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[CONTRIBUTION FROM THE NEW YORK STATE COLLEGE OF FORESTRY AND SYRACUSE UNIVERSITY.]

# ON THE QUINONE-PHENOLATE THEORY OF INDICATORS.[1] A SPECTROPHOTOMETRIC METHOD FOR MEASURING THE CONCENTRATIONS OF THE QUINOIDAL AND LACTOIDAL SALTS AND THE EQUILIBRIUM AND AFFINITY CONSTANTS OF THE PHENOLPHTHALEINS AND PHENOLSULFONPHTHALEINS.

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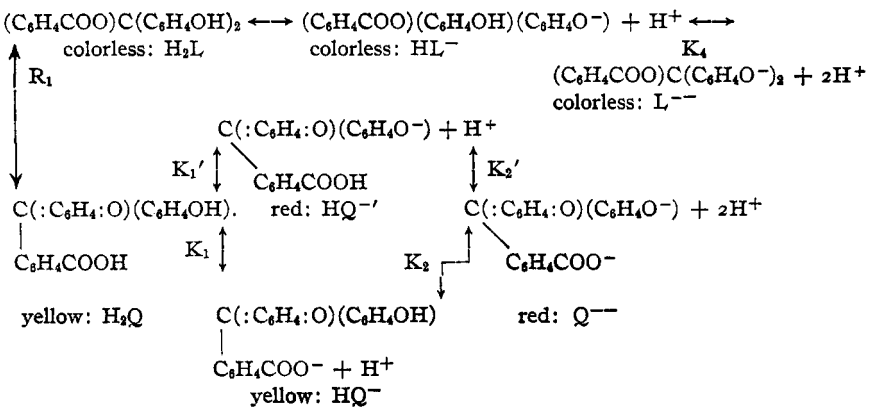
The quinone-phenolate theory[2] postulates that phenolphthalein and phenolsulfonphthalein indicators, with both phenol groups alike, exist in solutions in the following equilibrium. The equations for indicators with unlike phenols, and with a hydrated form, $HOOCC_6H_4C(OH)(C_6H_4OH)_2$, will be given in the general theoretical article now completed.

[1] This article is one of a series which we are publishing from the New York State College of Forestry at Syracuse University in coöperation with Dr. Haven Metcalf, in charge Forest Pathology, Bureau of Plant Industry, Dept. of Agriculture, on quantitative studies of the various chemical and physical factors governing the growth of fungi on culture media and trees.

[2] *Am. Chem. J.*, 37, 71 (1907); 38, 1 (1907); 39, 528 (1908); 42, 115 (1909); THIS JOURNAL, 38, 2772 (1916); 39, 648 (1917); 40, 1092 (1918); *Science*, 42, 101 (1915).




We have found that $HQ^{-\prime}$ and $Q^{--}$ give a strong absorption band in the green at about $1/\lambda = 1800$. In other words an intense red color is transmitted by $HQ^{-\prime}$ and $Q^{--}$, a faint yellow color is transmitted by solutions of $H_2Q$ and $HQ^-$, while $H_2L$, $HL^-$ and $L^{--}$ are colorless.

From the ionization and equilibrium equations for such tautomeric[1] compounds,

$$\frac{H \times HQ^-}{H_2Q} = K_1 \quad (1) \qquad \frac{H \times HQ'^-}{H_2Q} = K_1' \quad (2) \qquad \frac{H \times Q^{--}}{HQ^-} = K_2 \quad (3)$$

$$\frac{H \times Q^{--}}{HQ'^-} = K_2' \quad (4) \qquad \frac{H \times HL^-}{H_2L} = K_3 \quad (5) \qquad \frac{H \times L^{--}}{HL^-} = K_4 \quad (6)$$

$$\frac{H_2L}{H_2Q} = R_1 \quad (7).$$

By simple algebraic combination of two or more of these equations, we may obtain the equilibrium ratio between any one (or several) of the above forms (ions or molecules) and any other (or several other) forms. Certain of the more interesting of these ratios are given below, the important ratios being indicated for convenience by a new constant.

$$\frac{(H)^2 \times Q^{--}}{H_2Q} = K_1K_2 = K_1'K_2' = \frac{(H)^2 \times Q^{--} \times R_1}{H_2L} \quad (8)$$

$$\frac{(H)^2 \times L^{--}}{H_2L} = K_3K_4 \quad (9)$$

$$\frac{(H)^2 \times Q^{--}}{(H_2Q + H_2L)} = \frac{K_1K_2}{1 + R_1} \quad (10) \qquad \frac{(H)^2 \times L^{--}}{(H_2Q + H_2L)} = \frac{K_3K_4R_1}{1 + R_1} \quad (11)$$

$$\frac{H \times (HQ^- + HQ'^- + HL^-)}{(H_2Q + H_2L)} = \frac{K_1' + K_1 + R_1K_3}{1 + R_1} = M_1 \quad (12a)$$

$$\frac{H \times (Q^{--} + L^{--})}{(HQ^- + HQ'^- + HL^-)} = \frac{K_1K_2 + R_1K_3K_4}{K_1' + K_1 + R_1K_3} = M_2 \quad (12b)$$

$$\frac{(H)^2 \times (Q^{--} + L^{--})}{(H_2Q + H_2L)} = \frac{K_1K_2 + R_1K_3K_4}{1 + R_1} = M_1M_2 \quad (12c)$$

[1] *Am. Chem. J.*, **37**, 71 (1907); **38**, 1 (1907); **39**, 528 (1908); **42**, 115 (1909); THIS JOURNAL, **38**, 2772 (1916); **39**, 648 (1917); **40**, 1092 (1918); *Science*, **42**, 101 (1915).

The three Equations 12*a*, 12*b*, 12*c* give the "effective" ionization constants[1] ($M_1$ and $M_2$) obtained when one ignores the tautomerism, and considers simply the molecular, monovalent and divalent forms. Thus $M_1$ corresponds to $K_1K_1'$ or $K_3$, while $M_2$ corresponds to $K_2$, $K_2'$ or $K_4$. Similarly $M_1M_2$ corresponds to $K_1K_2 = K_1'K_2'$ or to $K_3K_4R_1$.

Equations 8 to 12*c* all involve a ratio between different steps of ionization, and so (H) or $(H)^2$ occurs in each equation. The following equations give some of the more interesting ratios where only one step of ionization is involved:

$$\frac{L^{--}}{Q^{--}} = \frac{R_1K_3K_4}{K_1K_2} = R_3 \quad \text{or} \quad \frac{R_3}{R_1} = \frac{K_3K_4}{K_1K_2} \tag{13}$$

$$\frac{L^{--}}{Q^{--} + L^{--}} = \frac{R_3}{R_3 + 1} \tag{14a}$$

$$\frac{Q^{--}}{L^{--} + Q^{--}} = \frac{1}{R_3 + 1} \tag{14b}$$

$$\frac{HL^-}{HQ^-} = \frac{R_1K_3}{K_1} = R_2 \quad \text{or} \quad R_2/R_1 = K_3/K_1 \tag{15}$$

$$\frac{HL^-}{HQ'^-} = \frac{R_1K_3}{K_1'} = R_2' \quad \text{or} \quad R_2'/R_1 = K_3/K_1' \tag{16}$$

