cent. ($\rho = 10^{-3}$) is desired, if the indicator is an acid and the fraction of it transformed at the end-point is 10 per cent. ($\alpha = 10^{-1}$), and if the concentration of the salt in the titrated solution is 0.05 normal ($C = 5 \times 10^{-2}$),

II. Titration of Monobasic Acids and Monacidic Bases.

7. *General Formulation of the Theory.*—We may now proceed to the solution of our main problem, which consists primarily in deriving expressions for the difference between the quantity of the acid HA and that of the base BOH which have to be brought together in order that the end-point may be reached, confining ourselves in the first instance to the case where the acid is monobasic and the base monacidic. A general solution of this problem involves the treatment of combinations involving any acid of ionization-constant K_A, any base of ionization constant K_B, and any value of the indicator-function k.

The ionization-constants of the acid and base are expressed by the equations:

$$(B^+)(OH^-) = K_B(BOH). \tag{19}$$

$$(H+)(A-) = K_A(HA). \tag{20}$$

The ionization-constant of water (K_W) is also involved in the subsequent considerations, since it furnishes a relation between the concentrations (H^+) and (OH^-). It is expressed by equation (12) given above. Replacing (H^+) in this equation by k we get:

$$(OH^-) = K_W/k. \tag{21}$$

It is to be noted that K_W has an extremely small value; namely, about 10^{-15} at 0°, 10^{-14} at 25°, 10^{-13} at 65°, and 5×10^{-13} at 100°.[1]

Let now the total concentration of the acid-constituent A in the solution titrated to the end-point be (ΣA) and that of the base-constituent B in that solution be (ΣB).[2]

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the concentration of the indicator must be less than 5×10^{-4} normal or 1/2000 normal; and if the volume of the titrated solution is 100 cc., less than 1/20,000 of a formula weight of indicator must be added to it.

That the concentration of the indicator is in practice ordinarily less than 1/2000 normal will be seen from the following facts: Solutions of indicators are usually prepared so as to contain 1 to 5 grams of the indicator per liter. This latter value corresponds to 0.016 of a formula weight per liter (assuming the average formula weight to be 300). Of such solutions less than 1.0 cc. is commonly added to say 80 cc. of the titrated solution. This makes the concentration of the indicator in the latter less than 0.0002 formal.

[1] The values of this constant at 0 and 25° given by Kanolt (THIS JOURNAL, **29**, 1414 (1907)) are somewhat lower, namely, 0.88×10^{-15} at 0° and 0.81×10^{-14} at 25°. Other investigators have, however, found higher values; thus Heydweiller (*Ann. Phys.*, [4] **28**, 512 (1909)) through a recalculation of the experiments made by him and Kohlrausch obtained 1.16×10^{-15} at 0° and 1.04×10^{-14} at 25° and Lundén (*Meddel. fr. k. sv. vet. Nobelinstitut*, Vol. 1, No. 8, p. 16 (1907)) found 1.05×10^{-14} at the latter temperature. Whatever may be the correct result, the round values are sufficiently accurate for the purposes of this investigation.

[2] The products obtained by multiplying these concentrations by the volume of the titrated solution represent evidently the quantities of the acid HA and base BOH which have been mixed in order to reach the end-point; and the ratio of these concentrations to each other represents the ratio of the said quantities to each other (provided no salt of the acid or base was originally present in either solution).

The different forms in which these two constituents exist in the solution are shown by the following equations which sum up the concentrations of those various forms:

$$(\Sigma B) = (B^+) + (BOH) + (BA). \tag{22}$$

$$(\Sigma A) = (A^-) + (HA) + (BA). \tag{23}$$

We have also a further relation expressing the equality of the sums of the concentrations of all the positive and of all the negative ions in the solution, as follows:

$$(B^+) + (H^+) = (A^-) + (OH^-). \tag{24}$$

It is to be noted that the quantities (H^+) and (OH^-) in a titrated solution are always small in comparison with the quantities (B^+) and (A^-). It is not, however, permissible to cancel them from this equation, since the difference $(B^+) — (A^-)$ is involved in the following derivation. In cases, however, where the value of (B^+) or (A^-) itself, and not their difference, is involved, no serious error will be made by assuming that (B^+) and (A^-) are equal.

8. *The Error in the Titration.*—In order to obtain an expression for the fractional error in the titration we may proceed as follows. We first subtract equation (23) from (22), whereby we obtain:

$$(\Sigma B) - (\Sigma A) = (B^+) - (A^-) + (BOH) - (HA). \tag{25}$$

We then substitute in this equation the value of $(B^+) — (A^-)$ given by equation (24), whereby we get:

$$(\Sigma B) - (\Sigma A) = (BOH) - (HA) + (OH^-) - (H^+). \tag{26}$$

Substituting the values of (BOH) and (HA) given by equations (19) and (20), we get:

$$(\Sigma B) - (\Sigma A) = \frac{(B^+)(OH^-)}{K_B} - \frac{(H^+)(A^-)}{K_A} + (OH^-) - (H^+).$$

Replacing in this equation (H^+) by k and (OH^-) by K_w/k, and putting $(B^+) = (A^-)$, which as stated above is justifiable so long as the difference between them is not involved, we get:

$$\frac{\Sigma B - \Sigma A}{(B^+) \text{ or } (A^-)} = \frac{K_w}{kK_B} - \frac{k}{K_A} + \frac{K_w}{k(B^+)} - \frac{k}{(A^-)}. \tag{27}$$

For the quantity (B^+) or (A^-) in equation (27) expressions in terms of (ΣB) or (ΣA) may be obtained from equations (22) and (23) by substituting for (BOH) and (HA) the same values that were introduced into equation (26) and by substituting for $(BA)/(B^+)$ the quantity $(1 - \gamma)/\gamma$, where γ evidently represents the ionization of the salt BA in the titrated solution. The so-obtained expressions for (B^+) and for (A^-) are:

$$(B^+) = \frac{(\Sigma B)}{\frac{1}{\gamma} + \frac{K_W}{kK_B}} \quad (28); \qquad \text{and } (A^-) = \frac{(\Sigma A)}{\frac{1}{\gamma} + \frac{k}{K_A}}. \quad (29)$$

By introducing these values into equation (27), an exact expression applicable to any combination of base and acid can be obtained.

The practically important cases are, however, those in which either the base or the acid is largely ionized, since such a base or acid is almost invariably employed as a standard solution in the titration. It is therefore worthy of note that in the expression for (B^+) the last term in the denominator, which is equal to the concentration ratio $(BOH)/(B^+)$, is negligible in comparison with the first term when K_B is even moderately large; and that in the expression for (A^-) the last term in the denominator, which is equal to the concentration-ratio $(HA)/(A^-)$, is negligible when K_A is even moderately large.[1] Taking into account these facts, we may write equation (27) in the following substantially exact form, applicable according as (ΣB) or (ΣA) is written in the denominator to the case where the base or the acid is largely ionized:

$$\frac{(\Sigma B) - (\Sigma A)}{(\Sigma B) \text{ or } (\Sigma A)} = \gamma\left(\frac{K_W}{kK_B} - \frac{k}{K_A} + \frac{K_W}{k\gamma(\Sigma B)} - \frac{k}{\gamma(\Sigma A)}\right). \quad (30)$$

This equation also gives approximate results, which are, however, sufficiently accurate for almost all purposes, when applied to the case in which the base and acid are both slightly ionized; for the error in this case is only that arising from neglecting the last term in the denominator of (28) or (29), and this will not give rise to an error in the first member of (30) of more than 1 or 2 per cent. for any combination for which even a very rough titration is possible. Equation (30) will therefore serve as a general basis for the following discussion of the accuracy of the titration and of the conditions determining it.

It will be noted that the first member, which expresses the difference between the concentrations of the basic and acid radicals divided by the concentration of the one or other of these, really represents the fractional error (FE) in the titration in the common case in which the acid and base titrated against each other are the only source of those radicals. That error can therefore be calculated for any combination of indicator, acid, and base by equation (30) or still better by the following, more perspicuous equation,[2] which is obtained from it by a simple transformation and by

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[1] Thus, if K_W/k in (28) or k in (29) has a value even as large as 10^{-4}, the last term will be entirely negligible when K_B or $K_A > 10^{-2}$. For the strongest bases like potassium hydroxide or the strongest acids like hydrochloric or nitric acid, the value of K_B or K_A at 0.1 normal is about 1, while for barium hydroxide it is about 0.3 and for the second hydrogen of sulphuric acid about 0.03.

[2] Consider, for example, the case where 0.1 normal ammonium hydroxide is titrated at 25° with 0.1 normal hydrochloric acid, using phenolphthalein as an indica-

the substitution of C, representing the normal concentration of the salt in the titrated solution, for (ΣB) and for (ΣA), which are obviously approximately equal to it and to each other so long as $\overline{FE}$ is even moderately small.

$$\overline{FE} = \frac{\gamma K_w}{kK_B}(1 + K_B/\gamma C) - \frac{\gamma k}{K_A}(1 + K_A/\gamma C). \qquad (31)$$

Of the quantities occurring in this equation it is to be noted that the ionization γ has nearly the same value at the same concentration for all salts of monobasic acids and monacidic bases, the average value for uniunivalent salts at various concentrations at 20° being approximately as follows:

Normal concentration......	0.50	0.20	0.10	0.05	0.02	0.01
Ionization (γ)............,	0.70	0.78	0.83	0.86	0.91	0.93

If the intermediate value 0.80 be employed, the result will be sufficiently accurate in almost all cases.

It may also be mentioned that all of the most completely ionized monacidic bases and monobasic acids (such as sodium and potassium hydroxides and hydrochloric and nitric acids) have an ionization at room temperature in 0.1 normal solution which corresponds to a ionization-constant of about unity.[1] The corresponding values of the parentheses $(1 + K_B/\gamma C)$ or $(1 + K_A/\gamma C)$ when K_B or $K_A = 1$ are 24 for $C = 0.05$, and 4.0 for $C = 0.5$. These are evidently the maximum values for these parentheses, since their values approach unity as K_B or K_A decreases.

9. *Error in the Titration when a Neutral Salt is Originally Present.*—Equation (30) is also applicable to the not uncommon case in which there

tor (for which $K_I = 2 \times 10^{-10}$), the indicator being at the end-point 10 per cent. transformed. In this case:

$$k = \frac{K_I(1-\alpha)}{\alpha} = \frac{2 \times 10^{-10} \times 0.90}{0.10} = 2 \times 10^{-9};\ \gamma = 0.86;\ C = 0.05;\ K_A = 1;$$

and $K_B = 1.8 \times 10^{-5}$.

Substituting the appropriate numerical values in equation (31) we get:

$$\overline{FE} = \frac{0.86 \times 10^{-14} \times 1}{(2 \times 10^{-9})(1.8 \times 10^{-5})} - \frac{0.86(2 \times 10^{-9})(1 + 1/0.043)}{1.0} = 0.24 = 24\%.$$

That is to say, an error of 24 per cent. will be made in the titration.

Suppose now that the same titration be made, using p-nitrophenol as indicator (for which $K_I = 9 \times 10^{-8}$), and causing it to be one per cent. transformed. Equation (31) then becomes:

$$\overline{FE} = \frac{0.86 \times 10^{-14} \times 1}{(9 \times 10^{-6})(1.8 \times 10^{-5})} - \frac{0.86(9 \times 10^{-6})(1 + 1/0.043)}{1.0} = 0.0005 = 0.05\%.$$

[1] The constant unity corresponds to an ionization-value 0.916 at 0.1 normal, while the ionization values at 18° derived from the conductivity measurements made in this laboratory are 0.926 for HCl, 0.918 for HNO_3, 0.902 for NaOH. Even if, as suggested by Noyes and Kato (THIS JOURNAL, 30, 334 (1908)), the ionization of these acids is as small as that of potassium chloride (86.0 per cent. at 0.1 normal), the ionization-constant would be of the same general magnitude; namely, 0.53 instead of 1.0.

is present in the original solution, together with the acid HA or base BOH which is to be titrated, some of the neutral salt BA. This is true since this equation expresses the equilibrium conditions prevailing in the solution in which the end-point has been reached, and since it evidently makes no difference whether all of the salt was produced by the titration or whether some of it was originally present. It is evident, however, that in the latter case equation (30) does not express the fractional error in the titration of the free acid or base, since the difference between the concentrations of the basic and acid constituents must then be referred, not to the total concentration (ΣB) or (ΣA) of either of them, which is substantially equal to the concentration C of the salt in the titrated solution, but to the concentration $C - C_0$ which has been produced in that solution through the addition of the standard base or acid (C_0 therefore corresponding to the quantity of salt originally present). We have therefore for the fractional error $\overline{FE}'$ in the titration in this case:

$$\overline{FE}' = \frac{(\Sigma B) - (\Sigma A)}{C - C_0} = \left(\frac{(\Sigma B) \text{ or } (\Sigma A)}{C - C_0}\right)\left(\frac{(\Sigma B) - (\Sigma A)}{(\Sigma B) \text{ or } (\Sigma A)}\right),$$

$$\text{or } \overline{FE}' = \frac{C}{C - C_0}\,\overline{FE}, \qquad (32)$$

the value of the last parenthesis or of $\overline{FE}$ being that expressed by equation (30) or (31).

