The use is obvious.   After the addition of substance from a buret the mixing is performed by sucking on a soda-lime tube attached to the outlet S.   This causes the electrolyte to rise into the bulb M.   The liquid is then allowed to run back into the cell jar B.   Two or three repetitions are sufficient for thorough mixing.

The lower part of the cell jar B is designed to allow the use of small amounts of solution, while with larger amounts the liquid can rise into the spherical shaped part of the cell jar without touching the upper neck F, contact with which may give capillary troubles.

The apparatus has given good service in the laboratories of Physics and of Chemistry[1] in this institution and is superior in several respects to one previously described.[2]   HAROLD E. ROBBINS.
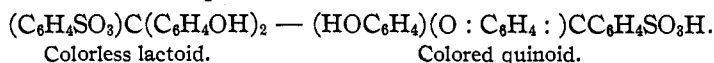
MASS. AGRICULTURAL COLLEGE,
   AMHERST, MASS.

ON THE QUINONE-PHENOLATE THEORY OF INDICATORS: THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF PHENOLSULFONPHTHALEIN AND OF ITS BROMO AND NITRO DERIVATIVES.

BY E. C. WHITE AND S. F. ACREE.

In the preceding papers[3] by us the assumption has been made that the sulfonphthaleins investigated exist largely, if not entirely, in the quinoid modification when in aqueous solution.

$$(C_6H_4SO_3)C(C_6H_4OH)_2 - (HOC_6H_4)(O : C_6H_4 :)CC_6H_4SO_3H.$$

  Colorless lactoid.   Colored quinoid.

This assumption was based upon the colors of the solutions of these substances, and of their salts.[4]   If this assumption is well founded, the solu-

[1] *Am. J. Sci.*, [4] **41**, 244 (1916).

[2] *Ibid.*, [4] **41**, 249 (1916).

[3] Acree and Slagle, *Am. Chem. J.*, **39**, 528, 789 (1906); **42**, 115 (1909); White and Acree, Address at New Orleans meeting of American Chemical Society, *Science*, **42**, 101, and unpublished dissertation 1915, University of Wisconsin; Lubs and Acree, THIS JOURNAL, **38**, 2772 (1916).

[4] Through absence and consequent failure to see the page proof of the article by Lubs and Acree, the third reference on page 2778 and the first on page 2779 were interchanged.   Through this mistake Dr. White was deprived of the credit due him for the experimental work in the table given, which was first reported at New Orleans. The theory of these titrations, of the change in affinity constant produced by substituent groups, and of the colors of the salts, was fully discussed in Dr. White's dissertation.   The developments by Lubs and Acree, and by Lubs and Clark in friendly cooperation with us, were of course subsequent to Dr. White's work, and his unpublished work was placed at the disposal of Lubs and Clark.   The article by Lubs and Acree was intended primarily as a contribution on the *quantitative* influence of substituent groups on the P_H values and affinity constants, and not as an exposition of the applica-

tions should show electrical conductivities comparable in magnitude with those of the strong sulfonic acids, because quinoidal sulfonphthaleins must contain a sulfonic acid group. The work in the present paper verifies these assumptions and the article of Lubs[1] and one of us on the P_H values and unpublished spectrophotometric measurements of our own and by Prof. J. S. Guy harmonize with the quinonephenolate theory.

In order to make the dyes dissolve it was necessary to heat the solution about three minutes. Hard glass beakers that had been previously thoroughly boiled out were used. The conductivity of the pure water after it was boiled the same length of time as was the solution, was measured and subtracted from that of the solution. In the case of phthaleins, which show slight conductivity, the variable errors due to the conductivity of the solvent might seriously vitiate the results but with the high conductivities of the sulfonphthaleins the error is small. This is made clear by the fact that the specific conductivity of the water was in all cases between 0.005 and 0.006, whereas the specific conductivities of the three phthalein solutions varied from 0.3816 to 0.4761.

The following are the average values of the molecular conductivities found at 25°. Although the substances were as pure as we could make them, their insolubility renders their absolute purification difficult. These values may, therefore, be found slightly different in the future work. At the dilutions used μ_v may be considered as practically equal to μ_∞ for the sulfonic acid group of the quinoidal form.