$$HQ'^-/HQ^- = K_1'/K_1 \tag{17}$$

$$HQ'^-/Q^{--} = HK_1'/K_1K_2. \tag{18}$$

The general method of measuring the absorption *at different frequencies* in the visible and ultraviolet regions, and at successive stages of neutralization to learn the amounts of the several salts present, was proposed in lectures and articles at various times from 1908 to the present. The plan was suggested for use with colored indicators and also with such tautomeric compounds as the colorless urazoles whose absorption spectra would be studied in the ultraviolet.[2] Schaeffer, Paulus, Hutchinson and Jones[3] measured the absorption at different frequencies by means of an improved suspended thermocouple method developed by Professor A. H. Pfund and Dr. J. S. Guy. Their studies substantiated the applicability of the theory in the best work yet published on rosolic acid, phenolphthalein and methyl orange. Pfund, Uhler, Anderson, Jones and Wood[4] had also used the photographic methods in the visible and ultraviolet in other studies, and Uhler and Wood photographed the spectra of a number of dyes. Hildebrandt[5] had used a spectrophotometer with phenolphthalein but made measurements at just one frequency in the red. Dr. H. A. Lubs prepared urazole esters and salts in 1914 for the

[1] The method of derivation of 12*a*, 12*b*, 12*c* and other similar complex equations will be discussed in the long theoretical article now ready for publication.

[2] See *Am. Chem. J.*, **42**, 123 (1909) and all of our more recent articles.

[3] THIS JOURNAL, **37**, 776, 1694 (1915).

[4] Carnegie Publications.

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

investigations as a part of his dissertation but did not have time to undertake the spectrophotometric measurements. These studies in the urazole series will now be continued.

In the quantitative use of indicators for measuring the acidity of solutions, as in studying reaction velocities or the growth of fungi on culture media, it becomes imperative to know the magnitude of the above constants and to vary them at will by introducing substituent groups which will make the indicators extremely sensitive and useful over a wide range of hydrogen ion concentration. In this article, therefore, we shall discuss especially the equilibrium and affinity constants and their relation to the intensity of the colors of various indicators at different hydrogen ion concentrations.

It is obvious that these constants and ratios can vary widely with different substituent groups and we therefore have a means of preparing different series of indicators that will (*a*) give varying intensities for definite equivalents of alkali and, (*b*) give their color changes at the different hydrogen ion concentrations or $P_H$ values. Up to this time it has not been possible for us to calculate with any certainty the relative concentrations of the colorless lactoidal, yellow quinoidal, and deeply colored quinone-phenolate salts in the acid or alkaline solutions of the phenolphthalein series. We did know from White's synthetic, conductivity and spectroscopic work[1] and Lubs'[2] $P_H$ values that the phenolsulfonphthaleins exist practically only as quinone-phenolates in alkaline solutions and consequently give brilliant color changes. But our own, and Guy's unpublished (finished 1916) spectrophotometric measurements and those of Howe and Gibson[3] now give us sufficient insight into the phenomena involved to enable us to begin to measure or calculate (*a*) the concentrations of the lactoidal ($H_2L$) and of the quinoidal ($H_2Q$) free indicator, (*b*) the colorless lactoidal mono- ($HL^-$) and dibasic ($L^{--}$) salts, (*c*) the yellow quinoidal mono-basic salt ($HQ^-$), (*d*) the deeply colored mono-basic quinone-phenolate salt ($HQ'^-$), and (*e*) the deeply colored dibasic quinone-phenolate salt ($Q^{--}$) of all indicators of this general type.

This is such a very important advance in the history of the study of the indicators that the results will now be outlined, together with some plans for future work on these tautomeric compounds.

## Discussion of the Phenolsulfonphthalein Series.

In order to aid the reader in following the discussion, it may be well to summarize the meaning and probable values of the various constants defined by Equations 1 to 7.

[1] White and Acree, New Orleans Address, *Science*, **42**, 101 (1915); THIS JOURNAL, **39**, 648 (1917); **40**, 1092 (1918).

[2] Lubs and Acree, *Ibid.*, **38**, 2772 (1916); Lubs and Clarke, *J. Wash. Acad. Sci.*, **5**, 609 (1916); **6**, 483 (1917); *J. Bact.*, **2**, 1, 109, 137 (1917).

[3] *Phys. Rev.*, **10**, 767, 779 (1918).

(*a*) $R_1$ gives the equilibrium between the lactoidal and quinoidal forms. Our work seems to indicate a value of about 1000 for phenolphthalein and of about unity for phenolsulfonphthalein.

(*b*) $K_1$ and $K_2'$ refer to the ionization constants of the sulfonic acid residue in phenolsulfonphthalein, or to the phthalic acid residue in phenolphthalein. They are very large, about $10^{-1}$, for phenolsulfonphthalein, and about $10^{-5}$ or $10^{-4}$ for phenolphthalein.

(*c*) $K_1'$ and $K_3$ refer to a primary phenol ionization. They are both very small, and probably of about the same order of magnitude, say $10^{-8}$ to $10^{-10}$, for phenols with no negative or positive substituent groups. The introduction of positive or negative groups into the phenol radical decreases or increases $K_1'$ and $K_3$.

(*d*) $K_2$ and $K_4$ refer to a secondary phenol ionization. They are therefore still smaller than $K_1'$ and $K_3$.

Equation 13 shows that in a series of indicators having the same absorption index for unit equivalent of quinone-phenolate ions, those indicators having the *largest* values of $K_1K_2$ and *smallest* values of $R_1K_3K_4$ should give the largest value $Q^{--}/L^{--}$, and the greatest absorption in the green and consequently the most intense transmitted red color. For that reason we chose the sulfonphthalein series with a large value for $K_1$, about $10^{-1}$, for the sulfonic acid group, with a *small* value for $R_1$, about 10 or less, and with $K_2$, $K_3$ and $K_4$ variable at will, as being one of the most promising groups of indicators for practical use as well as for the study of the general theory. The small ratio $R_1$ enables us to study the properties of the actual yellow quinoidal form, $H_2Q$ (which is not present in appreciable quantities in the phenolphthalein series), and of the monobasic yellow salts corresponding, $KHQ$, which have been made and described by White[1] (and which have not been *isolated* in the phenolphthalein series but which we shall measure spectrophotometrically in the alkaline solutions). The value of $K_1$ is so large in comparison with $R_1K_3$, $K_2$ and $K_4$ in the phenolsulfonphthalein that well over 90% of the indicator is titrated as a yellow quinoidal monobasic acid before the "turning point" or intense color change appears. To illustrate, to state that $K_1$ is large in comparison with $R_1K_3$ means from Equation 15 that little of the monovalent ions are lactoidal and colorless ($HL^-$). When $K_4$ is small in comparison with $K_1$, and $R_1K_3$ is likewise small, Equation 13 shows that little of the divalent ions are lactoidal and colorless ($L^{--}$). When $K_2/K_1$ is small, and $R_1K_3$ and $K_4$ are also small, Equations 1 and 3 give by division $K_2/K_1 = \frac{(H_2Q) \times (Q^{--})}{(HQ^{--})^2}$, which shows that no appreciable quantity of ($Q^{--}$), *the red salt*, can be formed while there is appreciably any unchanged indicator ($H_2Q$) remaining in solution with the

[1] Reference to article now in editor's hands.

large amount of ($HQ^-$) (over 90% at the first appearance of the red color). It is therefore certain that in *alkaline* solution practically only the quinone-phenolate dibasic salt ($Q^{--}$) is present, with no appreciable amount of the colorless lactoidal dibasic salt ($L^{--}$); *i. e.*, $R_3$ is very small. The alkaline solutions therefore exhibit unusually brilliant color changes because such a large per cent.[1] is in the quinone-phenolate form. The exact per cent. can be calculated from our theory when all the constants are known and shown to be practically 100% of the indicator salt for the sulfonphthalein series.

