Although the results given in Table IV cannot be considered as final and will need confirmation, they indicate one or two rather interesting points.

It will be noticed that the silica, soluble in hydrochloric acid, increases with the increase in the temperature at which the clinker is produced. The silica, soluble in sodium carbonate, however, reaches a maximum in sample No. 14, burned at 1352°. The total insoluble residue after treatment with sodium carbonate, usually reported as "undecomposed silicate," is smallest (0.54 per cent.) in this same sample. The amount of undecomposed silicates seems to increase with rise in temperature above 1352°, and the proportion of silica given off on treating these undecomposed silicates with hydrofluoric acid, is about one-half their weight.

These results would go to indicate that probably all of the original silicates were converted into readily decomposable basic silicates by the time a temperature of 1352° was reached, and that the increased amount of undecomposed silicates found in the high numbers may be due to the more acid silicates left in the magma, from which the tricalcium silicate or other true cement-forming material has separated.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

# THE THEORIES OF INDICATORS.[1]

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IN CONNECTION with the use of indicators in the titration of acids and alkalies there are two main questions of theoretical interest: First, what chemical change does the indicator undergo which causes it to change color, and, second, what is the cause of the characteristic differences in sensitiveness shown by such indicators as phenolphthaleïn and methyl orange towards the various acids and bases—differences which are of the greatest importance in laboratory practice.

Considering first the more interesting question as to the change of color, we find two distinct views held; but only one, the theory of Ostwald, has become generally known and has found a place

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[1] See Stieglitz, this Journal, **24**, 558 (1902).

and uniform acceptance in every modern text-book examined[1] which discusses the subject at all.[2] It is extremely probable, moreover, that this theory is wrong in so far as the interpretation of the cause of the change of color is concerned. The other view, growing out of researches with organic dyes and other colored substances, appears to be almost unknown, although work in more recent years is confirming results which had their origin over ten years ago. While most likely wrong in regard to the one question of change of color, Ostwald, in his theory of indicators, has undoubtedly laid down correctly the guiding principles of the proper theoretical treatment of the second, scientifically far more important, question, concerning the varying sensitiveness of the indicators to acids and bases. In this paper, it is proposed to discuss, critically, the two theories concerning the change of color and particularly to develop the relation of the newer interpretation of this phenomenon to Ostwald's fundamental views on the sensitiveness of indicators. It is thought that such a development may remove the main obstacle in the way of the general acceptance of what seems to the author the correct explanation of the color change.

## THE CHANGE OF COLOR OF INDICATORS.

*The Ionization Theory.*—All indicators used with acids and bases, as Ostwald pointed out, are themselves either bases or acids and capable of salt formation. A few, like methyl orange,[3] are at the same time both base and acid (amphoter), and able to form salts either with an acid or a base. There is an undoubted intimate connection between this salt formation and the change of color, but what is the real nature of the connection? According to Ostwald's theory,[4] which has found such wide acceptance, the change of color of an indicator, tersely expressed, is due to a change of its ionic condition. In the case of phenolphthaleïn, which may be used in illustration, the colorless molecule,

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[1] Ostwald's "Lehrbuch der allgemeinen Chemie," 1891, and "Scientific Foundations of Analytical Chemistry," 1900; Walker's "Introduction to Physical Chemistry," 1899; Nernst's "Theoretische Chemie," 1900; Arrhenius's "Electrochemie," 1901; Jones's "Elements of Physical Chemistry," 1902, and "Principles of Inorganic Chemistry," 1903.

[2] See, however, W. A. Noyes's "Organic Chemistry," published while this paper was being written, and referring to the other, probably correct view.

[3] The indicator characteristics of methyl orange are due essentially to its basic character (see below).

[4] Ostwald: *Loc. cit.*

$\underline{OCOC_6H_4C}(C_6H_4OH)_2$, (I), is supposed to produce the red negative ion, $\overline{OCOC_6H_4C}(C_6H_4OH)C_6H_4\overset{-}{O}$, (II). Phenolphthaleïn, which appears to be a very weak acid, can indeed be very little ionized in aqueous solution, and the dissociation constant for the condition of equilibrium,