The fractional error in the case where a neutral salt of the acid and base involved in the titration is originally present is therefore greater in the proportion which the sum of the quantity of that salt and of the quantity of acid or base used in the titration bears to the latter quantity.

It can furthermore be shown, by formulating the condition equations as in section 7, that the fractional error in the titration can be correctly calculated by equation (32) also in the following cases:

(*a*) When a not largely ionized acid HA is titrated with a largely ionized base BOH, and a neutral salt B′A of another largely ionized base B′OH is originally present.

(*b*) When a not largely ionized base BOH is titrated with a largely ionized acid HA, and a neutral salt BA′ of another largely ionized acid HA′ is originally present.

10. *The Best Value of the Indicator-Function.*—Equation (31) may be employed to determine what the value of the indicator-function is which will give the best result in titrating an acid of known ionization-constant K_A with a base of known ionization-constant K_B, when the titrated solution has a given concentration C. To determine this, we need only place FE equal to zero and solve for k. We thus obtain the following expression, in which this "best value" of k is represented by k_0:

$$k_0 = \left(\frac{K_W(1 + K_B/\gamma C)}{K_B}\right)^{\frac{1}{2}} \left(\frac{K_A}{1 + K_A/\gamma C}\right)^{\frac{1}{2}} = \sqrt{\left(\frac{K_W K_A}{K_B}\right)\left(\frac{1 + K_B/\gamma C}{1 + K_A/\gamma C}\right)}. \qquad (33)$$

It is evident from equation (33) that the best value of the indicator-function is equal to the square-root of the ionization-constant of water when the ionization-constants of the base and acid are equal, and that it is smaller than this when the acid is slightly ionized and larger when the base is slightly ionized. The best value can, of course, be exactly calculated for any given case.[1]

11. *Limiting Values of the Indicator-Function.*—It is evident from equation (33) that for any combination of acid or base whatever there is a value of the indicator-function which would theoretically make possible an exact titration. Yet it is a well-known fact that, if either the acid or base has too small an ionization-constant, accurate results can not in practice be obtained. This arises from the impossibility of realizing in the titration a value of the indicator-function identical with the best value, and from the sensitiveness of the titration in certain cases to the deviation of the actual value k from the best value k_0. What the realization of the desired value of the indicator-function involves will be seen by considering the following expression for the ratio k_0/k, which may be obtained by combining equations (33) and (14):

$$\frac{k_0}{k} = \frac{(K_W K_A/K_B)^{\frac{1}{2}}}{K_I(1 - \alpha)/\alpha} \left(\frac{1 + K_B/\gamma C}{1 + K_A/\gamma C}\right)^{\frac{1}{2}}. \qquad (34)$$

In order to make this expression as nearly as possible equal to zero, one would in practice first select an indicator with such an ionization-constant K_I that k_0/k can become zero when a practicable fraction of the indicator is transformed, then would calculate by (34) just what the fraction transformed α should be to make k_0/k equal to unity, and finally would attempt to realize in the titration this fraction transformed by comparison with a standard color so prepared as to correspond to it (see Section 5). It will be seen that there are two errors involved in this process; first, the error in the calculation of α arising from the errors in the assumed values of the various ionization-constants, of which errors that in K_I is likely with our present knowledge to be the largest; and second, the error in the experimental determination of α arising from the failure to titrate to the depth or shade of color which corresponds to the proper fraction transformed. For these reasons the ratio k_0/k will inevitably vary from

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[1] For example, suppose NH_4OH ($K_B = 1.8 \times 10^{-5}$) is to be titrated at 25° ($K_W = 10^{-14}$) with HCl ($K_A = 1$), the titrated solution of the salt being 0.05 normal ($C = 0.05$) and its ionization γ being 0.86. We then have:

$$k_0^2 = \frac{10^{-14} \times 1}{1.8 \times 10^{-5}} \times \frac{1}{24}; \text{ whence } k_0 = 4.8 \times 10^{-6}.$$

unity by a considerable amount; and it is therefore important to consider the conditions which determine the sensitiveness of the titration to this variation.

The practical problem may be concretely stated as follows: to determine how much the actual value of the indicator-function k may vary from the best value k_0 without causing a fractional error $\overline{FE}$ in the titration greater than the accuracy which is aimed at. To solve this problem we may multiply each of the terms of the second member of equation (31) by k_0/k_0, substitute in the denominator of the first and in the numerator of the second term the value of k_0 given by equation (33), and transform, whereby we get:

$$\overline{FE} = \gamma\left(\frac{k_0}{k} - \frac{k}{k_0}\right)\left(\frac{K_W}{K_A K_B}\right)^{\frac{1}{2}}\left(1 + \frac{K_B}{\gamma C}\right)^{\frac{1}{2}}\left(1 + \frac{K_A}{\gamma C}\right)^{\frac{1}{2}}. \qquad (35)$$

It is obvious that in equation (35) the value of the first parenthesis, which is nearly identical with k_0/k or k/k_0 when this is greater than (say) 3, must evidently for a given value of $\overline{FE}$ be smaller, the larger the values of the other three parentheses. The last two of these do not, however, vary very greatly from unity; thus in the rather extreme case in which K_B or $K_A = 1$ and $C = 0.05$, one or other of these factors has the value 4.9. It is therefore the very variable second factor $(K_W/K_A K_B)^{1/2}$ that mainly determines how large the arithmetical value of k_0/k or k/k_0 may be without causing the fractional error in the titration to exceed any given value. It is evident now that this factor increases as the product $(K_A K_B)$ of the ionization-constants of the acid and base decreases, and assumes a considerable magnitude only when the value of this product approaches that of the ionization-constant of the water. The percentage error in the titration therefore increases under the same conditions.[1]

The maximum value, which k_0/k or k/k_0 may be allowed to assume when a definite fractional accuracy ρ is desired in the titration, may be calculated for various values of $K_W/K_A K_B$, by substituting, in equation (35) for $\overline{FE}$ the given value of ρ and for $K_B/\gamma C$ and $K_A/\gamma C$ in the last two factors, the values which they have in the titration under consideration.

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[1] Compare, for example, the values of the percentage error (100 $\overline{FE}$) given in the last column of the following table for various combinations of acids and bases. In the calculations of these quantities by (35) it is assumed that $K_W = 10^{-14}$ as it is at 25°, that $C = 0.05$, that $\gamma = 0.86$, and that k_0/k or $k/k_0 = 5$, which is about as small a value as can be realized in practice without taking unusual precautions.

Acid.	Base.	K_A.	K_B.	$(K_W/K_A K_B)^{\frac{1}{2}}$.	100 $\overline{FE}$.
HCl	KOH	1	1	10^{-7}	0.001
$HC_2H_3O_2$	KOH	2×10^{-5}	1	2×10^{-5}	0.05
HCl	NH_4OH	1	2×10^{-5}	2×10^{-5}	0.05
HBO_2	KOH	7×10^{-10}	1	4×10^{-3}	9.0
$HC_2H_3O_2$	NH_4OH	2×10^{-5}	2×10^{-5}	5×10^{-3}	2.3

Such a calculation has been made under the assumption that $\rho = 0.1\ \%$ $= 0.001$, for the three following, practically limiting cases:

(1) K_B or $K_A = 1$ and $\gamma C = 0.86 \times 0.05 = 0.043$.
(2) K_B or $K_A = 1$ and $\gamma C = 0.70 \times 0.5 = 0.35$.
(3) $K_B/\gamma C$ and $K_A/\gamma C$ are negligible (less than 0.2).

The results of these calculations are given in the following table, the columns marked (1), (2), and (3) corresponding to the three cases just considered.[1]

TABLE I.—MAXIMUM VALUES OF THE RATIO BETWEEN THE ACTUAL AND BEST VALUES OF THE INDICATOR-FUNCTION FOR AN ACCURACY IN THE TITRATION OF 0.1 PER CENT.

$\frac{K_W}{K_AK_B}$.	K_AK_B at 25°.	Maximum value of k_0/k or k/k_0.			$\frac{K_W}{K_AK_B}$.	K_AK_B at 25°.	Maximum value of k_0/k or k/k_0.		
		(1)	(2)	(3)			(1)	(2)	(3)
10^{-12}	10^{-2}	214	720	..	10^{-7}	10^{-7}	1.44	2.7	4.2
10^{-11}	10^{-3}	74	230	..	10^{-6}	10^{-8}	1.13	1.43	1.8
10^{-10}	10^{-4}	24	73	..	10^{-5}	10^{-9}	1.04	1.12	1.22
10^{-9}	10^{-5}	7.6	23	40	10^{-4}	10^{-10}	1.011	1.04	1.06
10^{-8}	10^{-6}	2.7	7.4	13	10^{-3}	10^{-11}	1.004	1.01	1.02

These maximum values are valid for the case that the accuracy desired is 0.1 per cent. The table will hold true for an accuracy of about 1/3 per cent. if each value of K_w/K_AK_B be multiplied by 10, and it will hold true for an accuracy of 1 per cent. if each value of K_w/K_AK_B be multiplied by 100; and if correspondingly each value of K_AK_B at 25° be divided by 10 or 100.[2]

Attention may also be called to the fact that, since K_w increases rapidly with rising temperature, the maximum value of k_0/k or k/k_0 admissible when a given percentage accuracy is desired is for a given value of K_AK_B larger at lower than at higher temperatures. Thus the values of k_0/k or k/k_0 given in Table I correspond to values of K_AK_B one-tenth as large at 0° and ten times as large at 65° as the values of K_AK_B given in the same row in the table for 25° (since $K_w = 10^{-15}$ at 0° and $= 10^{-13}$ at 65°). Since K_A and K_B for weak acids and bases commonly change with the temperature in a direction opposite to that in which K_w changes (or, since when K_A and K_B change in the same direction they change in a smaller proportion than K_w), it is almost always true that greater accuracy will be secured with any combination of acid, base, and indicator that is sensitive to error by titrating at as low a temperature as possible.[3]

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[1] In these three cases γ was taken as 0.86, 0.70, and 0.80, respectively.

[2] It will be shown later that this table is also applicable to titrations in which a diacidic base or dibasic acid is involved, provided K_W/K_AK_B be replaced by an appropriate function of the ionization-constants.

[3] Exceptions to this statement may occasionally arise from an entirely different cause—namely, from the fact that the equilibrium of the indicator acid or base with its salt is too slowly established at the lower temperature, owing to a very slow rate of transformation of the two isomeric forms of the indicator into each other.

Certain other practical conclusions that may be drawn from Table 1 and equation (35) may be pointed out. A comparison of columns (1) and (2) shows that the titration is more sensitive to variations in the value of k, the more dilute the solution. It is therefore desirable to titrate in as strong a solution as possible, whenever the conditions are such that an error is likely to arise.

It will also be seen from the table that, as the product $K_A K_B$ decreases in value, greater care must be taken to approximate to the best value of the indicator-function by selecting a suitable indicator of known ionization-constant, using a measured quantity of it, and titrating to a standard color corresponding to the appropriate fraction transformed.