We shall make full use of this high per cent. of quinone-phenolate form to study the influence of all kinds of negative, basic and alkyl groups on the values of $K_1$ and $K_2$ and on the specific absorption index and hydration rate for the quinone-phenol, $—C(:C_6H_4:O)(C_6H_4OH)$, and quinone-phenolate groups, $—C(:C_6H_4:O)(C_6H_4O^-)$, of each "practically completely" quinoidal sulfonphthalein indicator. The mono-phenolic ethers and the sulfonic esters will also be investigated for the same purpose. Similar studies will be made with other simpler purely quinoidal groups, such as the aurines, sulfonated aurines, and mono-alkyl aurines, $(ROC_6H_4)$-$C(C_6H_4:O)(C_6H_4OH)$, and the esters of the phenolphthalein series, such as $ROOCC_6H_4C(:C_6H_4:O)(C_6H_4OH)$ and their substitution products and salts, in which various factors can be controlled and measured. These constants, taken together, will give us an extensive set of data by which to estimate what influence the substitution of such groups in the phenolic, and in the sulfonic ($—C_6H_4SO_3H$) and phthalic ($—C_6H_4COOH$) residues will have on the $K_1$ and $K_2$ and on the maximum absorption index of the quinone phenol $—C(:C_6H_4:O)(C_6H_4OH)$, and the quinone-phenolate $—C(:C_6H_4:O)(C_6H_4O^-)$ groups. The influence of substituent groups on the ionization constants $K_3$ and $K_4$ of the *lactoidal* form will be studied by using the hydrogen electrode to measure the primary and secondary ionization constants of the very closely related compounds such as the anilides $C_6H_4CO(NC_6H_5)C(C_6H_4OH)_2$, *phthalin* esters, $ROOCC_6H_4CH$-$(C_6H_4OH)_2$, and their monophenol ethers. With these various studies completed, we shall be in a much better position to calculate the true per cent. of mono- and dibasic quinoidal, lactoidal and hydrated salts given by any indicator of the quinonephenolate type, and we shall of course use these absorption indexes and other constants in measuring and calculating the equilibrium and affinity constants of all these indicators. The "salt effects" are now under investigation in coöperation with Dr. C. L. Brightman, assisted by Dr. M. R. Meacham and Mr. J. J. Hopfield.

But a further advantage of the sulfonphthalein series arises because of this same large ratio $K_1K_2/R_1K_3K_4$, namely the fact that the addition

[1] White, Lubs, *Loc. cit.*

of substituent groups in the phenolic residues causes a wide variation in the hydrogen ion concentrations, or useful $P_H$ ranges,[1] at which the indicator gives its *color changes* without appreciable *diminution* of its *color intensity*. For the above reasons we find, theoretically and experimentally, from the work of White and of Lubs that all of the phenolsulfonphthalein series yet made form, first, practically only the yellow monobasic salts and then the deeply colored dibasic salts, when treated with alkalies. Since the deeply colored dibasic salt or ion $^{-}O_3SC_6H_4C(:C_6H_4O)(C_6H_4O^{-})$ is formed chiefly by the ionization and the neutralization of the yellow ion-acid $^{-}O_3SC_6H_4C(:C_6H_4:O)(C_6H_4OH)$, it follows from Equation 22 (which becomes approximately $H\alpha'/(1 - \alpha') = K_2$ when the values for the constants are substituted) that the ionization constant $K_2$ of the phenolic group is the *chief determining* factor in causing the intense color change of the particular indicator. Since $K_2$ is then practically the determining factor in the "effective" affinity constant[2] of the indicator, the negative bromo or nitro groups or basic groups increase or decrease this affinity constant without thereby lowering appreciably the per cent. of quinone-phenolate form in the total dibasic salt and without lowering appreciably its *color intensity*,[3] or $Q^{--}/(Q^{--} + L^{--})$. These results are clear from the equation $L^{--}/Q^{--} = R_1K_3K_4/K_1K_2$. The introduction of halogen or nitro groups into the phenol residues increases $K_2$, $K_3$ and $K_4$ greatly without disturbing $K_1$ or $R_1$ very much. The

[1] Such a wide range of $P_H$ values in one series of brilliant indicators soluble in both water and alcohol makes the sulfonphthaleins the best class yet developed. We can make concentrated solutions of the yellow monobasic salts and these solutions can be titrated with more alkali to adjust them to any desired $P_H$ value. By so adjusting the indicator solution it is possible to mix the indicator with a solution known to have approximately the same $P_H$ value and thus prevent any appreciable change of the $P_H$, even when the solution has weak buffer properties.

[2] The theoretical work already completed will give a very full treatment of the general and special equations covering all known types of quinone-phenol indicators.

[3] If we designate the absorption index for the peak of the green band of any indicator existing completely in the quinone-phenolate form, when neutralized completely with alkali and when completely ionized, by the term *maximum absorption index* (for a one cm. cell and either 0.001 $N$ or $N$ solutions), we can call the expression (*maximum absorption index*) $\times\ Q^{--}/(Q^{--} + L^{--})$ the *specific absorption index* of the given indicator existing in alkaline solution in only the deeply colored ions $Q^{--}$ and the colorless ions $L^{--}$. The larger the value of *maximum absorption index* $\times\ Q^{--}/(Q^{--} + L^{--})$ the greater the *apparent color intensity* of the transmitted red color of the solutions. The physicist thinks *correctly* in terms of the *absorption* which he uses and measures, while the chemist thinks *conveniently* in terms of the *apparent intensity* of the *transmitted* colors which he uses and measures in applying indicators. We can then, for convenience, and by way of contrast, speak of the *maximum color intensity* and of the *specific color intensity* for the transmitted light. As shown in this article, the *maximum absorption index* and *maximum color intensity* probably do not vary greatly in the phenolphthalein and phenolsulfonphthalein series, but the *specific absorption index* and the *specific color intensity* vary very widely for the different substituent groups.