$$PH \rightleftarrows P' + H^{\cdot},$$

must be so small that a slight excess of hydrogen ions from any acid would be able to suppress almost completely the negative phenolphthaleïn ions. Its alkali salts, however, would be very highly ionized, like all alkali salts. We have, therefore, coincident with the change of color, a change also of phenolphthaleïn from the molecular to the ionic condition. It was, perhaps, a perfectly natural, although not a necessary, conclusion that the simultaneous change of ionic condition and color bear the relation to each other of cause and effect. This conclusion was, doubtless, even more readily reached and accepted because Ostwald had just shown,[1] with the aid of the spectroscope, that many of the characteristic changes of color which dry inorganic salts experience on treatment with water are almost certainly due to changes from the molecular form to the differently colored ions, so that solutions of all salts of a given metal like copper show identical absorption spectra when the salts are completely ionized.[2] In spite of this parallel with inorganic salts and, notwithstanding the striking coincidence mentioned above, on which this theory of the change of color of an indicator like phenolphthaleïn is based, facts have been known for ten years and new ones have become known more recently, which prove that the change is not primarily due to a change of ionic condition, but to a very important change of constitution of the phenolphthaleïn molecule when it goes from the colorless into the red condition.

*The "Chromophoric Theory."*—In view of what chemists have known for over a quarter of a century about the intimate connection between color production and constitution of organic compounds, the explanation that phenolphthaleïn (I) without a single chromophoric group should become intensely red by forming the ion (II) without any chromophoric group, appeared from the

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[1] In the "Lehrbuch," p. 799, the theory of indicators follows immediately the discussion of the color of inorganic salts.

[2] See, however, Kastle, *Am. Chem. J.*, 16, 326 (1894).

outset as extremely unlikely. As early as 1892, a year after Ostwald's theory was published, Bernthsen[1] made it appear practically certain that whereas phenolphthaleïn in its colorless solution has the constitution of a lactone, as expressed by (I), its red salts are the salts of a carboxyl acid, not a phenol, and have the constitution.[2] $(MeOOC.C_6H_4)(HOC_6H_4)C:C_6H_4:O$. The strongly chromophoric quinoid complex $(:C_6H_4:O)$ gives us an explanation of the production of intense color, which is entirely adequate, in view of the general laws governing color in organic compounds. The sodium salt is, no doubt, incidentally ionized in solution, but that this ionization is merely a coincidence and not a cause is established by the fact that the solid, dry, non-ionized silver salt is also intensely colored (violet). Other strong proof that the view first presented by Bernthsen is the correct one, lies in the fact that Nietzki and Burckhart[3] have prepared colored, non-ionized ethers of tetrabromphenolphthaleïn,

$$(C_2H_5O_2C.C_6H_4)(HOC_6H_2Br_2).C:C_6H_2Br_2:O$$

and

$$(C_2H_5O_2C.C_6H_4)(C_2H_5OC_6H_2Br_2).C:C_6H_2Br_2:O,$$

with quinoid molecules, and colorless lactoid ethers, isomeric with the colored one, namely,

$$\underbrace{OCOC_6H_4C}(C_6H_4Br_2OH)(C_6H_2Br_2OC_2H_5)$$

and

$$\underbrace{OCOC_6H_4C}(C_6H_2Br_2OC_2H_5)_2.$$

In the absence of the chromophoric quinoid group, color is also absent, but the question of ionization has no effect at all on the matter of color or absence of color.

Similarly, it has long been known that the intensely colored salts of the rosaniline series of dyes are quinone derivatives, *e. g.*, the hydrochloride of pararosaniline,

$$(H_2NC_6H_4)_2C:C_6H_4:NH_2Cl,$$

and that the corresponding free base is more or less rapidly converted into the isomeric, colorless carbinol,

$$(H_2NC_6H_4)_3C(OH),$$

the color disappearing again with the quinone complex. The

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[1] *Chem. Ztg.*, p. 1956 (1892). *Vide* also Friedländer: *Ber. d. chem. Ges.*, **26**, 172, 2258 (1893).

[2] The lactone ring is saponified very readily by alkalies, as are lactones in general.

[3] *Ber. d. chem. Ges.*, **30**, 175 (1897).

difference between the behavior of phenolphthaleïn and rosaniline, as will be shown, is essentially a difference in the speed of the change of constitution. More recently, Hantzsch[1] has shown that, in general, the change of colorless organic compounds into highly colored salts is invariably accompanied by a modification of the constitution affecting a chromophoric group. Reference need only be made to the formation of red salts,

$$RC(NO_2) : NONa,$$

from the colorless nitrolic acid,

$$RCH(NO_2)NO.$$

## THE CHANGE OF COLOR OF INDICATORS SHOWING TWO COLORS.

*The Ionization Theory.*—Turning to the consideration of a second kind of indicators, such as methyl orange and litmus, which change from one color to another, we again find the two theories confronting each other. According to Ostwald's views,[2] as slightly modified by Küster,[3] the yellow color of methyl orange in alkaline solution is due to the formation of an intensely yellow, negative ion,

$$\overset{-}{O}_3SC_6H_4N : NC_6H_4N(CH_3)_2,$$

methyl orange, which is amphoter, behaving in this case as an acid. In acid solution, we have an ion which carries both a negative and a positive charge,

$$\overset{-}{O}_3SC_6H_4N : NC_6H_4N(C\overset{+}{H}_3)_2H,$$

and which is said to have a not very intense red color. The difference between the two colored substances is supposed to be simply one of ionization; both are supposed to have essentially the same chromophoric complex (the azo groups, $N : N$), but different electric charges.