Another, more direct, method of treating the problem of determining the limits between which the indicator-function k may vary when a certain accuracy in the titration is desired is as follows. Representing the limits between which the fractional error permissible in the titration lies by ρ and $-\rho$, substituting $\pm\rho$ for $\overline{\text{FE}}$ in equation (31), and transforming, we get:

$$\frac{K_W K_A}{K_B}\left(\frac{1 + K_B/\gamma C}{1 + K_A/\gamma C}\right) = k^2 \pm \frac{\rho K_A}{\gamma(1 + K_A/\gamma C)}\, k.$$

Adding $\dfrac{\rho^2 K_A^2}{4\gamma^2(1 + K_A/\gamma C)^2}$ to both members to complete the square in the second member, taking the square-root of both members, and transforming, we get the following exact expression:

$$k\begin{smallmatrix}(\text{Max.})\\(\text{Min.})\end{smallmatrix} = \frac{\rho K_A}{2\gamma(1 + K_A/\gamma C)} \times$$

$$\left(\pm 1 + \sqrt{1 + \frac{4\gamma^2}{\rho^2}\,\frac{K_W}{K_A K_B}\,(1 + K_A/\gamma C)(1 + K_B/\gamma C)}\right). \quad (36)$$

The second term under the square-root sign is considerably smaller than unity in any case in which the titration is practicable. Thus it may be seen from column (1) of Table 1, when $\rho = 0.001$, $C = 0.05$, and K_A or $K_B = 1$, and k_0/k or $k/k_0 > 2.7$, that $K_W/K_A K_B$ must be less than 10^{-8}; under these circumstances, however, the value of the second term in question is less than 0.72. In this case (where $K_W/K_A K_B < 10^{-8}$) it can readily be shown that expression (36) reduces to the following approximate, but sufficiently accurate forms:[1]

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[1] This follows from the fact that $(1 + x)^{\frac{1}{2}}$ = approx. $(1 + {}^1/_2 x)$, when x is small. The whole parenthesis in (36) then has a maximum value of $1 + 1 + \frac{1}{2}x$ = approx. 2, and a minimum value of approx. $-1 + 1 + \frac{1}{2}x$ = approx. $\frac{1}{2}x$, where x represents the second term under the square-root sign. Even in the limiting case where $x = 0.72$ the error in the maximum and minimum values of k when calculated by the approximate expressions (37) and (38) would be only 13 and 16 per cent. respectively.

$$k < \frac{\rho K_A}{\gamma(1 + K_A/\gamma C)}. \qquad (37)$$

$$k > \frac{\gamma K_W(1 + K_B/\gamma C)}{\rho K_B}. \qquad (38)$$

By means of these expressions the limits between which k must lie in order to give any desired accuracy ρ can evidently be calculated for any given values of K_W, K_A, K_B, and C.[1]

Expressions (37) and (38) show that the lower limit for k is determined by the ionization constant (K_B) of the base, and the upper limit by the ionization-constant (K_A) for the acid.

It is also worthy of note that, since the maximum value of K_B or K_A possessed by any base or acid is unity, since the concentration of the titrated solution can hardly in practice be made greater than 0.5 normal, and since an accuracy at least as great as 1/3 per cent. is almost always essential, the indicator-function k must at 25° under all circumstances have a value lying between the limits of 10^{-3} and 10^{-11}, and the ionization-constant of the indicator must have such a value as will make this possible.

In the important case in which K_A or K_B is even moderately small, say less than 0.1 C, the corresponding expression (37) or (38) remains sufficiently accurate for practical purposes, when written in the still simpler, easily remembered form:

$$k < \rho K_A; \text{ or } k > \frac{K_W}{\rho K_B}. \qquad (39)$$

That is, in titrating any not largely ionized acid, the value of the indicator-function must be less than the product of the ionization-constant of the acid by the fractional error permissible in the titration; and in titrating any not largely ionized base, the value of the indicator-function must be greater than the ratio of the ionization-constant of water to the product of the ionization-constant of the base by the fractional error permissible in the titration.

12. *Limits beyond which the Titration is Impracticable.*—Considered from the converse point of view, equation (35) may be utilized to furnish an estimate of the minimum values below which the ionization-constants of the acid and base may not fall if the error in the titration is to be less than any assigned value ρ. For if we represent by β the smallest value

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[1] As an example, consider first that acetic acid ($K_A = 1.8 \times 10^{-5}$) is to be titrated with potassium hydroxide ($K_B = 1$) at 25° ($K_W = 10^{-14}$) with an accuracy of 0.1 per cent. ($\rho = 0.001$), the resulting salt solution being 0.05 normal ($C = 0.05$ and $\gamma = 0.86$). By substituting these values in (37) and (38) we get:

$$k < 2.1 \times 10^{-8}, \text{ and } k > 2.1 \times 10^{-10}.$$

Consider secondly that ammonium hydroxide ($K_B = 1.8 \times 10^{-5}$) is to be titrated with hydrochloric acid ($K_A = 1$) under the same conditions. We then find:

$$k < 4.8 \times 10^{-5}, \text{ and } k > 4.8 \times 10^{-7}.$$

of $(k_0/k - k/k_0)$ that one can hope to realize in practice, even when reasonable care is taken in choosing a suitable indicator and in securing the proper fraction transformed, equation (35) may be replaced by the following expression:

$$\frac{K_W}{K_A K_B}\gamma^2(1 + K_A/\gamma C)(1 + K_B/\gamma C) < \frac{\rho^2}{\beta^2}. \qquad (40)$$

Since one can hardly count on making k_0/k or k/k_0 less than 3.5,[1] and since in this case $\beta^2 = 10$, we may conclude that the first member of the preceding inequality must always be less than $^1/_{10}\,\rho^2$; that is, less than 10^{-7} for $\rho = {}^1/_{10}$ per cent., less than 10^{-6} for $\rho = {}^1/_3$ per cent., and less than 10^{-5} for $\rho = 1$ per cent. If, furthermore, either the acid or base is nearly completely ionized (K_A or $K_B = 1$) and the concentration C of the titrated solution is not greatly different from 0.1 normal, we may assign the medium value 10 to the product of the last three factors in the first member of (40), and write the inequality in the simple form:

$$\frac{K_W}{K_A K_B} < \frac{1}{100}\rho^2.$$

From this it follows that at 25°, where $K_W = 10^{-14}$, the product $K_A K_B$ must not have a smaller value than 10^{-6}, 10^{-7}, or 10^{-8} if an accuracy of $^1/_{10}$, $^1/_3$, or 1 per cent., respectively, is to be secured. These values therefore represent the practical limits below which the ionization-constant (K_A or K_B) of an acid or base may not fall if it is to be titrated at 25° with the stated accuracy, even with one of the most largely ionized bases or acids, such as sodium hydroxide or hydrochloric acid (for which K_B or K_A = approx. 1).

III. Titration of Two Monobasic Acids or of Two Monacidic Bases in the Presence of Each Other.

13. *Separate Titration of the More Ionized Acid.*—A special case that occurs not infrequently in practice is the titration of an acid HA in the presence of another, much less ionized acid HA′, or of a base BOH in the presence of another, much less ionized base B′OH. It is therefore of interest to determine the conditions under which such a titration can be

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[1] That this is a reasonable estimate will be seen from the following considerations. It has already been pointed out in discussing equation (34) that the deviation of k_0/k or k/k_0 from unity is likely to arise mainly from the error in the value of K_I assumed in the calculation of the best value of α, and from the error in the experimental realiza- f the so-calculated value of α. Now there are probably few indicators for which now the ionization-constant more closely than within one-half or twice its true ue; and without taking unusual care in the titration to match the color of the indicator with a standard we can hardly realize any desired value of $(1 - \alpha)/\alpha$ nearer than within one-half or twice that value: and from the combination of these two errors a value of k_0/k or k/k_0 as large as 3.5 is not unlikely to arise. This becomes even more probable when the error likely to be involved in the ionization-constants of very weak bases or acids is also considered.

made without incurring a fractional error greater than any assigned value, especially for the case where a nearly completely ionized base BOH or acid HA is employed as the standard solution.

A general expression for the fractional error analogous to (31) can be readily derived for the case of the two acids in an entirely similar manner, as follows.

It will be noted that the following condition equations corresponding to (22), (23) and (24) hold true in this case:

$$(\Sigma B) = (B^+) + (BOH) + (BA) + (BA'). \qquad (41)$$

$$(\Sigma A) = (A^-) + (HA) + (BA). \qquad (42)$$

$$(B^+) + (H^+) = (A^-) + (A'^-) + (OH^-). \qquad (43)$$

Combining these equations, we get:

$$(\Sigma B) - (\Sigma A) = (BOH) - (HA) + (A'^-) + (BA') + (OH^-) - (H^+). \quad (44)$$

In this case we have to consider also the additional equilibrium equation:

$$(H^+)\,(A'^-) = K_{A'}(HA'). \qquad (45)$$

Since we may without serious error put (HA') = (ΣA') or = C' when only an inconsiderable proportion of the acid HA' is converted into its salt, (45) may be written also in the form:

$$(A'^-) = C'K_{A'}/k. \qquad (46)$$

Dividing both members of (44) by (ΣB), substituting $(A'^-)/\gamma$ for $(A'^-) + (BA')$, eliminating (A'^-) by means of (46), writing C for (ΣB) and (ΣA), expressing the other quantities as before in terms of the appropriate constants, and transforming, we get:

$$\overline{\text{FE}} = \frac{(\Sigma B) - (\Sigma A)}{(\Sigma B)} = \frac{\gamma K_W(1 + K_B/\gamma C)}{kK_B} + \frac{C'K_{A'}}{\gamma\, Ck} - \frac{\gamma k(1 + K_A/\gamma C)}{K_A}. \qquad (47)$$

It will be seen that this equation differs from (31) only in the respect that it contains the additional term $+ C'K_{A'}/\gamma Ck$. (In this term C'/C is equal to the ratio of the quantities of two acids HA' and HA originally present, and $K_{A'}$ is the ionization-constant of the acid HA'.)

Exact expressions for the best value and the limiting values of the indicator-function can therefore be written down simply by replacing in expressions (33) to (40) the quantity

$$\frac{\gamma K_W(1 + K_B/\gamma C)}{K_B} \text{ by } \frac{C'K_{A'}}{\gamma C} + \frac{\gamma K_W(1 + K_B/\gamma C)}{K_B}.$$

Instead of reproducing these somewhat complex exact expressions here, the simpler approximate expressions may be considered that are applicable: first, to the case where the first term in the last expression is smaller than one-tenth of the second term; and second, to the case where the first term is larger than the second term; so that the smaller of these two terms may be neglected without serious error.

In the first case, where

$$\frac{C'K_{A'}}{C} < \frac{\gamma^2 K_w(1 + K_B/\gamma C)}{10K_B}, \text{ or } < 10^{-14} \text{ at } 25° \text{ when } K_B = 1 \text{ and } C = 0.1,$$

the presence of the acid HA′ evidently has only a relatively small effect on the result of the titration, and no large error will be made by neglecting the term containing $K_{A'}$ and by employing equations (33) to (39), for computing the best value and the limiting values of the indicator-function. This merely signifies that at 25° the presence of an acid whose ionization-constant is less than about 10^{-14} can be disregarded (unless its concentration C' is much larger than that C of the acid to be titrated.)

In the second case, where

$$\frac{C'K_{A'}}{C} > \frac{10\gamma^2 K_w(1 + K_B/\gamma C)}{K_B}, \text{ or } > 10^{-12} \text{ at } 25° \text{ when } K_B = 1 \text{ and } C = 0.1,$$

a large error will not be made by neglecting in (47) the term containing K_w and K_B in comparison with that containing $K_{A'}$. When this is done equation (47) becomes:

$$\mathrm{FE} = \frac{C'K_{A'}}{\gamma\, Ck} - \frac{\gamma k(1 + K_A/\gamma C)}{K_A}. \tag{48}$$

Putting $\overline{\mathrm{FE}} = 0$ and solving for k, we get for the best value of the indicator-function:

$$k_0 = \frac{1}{\gamma}\left(\frac{C'K_{A'}K_A}{C(1 + K_A/\gamma C)}\right)^{\frac{1}{2}}. \tag{49}$$

The expressions for the limiting values of k which will give a fractional error not greater than ρ are found, for any case in which the titration is practicable, to be as follows:

$$k < \frac{\rho K_A}{\gamma(1 + K_A/\gamma C)} \quad (50); \qquad \text{and } k > \frac{C'K_{A'}}{\rho\gamma C}. \tag{51}$$

The following expression for $\overline{\mathrm{FE}}$ in terms of k_0/k is also readily obtained from (48) and (49):

$$\overline{\mathrm{FE}} = \left(\frac{k_0}{k} - \frac{k}{k_0}\right)\left(\frac{C'K_{A'}}{CK_A}\right)^{\frac{1}{2}}\left(1 + \frac{K_A}{\gamma C}\right)^{\frac{1}{2}}. \tag{52}$$

From this equation, if we represent by ρ the fractional error permissible in the titration and by β the smallest value of $(k_0/k) - (k/k_0)$ that one can hope to realize, we may obtain by substitution the following expression showing the limiting condition at which the titration ceases to be practicable:

$$\frac{C'K_{A'}}{CK_A}(1 + K_A/\gamma C) < \frac{\rho^2}{\beta^2}. \tag{53}$$

Assuming $\beta = 3.5$ it follows from this expression for the case that $K_A = 1$

and C = about 0.1 that $C'K_{A'}/CK$ must be less than 10^{-8}, 10^{-7}, and 10^{-6} for accuracies in the titration of $^1/_{10}$, $^1/_3$, and 1 per cent., respectively; and for the case that $K_A < {}^1/_{10}C$ (when the parenthesis becomes substantially equal to unity), that $C'K_{A'}/CK_A$ must be less than 10^{-7}, 10^{-6}, and 10^{-5} for accuracies of $^1/_{10}$, $^1/_3$, and 1 per cent., respectively.