affinity constant of phenol is approximately $10^{-10}$ at 25°, whereas that of *o*-chlorophenol is $7.7 \times 10^{-10}$, that of *o*-nitrophenol is $700 \times 10^{-10}$, that of 2,4,6-trichlorophenol is $260 \times 10^{-10}$, and that of 2,6-dinitrophenol is $2{,}700{,}000 \times 10^{-10}$. It is clear then that the introduction of these negative groups into the phenolic radicals of the sulfonphthalein series will very greatly increase $K_3$. $K_2$ and $K_4$ are both secondary ionization constants arising from the phenol groups and their values will also be greatly increased. As they will both be enlarged in a similar manner and as the data on the secondary ionization constants of dibasic acids show that the ratio $K_2/K_4$ will not vary to any extent comparable with the change in $K_3$, it is clear that the per cent. of lactoidal salt or $L^{--}/(Q^{--} + L^{-})$ will be increased *manifold* by the introduction of the negative groups and is chiefly governed by $K_3/K_1$, $R_1$ apparently changing very little in comparison. If, however, in phenolsulfonphthalein $R_1K_3K_4/K_1K_2$ were of the order $10^{-10}/10^{-1} = 10^{-9}$ it is clear that this value could be increased a *millionfold*, or $10^6$ fold, and there would still be only $10^{-3}$ or 0.10% of the lactoidal salt and hence 99.9% of the quinone-phenolate salt in the alkaline solution. While $K_3/K_1$ is increasing $K_2$ is becoming larger in the desired degree illustrated in the following examples,[1] the $P_H$ range of course decreasing. Phenolsulfonphthalein has a useful indicator range corresponding to $P_H$ values of 6.50 to 8.50, and a $K_2$ of about $2.0 \times 10^{-8}$. The introduction of isopropyl groups in the thymolsulfonphthalein raises this $P_H$ range to 8.0–9.5. The introduction of two bromines into the thymolsulfonphthalein lowers the $P_H$ range to 6.0–7.6. Two bromines and two methyls in the ortho positions in dibromo-*o*-cresolsulfonphthalein lower the $P_H$ range to 5.2–6.8, whereas 4 bromines in tetrabromophenolsulfonphthalein lower the $P_H$ range to 2.8–4.6. The 4 nitro groups in tetranitro-phenolsulfonphthalein lower the $P_H$ range to $<2.0$. The introduction of a nitro group into the benzenesulfonic radical of phenolsulfonphthalein and thymolsulfonphthalein increases $K_1$ but does not appreciably change $K_2$ for the phenolic group and hence the $P_H$ ranges 6.8–8.4 and 8.0–9.5, respectively, remain unchanged. These different indicators give color changes, then, at $P_H$ ranges varying from about 10 to $<2$, the $K_2$ values increasing simultaneously, and in all cases the color changes are *brilliant* because practically all of the indicator is in the deeply colored quinone-phenolate form and very little is in the colorless lactoidal form. These satisfactory results were predicted from the theory just as the *low color intensities* of the corresponding halogenated phenolphthaleins observed by Howe and Gibson were forecast.

One other point is predicted and will be studied. The introduction of negative groups into the phenol groups will increase very greatly (and

[1] Lubs and Acree, THIS JOURNAL, **38**, 2772 (1916); Lubs and Clark, *J. Bact.*, 2, 114.

by about the same factor) the primary phenol ionization constants $K_1'$ and $K_3$ and the secondary phenol constants $K_2$ and $K_4$ without appreciably altering $K_1$. It therefore follows that the *color intensity* $\left(\text{given by } \frac{Q^{--}}{L^{--} + Q^{--}} = \frac{K_1K_2}{R_1K_3K_4 + K_1K_2}\right)$ will be lowered, since $K_2$, $K_3$ and $K_4$ in the denominator increase, while only $K_2$ in the numerator increases. But at the same time a greater portion of the intense color will come from $HQ'^{-}$. For the ratio of $HQ'^{-}$ to all quinoidal form is given by

$$\frac{HQ^{-\prime}}{H_2Q + HQ^{-} + HQ^{-\prime} + Q^{--}} = \frac{K_1'}{H + K_1 + K_1' + K_2K_1/H} \quad (21)$$

In this expression, the numerator increases directly, under the above condition, while the denominator (of which $K_1$ is the largest term, except for *very* small H) increases less rapidly than in a direct ratio. For sufficiently small H, practically all the intense red color must of course come from $Q^{--}$, regardless of the probable values of the various constants, but for all intermediate values of H the $HQ^{-\prime}$ will thus play a more and more important role, as negative groups are introduced into the phenol group. Also, $HQ^{-\prime}$ *decreases* as the first power of the hydrogen ion concentration *increases*, while $Q^{--}$ changes with the second power of the hydrogen ion concentration. We thus have a ready means of determining the relative concentrations of $HQ^{-\prime}$ and $Q^{--}$.

This same theory shows why the introduction of negative chloro, bromo, etc., atoms into the phenolic groups of phenolphthalein and of phenoltetrachlorophthalein still further and very greatly lowers the color intensity of these indicators in alkaline solution. The proof of the theory has now been developed by an interpretation of the fine work of Howe and Gibson on the phenolphthalein series, which will now be discussed.

## Discussion of the Phenolphthalein Series.

Howe and Gibson[1] have observed, in an excellent study by a combination of visual and photographic methods, the complete absorption curves in neutral and alkaline solutions of seven substances of the phenolphthalein series of indicators and of phenolsulfonphthalein, all of the chemicals having been prepared by Professor W. R. Orndorff and Dr. S. A. Mahood. The absorption curves were determined from about 2000 Å. in the ultraviolet to 6500 Å. in the red. The curves show that all of these substances in the free state possess the expected lactoidal phenolic absorption bands in the ultraviolet, even if they have none in the visible spectrum. In this article however we are concerned with these substances chiefly in relation to their use as indicators. We shall therefore discuss fully only the green band centering at about $1/\lambda = 1800$ and arising from the quinone-phenolate group. This band grows up in alkaline solution with

[1] *Loc. cit.*

increasing quantities of added base and its presence and magnitude is practically the sole determining factor. The band $1/\lambda = 2700$ in the ultraviolet arising from the quinone-phenolate group will change along with the green band. Both of these bands are present, either more or less sharply or merged together, in the alkaline solutions of aurine, rosolic acid, tetrabromorosolic acid, fluorescein and its derivatives, phenolsulfonphthalein and its derivatives, alizarine, and a large number of other compounds whose color changes have been shown[1] by spectrophotometric methods to arise from the quinone-phenolate group. If both of these bands come solely from the quinone-phenolate group we should expect them to be formed in constant ratio from any given indicator as more and more alkali is added, and we might even expect different indicators of the same general type to give comparable ratios from these two bands. Of course, we should expect the position and ratio of these bands to vary to some extent with different substituent groups, as Howe and Gibson discussed. Furthermore there is a general absorption in the ultraviolet which masks the bands and makes any conclusions valuable only as first approximations. That there is a *general* constancy for this ratio is shown in the following Table I which was calculated from the data of Howe and Gibson by Professor C. L. Brightman who is now coöperating with us in this work. Both of these bands should be measured and compared accurately for a large number of these indicators to test the theory, but in all practical use of the indicators the large green band is the one most easily studied by spectrophotometric methods.

We have also hoped that the phenolate ions of the colorless lactoidal salts will show characteristic bands in the ultraviolet whose magnitude and position will enable us to measure the concentration of such ions. It seems to us that the data of Howe and Gibson do not permit us to draw definite conclusions as to whether the ultraviolet band at about $1/\lambda = 3200$ is connected with the phenolate ions (as against carboxylate or sulfonate salts). If such proves to be the case and accurate measurements can be made we shall then be able to study carefully the concentrations of the free lactoidal form, the lactoidal phenolate ions, the quinoidal form and its salts, and the quinone-phenolate ions, and hence we will be able to measure the tautomeric equilibrium and affinity constants of all these substances. Howe and Gibson make no attempt to interpret their data in this respect. As a matter of fact, it is impossible to interpret the data without the use of certain general equations which we have developed fully.