*The "Chromophoric Theory."*—In view of what has been explained above as to the change of constitution and of chromophoric complexes attending the change of phenolphthaleïn, the rosanilines, etc., from a colorless to a colored condition, we are justified in questioning the adequateness of the ionization explanation of the change of color, also, of bicolored indicators like methyl orange. We may ask whether analogous, constitutional and chromophoric changes of the molecule of methyl orange do not

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[1] *Ibid.*, **32**, 583. 3085 (1899), etc.

[2] "Scientific Foundations of Analytical Chemistry."

[3] *Ztschr. anorg. Chem.*, **13**, 135 (1897); *Vide* Bredig: *Ztschr. Elektrochem.*, **6**, 33 (1899).

accompany its transition from yellow to red, and vice versa. As a matter of fact, for reasons quite distinct from the sole question of color, chemists have for a number of years been seriously divided as to the true constitution of dyes of the class of methyl orange (amino and hydroxyazobenzene dyes). There are two possible constitutions for methyl orange:

(I) $HO_3SC_6H_4N:NC_6H_4N(CH_3)_2$

which represents an aminoazobenzene with a chromophoric azo group ($N:N$), and

(II) $\underbrace{O_3SC_6H_4NH.N:C_6H_4:N(CH_3)_2}$,

the inner salt (sulphonate) of a phenylhydrazone of an iminoquinone, containing the chromophoric quinoid group ($:C_6H_4:$). It seems extremely probable that in alkaline solutions we have yellow, metal salts of methyl orange of the constitution (I), with the azo group, and, in acid solution, red salts of the quinoid constitution (II) or, in the presence of an excess of acid, the perfectly analogous red salts of other acids, such as

(II') $HO_3SC_6H_4NH.N:C_6H_4:N(CH_3)_2Cl$.

The change of color would then be attended by a profound change of chromophoric complexes. Aside from the general considerations of analogy to phenolphthaleïn and other dyes, and of agreement with the general laws governing color in organic compounds, the chief support for this "chromophoric theory" of the change of color of bicolored indicators is found in the fact that for hydroxyazobenzene, which structurally is entirely analogous to methyl orange, Hantzsch[1] has recently proved that in alkaline solutions it is, indeed, the salt of an azophenol,

$$C_6H_5N:NC_6H_4ONa,$$

but in neutral and acid solutions a phenylhydrazone of quinone, *e. g.*,

$$(HClC_6H_5NH).N:C_6H_4:O.$$

The dry sodium salt is orange, the dry hydrochloride a deep purple-red. With the change of constitution we have, therefore, again a marked change of color.

## THE CHANGE OF COLOR AND OF IONIZATION A COINCIDENCE.

Results of the last ten years in the field of organic chemical research, such as the work of Nef on the salts of acetoacetic and

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[1] *Ber. d. chem. Ges.*, **32**, 590, 3089 (1899).

malonic ethers,[1] and of Hantzsch on pseudo-acids and bases, enable us to understand also very readily why there should be this striking coincidence between the change of color of indicators and the change of the ionic condition without any strictly causal relation between the two facts. The coincident is simply due to the fact that many organic acids, and among them indicators that are acids, are extremely unstable in the form of *free acids,* and readily suffer a change of constitution to closely allied, isomeric (tautomeric) substances, which are no true acids (not ionized). Analogous relations are known to exist for many organic bases. The *salts,* however, of such acids or bases are stable, whether in solution (ionized) or dry (non-ionized). Thus nitrophenylmethane is known in two forms;[2] isonitrophenylmethane,

$$C_6H_5CH:NOOH,$$

a rather strong acid, which is precipitated when the solutions of its salts are rapidly and strongly acidified, but which changes gradually and spontaneously to a stable, neutral isomer, nitrophenylmethane,

$$C_6H_5CH_2.NO_2.$$

In other cases of this kind, the isomerization is instantaneous.