If the two acids were originally present in equivalent quantities ($C = C'$), these same statements are approximately true of the ratio $K_{A'}/K_A$.[1]

14. *Separate Titration of the More Ionized Base.*—The corresponding case involving the titration of a base BOH of ionization-constant K_B and concentration C in the presence of another much less ionized base B'OH of ionization-constant $K_{B'}$ and concentration C' with a nearly completely ionized acid HA can be similarly treated. The resulting expression for the fractional error corresponding to (47) is

$$\text{FE} = \frac{\gamma K_w(1 + K_B/\gamma C)}{kK_B} - \frac{\gamma k(1 + K_A/\gamma C)}{K_A} - \frac{kC'K_{B'}}{\gamma CK_w}. \qquad (54)$$

In the case where

$$\frac{C'K_{B'}}{C} < \frac{\gamma^2 K_w(1 + K_A/\gamma C)}{10K_A} \text{ or } < 10^{-14} \text{ at } 25° \text{ when } K_A = 1 \text{ and } C = 0.1,$$

the influence of the base B'OH on the titration can without serious error be disregarded.

In the case where

$$\frac{C'K_{B'}}{C} > \frac{10\gamma^2 K_w(1 + K_A/\gamma C)}{K_A}, \text{ or } < 10^{-12} \text{ at } 25° \text{ when } K_A = 1 \text{ and } C = 0.1,$$

the middle term in the second member of equation (54) is relatively small, and that equation assumes the approximate form:

$$\text{FE} = \frac{\gamma K_w(1 + K_B/\gamma C)}{kK_B} - \frac{kC'K_{B'}}{\gamma CK_w}. \qquad (55)$$

The best values and limiting values corresponding to this case are:

$$k_o = \gamma K_w\left(\frac{C(1 + K_B/\gamma C)}{C'K_{B'}K_B}\right)^{\frac{1}{2}}. \qquad (56)$$

$$k < \frac{\rho\gamma CK_w}{C'K_{B'}} \quad (57). \qquad \text{and } k > \frac{\gamma K_w(1 + K_B/\gamma C)}{\rho K_B} \qquad (58)$$

It can also be readily shown that, as in the case of the two acids, the titration will be practicable with accuracies of $^1/_{10}$, $^1/_3$, and 1 per cent.

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[1] Thus the ionization-constant for the first hydrogen of carbonic acid, according to Walker and Cormack, is 3×10^{-7}. Hence only the most completely ionized acids for which $K_A = 1$, such as HCl and HNO_3, can be titrated at 25° in the presence of an equal number of mols of H_2CO_3, and these only with an accuracy of about $^1/_2$ per cent., even where care is taken to secure a value of k not greater than about 3.5 k_0 and not less than about $^1/_{3.5}$ k_0. The best value k_0 for this case is calculated by equation (49) to be 2.1×10^{-4} (for $C = C'$ = about 0.1).

only when $C'K_{B'}/CK_B$ is less than 10^{-8}, 10^{-7}, and 10^{-6} when $K_B = 1$, and less than 10^{-7}, 10^{-6}, and 10^{-5} when $K_B < {}^1/_{10}\gamma C$.

15. *Titration of the Less Ionized Acid or Base.*—It is evident, in the titration of a mixture of two acids HA and HA′ with a largely ionized base, or of two bases BOH and B′OH with a largely ionized acid, that the more ionized acid HA or base BOH will first be converted into its salt, after which the titration of the less ionized acid HA′ or base B′OH will take place substantially as if it had been alone present.[1] The error in its titration, the conditions under which it is practicable, and the best value and limiting values of the indicator-function will therefore be determined by the considerations presented in Part II. Thus in accordance with expressions (39) it is necessary for the titration of HA′ that $k < \rho K_{A'}$, and for the titration of B′OH that $k > \frac{K_w}{\rho K_{B'}}$; and in accordance with equation (40) and the discussion following it, it is practically necessary that at 25° at 0.1 normal $K_{A'}$ or $K_{B'}$ be not smaller than 10^{-6}, 10^{-7}, and 10^{-8} for accuracies of ${}^1/_{10}$, ${}^1/_3$, and 1 per cent.

It is to be noted that an indicator-function which will give accuracy in the titration of HA′ or B′OH will also be suitable for the titration of the more ionized acid HA or base BOH; and that therefore the sum of the quantities of the two acids or bases can be accurately determined provided the conditions are such that the quantity of the less ionized acid or base can be so determined.

In order that, with the aid of two indicators, the quantity of each of the two acids or each of the two bases may be separately determined with any given accuracy, their ionization-constants must be sufficiently different to satisfy the requirement stated at the end of Sections 13 and 14; and yet, as just stated, the ionization-constant $K_{A'}$ or $K_{B'}$ of the less ionized acid or base must be large enough to satisfy equation (40), namely, at 25° and 0.1 normal it must be as large as 10^{-6}, 10^{-7} and 10^{-8} for accuracies of ${}^1/_{10}$, ${}^1/_3$ and 1 per cent. It follows from these two requirements that at 25° when $C = C' = 0.1$ normal, for an accuracy of ${}^1/_3$ per cent. (the greatest attainable under any conditions), the ionization-constant K_A or K_B of the more ionized acid or base must be as large as unity, and that $K_{A'}$ or $K_{B'}$ of the less ionized acid or base must be in the neighborhood of 10^{-7}; also that for an accuracy of 1 per cent., K_A or K_B may lie between 1 and 10^{-3} and $K_{A'}$ or $K_{B'}$ between 10^{-6} and 10^{-8} provided the ratio between them is as large as 10^5.

IV. Titration of Dibasic Acids with Monacidic Bases.

16. *General Formulation of the Theory.*—Thus far only monobasic acids and monacidic bases have been discussed. The case may now be

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[1] The neutral salt BA present will not affect the result materially, since it is a salt of the acid HA and not of HA′, or of the base BOH and not of B′OH.

considered in which the acid has two replaceable hydrogens, as indicated by the symbol H_2A. In this case, the condition equations, corresponding to (22), (23), and (24) evidently are:[1]

$$(\Sigma B) = (B^+) + (BOH) + (BHA) + 2(B_2A). \qquad (59)$$

$$(\Sigma A) = (A^=) + (HA^-) + (H_2A) + (BHA) + (B_2A). \qquad (60)$$

$$(B^+) + (H^+) = (HA^-) + 2(A^=) + (OH^-). \qquad (61)$$

17. *Error in the Titration of the First Hydrogen.*—To derive an expression for the titration of the first hydrogen, we may first subtract (60) from (59) and substitute in the result for (B^+) its value given by (61), whereby we get:

$$(\Sigma B) - (\Sigma A) = (BOH) + (A^=) + (B_2A) - (H_2A) + (OH^-) - (H^+). \qquad (62)$$

It is now to be noted that, when (ΣB) is equal or nearly equal to (ΣA), as it is in even a rough titration of the first hydrogen, this equation represents the condition in which the acid H_2A has been nearly completely converted into its acid salt BHA. It is therefore true that $(A^=)$ is a relatively small quantity. We may therefore, when the difference between them is not involved, place $(B^+) = (HA^-)$, thus neglecting in this case the quantities $2(A^=) + (OH^-) - (H^+)$ in equation (61). We may therefore divide all the terms of equation (62) either by (HA^-) or by its substantial equivalent (B^+), whereby we get:

$$\frac{(\Sigma B) - (\Sigma A)}{(B^+)} = \frac{(BOH)}{(B^+)} + \frac{(A^=) + (B_2A)}{(HA^-)} - \frac{(H_2A)}{(HA^-)} + \frac{(OH^-)}{(B^+)} - \frac{(H^+)}{(HA^-)}. \qquad (63)$$

Other expressions for the ratios in the second member may be obtained from the following equations:

$$\frac{(B^+)(OH^-)}{(BOH)} = K_B \quad (64); \qquad \frac{(H^+)(HA^-)}{(H_2A)} = K_{A_1} \quad (65);$$

$$\frac{(H^+)(A^=)}{(HA^-)} = K_{A_2} \quad (66); \qquad (H^+)(OH^-) = K_W \quad (67);$$

$$(H^+) = k \quad (68); \text{ and } \quad (A^=) + (B_2A) = (A^=)/\gamma_2 \quad (69);$$

where k is the indicator-function defined as before by equation (14), and γ_2 is the ionization of the salt B_2A of the unibivalent type.[2]

[1] The assumption is here made that the concentration of the intermediate ion BA^- is negligible. There is as yet no evidence that such ions exist in appreciable quantity in the case of salts, at any rate up to moderate concentrations.

[2] Unibivalent salts differ from one another in ionization more than uniunivalent ones. The following average values are, however, sufficiently accurate for the purposes here under discussion:

Normal concentration	0.50	0.20	0.10	0.05	0.02	0.01
Ionization γ_2	0.50	0.64	0.72	0.76	0.85	0.88

Making obvious substitutions, writing $\gamma_1 C$ for (B^+) and (HA^-), multiplying both members by γ_1, and uniting the first and fourth and the third and fifth terms, equation (63) becomes:

$$\overline{\text{FE}} = \frac{(\Sigma B) - (\Sigma A)}{(\Sigma B)} = \frac{\gamma_1 K_W(1 + K_B/\gamma_1 C)}{kK_B} + \frac{\gamma_1 K_{A_2}}{\gamma_2 k} - \frac{\gamma_1 k(1 + K_{A_1}/\gamma_1 C)}{K_{A_1}}. \quad (70)$$

18. *Best Value and Limiting Values of the Indicator-Function for Titration of the First Hydrogen.*—It will be noticed that equation (70) differs from equation (31) only in the respect that it contains the additional term $(+\ \gamma_1 K_{A_2}/\gamma_2 k)$. By considering this term associated with the positive term preceding it, which also contains k in the denominator, and which therefore can be treated like it in deriving expressions for k, we may write down at once relations corresponding to (33) to (40). More specifically stated, this may be done by substituting in those equations for the quantity

$$\frac{K_W(1 + K_B/\gamma_1 C)}{K_B}, \text{ the quantity } \frac{K_W(1 + K_B/\gamma_1 C)}{K_B} + \frac{K_{A_2}}{\gamma_2}.$$

It is therefore not necessary to write out these exact general expressions. We will, however, consider the two following cases: (1) that in which the second term in the last quantity is much smaller, and (2) that in which it is much larger than the first term; so that a serious error will not be made by neglecting the smaller of the two terms. It may be assumed that the error will be negligible when one term is as small as one-tenth of the other.

In the case where

$K_{A_2} < \frac{1}{10}\gamma_2(K_W/K_B)(1 + K_B/\gamma_1 C)$, or $< 10^{-14}$ at 25° when $K_B = 1$ and $C = 0.1$, the acid may be treated as a monobasic acid, the ionization of its second hydrogen being disregarded.