The 7 phenolphthaleins used by Howe and Gibson are: Phenolphthalein, tetrachloro-phenolphthalein, tetrabromo-phenolphthalein, tetra-

[1] See the first article by White and Acree, THIS JOURNAL, **40**, 1092 (1918), and work appearing later by Professors Guy and Brightman in coöperation with us.

iodo-phenolphthalein, phenoltetrachloro-phthalein, tetrabromo-phenol-tetrachloro-phthalein, tetraiodo-phenoltetrachloro-phthalein. These substances are but slightly soluble in aqueous, non-alkaline, solution. They therefore used them in alcoholic solution with no alkali, and then with 2, 4, and 10 molecules of alkali. They also obtained curves in aqueous solution with 4 to 10 mols of added alkali. They give no curves for the free acid in aqueous solution, doubtless because of the small solubility.

TABLE I.

| | Aqueous solution. | | | | Alcoholic solution. | | | |
|---|---|---|---|---|---|---|---|---|
| Indicator. | Mols of alkali. | Absorption. Index $B$. $1/\lambda=1800$. | Absorption. Index $B'$. $1/\lambda=2700$. | Ratio. $B/B'$. | Mols of alkali. | Absorption. Index $B$. $1/\lambda=1800$. | Absorption. Index $B'$. $1/\lambda=2700$. | Ratio. $B/B'$. |
| Phenolphthalein..... | 10. | 2.7 | 0.47 | 5.84 | 10 | 0.7 | 0.12 | 5.83 |
| Tetrachloro-phenolphthalein... | * | * | * | * | * | * | * | * |
| Tetrabromo-phenolphthalein... | * | * | * | * | * | * | * | * |
| Tetraiodo-phenolphthalein..... | * | * | * | * | * | * | * | * |
| Phenoltetrachloro-phthalein... | 4. | 5.85[d] | 0.8 | 7.18 | 2 | 1.4 | 0.3 | 4.6 |
| | | | | | 4 | 2.6 | 0.5 | 5.2[a] |
| | | | | | 10 | 4.0 | 0.85 | 4.7 |
| Tetrabromo-phenoltetrachloro-phthalein..... | 10. | 1.0 | 0.15 | 6.65 | * | * | * | * |
| Tetraiodo-phenoltetrachloro-phthalein..... | 4. | 2.4 | 0.25 | 9.6 | * | * | * | * |
| Phenolsulfonphthalein..... | 1.5 | 3.6 | 0.65 | 5.54 | 10 | 5.2 | 0.80 | 6.5[b] |
| | 2.0 | 4.4 | 0.75 | 5.86 | 10 | 5.2 | 0.5 | 10.4[c] |

In the case of the phenolsulfonphthalein series of indicators, which the present authors are studying in detail, it is possible to obtain aqueous, non-alkaline solutions, and to observe accurately the gradual change in absorption spectrum as alkali, acid, or salt, is added. Howe and Gibson studied phenolsulfonphthalein by the titration method developed by White and Lubs[1] in coöperation with us for the entire sulfonphthalein series, and observed the absorption curves for 0, 1, 1.5, and 2 mols of added alkali. Their results check roughly with those of White (1915), Guy (1916), and the present authors (1917–18), which were obtained and interpreted before

* In these cases the band was too weak to give a good value of the index on the curve.

[a] This calculation was made on the assumption that the D curve in the ultraviolet and the O curve in the visible regions are for the same solution.

[b] Calculated from the total heights of the bands.

[c] Calculated from the increased heights of the bands.

[d] The reading in Fig. 6, p. 772, corresponds to about 5.85, whereas Howe and Gibson give 5.95 in Fig. 8. This and other similar discrepancies are too small to warrant discussion.

[1] *Loc. cit.*

the article by Howe and Gibson appeared, and which will be discussed in full in another article. We will here consider only the interpretation of the results for the 7 phenolphthalein compounds mentioned above.

All of these indicators are dibasic, tautomeric acids, and their behavior depends on the relative magnitudes of the various affinity constants of the acid radicals and upon the equilibrium constants. In the preceding section on sulfonphthaleins we concluded that adding chloro, bromo, nitro, etc., to the phthalic acid residue strengthens this group but does not appreciably affect the strength of the acid phenolic group, the phenolsulfonphthalein and phenolnitro-sulfonphthalein having the same $P_H$ range 6.8–8.4 and thymolsulfonphthalein and thymolnitro-sulfonphthalein having about the same $P_H$ range, namely, about 8.0 to 9.5. But adding bromo and iodo groups to the phenol residue raises the phenolic affinity constant without appreciably disturbing the $K_1$. When at the same time chloro groups are added to the phthalic acid residue, and chloro, bromo or iodo groups to the phenol residue, the same general relations can be roughly predicted.

Now according to the quinone-phenolate theory, the intensity of this green band, which is present in all of these compounds, is a measure of the amount of quinone-phenolate ion present. In very dilute solutions the quinone-phenolate salt can be considered as practically completely ionized, especially if the molecular salt is also assumed to have the same color. This red ion is formed from the yellow quinoid, $H_2Q$, as has been shown in the preceding articles, and can exist in the two forms $HQ'^-$ (quinoidal-phenolate primary ion) and $Q^{--}$ (quinoidal-phenolate secondary ion). We can assume as a first approximation that if *all* of the indicator were in the form $Q^{--}$, for high alkalinity, the intensity of the green band (at its center point) would be nearly the same for all substances of the phenolphthalein and phenolsulfonphthalein series of indicators. This assumption is based on experimental facts which will be developed in the following.

Let us, as before, assume equilibrium between the molecular lactoidal and quinoidal form $(H_2L)/(H_2Q) = R_1$.

Then, as shown, the equilibrium between the dibasic ions is given by $L^{--}/Q^{--} = R_3 = R_1K_3K_4/K_1K_2$ (13).

For high acidity the ratio of all lactoidal to all quinoidal forms is given by $R_1$, for high alkalinity by $R_3$. This has been shown in Equations 7 and 13. The phenolphthalein, as a free acid, is colorless and is therefore considered to exist almost entirely in the colorless lactoidal form. Certainly the absorption is hardly more than the experimental errors involved in the measurements, namely at least 0.1 or 0.2%. Therefore $R_1$ is large. Furthermore, an analysis of the work of Rosenstein, together with that of Howe and Gibson, indicates that $R_1$ is $10^3$ or greater, also