Such a substance, to be serviceable as an indicator, must suffer isomerization from the acid (or basic) condition to the pseudo (neutral) condition or vice versa, practically *instantaneously* and the isomerization *must also affect a chromophoric group.* In the case of phenolphthaleïn, which may again serve in illustration, we must have a true acid form,

$$H^*OOCC_6H_4(HOC_6H_4)C:C_6H_4:O,$$

from which the colored metallic salts are derived, but which in

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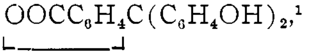
[1] Vorländer (*Ber. d. chem. Ges*, **36**, 268 (1903)), having proved malonic ether to be a true weak acid in aqueous solution, supposed that this fact proves also that the salts of malonic ether have the constitution $MeCH(COOR)_2$ and not $ROOC.CH:C(OMe)OR$, as advocated by Nef. As a matter of fact, the evidence merely shows that malonic ether is somewhat ionized in aqueous solution and a very weak acid. The assumption that an oxygen acid, $ROOC.CH:C(OH)OR$, must be a strong acid is entirely unwarranted; but, moreover, the important fact is left entirely out of consideration that in an aqueous solution, two forms of malonic ether would be in equilibrium with each other, *viz.*,

$$ROOC.CH_2COOR \rightleftarrows ROOC.CH:C(OH)OR.$$

If there were very little of the latter acid found present, malonic acid would appear to be a very weak acid, even if the acid form ionized quite easily (see below). The results of Vorländer are, therefore, evidence neither for nor against Nef's views as to the constitution of the salts, and taken in connection with Hantzsch's work on pseudo-acids rather confirm Nef's conclusions.

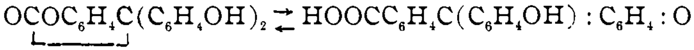
[2] Hantzsch: *Ber. d. chem. Ges.*, **29**, 699, 2251 (1896).

the free acid condition must go, practically, instantly over into the colorless lactoid form,



$$OOCC_6H_4C(C_6H_4OH)_2,$$[1]

the hydrogen atom, H*, suffering a change of position. The lactone is the more stable of the two isomers, belonging, as it does, to the most stable class of lactones, the $\gamma$-lactones. However, in an aqueous solution of phenolphthaleïn we must have, as in the case of all such tautomeric substances, a condition of equilibrium between the lactoid and quinoid forms:



$$OCOC_6H_4C(C_6H_4OH)_2 \rightleftarrows HOOCC_6H_4C(C_6H_4OH):C_6H_4:O \quad (1)$$

The condition of equilibrium favors the lactoid form, since the solution is colorless, and only minimal quantities of the quinoid acid can be present. This trace of quinoid acid is ionized and in equilibrium with its ions:

$$HOOCC_6H_4C(C_6H_4OH):C_6H_4:O \rightleftarrows H^{\cdot} + \overset{-}{O}OCC_6H_4C(C_6H_4OH):C_6H_4:O \quad (2)$$

The addition of an alkali causes the hydrogen ions (equation 2) to disappear; more of the quinoid molecules (equations 1 and 2) must be ionized to preserve equilibrium and the quinoid molecules, in turn, be reproduced from the lactoid (equation 1) as fast as the former are converted into the salt. The effect of the alkali, therefore, is to suppress the colorless lactoid isomer by converting the unstable, free quinoid acid into its stable quinoid salt, which is colored red and is incidentally ionized. That it is only a question of stability of the salt and not of ionization is proved by the fact that the dry salts are as intensely colored as the solution. The case is obviously entirely analogous to that of carbonic acid, whose neutral alkali salts, the carbonates, whether ionized in solution, or non-ionized in a dry state, are so very much more stable than the free acid. In fact, in both cases, the dry, non-ionized condition is rather more favorable to stability and, therefore, in the case of phenolphthaleïn, to the maximum formation of color, since in consequence of the ionization in aqueous solution we have hydrolysis and a reversal of equations (1) and

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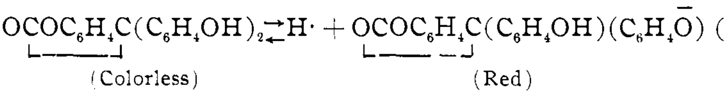
[1] It is possible that the unstable isomer, the true carboxylic acid, will some day be isolated; but this is not at all essential for the theory, as analogous unstable isomers, such as isonitrophenylmethane, have been isolated and their spontaneous change studied.

(2) for phenolphthaleïn and an analogous change of the carbonates.

The equilibrium equations (1) and (2), as just developed, enable us to put the two theories of the cause of the change of color of indicators briefly, thus: Ostwald's theory takes an equation analogous to (2), *viz.*,



$$\underbrace{OCOC_6H_4C}(C_6H_4OH)_2 \rightleftarrows H^{\cdot} + \underbrace{OCOC_6H_4C}(C_6H_4OH)(C_6H_4\bar{O}) \quad (2'),$$

(Colorless) (Red)

alone into account, ascribing the change of color to the shifting of equilibrium according to (2'); the "chromophoric theory" takes both equations, (1) and (2), into account and ascribes the *change of color* to the shifting of equilibrium according to (1).