In the case where

$K_{A_2} > 10\gamma_2(K_W/K_B)(1 + K_B/\gamma_1 C)$ or $> 10^{-12}$ at 25° when $K_B = 1$ and $C = 0.1$, the approximate, but sufficiently accurate expressions for the best value and limiting values of the indicator-function corresponding to (33), (37), and (38) are as follows:

$$k_\circ = \left(\frac{K_{A_1} K_{A_2}}{\gamma_2(1 + K_{A_1}/\gamma_1 C)}\right)^{\frac{1}{2}}. \quad (71)$$

$$k < \frac{\rho K_{A_1}}{\gamma_1(1 + K_{A_1}/\gamma_1 C)} \quad (72); \quad \text{and } k > \frac{\gamma_1 K_{A_2}}{\gamma_2 \rho}. \quad (73)$$

In the case, usual with dibasic acids, in which the first hydrogen is only moderately dissociated (thus where $K_{A_1} < {}^1/_{10}\ C$), equation (71) is substantially accurate in the still simpler form:

$$k_0 = \sqrt{K_{A_1}K_{A_2}}. \qquad (74)$$

It is evident therefore that, provided the second hydrogen is appreciably dissociated, it is the product $K_{A_1}K_{A_2}$ which mainly (equation (71)) or wholly (equation (74)) determines the best value of the indicator-function for the titration of the first hydrogen.[1]

In this case (where $K_{A_1} < {}^1/_{10}\,C$) the expressions for the limiting values permissible assume the following approximate, but sufficiently accurate forms:

$$k < \frac{\rho K_{A_1}}{\gamma_1}, \text{ and } k > \frac{\gamma_1 K_{A_2}}{\gamma_2 \rho}. \qquad (75)$$

Thus the smallest value which k may have is determined by the ionization-constant for the second hydrogen, and the largest value by that for the first hydrogen.

In analogy with equation (35), the expression for the fractional error in the titration of the first hydrogen of a dibasic acid may be written in the following form in the case where $K_{A_2} > 10(K_w/K_B)\ (1 + K_B/\gamma_1 C)$:

$$\overline{FE} = \gamma_1 \left(\frac{k_0}{k} - \frac{k}{k_0}\right) \left(\frac{K_{A_2}}{\gamma_2 K_{A_1}}\right)^{\frac{1}{2}} (1 + K_{A_1}/\gamma_1 C)^{\frac{1}{2}}. \qquad (76)$$

It is therefore in this case the quantity K_{A_2}/K_{A_1} (instead of $K_w/K_A K_B$) that mainly determines how large the value of k_0/k or k/k_0 may be without causing the fractional error in the titration to exceed any assigned value. Therefore column (3) of Table I in Section 11 will show the maximum values of k_0/k or k/k_0 permissible, if an accuracy of 0.1 per cent. is to be secured in the titration of the first hydrogen of a dibasic acid (for which $K_{A_1} < {}^1/_{10}\,C$ and $K_{A_2} > 10^2 K_w$) with a nearly completely ionized base, if it be understood that the figures in the columns headed $K_w/K_A K_B$ are in this case the values of K_{A_2}/K_{A_1}.

In analogy with expression (40), we may derive from (76) the following expression showing the condition that must be fulfilled in order that the titration may be practicable with any given accuracy ρ:

$$\frac{K_{A_2}}{K_{A_1}} \left(\frac{\gamma_1{}^2}{\gamma_2}\right) (1 + K_{A_1}/\gamma_1 C) < \frac{\rho^2}{\beta^2}. \qquad (77)$$

Assuming as before that β_2 can hardly be made smaller than 10 and that

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[1] Thus in the case of carbonic acid, for which the ionization-constants for the two hydrogens are $K_{A_1} = 3 \times 10^{-7}$ and $K_{A_2} = 3 \times 10^{-11}$, the best value for the indicator-function is $k_0 = (3 \times 10^{-7} \times 3 \times 10^{-11})^{\frac{1}{2}} = 3 \times 10^{-9}$. In the case of phosphoric acid, for which according to Abbott and Bray (THIS JOURNAL, 31, 760 (1909)) $K_{A_1} = 10^{-2}$ and $K_{A_2} = 2 \times 10^{-7}$, one finds by equation (71) for $C = 0.05$ that

$$k_0 = \left(\frac{K_{A_1}K_{A_2}}{1 + 10^{-2}/(0.86 \times 0.05)}\right)^{\frac{1}{2}} = 0.90(K_{A_1}K_{A_2})^{\frac{1}{2}} = 4.0 \times 10^{-5}.$$

(In the case of tribasic acids, the ionization of the third hydrogen is so much smaller than that of the second hydrogen that it does not affect appreciably the conditions determining the titration of the first hydrogen.)

$K_{A_1} < {}^1/_{10}C$, it follows (since γ_1^2/γ_2 = approx. 1) that the titration can not be made with an accuracy as great as ρ unless $K_{A_2}/K_{A_1} < {}^1/_{10}\rho^2$. Therefore K_{A_2}/K_{A_1} must be less than 10^{-7}, 10^{-6}, and 10^{-5} for accuracies of ${}^1/_{10}$, ${}^1/_3$, and 1 per cent. respectively.[1]

19. *Error in the Titration of the Total Hydrogen.*—An expression applicable to the titration of the total hydrogen may be obtained in a similar way. Namely, by multiplying equation (60) through by 2, subtracting the result from equation (59), and substituting for (B^+) the value of it given by equation (61), we get:

$$(\Sigma B) - 2(\Sigma A) = (BOH) - (HA^-) - (BHA) - 2(H_2A) + (OH^-) - (H^+). \quad (78)$$

Taking into account the fact that in this case (HA^-) is small, so that (B^+) may be placed equal to $2(A^=)$ when the difference between them is not involved, dividing through by (B^+) or its substantial equivalent $2(A^=)$, and putting $(HA^-) + (BHA) = (HA^-)/\gamma_1$ we get:

$$\frac{(\Sigma B) - 2(\Sigma A)}{(B^+)} = \frac{(BOH)}{(B^+)} - \frac{(HA^-)}{2\gamma_1(A^=)} - \frac{(H_2A)}{(A^=)} + \frac{(OH^-)}{(B^+)} - \frac{(H^+)}{2(A^=)}. \quad (79)$$

Substituting for the ratios in the second member their values as given by equations (64) to (68) and for (B^+) or $2(A^=)$ the quantity $\gamma_2 C$ (where C therefore represents the *equivalent* concentration of the salt), and multiplying through by γ_2, the ionization of the unibivalent salt, we get:

$$\frac{(\Sigma B) - 2(\Sigma A)}{(\Sigma B) \text{ or } 2(\Sigma A)} = \gamma_2\left(\frac{K_W}{kK_B} - \frac{k}{2\gamma_1 K_{A_2}} - \frac{k^2}{K_{A_1}K_{A_2}} + \frac{K_W}{k\gamma_2 C} - \frac{k}{\gamma_2 C}\right). \quad (80)$$

This equation evidently expresses the fractional error in the titration of the total hydrogen in the ordinary case in which no salt of the acid or base is originally present in the solutions.

Since equation (80) is a cubic with respect to k, a rigorous discussion of the best value and of the limiting values of the indicator-function would be attended with mathematical difficulties. It is therefore of importance to note that the third term in the parenthesis is in practice entirely negligible in comparison with the second term, whenever even a very rough titration is possible. This is true since the ratio of the third to the second term is $2\gamma_1 k/K_{A_1}$, since it may be shown (by sub-

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[1] Therefore in the case of carbonic acid for which $K_{A_2} = 10^{-4}\,K_{A_1}$ the titration of the first hydrogen is not possible with even a moderate degree of accuracy. But in the case of phosphoric acid, for which $K_{A_2} = 2 \times 10^{-5}\,K_{A_1}$ the titration of the first hydrogen should be possible with an accuracy of not far from 1 per cent. by taking care to secure a value of the indicator-function as nearly as possible equal to the best value. In the case of nearly all the organic dibasic acids, the ionization-constants for the first and second hydrogens do not differ from each other sufficiently to make a titration of the former at all possible.

stituting $2\gamma K_{A_2}$ for K_A in (37)) that $k/2K_{A_2}$ must be less than the fractional error, and since for all dibasic acids K_{A_1} is much larger than K_{A_2}. (Considered from the standpoint of the chemical composition as expressed by equation (78), this signifies that $2(H_2A)$ is negligible in comparison with (HA^-) in a solution in which the acid has been almost wholly converted into the salt B_2A or its ions.) Neglecting the third term in the parenthesis and writing $\overline{FE}$ for the first member, equation (80) becomes:

$$\overline{FE} = \frac{\gamma_2 K_W}{kK_B}(1 + K_B/\gamma_2 C) - \frac{\gamma_2 k}{2\gamma_1 K_{A_2}}(1 + 2\gamma_1 K_{A_2}/\gamma_2 C). \qquad (81)$$

This will be seen to be identical with equation (31) expressing the error in titrating a monobasic acid, except that it contains $2\gamma_1 K_{A_2}$ in place of K_A, and γ_2 in place of γ. It will also be noted that in the titration of a dibasic acid it is the constants for the base and for the second hydrogen which determine the error, that for the first hydrogen having dropped out.

20. *Best Value and Limiting Values of the Indicator-Function for Titration of the Total Hydrogen.*—In view of the close correspondence of equations (81) and (31) just referred to, all the conclusions drawn from the latter in regard to the best value and the limiting values of the indicator-function for the titration of monobasic acids can be made to apply directly to the titration of the total hydrogen of dibasic acids by substituting $2\gamma_1 K_{A_2}$ for K_A and γ_2 for γ, in expressions (33) to (40), in Table I, and in the discussions of those expressions and of that table. It is therefore unnecessary to consider in detail the conditions relating to the titration of the total hydrogen.

V. Titration of Diacidic Bases with Monobasic Acids.

21. *Error in the Titration of the First Hydroxyl.*—By a method entirely analogous to that just described for dibasic acids expressions may be obtained for the error in the titration of both the first and total hydroxyl of a diacidic base $B(OH)_2$ with a monobasic acid HA, the ionization-constants for the first and second hydroxyls being represented by K_{B_1} and K_{B_2} and defined by the equilibrium equations:

$$\frac{(BOH^+)(OH^-)}{B(OH)_2} = K_{B_1} \quad (82); \quad \frac{(B^{++})(OH^-)}{(BOH^+)} = K_{B_2}. \qquad (83)$$

The so-obtained expression for the first hydroxyl is:

$$\overline{FE} = \frac{(\Sigma B) - (\Sigma A)}{(\Sigma B) \text{ or } (\Sigma A)} = \frac{\gamma_1 K_W(1 + K_{B_1}/\gamma_1 C)}{kK_{B_1}} - \frac{\gamma_1 k(1 + K_A/\gamma_1 C)}{K_A} - \frac{\gamma_1 k K_{B_2}}{\gamma_2 K_W} \qquad (84)$$

22. *Best Value and Limiting Values of the Indicator-Function for Titration of the First Hydroxyl.*—It will be seen that equation (84) corresponds

closely with (70), and differs from (31) only in the respect that it contains the additional term $(-\gamma_1 k K_{B_2}/K_w \gamma_2)$. By a treatment entirely analogous to that described in Section 18 expressions may be obtained for the best value and the limiting values of the indicator-function. The following are the forms applicable to the case where

$K_{B_2} \times 10(K_w/K_A)(1+K_A/\gamma_1 C)$ or $> 10^{-12}$ at 25° when $K_A = 1$ and $C = 0.1$:

$$k_o = \left(\frac{\gamma_2 K_w^2}{K_{B_1} K_{B_2}}\right)^{\frac{1}{2}} (1 + K_{B_1}/\gamma_1 C)^{\frac{1}{2}} = \text{appr.}\ \frac{K_w}{\sqrt{K_{B_1} K_{B_2}}} \text{ when } K_{B_1} < \frac{1}{10} C. \quad (85)$$

$$k < \frac{\rho \gamma_2 K_w}{\gamma_1 K_{B_2}} \quad (86); \qquad \text{and } k > \frac{\gamma_1 K_w (1 + K_{B_1}/\gamma_1 C)}{\rho K_{B_1}} \quad (87)$$

$$\text{or } k > \frac{\gamma_1 K_w}{\rho K_{B_1}} \text{ when } K_{B_1} < \frac{1}{10} C. \quad (87a)$$

$$\overline{\text{FE}} = {}_1\left(\frac{k_o}{k} - \frac{k}{k_o}\right) \left(\frac{K_{B_2}}{\gamma_2 K_{B_1}}\right)^{\frac{1}{2}} (1 + K_{B_1}/\gamma_1 C)^{\frac{1}{2}}. \quad (88)$$

$$\frac{K_{B_2}\gamma_1^2}{K_{B_1}\gamma_2} (1 + K_{B_1}/\gamma_1 C) < \frac{\rho^2}{\beta^2}. \quad (89)$$

23. *Titration of the Total Hydroxyl.*—For the error in this titration the following expression analogous to equations (31) and (81) may be obtained by a similar method of procedure:

$$\overline{\text{FE}} = \frac{\gamma_2 K_w}{2k\gamma_1 K_{B_2}} (1 + 2\gamma_1 K_{B_2}/\gamma_2 C) - \frac{\gamma_2 k}{K_A} (1 + K_A/\gamma_2 C). \quad (90)$$

This will be seen to differ from equation (31) only in the respects that it contains $2\gamma_1 K_{B_2}$ in place of K_B, and γ_2 in place of γ. The conclusions drawn from that equation therefore all apply, after making these substitutions, to the titration of the total hydroxyl of a diacidic base.