that $K_1$ is of the order $10^{-6}$ and $K_3$ is about $10^{-9}$. $K_2$ and $K_4$ must be of the same order and $R_3 = L^{--}/Q^{--} = R_1K_3K_4/K_1K_2$ can easily become $R_3 = 1$, as shown below by the experimental data. If $R_3 = R_1K_3K_4/K_1K_2 = .1$ it follows that the introduction of halogens into the phenol groups will increase $K_3K_4/K_2$ very greatly, say from 10 to $10^2$ fold, without changing $K_1$ materially. If we assume[1] for the moment that $R_1$ remains constant it follows that $L^{--}/Q^{--}$ must increase 10 to $10^2$ fold and that the per cent. of quinone-phenolate salt must decrease to a value of from 10 down to 1%. In other words, the indicator will be practically lactoidal and faintly colored in alkaline solution. That this theory is correct is shown in Table II where it is seen that not over 2% of the tetrachloro-, bromo-, or iodophenolphthalein forms the quinone-phenolate salt in alkaline solution. If on the other hand, $K_1$ is made larger by the 4 chlorines in phenoltetrachloro-phthalein and $R_3$ becomes 1/10 as large as for phenolphthalein, then 90% or more of the phenoltetrachloro-phthalein would be in the quinone-phenolate form in alkaline solution. This is shown in Table II below. The introduction of halogens into the phenol groups of phenoltetrachloro-phthalein would then raise the value of $R_3$, as above, and decrease the per cent. of quinone-phenolate salt to the 17 and 40% given for tetrabromo-phenoltetrachloro-phthalein and the tetraiodo compound in Table II. The halogen derivatives of phenoltetrachloro-phthalein have therefore a greater specific color intensity than the corresponding ones of phenolphthalein but a smaller specific color intensity than the corresponding phenolsulfonphthalein derivatives. We thus have three classes of indicators giving a wide range of per cent. of quinone-phenolate salt in the alkaline solution, the determining factors most apparent being the different values for $R_1$ and the increasing value of $K_1$ for the phthalic acid, tetrachloro-phthalic acid, and phenolsulfonic acid residues. These classes will give interesting measurements.

For phenoltetrachloro-phthalein, we have the strongest phthalic acid group, and the relatively weakest phenol group. Therefore $K_1$ is much greater than the $K_1$ for the phenolphthalein and therefore proportionately greater than the $K_3$ of the phenoltetrachloro-phthalein and unless $R_1$ is very large, the substance will exist almost entirely in the quinoidal form, for high alkalinity. In aqueous solution and at high alkalinity the intensity of the green band for this substance, in the units used by Howe and Gibson, is 5.95. They found the intensity of the same band for phenolsulfonphthalein, which is known from our previous work to be practically entirely in the quinoidal form at high alkalinity, to be 4.50 with 2 mols alkali in water, and 5.2 with 10 mols alkali in alcohol. Howe and Gibson did not reach the true "end-point"[2] with phenolsulfon-

[1] See the discussion of $R_1$ and $R_3$ on page 1047.

[2] By the "end-point" we mean obviously the stage of neutralization of the indi-

phthalein as it is necessary to add more than 2 mols alkali to do this with 0.0001 $N$ aqueous solutions. The work of the present authors also shows that when all the substance is evidently in the quinoidal form, at high alkalinity, the intensity of the green band is approximately the same for various different indicators of the phenolsulfonphthalein series. We can at first therefore take 5.95 as an approximate *measure* of the intensity of this band when we have 0.000,1 $N$ concentration of quinone-phenolate ions in a one cm. cell, the unit used by Howe and Gibson.

Then since for *phenolphthalein* the intensity in water is only 2.62, it indicates that only about $^1/_2$ *this indicator salt is in the quinoidal form, even for very high alkalinity.* This is contrary to the conclusion[1] of past investigators, but the very accurate data of Howe and Gibson and our own measurements allow of no other interpretation, so far as we can see. $R_3$ is therefore approximately unity, and it is difficult to see how it could be greater than two or less than 0.5. This fact, combined with Rosenstein's data (to be later discussed) yields the approximate values of the primary ionization constants given above.

All of the other substances used by Howe and Gibson can be similarly studied and interpreted. For tetrabromo-phenolphthalein the phenol affinity constant ($K_3$) is probably fully as large if not larger than $K_1$ and therefore if 1% is in the quinoidal form at the start (high acidity) only 1% or less will be in that form at the end (high alkalinity). The intensity of the band is 0.033 and so about 0.5% is in the quinoidal form at the end.

We have calculated Howe and Gibson's results in the following way: First, we have assumed a value 5.95 for the index of any indicator existing in any solvent entirely as the quinone-phenolate form. We have then used Howe and Gibson's data to calculate the per cent. of each indicator actually present in the quinone-phenolate form, $Q^{--}$, when varying quantities of alkali are added, the difference between unity and the per cent. of quinone-phenolate giving the per cent. of lactoidal dibasic colorless ion $L^{--}$. The ration $R_3 = L^{--}/Q^{--}$ is then readily calculated and is given for both alcohol and water in Table II, which was computed by Professor Bright.

cator at which the quinone phenol $-C(:C_6H_4:O)(C_6H_4OH)$ (and its tautomer, if any) is fully converted into the corresponding quinone-phenolate ion (and its tautomer, if any). In measuring this "end-point" spectrophotometrically within any given experimental error a correction must be made for any unchanged quinone phenol (and tautomer, if any) and for any substance (such as the colorless hydrated salt) which is formed from the quinone-phenolate (or tautomer, if any) and whose concentration depends upon the concentration of the hydrogen (hydroxyl) ions or upon a "salt effect." See also Brightman, Hopfield, Meacham and Acree, THIS JOURNAL, 40, 1940 (1918).

[1] For example, see an excellent discussion by A. A. Noyes, THIS JOURNAL, 32, 816, 817 (1910).

man. As discussed below, $Q^{--}$ is too small, and $L^{--}$ is too large because it really involves the unchanged indicator, the colorless and yellow monobasic salts and any hydrated or alcoholated colorless salt. Consequently $R_3$ will probably be lowered in all cases when the true "end-point" for each substance is measured. The results for the aqueous solutions are probably much nearer the "end-point" than those for the alcoholic solutions.

It seems that the following preliminary conclusions can be drawn from the tables: First, as indicated in Table I, the addition of increasing quantities of alkali, up to 20 mols in some cases, increases the quinone-phenolate concentration and hence the absorption index, until the "end-point" is reached, at which all of the indicator is converted into the dibasic lactoidal and quinone-phenolate salts. Howe and Gibson followed the "titration method" of White[1] and found the greatest change in phenolsulfonphthalein between one and two mols of alkali in aqueous solution, which accords with the prior work of White and Guy and ourselves and with the theory. This gradual increase in absorption index with increase in alkali up to and beyond the "turning point" has been investigated very extensively with a number of sulfonphthalein indicators by

TABLE II.—PER CENT. OF VARIOUS INDICATORS IN QUINONE-PHENOLATE FORM IN ALKALINE AQUEOUS AND ALCOHOLIC SOLUTIONS.