## THE SENSITIVENESS OF INDICATORS.

This condensed contrast of the two theories enables us to proceed to the second question raised in the opening paragraph of this paper, to the question as to the different degrees of sensitiveness of the various indicators to weak acids and bases.

In this, the more important of the two questions raised, Ostwald has brilliantly laid the foundations for a correct theoretical interpretation and practical application of the varying phenomena, and we need only consider in what relation the new interpretation of the cause of the change of color stands to his views on the sensitiveness of indicators.

*The Ionization Theory.*—According to Ostwald, the indicators, as acids and bases, take part in the changes of chemical equilibrium in the solution by forming salts and are subject to the general laws governing equilibrium and notably to that of mass action. The sensitiveness of an indicator, consequently, must depend chiefly on the numerical size of its ionization constant as an acid or base. For instance, according to (2')

$$C_H \times C_L = K \times C_{LH}, \qquad (3)$$

if $C_H$, $C_L$, and $C_{LH}$ represent, respectively, the concentrations of the hydrogen ions, the complex organic negative ions and the non-ionized molecules of an acid indicator, and K its ionization constant according to Ostwald's dilution law for organic acids. If, as in the case of phenolphthaleïn, the colored substance is the complex negative ion, the formation and intensity of color would be measured by $C_L$. As explained above, by the suppression of the hydrogen ions ($C_H$) and the formation of metal salts, which are largely ionized, $C_L$ would become very large. Now, if the ionization constant K is exceedingly small and the indicator, therefore, a very weak acid, it cannot be sensitive to very weak bases, because the nearer the dissociation constants of base and acid approach that of water itself, the less readily are salts formed; water prevents their formation by hydrolysis according to the well-known equation:

$$\overset{+}{\mathrm{Me}} + \overset{-}{\mathrm{L}} + \mathrm{H_2O} \rightarrow \mathrm{LH} + \mathrm{MeOH}. \qquad (4)$$

In the same way, the smaller the dissociation constant K or the weaker the indicator is as an acid, the more sensitive and, therefore, the more serviceable will it be in the titration of ordinarily weak acids, such as oxalic, acetic and carbonic; the small excess of hydrogen ions formed by these acids would be sufficient to drive the indicator out of its colored salts into the colorless molecules, since $C_L$ grows smaller, according to (3), as $C_H$ grows larger, and it does so the more rapidly the smaller K is.

By the same process of reasoning, it would follow, vice versa, that an indicator which is a moderately strong acid with a large dissociation constant, as methyl orange was supposed to be, or one which is a very weak base, with a very small dissociation constant as a base, as methyl orange really is,[1] would be an excellent indicator for strong or weak bases, but a very poor one for weak acids.

These conclusions, as developed from Ostwald's statements, agree in the main with the facts as far as they are known. Observations have been chiefly of a qualitative nature, and quantitative measurements of the dissociation constants of our most important indicators are extremely desirable,[2] but there is no reason to expect that they will modify in any way Ostwald's views which have just been described.

*The "Chromophoric Theory."*—The above views are based, however, on Ostwald's theory as to the change of color, briefly, for phenolphthaleïn, on equation (2'). But it is almost certain that this part of the theory is wrong and that the two equations, (1) and (2), express the changes in an indicator, and (1) in par-

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[1] As explained below, the value of methyl orange as an indicator is due rather to its weak basic functions than to its acid character.

[2] *Vide* Bredig: *Loc. cit.*

ticular expresses the cause of the change of color. A brief consideration will show that this new view does not modify, in any fundamental respect, the result of the application of the laws of chemical equilibrium to the indicators, but simply introduces one or more new constant factors into the final equilibrium equation, factors which are rather helpful than otherwise in the interpretation of the facts.

Using phenolphthalein again as an illustration, we have two conditions of equilibrium occurring simultaneously in solution. First, according to equation (1), (p. 1119),

$$C_{QH} = k \times C_{LH}, \qquad (5)$$

if $C_{LH}$ and $C_{QH}$ represent the concentrations of the lactoid and quinoid forms of phenolphthaleïn and $k$ is a constant. Again for equation (2), (p. 1119), we have

$$C_Q \times C_H = K' \times C_{QH}, \qquad (6)$$

if we express the concentrations of the negative quinoid ions and of the hydrogen ions by $C_Q$ and $C_H$, that of the undissociated quinoid molecules again by $C_{QH}$, and the ionization constant of Ostwald's dilution law by K'.