VI. Summary.

24. *Summary.*—It seems desirable to sum up the conclusions reached in this article which are of most direct application to the problems of volumetric analysis.

The equilibrium relations of the two differently colored structural forms in which all indicators probably exist, and the equilibrium conditions under which such a pair of tautomeric substances can show sharply differentiated colors in acid and alkaline solution were first discussed (see Section 2). It was shown that, provided these conditions are fulfilled, the indicator can be treated in titrations as if it were a single acid or base having an ionization-constant which, though really a function of three equilibrium-constants, can be directly determined either from the color-changes exhibited by it in solutions of various hydrogen-ion concentration, or by any of the other methods commonly employed—for example, by measurement of the conductivity of the indicator acid or base or by a study of the hydrolysis of its salt.

The well-known principle of the theory of indicators was then formulated (in Section 3), according to which the proportion of the indicator acid converted into its salt, or of the indicator base liberated from its salt, is determined solely by its ionization-constant (K_{IA} or K_{IB}) and by the hydrogen-ion concentration (H^+) in the solution; and a series of lecture experiments illustrating this were described in Section 4. Defining the end-point of the titration as the condition where a definite proportion (α) of the indicator, as shown by the color, is so transformed, the equilibrium prevailing at the end-point is then expressed by the equations:

$(H^+) = K_{IA}(1 - \alpha)/\alpha\gamma = k$, for an acid indicator; or

$(H^+) = (K_w/K_{IB})(\gamma(1 - \alpha)/\alpha) = k$, for a basic indicator;

where $K_w = (H^+)(OH^-)$, and γ represents the ionization of the indicator salt, which may be assumed to be equal to that of other salts of the same type.

The symmetry in the equilibrium relations of acid and basic indicators and the impossibility of distinguishing them by their behavior in titrations was pointed out; and the term apparent ionization-constant (K_I) was introduced, this being defined for acid and basic indicators by the equations $K_I = K_{IA}/\gamma$ and $K_I = \gamma K_w/K_{IB}$, respectively, where γ represents the ionization of the indicator salt in any solution in which its color serves as a measure of its concentration. We then have for either an acid or basic indicator: $(H^+) = K_I(1 - \alpha)/\alpha = k$.

Throughout the article the letter k is written in place of the lengthy expression preceding it in this equation; and it is designated the indicator-function. This fundamental quantity was fully discussed in Section 5, the fact being emphasized that it depends on two factors, the ionization-constant of the indicator and the fraction of it transformed at the end-point. The limits within which the fraction transformed can be varied in practice were considered, it being pointed out that the experimental determination of these limits for each indicator would supplement in an important way that of its ionization-constant. In the absence of such experimental data, it was suggested as a reasonable estimate that in the case of sufficiently soluble one-color indicators, like *p*-nitrophenol, the fraction transformed might be varied from 0.1 to 25 per cent., corresponding to a variation of k from 1000 K_I to $3K_I$. When, however, the indicator has a limited solubility S, the largest value of k that can be secured is equal to $K_I(S - I)/I$, where I represents that concentration of the transformed part of the indicator which gives the depth of color suitable for the end-point. Attention was called to the facts that in the case of two-color indicators, like methyl orange, the range was much smaller, since the fraction transformed must have a considerable value in order that its color may not be entirely obscured by the color of the untransformed part of the indicator; and that, on the other hand, such indicators could sometimes be employed at both ends of their transformation, being in one case say 10 per cent. transformed in the direction from acid to alkaline and in the other case 10 per cent. transformed in the other direction, thus giving two values of k equal to about $10K_I$ and $^1/_{10}K_I$, respectively.

It was shown in Section 6 that, if the indicator itself is not to require for its neutralization an appreciable proportion of the base or acid used in the titration, its concentration (ΣIn) in the titrated solution must be less than $\rho C/\alpha$ for an acid indicator, or less than $\rho C/(1 - \alpha)$ for a basic indicator, where C represents the concentration of the salt, ρ the fractional error permissible in the titration, and α the fraction of the indicator transformed in the direction from acid to alkaline.

Through formulation of the equilibrium and condition equations involved and the combination of these, the following practically exact expression was derived in Sections 7 and 8 for the fractional error $\overline{\mathrm{FE}}$[1] incurred in the titration of any monobasic acid HA of ionization-constant K_A and of any monacidic base BOH of ionization-constant K_B when the indicator-function has any value k, the salt in the titrated solution having an equivalent concentration C and an ionization γ_1:

$$\overline{\mathrm{FE}} = \frac{\gamma K_W}{k K_B}(1 + K_B/\gamma_1 C) - \frac{\gamma k}{K_A}(1 + K_A/\gamma_1 C). \qquad (31)$$

It was shown in Section 9 that, when a neutral salt BA of the acid and base is originally present in the solution to be titrated, the fractional error in the titration is equal to that calculated by equation (31) multiplied by the ratio which the sum of the quantity of that salt and of the quantity of acid or base used in the titration bears to the latter quantity. This also holds true when a neutral salt (BA′ or B′A) is present which is a salt of a different acid or base (HA′ or B′OH) provided the latter is of the largely ionized type.

In later sections were derived expressions for the fractional error in the titration of combinations of other types of acids and bases, as follows:

For the total hydrogen of a dibasic acid H_2A with a monacidic base BOH, replace in (31) K_A by $2\gamma_1 K_{A_2}$ and γ_1 by γ_2. (81)

For the total hydroxyl of a diacidic base $B(OH)_2$ with a monobasic acid HA, replace in (31) K_B by $2\gamma_1 K_{B_2}$ and γ_1 by γ_2. (90)

For the first hydrogen of a dibasic acid H_2A with a monacidic base BOH:

$$\overline{\mathrm{FE}} = \frac{\gamma_1 K_W}{k K_B}(1 + K_B/\gamma_1 C) - \frac{\gamma_1 k}{K_{A_1}}(1 + K_{A_1}/\gamma_1 C) + \frac{\gamma_1 K_{A_2}}{\gamma_2 k}. \qquad (70)$$

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[1] Meaning thereby the difference between the quantity of acid or base originally present and the quantity of standard base or acid added when the end-point has been reached, divided by either of these quantities. The percentage error is, of course, equal to 100 $\overline{\mathrm{FE}}$.

For the first hydroxyl of a diacidic base $B(OH)_2$ with a monobasic acid HA:

$$\overline{FE} = \frac{\gamma_1 K_w}{k K_{B_1}} (1 + K_{B_1}/\gamma_1 C) - \frac{\gamma_1 k}{K_A} (1 + K_A/\gamma_1 C) - \frac{\gamma_1 k K_{B_2}}{\gamma_2 K_w}. \qquad (84)$$

In these expressions K_{A_1} and K_{A_2} represent the ionization-constants for the first and second hydrogens of the acid as defined by the equations $(H^+)(HA^-)/(H_2A) = K_{A_1}$ and $(H^+)(A^{--})/(HA^-) = K_{A_2}$, K_{B_1} and K_{B_2} represent the ionization-constants for the first and second hydroxyls of the base correspondingly defined; C represents the equivalent concentration of the salt in the titrated solution; and γ_1 and γ_2 represent the degrees of ionization in the titrated solution of the salts of the uni-univalent and unibivalent types. Average values of these degrees of ionization at various concentrations will be found in tables given in Sections 8 and 17.

For the titration of a more ionized acid HA in the presence of a less ionized acid HA′ with a monacidic base BOH:

$$\overline{FE} = \frac{\gamma_1 K_w}{k K_B} (1 + K_B/\gamma_1 C) - \frac{\gamma_1 k}{K_A} (1 + K_A/\gamma_1 C) + \frac{C' K_{A'}}{\gamma_1 C k}. \qquad (47)$$

For the titration of a more ionized base BOH in the presence of a less ionized base B′OH with a monobasic acid HA:

$$\overline{FE} = \frac{\gamma_1 K_w}{k K_B} (1 + K_B/\gamma_1 C) - \frac{\gamma_1 k}{K_A} (1 + K_A/\gamma_1 C) - \frac{k C' K_{B'}}{\gamma_1 C K_w}. \qquad (54)$$

The C'/C occurring in the last terms of these equations is equal to the ratio of the quantities of the two acids HA′ and HA, or of the two bases B′OH and BOH, originally present in the solution to be titrated; and $K_{A'}$ and K_A, or K_B and $K_{B'}$, are the ionization-constants of these two acids or bases.

By these expressions the fractional error can be readily calculated in any case where the values of the ionization-constants involved and of the indicator-function are known. The error can evidently be reduced by securing an appropriate value of the indicator-function, which may be done by choosing a suitable indicator and taking care that the proper fraction of it is transformed at the end-point. Other sections of the article are therefore devoted to the derivation of expressions for the best value of the indicator-function and for the limiting values permissible in the different cases, and to a consideration of the conditions, under which the titration ceases to be practicable with any indicator.

By placing in each of the seven equations just considered the first member $\overline{FE}$ equal to zero, and solving the equation for k, expressions were obtained for the value which the indicator-function k must have in order that the titration may be perfect. The expressions for the "best values" (k_0) of k so obtained are for the seven cases as follows:

For the titration of a monobasic acid and a monacidic base:

$$k_o = \left(\frac{K_w(1+K_B/\gamma_1C)}{K_B}\right)^{\frac{1}{2}} \left(\frac{K_A}{1+K_A/\gamma_1C}\right)^{\frac{1}{2}}. \qquad (33)$$

For the titration of the total hydrogen of a dibasic acid with a monobasic acid, replace in equation (33) K_A by $2\gamma_1K_{A_2}$ and γ_1 by γ_2.

For the titration of the total hydroxyl of a diacidic base with a monobasic acid, replace in equation (33) K_B by $2\gamma_1K_{B_2}$ and γ_1 by γ_2.

For the titration of the first hydrogen of a dibasic acid with a monacidic base, when $K_{A_2} > 10(K_w/K_B)\ (1 + K_B/\gamma_1C)$:

$$k_o = \left(\frac{K_{A_1}K_{A_2}}{\gamma_2(1+K_{A_1}/\gamma_1C)}\right)^{\frac{1}{2}}. \qquad (71)$$

For the titration of the first hydroxyl of a diacidic base with a monobasic acid, when $K_{B_2} > 10(K_w/K_A)\ (1 + K_A/\gamma_1C)$:

$$k_o = \left(\frac{\gamma_2K_w^2}{K_{B_1}K_{B_2}}\right)^{\frac{1}{2}} (1+K_{B_1}/\gamma_1C)^{\frac{1}{2}}. \qquad (85)$$

For the titration of a more ionized acid HA in the presence of a less ionized one HA′, when $(K_{A'}C'/C) > 10(K_w/K_B)\ (1 + {}_{B}K/\gamma_1C)$:

$$k_o = \frac{1}{\gamma_1}\left(\frac{C'K_{A'}K_A}{C(1+K_A/\gamma_1C)}\right)^{\frac{1}{2}}. \qquad (49)$$

For the titration of a more ionized base BOH in the presence of less ionized one B′OH, when $(K_{B'}C'/C) > 10(K_w/K_A)\ (1 + K_A/\gamma_1C)$:

$$k_o = \gamma_1K_w\left(\frac{C(1+K_B/\gamma_1C)}{C'K_{B'}K_B}\right)^{\frac{1}{2}}. \qquad (56)$$

The applicability of the last four equations is not greatly limited by the restriction that the ionization-constant for the hydrogen that is *not* to be titrated must be greater than $10(K_w/K_{A\text{ or }B})\ (1 + K_{A\text{ or }B}/\gamma C)$; for this quantity has at 25° (where $K_w = 10^{-14}$) a value of only about 10^{-12} when the titration is made, as it usually is, with an almost completely ionized univalent base or acid (for which K_B or K_A = 1), such as sodium hydroxide or hydrochloric acid. (This restriction and these statements in regard to it apply also to the corresponding equations presented below.) If K_{A_2} or K_{B_2} is smaller than $^1/_{100}$ of this quantity (thus smaller than 10^{-14} at 25°) the dibasic acid or diacidic base may be treated as a monobasic or monacidic one; and if $(K_{A'}C'/C)$ or $(K_{B'}C'/C)$ is smaller than $^1/_{100}$ of this quantity, the presence of the less ionized acid or base can be disregarded. In the intermediate case more complex formulas than those given above must be used, in regard to which reference may be made to Sections 18, 22, 13, and 14.