Phenoltetrachloro-phthalein Taken as 100% Quinoidal in Aqueous Solution with an Absorption Index 5.95.

| | Aqueous. | | Alcoholic. | | | | |
|---|---|---|---|---|---|---|---|
| Indicator. | Mols alkali. | % in quinone-phenolate form. | Mols alkali. | % in quinone-phenolate form. | Aqueous. $R_3$. | Alcoholic. $R'_3$. | Ratio $R'_3/R_3$. |
| Phenolphthalein | 10 | 0.44 | 4 | 1.5 | | | |
| | | | 10 | 11.3 | 1.27 | 7.88 | 6.20 |
| Tetrachloro-phenolphthalein | 4 | 0.354 | 10 | 0.0354 | 282 | 2820 | 10.0 |
| Tetrabromo-phenolphthalein | 4 | 0.555 | 10 | 0.095 | 180 | 1052 | 5.85 |
| Tetraiodo-phenolphthalein | 4 | 1.68 | 10 | 0.208 | 58.5 | 481 | 8.2 |
| | | | 2 | 23.5 | | | |
| | | | 4 | 43.3 | | | |
| Phenoltetrachloro-phthalein | 2 | 100 (by definition) | 10 | 67.2 | 0 | 0.49 | ... |
| Tetrabromo-phenoltetrachloro-phthalein | 4 | 17 | 4 | 2.34 | | | |
| | | | 20 | 3.3 | 4.88 | 29.2 | 6.0 |
| Tetraiodo-phenoltetrachloro-phthalein | 4 | 40 | 5 | 4.58 | 1.50 | 20.6 | 13.7 |
| Phenolsulfonphthalein | 1 | 11.3 | 10 | 86.6 | .... | .... | ... |
| | 1.5 | 60.5 | | | | | |
| | 2 | 74.8 | | | | | |

[1] *Loc. cit.*, see also Lubs and Acree, THIS JOURNAL, 38, 2772 (1916).

Professor J. S. Guy in 1916 in coöperation with our own work and has been used in calculating the affinity constants. Secondly, as far as we can judge until the indexes for the true "end-points" are measured, all of these tables and figures show clearly the following: the larger the ratio of $K_1$, the ionization constant for the carboxyl or sulfonic acid group, to $K_3$, the ionization constant of the first phenol of the lactoid form, the larger the absorption index and per cent. of quinone phenolate in the alkaline solution. The larger the values of $K_3K_4$ are made, in comparison with $K_1K_2$, by the introduction of negative groups into the phenolic residues ($R_1$ remaining constant), the larger the per cent. of lactoidal colorless salt in the alkaline solutions and the smaller the absorption index. It is hoped that in time methods for the direct measurement of the concentration of the lactoidal colorless salts will be developed and that more will be learned about $R_1$.

We see that Howe and Gibson's results for aqueous and alcoholic solutions are similar, but the $R_3$ (alc.) is in all cases larger than $R_3$ (aq.), and as the last column shows, the ratio $R_3$ (alc.)/$R_3$ (aq.) is not constant. But this result is not unexpected for the formation of the alcoholate and especially alcoholysis tend to prevent the "end-point" being reached unless a larger number of moles of alkali are added. But, as the data of Howe and Gibson show, 10 mols of alkali were added for the first indicators, but only 4 moles of alkali for the last 3 indicators. The concentrations used are also different for different indicators, and our results have shown that the number of moles of alkali necessary to reach the true "end-point" depends radically upon the concentration. Their curves show clearly that 4 and even 20 mols of alkali have not produced the full color change in alcohol and the ratios given for the last two indicators may be proportionately too large. With complete data it will be very important to study these ratios and the equilibrium and affinity constants in water, alcohol, acetone, etc., as we have proposed in an earlier article[1] to do. By determining the ion product $K_{alc.} = H \times OC_2H_5$ for pure ethyl alcohol and using sodium, potassium and lithium ethylates it will be possible to measure the alcoholysis and affinity constants of a large number of weak acids (phenols, ketones, amines, etc.), many of which are insoluble in water.

Besides the changes of intensity of the green band, there is also the usual shift in position, due to loading down the molecule. Howe and Gibson discussed this shift and show that it increases with the atomic weight of the added group.

An examination of Equations 13 and 7 shows that we are now in a position to begin to calculate the values of $R_1$, $R_3$, and $K_3K_4/K_1K_2$ ap-

[1] *Am. Chem. J.*, 39, 542 (1908), and later articles.

proximately from the experimental data on some of these constants instead of having to rely on the obviously weak assumption used above that $R_1$ does not change in some cases. The equations become $H_2L/H_2Q = R_1 = R_3K_1K_2/K_3K_4$ or $H_2Q = H_2LK_3K_4/R_3K_1K_2$. For colorless indicators of the phenolphthalein type, $H_2Q$ is too small to be measured directly today. But $H_2L$ is practically the concentration of the free indicator, $R_3$ can now be approximately measured by the methods outlined in this paper; by measuring $K_1K_2/K_3K_4$ we can calculate $H_2Q$ and hence $R_1$. In the sulfonphthalein series we shall probably be able to measure $R_1$ and $R_3$, or one of its components, directly and hence secure better experimental data on all these constants.

More light on the values of $R_1$ and $R_3$ is greatly needed. For example, the introduction of 4 bromines into the phenol groups of the phenolsulfonphthalein does not materially change the per cent. of $Q^{--}$ in alkaline solutions, and the useful $P_H$ range corresponding to $K_2$ is therefore *lowered greatly*,[1] from 6.5–8.5 to 2.8–4.6. But the introduction of 4 bromines into phenolphthalein lowers the midpoint of the $P_H$ range from about 9 to only about 8, or only $1/4$ the change for phenolsulfonphthalein. This apparent discrepancy becomes clear from the equation for expressing the change of color with change in (*a*) concentration of the hydrogen ions and in (*b*) the equilibrium and ionization constants, which will be developed fully in a later article. The equation shows clearly that the hydrogen ion

$$(H[H(K_1'R_3 - K_3R_1 - K_1)/(R_1 + 1)][\alpha'/(1 - \alpha')] = (K_1K_2 + K_1'H)(R_3 + 1)/(R_1 + 1) \quad (22)$$

concentration necessary to produce 50%[2] of the specific absorption index (or specific color intensity) depends not only on $K_1$, and on $K_1'$, $K_2$, and $K_3$, which are ionization constants for phenols increased in strength by the bromines, but also on $(R_3 + 1)/(R_1 + 1)$. Considering the right side of the equation, we see that the $P_H$ range can be *lowered greatly* by introducing the 4 bromines (as in tetrabromo-phenolsulfonphthalein) provided the *increases* in $K_1'$ and $K_2$ are not offset by a *decrease* in $(R_3 + 1)/(R_1 + 1)$, or can be *lowered slightly* (as in tetrabromo-phenolphthalein) or even *increased*, provided a *decrease* in $(R_3 + 1)/(R_1 + 1)$ more than offsets *increases* in $K_1$, $K_2$ and $K_3$. We have seen from Table II that $(R_3 + 1)$ = about $(1.25 + 1.0) = 2.25$ for phenolphthalein becomes $(R_3 + 1)$ = about $(180 + 1) = 181$ for tetrabromo-phenolphthalein. This increase

[1] Lubs, White and Acree, THIS JOURNAL, **38**, 2779 (1916); **39**, 649, 651 (1917); Lubs and Clark, *Loc. cit.*

[2] 50% neutralization of the indicator by a base does not necessarily correspond to 50% of the specific absorption index. Thus 50% neutralization of phenolsulfonphthalein gives the yellow monobasic salt and only a few per cent. of the dibasic quinone-phenolate salt, and it requires around 75% of neutralization to give 50% of the specific absorption index.

of 80-fold multiplied by 3,000,[1] the increase in the ionization constant $K_2$ for the phenolic group by the introduction of the 4 bromines, gives a change of say 240,000-fold[2] in the numerator and the $(R_1 + 1)$ must therefore increase 24,000-fold to balance the change of the hydrogen ion concentration from $10^{-9}$ for phenolphthalein to $10^{-8}$ for tetrabromo-phenolphthalein. The left side of the equation must be treated in the same way, and this example serves to illustrate the underlying ideas which will be applied later in detail. Since $(R_1 + 1)$ is already large for phenol-phthalein, say 1000 or larger, an increase of 24,000 fold means simply that free tetrabromo-phenolphthalein has practically no quinoidal component in the aqueous or alcoholic solution.