Combining (5) and (6) we have:

$$C_Q \times C_H = k \times K' \times C_{LH} \qquad (7)$$

or

$$C_Q \times C_H = K'' \times C_{LH}. \qquad (7')^1$$

This is the same form of equation as developed above for the sensitiveness of the indicators (equation 3), with this simple difference that in equation (3) the constant K is only the ionization constant, in equation (7'), K" is the product of the true ionization constant K' of the quinoid acid and the stability constant $k$ of the two tautomeric forms of phenolphthaleïn. Equation (7') tells us, therefore, that such an acid as phenolphthaleïn is in its effect only as strong an acid as the joint action of ionization and possibility of molecular existence in solution make it. Its tend-

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[1] In this expression, for an aqueous solution of phenolphthalein, $C_Q$ and $C_H$ are not equal to each other, as hydrogen ions are formed not only by the carboxyl group of the quinoid acid but also by its phenolhydroxyl group as well as by the two phenolhydroxyl groups of the lactoid acid. The effect of this increase of hydrogen ions is to make phenolphthaleïn, as indicator, react as a still weaker acid than it otherwise would, that is, it is less sensitive to alkalies, more sensitive to acids. Thus phenolphthaleïn is affected favorably in the very direction in which it is of particular value as an indicator. A most instructive quantitative study of similar relations has been carried out for carbonic acid by H. N. McCoy, *Am. Chem. J.*, **29**, 437 (1903).

ency to produce the red color is measured by the same constant K". Entirely analogous relations and equilibrium equations, it may be added, exist for ammonium hydroxide, which also is unstable in solution.[1]

It is obvious from a comparison of equations (7') and (3). that all of the conclusions as to sensitiveness which were based on equation (3) apply equally well to the new equation (7'). The substitution of (7) for (3) shows us further, however, the great importance of the stability constant *k*, for the smaller *k* is the more difficult will it be to obtain the quinoid acid and its salts, to which the red color of the alkaline phenolphthaleïn solution is due, and consequently the less sensitive will the indicator be to alkalies. It is very probable, indeed, that phenolphthaleïn in its quinoid form with a carboxyl group is not such a very weak acid in itself, but the minute quantities in which it is able to exist in the free state make it appear and react as such.

But a still more important conclusion concerning indicators can be drawn from the substitution of equation (7') for (3) and the introduction of the stability constant *k* into the final equilibrium equation. Whereas changes involving only new conditions of equilibrium of ions always take place practically instantaneously (equation 6), reactions involving the transformation of one isomer into another (equation 5) show the widest range of difference as regards the velocities of the changes. The constant *k* of this equation (5), as is well known, is merely the ratio of the velocities of the two opposite reactions; the same ratio may be the result of two exceedingly great or two very small velocities. Now the velocities of change for serviceable indicators, no matter what their ratio is, must be exceedingly great in either direction, and practically of the order of the velocity of ionic changes. It is very probable that in the case of the indicators actually used the velocities are not only very great in both directions, but are increased by the catalytic action of hydroxyl and hydrogen ions[1] in such a way that complete equilibrium, according to (5) and (6), is reached instantaneously. This consideration shows us wherein an indicator differs from other intensely colored sub-

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[1] Kohlrausch: Wied. *Ann*. **26**, 197 (1885): Ostwald: *J. prakt. Chem.* (2), **33**, 358 (1886). and *Ztschr. phys. Chem.*, **2**, 36 (1888): Hantzsch: *Ibid.*, **30**, 258 (1899).

[2] Cameron's observation (*Am. Chem. J.*, **23**, 477 (1900)) that the red color of phenolphthaleïn is rather slowly discharged by carbonic acid may be the result of such an action. His own interpretation is surely wrong.

stances, such as rosaniline, which shows as striking color changes as phenolphthaleïn; it is intensely red in solution, colorless (as carbinol) in alkaline solution, but the transformations are much too slow,[1] at ordinary temperatures, to make rosonaline available as an indicator in acidimetry.[2]

For methyl orange, which exhibits a sensitiveness in extreme contrast to that of phenolphthaleïn and which, incidentally, is a bicolored indicator, relations exist which are entirely analogous to those developed above for phenolphthaleïn. It is always used in neutral solution in the form of a sodium salt and it is in this sensitive neutral solution that we must have a condition of equilibrium between the two tautomeric forms of methyl orange, which were previously discussed (p. 1117). It can best be expressed as follows:[3]

$$SO_3C_6H_4N:NC_6H_4N(CH_3)_2HOH \rightleftarrows \qquad (8)$$
$$SO_3C_6H_4NH.N:C_6H_4:N(CH_3)_2OH,$$

or

$$AzOH \rightleftarrows QOH.$$

The azo derivative on the left hand of the equation is yellow, as the solid sodium salt, which can only be

$$NaSO_3C_6H_4N:NC_6H_4N(CH_3)_2,$$

is yellow; the quinoid form on the right hand is red, for instance, in the form of the solid free sulphonate,

$$\underbrace{SO_3.C_6H_4NH.N:C_6H_4N(CH_3)_2}.$$

as explained above.