By placing in each of the seven equations for the fractional error the first member $\overline{FE}$ equal to $\pm\rho$ and solving for k, expressions can be directly obtained for the maximum and minimum values which the indicator-function k may have without giving rise to a fractional error numerically greater than any assigned value ρ. The expressions so obtained are:

For the titration of a monobasic acid with a monacidic base, or the reverse:

$$k < \frac{\rho K_A}{\gamma_1(1+K_A/\gamma_1 C)} \quad (37), \text{ and } k > \frac{\gamma_1 K_W(1+K_B/\gamma_1 C)}{\rho K_B}. \quad (38)$$

For the titration of the total hydrogen of a dibasic acid, replace in (37) K_A by $2\gamma_1 K_{A_2}$ and γ_1 by γ_2; and for the titration of the total hydroxyl of a diacidic base, replace in (38) K_B by $2\gamma_1 K_{B_2}$ and γ_1 by γ_2.

For the titration of the first hydrogen of a dibasic acid with a nearly completely ionized base:

$$k < \frac{\rho K_{A_1}}{\gamma_1(1 + K_{A_1}/\gamma_1 C)} \quad (72); \quad \text{and } k > \frac{\gamma_1 K_{A_2}}{\gamma_2 \rho} \quad (73).$$

For the titration of the first hydroxyl of a diacidic base with a nearly completely ionized acid:

$$k < \frac{\gamma_2 \rho K_W}{\gamma_1 K_{B_2}} \quad (86); \quad \text{and } k > \frac{\gamma_1 K_W(1 + K_{B_1}/\gamma_1 C)}{\rho K_{B_1}} \quad (87).$$

For the titration of an acid HA in the presence of another acid HA′, with a nearly completely ionized base:

$$k < \frac{\rho K_A}{\gamma_1(1 + K_A/\gamma_1 C)} \quad (50); \quad \text{and } k > \frac{C' K_{A'}}{\rho \gamma_1 C} \quad (51).$$

For the titration of a base BOH in the presence of another base B′OH, with a nearly completely ionized acid:

$$k < \frac{\rho \gamma_1 C K_W}{C' K_{B'}} \quad (57); \quad \text{and } k > \frac{\gamma_1 K_W(1 + K_B/\gamma_1 C)}{\rho K_B} \quad (58).$$

By these expressions the practical limits between which the indicator-function must lie can be readily calculated for any given combination of acid and base. It will be observed that in the first three cases, where the total acid or base present is to be titrated, the upper limit for k is determined by the ionization-constant of the acid and the lower limit by that of the base; that, in the case of the titration of the first hydrogen of a dibasic acid or of one monobasic acid in the presence of another, the upper limit is determined by the ionization-constant for the hydrogen that is to be titrated, and the lower limit by that for the hydrogen that is not to be titrated; and that the reverse is true in the case of the titration of the first hydroxyl of a diacidic base, or of one monacidic base in the presence of another.

It has been shown that, although theoretically there is a value of the indicator-function which would make a perfect titration possible for any combination of acid and base, yet in practice, since that best value k_o can be only approximately realized, it ceases to be possible to make the titration with reasonable accuracy when the ionization-constants of the base and acid assume too small values. The following expressions were derived in order to show how great the ratio of the actual value k to the

best value k_0 may become without causing the fractional error in the titration to exceed any assigned value:
For the titration of a monobasic acid and a monacidic base;

$$\overline{\mathrm{FE}} = \gamma_1\left(\frac{k_0}{k} - \frac{k}{k_0}\right)\left(\frac{K_W}{K_A K_B}\right)^{\frac{1}{2}}(1+K_B/\gamma_1 C)^{\frac{1}{2}}(1+K_A/\gamma_1 C)^{\frac{1}{2}}. \qquad (35)$$

For the titration of the total hydrogen of a dibasic acid or the total hydroxyl of a diacidic base, replace in this equation γ_1 by γ_2 and K_A by $2\gamma_1 K_{A_2}$, or γ_1 by γ_2 and K_B by $2\gamma_1 K_{B_2}$, respectively.
For the titration of the first hydrogen of a dibasic acid:

$$\overline{\mathrm{FE}} = \gamma_1\left(\frac{k_0}{k} - \frac{k}{k_0}\right)\left(\frac{K_{A_2}}{\gamma_2 K_{A_1}}\right)^{\frac{1}{2}}(1+ K_{A_1}/\gamma_1 C)^{\frac{1}{2}}. \qquad (76)$$

For the titration of the first hydroxyl of a diacidic base, replace in this equation K_{A_2} by K_{B_2} and K_{A_1} by K_{B_1}. (88)
For the titration of one monobasic acid HA in presence of another, less ionized one HA′,

$$\overline{\mathrm{FE}} = \left(\frac{k_0}{k} - \frac{k}{k_0}\right)\left(\frac{C'K_{A'}}{CK_A}\right)^{\frac{1}{2}}(1 + K_A/\gamma_1 C)^{\frac{1}{2}}. \qquad (52)$$

For the titration of one monacidic base BOH in presence of another less ionized one B′OH, one should replace $K_{A'}$ by $K_{B'}$ and K_A by K_B in this equation.

Since the factors of the form $(1 + K/\gamma_1 C)^{\frac{1}{2}}$ never have a value very different from unity, how small k_0/k or k/k_0 must be to prevent the error $\overline{\mathrm{FE}}$ from exceeding any assigned value depends mainly on how small the value is of $\frac{K_W}{K_A K_B}$, $\frac{K_W}{2K_{A_2}K_B}$, $\frac{K_W}{2K_A K_{B_2}}$, $\frac{K_{A_2}}{K_{A_1}}$, $\frac{K_{B_2}}{K_{B_1}}$, $\frac{C'K_{A'}}{CK_A}$, or $\frac{C'K_{B'}}{CK_B}$.

The numerical values of k_0/k or k/k_0 corresponding to a fractional error of 0.1 per cent., to a series of values of $K_W/K_A K_B$ or of any other of these seven quantities, and to different values of $(1 + K/\gamma_1 C)$ have been calculated and tabulated on page 836. This table shows that as any of these seven quantities increases, greater care must be taken to bring the actual value k of the indicator-function closer to the best value k_0, and when any of them becomes as large as 10^{-8}, the ratio k_0/k or k/k_0 must be given a value so small as to approach the practically attainable limit; namely, a value less than 7.4 when K_A or K_B = 1 and C = 0.5, and one less than 2.7 when K_A or K_B = 1 and C = 0.05. The table, as illustrated by this example, also shows that the smaller the concentration C of the titrated solution, the smaller is the limiting value of k_0/k or k/k_0 at which the titration is still possible with a given accuracy, and therefore that it is advantageous to titrate in a solution as concentrated as possible whenever the titration is sensitive to error and a strong base or acid is involved in it.

It was also pointed out, since the actual value of the indicator-function must be made to approach the best value more closely as K_W/K_AK_B, $K_W/2K_{A_2}K_B$ or $K_W/2K_AK_{B_2}$ increases, and since K_W increases very rapidly with rising temperature (thus from 10^{-15} at 0° to 10^{-14} at 25° and 10^{-13} at 65°), that it is advantageous to make the titration at as low a temperature as possible, provided the total acid or base present is to be titrated.

The following expressions, showing the maximum values which any of the seven quantities above referred to may have without causing the titration to become impracticable, were obtained from the equations for FE by denoting the minimum value of $(k_0/k - k/k_0)$ which one can hope to realize in practice by β and representing the fractional error permissible in the titration by ρ, and transforming:

For the titration of a monobasic acid and monacidic base:

$$\frac{K_W}{K_AK_B}\gamma_1^2(1+K_A/\gamma_1C)(1+K_B/\gamma_1C) < \frac{\rho^2}{\beta^2}. \qquad (40)$$

For the titration of the first hydrogen of a dibasic acid:

$$\frac{K_{A_2}}{K_{A_1}}\left(\frac{\gamma_1^2}{\gamma_2}\right)(1+K_{A_1}/\gamma_1C) < \frac{\rho^2}{\beta^2}. \qquad (77)$$

For the titration of one monobasic acid HA in the presence of another less ionized one HA′:

$$\frac{C'K_{A'}}{CK_A}(1+K_A/\gamma_1C) < \frac{\rho^2}{\beta^2}. \qquad (53)$$

For the titration of the other combinations the same substitutions are to be made in these expressions as in the previous cases.

It was shown in Section 12 that the smallest value of k_0/k or k/k_0 that one can ordinarily hope to realize may be fairly estimated to be in the neighborhood of 3.5. Since under this assumption β^2 is equal to 10, we may conclude that the first members of the preceding inequalities must not have a larger value than 10^{-7}, 10^{-6}, and 10^{-5} if the error (ρ) in the titration is not to exceed $^1/_{10}$, $^1/_3$, and 1 per cent., respectively.

By the first of these inequalities one can also calculate the minimum value which the product K_AK_B may have under various conditions. It is evident that this minimum value will be smaller, the greater the concentration C of the titrated solution and the lower the temperature (owing to the variation of K_W with the latter). It may also be pointed out that under ordinary conditions (say at 25° with the concentration 0.1 normal) the minimum value which K_A or K_B may have is about 10^{-8}, 10^{-7}, or 10^{-6} if the acid or base is to be titrated with an accuracy of $^1/_{10}$, $^1/_3$, or 1 per cent. with one of the nearly completely ionized bases or acids. The same statements apply to the product $2K_{A_2}K_B$ in the case of a dibasic acid, and to the product $2K_AK_{B_2}$ in the case of a diacidic base; also to the values of $2K_{A_2}$ and $2K_{B_2}$.

The more important of the foregoing considerations relating to the best value and the limiting values of the indicator-function may be expressed in the form of simple practical rules which, though only approximately correct, have sufficient accuracy for almost all purposes. These rules may be derived from the equations for k_0 and from the inequalities containing k and ρ by putting γ equal to unity, by putting also the expressions of the form $1 + K/\gamma C$ equal to unity when they refer to acids or bases that are not largely ionized, and by assigning to expressions of the form $\gamma(1 + K/\gamma C)/K$ the medium value[1] 10 and to K_A or K_B the value unity when they refer to the most completely ionized acids or bases. The rules are as follows:

In order that a not largely ionized acid or base may be titrated with one of the most largely ionized bases or acids with a fractional error not greater than ρ, it is essential that the indicator-function k have a value which is greater than the "minimum value" and less than the "maximum value" given in the following table; and in order to assure the fulfilment of this requirement, it is advisable in any titration sensitive to error to aim to secure a value of the indicator-function as nearly as possible equal to the "best value," whose square is given in the table.[2]

TABLE 2.—APPROXIMATE EXPRESSIONS FOR THE MAXIMUM, MINIMUM, AND BEST VALUES OF THE INDICATOR-FUNCTION.

Titration, with a largely ionized base or acid, of:	Square of best value.	Maximum value.	Minimum value.	Function for limit of titratability
A monobasic acid	$10K_WK_A$	ρK_A	$10K_W/\rho$	$10K_W/K_A$
A monacidic base.........	$^1/_{10}K_W/K_B$	$^1/_{10}\rho$	$K_W/(\rho K_B)$	$10K_W/K_B$
The total hydrogen of a dibasic acid..............	$10K_W2K_{A_2}$	$\rho 2K_{A_2}$	$10K_W/\rho$	$10K_W/2K_{A_2}$
The total hydroxyl of a diacidic base.............	$^1/_{10}K_W/2K_{B_2}$	$^1/_{10}\rho$	$K_W/(\rho 2K_{B_2})$	$10K_W/2K_{B_2}$
The first hydrogen of a polybasic acid..........	$K_{A_1}K_{A_2}$	ρK_{A_1}	K_{A_2}/ρ	K_{A_2}/K_{A_1}
The first hydroxyl of a polyacidic base.........	$\dfrac{K_W^2}{K_{B_1}K_{B_2}}$	$\dfrac{\rho K_W}{K_{B_2}}$	$\dfrac{K_W}{\rho K_{B_1}}$	K_{B_2}/K_{B_1}
One monobasic acid (HA) in the presence of another (HA′)............	$\dfrac{K_AK_{A'}C'}{C}$	ρK_A	$\dfrac{K_{A'}C'}{\rho C}$	$\dfrac{K_{A'}C'}{K_AC}$
One monacidic base (BOH) in the presence of another (B′OH)...........	$\dfrac{K_W^2C}{K_BK_{B'}C'}$	$\rho\dfrac{CK_W}{C'K_{B'}}$	$\dfrac{K_W}{\rho K_B}$	$\dfrac{K_{B'}C'}{K_BC}$

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[1] When $K = 1$ as it is approximately for such acids as HCl and HNO_3 and such bases as NaOH and KOH at 0.1 normal, the value of $\gamma(1 + K/\gamma C)/K$ varies from about 3 when the titrated solution is 0.5 normal, to about 21 when it is 0.05 normal.