Our own absorption spectra, and those of Howe and Gibson, for phenol-sulfonphthalein give further very important evidence on the question whether the quinone group remains free or combines[3] with the phenolate ion or salt to form intensely colored double compounds very much like those which Jackson[4] made by the union of quinones with phenol salts. The free sulfonphthaleins with nonionized phenols give an absorption band in the violet centering at about 2300 and another in the ultra-violet at 3770. The specific absorption index for the violet band [apparently about two for phenolsulfonphthalein] will be used in this entire series for measuring the per cent. of free quinoidal acid, $H_2Q$. This violet band practically disappears in alkaline solution and new bands are formed at about 1800, 2800 and 3500. It therefore seems certain that the quinone group, or quinonephenol group, $-C(:C_6H_4:O)(C_6H_4OH)$, disappears and is changed into the quinone-phenolate group, $-C(:C_6H_4:O)(C_6H_4OK)$, as described in the earlier articles. This phase

of the theory needs and will receive very close attention.

In the above calculations it was assumed that the colorless salts are lactoidal, and not hydrated (alcoholated in alcohol) tribasic salts $KOOCC_6H_4C(OH)(C_6H_4OK)_2$. The fine work of Kober and Marshall[5] on the fading of phenolphthalein shows that an excess of alkali causes

[1] This is the increase in $K_2$ observed by introducing the 4 bromines into phenol-sulfonphthalein and is used here for illustration. It will be very important to see how $K_2$ and the other constants are changed by the introduction of the same substituent groups, in the aurine, phenolphthalein, phenolsulfonphthalein and similar series.

[2] This factor omits $K'_1H$ as small in comparison with $K_1K_2$ in the numerator.

[3] *Am. Chem. J.*, **39**, 534 (1908); **42**, 122 (1909). White and Acree, THIS JOURNAL, **39**, 650 (1917); **40**, 1092 (1918), and forthcoming dissertation. Lubs and Acree, *Ibid.*, **38**, 2773, 2783 (1916).

[4] *Am. Chem. J.*, **18**, 1 (1896); **34**, 441 (1905). Wichelhaus, *Ber.*, **5**, 849 (1872); Posner, *Ann.*, **336**, 85 (1904).

[5] THIS JOURNAL, **33**, 59 (1911). See also Slagle and Acree, *Am. Chem. J.*, **39**, 533, 542 (1908); **42**, 126, 137–9 (1909).

quick fading of the color and that the final intensity varies inversely as the concentration of the free alkali. Since Howe and Gibson doubtless used the most refined spectrophotometric technique they would certainly have discovered any fading and we have assumed therefore that no fading and formation of hydrated salts took place. If in any case (*e. g.*, of low color intensity) there is doubt as to whether sufficient alkali has been added to reach the "end-point" or whether some of the colorless hydrated salt is already present the point can be checked by adding more alkali (ethylate in alcohol) to see whether the color increases or decreases according to theory. This check and the study of fading should be applied most carefully in all cases for short- and long-time periods to correct for the true "end-point" and has been given the closest scrutiny in our own work.[1]

It will be recalled[2] that phenolphthalein ethers, $(C_6H_4COO)C(C_6H_4OR)(C_6H_4OH)$, *p*-oxydiphenyl-phthalid, $(C_6H_4COO)C(C_6H_5)(C_6H_4OH)$, and similar substances dissolve in alkalies as faintly colored or colorless solutions. Green[3] believed that the hydrated salt $KOOCC_6H_4C(OH)(C_6H_4OK)(C_6H_4OR)$ is formed in such cases and one of us has pointed out the evidence[4] on the question whether there may not be a lactoidal salt formed. These are very important cases for the general theory and it is proposed to study the affinity constants of the indicators forming such faintly colored solutions by (*a*) adding the proper indicators to such (nearly) colorless solutions and seeing spectrophotometrically how much indicator salt and colorless salt are formed and hence telling whether the affinity constant of the colorless substance in solution corresponds to the weak phenolic group of the lactoidal form or to a *much stronger* ($10^3$- to $10^6$-fold) carboxyl group of a hydrated form; and by (*b*) using partition between two solvents to measure the hydrolysis and affinity constants to get the same data. It is clear that all of these different phases of the theory must and will be studied in order to get a clear vision of the fundamental underlying causes of these color changes.

## Conclusions.

1. Equations are given to show the relation between the specific absorption index (or specific color intensity), or per cent. of intensity colored quinone-phenolate salt, and the equilibrium and affinity constants of the two acid groups of phenolphthalein and phenolsulfonphthalein indicators.

2. A spectrophotometric method is proposed for measuring the concentration of the monobasic yellow quinone phenol salt and of the dibasic intensely colored quinone-phenolate salt in any solution, and the per cent.

[1] Brightman, Hopfield, Meacham and Acree, THIS JOURNAL, 40, 1940 (1918).

[2] *Ann.*, 354, 171 (1907); *Ber.*, 40, 3728 (1907); *Ibid.*, 30, 177 (1897).

[3] Green and King, *J. Chem. Soc.*, 85, 398 (1904); *Ber.*, 40, 3724 (1907).

[4] *Am. Chem. J.*, 39, 532 (1908); 42, 126, 137–9 (1909).

of any indicator transformed into the quinone-phenolate salt in alkaline solution.

3. By the use of the equations and the spectrophotometric data by Howe and Gibson and by ourselves, we have shown that sulfonphthalein indicators are transformed practically completely into quinone-phenolate salts and are therefore very fine, intensely colored indicators. Phenolphthalein is changed to the extent of only about 44% into the intensely colored quinone-phenolate salt, the remainder forming the colorless lactoidal (and hydrated) salts. Tetrachloro-, tetrabromo-, and tetraiodophenolphthalein form only about 1 to 2% of the intensely colored quinone-phenolate salt, the remaining 98 or 99% forming the colorless lactoidal (and hydrated) salts. These indicators are therefore very poor for analytical work. The introduction of 4 chlorines into the phthalic acid residue of phenolphthalein makes phenoltetrachloro-phthalein an excellent indicator which changes to probably 90% or more into the intensely colored quinone-phenolate salt. The introduction of halogens into the phenol groups of phenoltetrachloro-phthalein gives bromo and iodo derivatives, for example, which can give only 17 and 40%, respectively, of the intensely colored quinone-phenolate salt in alkaline solution.

4. We have pointed out how the application of spectrophotometric methods, and the proper equations derived by the use of the mass law, to these indicators gives us for the first time an approximate measure of the real equilibrium and affinity constants of the two acid groups in indicators of the phenolphthalein and the phenolsulfonphthalein types.

5. The disappearance of the violet band at 2300 for phenolsulfonphthalein indicates that in alkaline solution the quinone, or quinone-phenol, group is changed into a quinone-phenolate complex ion like the intensely colored double compounds which Jackson made by the union of quinone and phenolate salts.

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