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[1] It is also too strong a base to be very sensitive.

[2] NOTE.—In his work on the pseudo-acids and -bases, Hantzsch uses the method of comparing the affinity constant, for instance, of an acid as determined from the measurement of the hydrolysis of its salt, with the affinity constant as ascertained by conductivity measurements in the aqueous solution of the pseudo-acid and decides, on the basis of the great differences in the values obtained, that the free acid must be a different substance (isomeric or tautomeric) from the acid in the salt. This conclusion is perfectly justified and the method an admirable one. But it is never clearly emphasized by Hantzsch—perhaps inadvertently—that such differences can result only if measurements are made before a final condition of equilibrium can possibly have been reached in all the solutions used. Equation (7′), as used in the text, rests, therefore, less on quantitative work done with tautomeric substances than on the experimental work of Kohlrausch (*Loc. cit.*) and Ostwald (*Loc. cit.*) on the ionization of ammonium hydroxide and on that of Bodländer (*Ztschr. phys. Chem.*, **35**, 32) and McCoy (*Loc. cit.*) on carbonic acid as well as on the laws of chemical equilibrium.

[3] The sulphonate group, $SO_3Na$, is ionized and has absolutely nothing to do with the color changes, as was at first supposed; dimethylaminoazobenzene may be used in place of its sulphuric acid derivative, methyl orange. *Vide* Bredig: *Loc. cit.*

If we represent the concentrations in the usual way, we obtain from (8) the equilibrium equation

$$k \times C_{AzOH} = C_{QOH}. \qquad (9)$$

As the solution is yellow, the second quinoid form can only be present in very small quantities and the stability constant $k$ must be exceedingly small.

The red quinoid form is also ionized as an ammonium base, according to

$$QOH \rightleftarrows \overset{+}{Q} + \overset{-}{O}H. \qquad (10)$$

We have, then,

$$C_Q \times C_{OH} = K \times C_{QOH}, \qquad (11)$$

and combining (9) and (11),

$$C_Q \times C_{OH} = k \times K \times C_{AzOH}, \qquad (12)$$

$$C_Q \times C_{OH} = K' \times C_{AzOH}. \qquad (12')^1$$

This is the same form of equation as was developed above for phenolphthaleïn (equation 7 and 7'), only we are dealing in this case with a base rather than with an acid. The ion Q and its salts are red and the red color of the acid methyl orange solution depends on the presence of Q and its development is subject to the equilibrium equation (12) or (12').

The whole behavior of the red, quinoid form of methyl orange (its sodium salt) is that of a *very weak* base, analogous to that of dimethylaminoazobenzene[2] or to the sodium salt of aminoacetic acid.[3] It does not form salts readily with weak acids, such as carbonic and acetic acids; the red carbonate,

$$(NaSO_3.C_6H_4NH.N:C_6H_4:N(CH_3)_2)_2CO_3,$$

is practically completely hydrolyzed and incapable of existence, the liberated base reverting, according to (8) and (9), to the stable yellow isomer. That is why methyl orange is not a sensitive indicator for weak acids. As a very weak base, it will be driven readily out of its red salts by other bases, even weak ones, and the free, red base will revert again, according to (8) and (9), to the yellow form, the result being that methyl orange is an ex-

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[1] As the amino group of the azo form is basic and forms some hydroxyl ions, $C_{OH}$ is somewhat larger than $C_Q$ in an aqueous solution. This fact, in the same way as explained above for phenolphthaleïn, favors the sensitiveness of methyl orange to weak bases, its most important characteristic.

[2] Bredig: *Loc. cit.* *Vide*, however, Ostwald: *Loc. cit.*, and Küster: *Loc. cit.*

[3] Lengfeld and Stieglitz: *Am. Chem. J.*, **15**, 516 (1893).

cellent sensitive indicator for weak bases. Accordingly, K', of equation (12'), must have a very small value, of the order of K'' for phenolphthaleïn in equation (7'). As the ionization constant K (equation 11) of the quaternary ammonium hydroxide must be a rather large one, the very small value of K' is evidently due to the exceedingly small size of the stability constant *k*, which is shown, qualitatively at least, by the color of the neutral methyl orange solution.