[2] For the significance of the various K's and C's in this table see the third and fourth pages of this Summary. For an example illustrating the use of the table, see the foot-note at the end of the article.

The table also contains in the last column that function of the ionization-constants whose value determines the limit beyond which the titration becomes impracticable. This limit depends also on how small a value of $(k_0/k - k/k_0)$ it is possible to realize. If we represent by β the minimum value of the latter quantity attainable, the following rule in regard to the limit may be stated:

In order that the titration of a not largely ionized acid or base with one of the most completely ionized bases or acids may be made with a fractional error not greater than ρ, it is essential that the quantity given in the last column of the table have a value less than that of the ratio ρ^2/β^2. If we adopt the estimate that the value of k_0/k or k/k_0 may be made as small as 3.5, but not smaller without taking unusual precautions, then $\beta^2 = 10$ approximately; and we may conclude that the titration ceases to be practicable with an accuracy ρ when any of the functions of the ionization-constants given in the preceding list become greater than $^1/_{10}\rho^2$; thus greater than 10^{-7} for an accuracy of $^1/_{10}$ per cent., greater than 10^{-6} for an accuracy of $^1/_3$ per cent., and greater than 10^{-5} for an accuracy of 1 per cent.

VII. Appendix.

25. *Values of the Ionization-Constants of Indicators.*—The application of the principles developed in this article to the various practicable titrations involves the use of a series of indicators with ionization-constants varying in value by gradations from about 10^{-3} to 10^{-11}. Unfortunately, our knowledge of the ionization-constants of the numerous available indicators is at present for the most part inexact, and needs to be supplemented by further careful investigations. Extensive preliminary studies of indicators in this direction were first made by Friedenthal,[1] Salessky,[2] Fels,[3] and Salm,[4] who have published tables showing roughly the hydrogen-ion concentration at which a large number of indicators undergo change in color, in connection with which it may be recalled that the ionization-constant of an indicator is equal to the hydrogen-ion concentration at which it is one-half transformed into its salt. A more careful investigation by the colorimetric method has been made by Saim[5] with the object of obtaining better values of the constants for several of the more important indicators. A quantitative study of phenolphthalein has also been

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[1] *Z. Elektrochem.*, 10, 113 (1904).

[2] *Ibid.*, 10, 204 (1904).

[3] *Ibid.*, 10, 208 (1904).

[4] *Ibid.*, 10, 344 (1904).

[5] *Z. physik. Chem.*, 57, 492–7 (1907).

made colorimetrically by McCoy,[1] Hildebrand,[2] and Wegscheider;[3] and the ionization-constant for *p*-nitrophenol has been determined by the ordinary conductivity method by Bader,[4] Hantzsch,[5] Holleman,[6] and Lundén.[7]

The following table contains the values of the apparent indicator-constant K_I (as defined at the end of Section 3) derived from these quantitative investigations, the data being those of Salm, except in the case of phenolphthalein where the geometrical mean of the values obtained by him, McCoy, and Hildebrand,[8] is given, and except in the case of *p*-nitrophenol where the ratio of the mean value[9] (excluding Bader's) derived from the various conductivity investigations to 0.83 (the value of γ at 0.1 normal) is adopted. In the case of the basic indicators, the value given is that which the constant would have if the indicator were regarded as an acid.

TABLE 3.—IONIZATION-CONSTANTS OF INDICATORS.

Dimethylaminoazobenzene	7×10^{-4}	Alizarin	9×10^{-9}
Methyl orange	5×10^{-4}	Cyanin	2×10^{-9}
p-Nitrophenol	9×10^{-8}	Phenolphthalein	2×10^{-10}
Rosolic acid	1×10^{-8}		

It is to be borne in mind that it is not the ionization-constant itself, but the product obtained by multiplying it by $(1 - \alpha)/\alpha$, where α is the fraction of the indicator transformed into its salt at the end-point, that is directly involved in the applications of the theory to volumetric analysis. It is therefore important to know also the limits between which the fraction transformed and therefore this product, designated throughout this article the indicator-function k, can in practice be varied, by adding different quantities of the indicator. In accordance with the considerations of Section 5 and the experiments communicated in the foot-notes thereto, the following values may be provisionally given as representing

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[1] *Am. Chem. J.*, **31**, 503 (1904).

[2] *Z. Elektrochem.*, 14, 351 (1908).

[3] *Ibid.*, 14, 510 (1904).

[4] *Z. physik. Chem.*, **6**, 297 (1890).

[5] *Ber.*, **32**, 3070 (1899).

[6] *Rec. trav. chim. Pays. Bas*, **21**, 444 (1902).

[7] *J. chim. physique*, **5**, 586 (1907).

[8] Salm's value is 8×10^{-10}, McCoy's 0.8×10^{-10}, Hildebrand's 1.7×10^{-10}, and Wegscheider's 1.8×10^{-10}. This disagreement illustrates the uncertainty which is probably attached to the other values obtained by the Salm method, which involved electromotive-force measurements with hydrogen-gas cells.

[9] The separate values are 12×10^{-8} (Bader), 9.6×10^{-8} (Hantzsch), 6.5×10^{-8} (Holleman), and 7.0×10^{-8} (Lundén).

roughly the values of the indicator-function *k* practically attainable with certain indicators.

TABLE 4.—PROVISIONAL VALUES OF THE INDICATOR-FUNCTION ATTAINABLE WITH VARIOUS INDICATORS.

Dimethylaminoazobenzene: 0.1 K_I or 7×10^{-5}.
Methyl orange: 0.1 K_I or 5×10^{-5}.
p-Nitrophenol: 1000 K_I to $3K_I$ or 9×10^{-5} to 3×10^{-7}.
Phenolphthalein: $20K_I$ to $3K_I$ or 4×10^{-9} to 6×10^{-10}.

26. *Values of the Ionization-Constants of Acids and Bases.*—To facilitate the application of the principles and formulas derived in this article to actual titrations, the ionization-constants of most of the important inorganic acids and bases at or near 25° have been brought together in the following table, and references to summaries of those of the organic acids and bases are given below.

TABLE 5.—IONIZATION-CONSTANTS OF INORGANIC ACIDS AND BASES.

Monobasic acids.	K_A.	Polybasic acids.*	K_{A_1}.	K_{A_2}.
HCl, HBr, HI	1	H_2SO_4[6]	1	3×10^{-2}
HNO_3, $HClO_3$, $HClO_4$	1	H_2CrO_4[7]	1	6×10^{-7}
HNO_2[1]	5×10^{-4}	H_2SO_3[8]	1.7×10^{-2}	......
HClO[2]	4×10^{-8}	H_3PO_4[9]	1.1×10^{-2}	2×10^{-7}
HCN[3]	7×10^{-10}	H_3AsO_4[10]	5×10^{-3}	......
HH_2BO_3[4]	7×10^{-10}	H_2CO_3[3, 11]	3.0×10^{-7}	3×10^{-11}
HH_2AsO_3[5]	6×10^{-10}	H_2S[12]	9.1×10^{-8}	1×10^{-15}

Monacidic bases.	K_B.
KOH, NaOH	1
(½Ba)OH, (½Ca)OH[13]	0.3
NH_4OH	1.8×10^{-5}

* K_{A_1} = ionization-constant for the first hydrogen, K_{A_2} = that for the second hydrogen.

[1] Schumann, *Ber.*, 33, 582 (1900); Blanchard, *Z. physik. Chem.*, 41, 706 (1902); Bauer, *Ibid.*, 56, 220 (1906).

[2] Sand, *Z. physik. Chem.*, 48, 614 (1904).

[3] Walker, *Ibid.*, 32, 137 (1900); Madsen, *Ibid.*, 36, 293 (1901).

[4] Lundén, *J. chim. physique*, 5, 580 (1907).

[5] Wood, *J. Chem. Soc.*, 93, 411 (1908).

[6] Noyes and Eastman, *Carnegie Institution Publications*, 63, 274 (1907).

[7] Sherrill, THIS JOURNAL, 29, 1673 (1907). In the case of H_2CrO_4 the relations are somewhat complicated by the fact that the $HCrO_4^-$ ion goes over partly into Cr_2O_7 by dehydration.

[8] Kerp, *Chem. Abstracts*, 4, 442 (1910); Drucker, *Z. physik. Chem.*, 49, 581 (1904).

[9] Abbott and Bray, THIS JOURNAL, 31, 760 (1909). K_{A_3} for $H_3PO_4 = 3.6 \times 10^{-13}$.

[10] Luther, *Z. Elektrochem.*, 13, 297 (1907).

[11] Bodländer, *Z. physik. Chem.*, 35, 23 (1900); McCoy, *Am. Chem. J.*, 29, 455 (1903).

[12] Auerbach, *Z. physik. Chem.*, 49, 220 (1904); Knox, *Trans. Faraday Soc.*, 1908, 43.

[13] Since barium and calcium hydroxides, like the tri-ionic salts, apparently do not dissociate in stages with formation of the intermediate ions $BaOH^+$ or $CaOH^+$, they can be regarded as monacidic bases.

A comprehensive list of the ionization-constants for organic monobasic acids, for the first hydrogen of organic polybasic acids, and for organic monacidic bases, is given in Kohlrausch and Holborn's "Leitvermögen der Electrolyte" (pp. 176–94); and a more nearly complete one will be found in Lundén's monograph on "Affinitäts-messungen an schwachen Säuren und Basen" (pp. 81–102) in Ahrens' *Sammlung chemischer und chemisch-technischer Vorträge.* Values for the specific acids and bases will also be found under them in Beilstein's and in Meyer and Jacobson's "Handbücher der organischen Chemie." The facts must not, however, be overlooked that the values given in all these books except Lundén's are 100 times the true ionization-constants, which have been employed throughout this article; and that in the case of dibasic acids the values given are ordinarily those for the first hydrogen, while it is those for the second hydrogen that are involved when the total acid is to be titrated. Values for the constants for the second hydrogen of many dibasic acids will be found in an article in THIS JOURNAL by Chandler.[1]

With the aid of Table 2, given near the end of the summary, and the data presented or referred to in this section and the preceding one, the conditions for realizing a satisfactory titration of any particular slightly ionized acid or base may be readily derived; or, if the titration is not practicable, the fact that such is the case may be determined.[2]

BOSTON, May 1910.

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[1] THIS JOURNAL, 30, 713 (1908).

[2] A concrete example may facilitate the application of these considerations by analysts. Suppose that butyric acid is to be titrated with sodium hydroxide. We find by reference to the summaries of Kohlrausch and Holborn or Lundén or to Meyer and Jacobson's text-book that the ionization-constant K_A for this acid is 1.5×10^{-5}. Referring to the first row of Table 2, we find that the best value of the indicator-function k for the titration of a monobasic acid by a largely ionized base is equal to $10K_WK_A$; therefore for this acid at 25° where $K_W = 10^{-14}$, it is $10 \times 10^{-14} \times 1.5 \times 10^{-5}$ or 1.2×10^{-9}. Reference to Table 3, in Section 25, shows that this value may be secured by using phenolphthalein (for which K_I is 2×10^{-10}) and causing it to be about 14 per cent. transformed into its salt at the end-point (since $k = K_I(1 - \alpha)/\alpha = 2 \times 10^{-10} \times 0.86/0.14 = 1.2 \times 10^{-9}$), and reference to Table 4 in Section 25 shows that it is practicable to secure with phenolphthalein this fraction transformed (since it corresponds to a value of k equal to $6K_I$).

The succeeding expressions in the first row of Table 2 show also that the maximum and minimum values which the indicator-function must have, if an accuracy ρ is to be secured, are $K_A\rho$ and $10K_W/\rho$, respectively; so that in this case if an accuracy of 0.1 per cent. ($\rho = 0.001$) is to be secured, the value of the indicator-function must be between the limits 1.5×10^{-8} and 10^{-10}. This shows that the attained value of the indicator-function must not be greater than 10 times the best value just calculated or smaller than one-tenth of that best value.