Our two most valuable indicators, phenolphthaleïn and methyl orange, which form an extreme contrast, do so as a very weak acid and a very weak base, respectively, in their *quinoid* (red) forms, as shown in equations (7') and (12'); and their weakness is due in largest measure to the *instability* of the quinoid isomers in the form of free acid or free base, respectively.

These considerations give us a complete survey of the chemistry of the different sensitiveness of our two most important indicators on the basis of the conclusions reached in the first part of this paper that the color change must be primarily due to a change of constitution involving a chromophoric complex. An experimental determination of the constants and verification of these views would be very important.[1] They rest, so far, on the work of Bernthsen, Nietzki, and Burckhardt on the phenolphthaleïns; on Hantzsch's investigation of the pseudo-acids and -bases, and on the quantitative study of the equilibrium conditions of ammonium hydroxide and of carbonic acid in solution, as quoted above. An experimental study of the peculiarities of indicators, such as the disappearance of the color of phenolphthaleïn in the presence of a large excess of alkali, would also be profitable and the quinone complex, with its well-known reactivity, would probably be found to be the seat also of this change.[2]

In conclusion, in connection with the discussion of the sensitiveness of our indicators, too much emphasis cannot be laid on the fact that the lack of sensitiveness of phenolphthaleïn in laboratory practice in the titration of a weak base like ammonia or of methyl orange in the titration of a weak acid like acetic acid is

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[1] Bredig (*Loc. cit.*) has announced an experimental study of methyl orange from Ostwald's point of view, and Dr. H. N. McCoy, of this laboratory, in connection with his work on the affinity constants of carbonic acid, has taken up the determination of the affinity constant of phenolphthaleïn. The author feels obliged to refrain from pursuing his subject experimentally until these researches are completed.

[2] The colorless solution probably contains the salt $KO_2C.C_6H_4C(OH)(C_6H_4OK)_2$. The corresponding triacetate of aurine, $C(OH)(C_6H_4OC_2H_3O)_3$, is known and is colorless.

ultimately due chiefly to the fact that a weak base or a weak acid is very much weaker (less ionized) in the presence of its own salts than in pure aqueous solutions.[1] Phenolphthaleïn will readily show the presence of 0.01 cc. N/10 free ammonia in 100 cc. of pure boiled water, to which only 1 milligram of phenolphthaleïn has been added. But in titrating ammonia with N/10 hydrochloric acid, very long before all but that small amount has been neutralized, the red color of phenolphthaleïn disappears, owing to the formation of ammonium chloride. The isothermic equation for ammonium hydroxide is

$$C_{NH_4} \times C_{OH} = k \times C_{NH_3},$$

in which $C_{NH_4}$. $C_{OH}$, $C_{NH_3}$ represent the concentrations of the ammonium ions, the hydroxyl ions and the non-ionized ammonia, and $k$ ($= 1 : 53{,}750$)[2] is the ionization constant. It shows how readily the hydroxyl ions must disappear when an easily ionized salt like ammonium chloride is added to a solution of ammonia. A striking insight into the matter is obtained from the result of the following calculation, made with the aid of the isothermic equation and its known constant and of the known degrees of dissociation of solutions of ammonium chloride: If 10 cc. normal ammonium hydroxide are half neutralized by 5 cc. normal hydrochloric acid, the resulting solution, instead of being one-half as effective as a base, as it would have been if sodium hydroxide had been used, contains very nearly only one-hundredth as many hydroxyl ions as the original solution and is, therefore, only one-hundredth as effective as a base. The same result would be attained if to 10 cc. normal ammonium hydroxide 0.32 gram solid ammonium chloride (= 6 cc. normal ammonium chloride) is added in place of all the acid. In other words, in these concentrations ammonia is weakened fifty times more by the neutral salt ammonium chloride than by the hydrogen ions (in their neutralizing effect) of a nearly equivalent[3] amount of hydrochloric acid. Analogous relations hold for the neutralizing of acetic acid by sodium hydroxide, the affinity constant of acetic acid (1 : 55,000) being nearly the same as that of ammonia.

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[1] Arrhenius: *Ztschr. phys. Chem.*, **2**, 287 (1888); Küster: *Ztschr. Elektrochem.*, **4**, 110 (1897); Stieglitz: *Am. Chem. J.*, **23**, 406 (1900).

[2] Kohlrausch: *Loc. cit.*; Ostwald: *Loc. cit.*

[3] Equivalent to the ammonium chloride.

CHICAGO, April, 1903.