Substance.	Normality of solution.	μ_v.	P_H.
Phenolsulfonphthalein...................	0.0014	268	6.5–8.5
Tetrabrom phenolsulfonphthalein..........	0.0011	299	3.2–4.5
Tetranitrophenolsulfonphthalein..........	0.0011	427	Too low to measure accurately

Since the values of μ_∞ for sulfonic acids are somewhere around 360 to 370 these results show conclusively that the sulfonphthaleins in aqueous solution exist largely in the quinoid modification. The conductivity due to any portion existing in the lactoid form would be extremely slight, because the two phenol hydroxyls are weak acids.
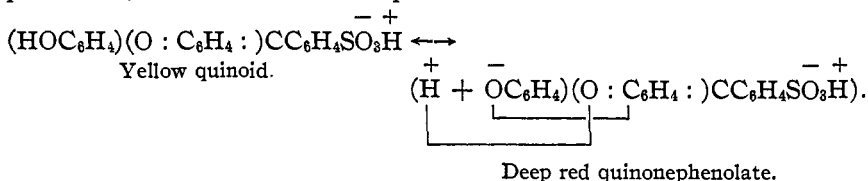
The relative magnitudes of the three molecular conductivities obtained afford a striking confirmation of the idea expressed previously[2] that the distinct *yellow* color develops with the rearrangement into the quinoidal form, attended in these cases by a *primary ionization*, that of the sulfonic

tion of the quinone-phenolate theory to the sulfonphthaleins, which had already been developed in White's dissertation and firmly established by his experimental material.   S. F. ACREE.

[1] THIS JOURNAL, **38**, 2777 (1916).

[2] *Am. Chem. J.*, **39**, 528, 789 (1906); see especially White and Acree, *Loc. cit.*, and Lubs and Acree, THIS JOURNAL, **38**, 2775 (1916).

acid group, whereas the *intense red or blue* color of the indicator solution develops simultaneously with the *secondary* ionization of the sulfonphthaleins, and the formation of *phenolate ions*.

$$(HOC_6H_4)(O : C_6H_4 :)CC_6H_4SO_3H \overset{- \; +}{\longleftrightarrow}$$

Yellow quinoid.

$$(H + OC_6H_4)(O : C_6H_4 :)CC_6H_4SO_3H).$$

Deep red quinonephenolate.

Phenolsulfonphthalein and tetrabromo phenolsulfonphthalein show values comparable with those found by Ostwald for acids like benzene sulfonic acids. The fact that the values for these two sulfonphthaleins are lower than that of benzene sulfonic acid may be attributed (1) to the slightly smaller velocity of the more complex anion of the sulfonphthalein and possibly to a slightly smaller percentage of ionization, and (2) especially to an equilibrium involving about 60 to 75% in the strongly acid quinoid form and the remainder in the weakly acid lactoid form. When we compare the values of μ_v and the colors of these two sulfonphthaleins there is every indication that the secondary ionization is not great in either case, but that it is somewhat greater in the case of the bromine derivative. The colors of the solutions of these two substances, at the dilution used, are not intense, but become so only when sufficient alkali is added or when, especially in the case of the bromine derivative, the solution is diluted. The tetranitro compound, on the other hand, shows an intensity of color in the solution used which is not appreciably increased by the addition of alkalies. We should, therefore, suppose that the secondary ionization of the dinitrophenol group had progressed to a large extent. The exceedingly high value of the molecular conductivity indicates that such is the case. Indeed, the fact that this value is much higher than that of even such a strong acid as hydrochloric acid can be explained only on the basis that tetranitrophenolsulfonphthalein functions chiefly as a dibasic acid. This high acidity doubtless arises from the ionization of the two potential 1,2,6-dinitrophenol groups and it is interesting to compare the tetranitrophenolsulfonphthalein with the nitrophenols. The 2,6-dinitrophenol is 41% ionized in 0.001 N solution. If we assume that the 2,6-dinitrophenol group of the tetranitrophenolsulfonphthalein has the same affinity constant, the calculation of the suppression of its ionization by the sulfonic acid group gives a conductivity around 420–30, which is very close to the 427 observed.

It is instructive to compare the molecular conductivities of these three phenolsulfonphthaleins with their corresponding P_H values. If both the increasing molecular conductivity and the increased amount of deep color (characteristic of the dibasic salts) depend upon the increased

ionization of the phenol groups we should expect the P_H value to *decrease* with *increasing* affinity constant of the phenol group, and, in this case, with *increasing* molecular conductivity. The above table and other data by Lubs[1] and one of us, and the excellent work along this line by Lubs[2] and Clark show clearly that these relations hold in general.

Prof. J. S. Guy has obtained some unpublished spectrophotometric data over the entire spectrum for varying P_H values, and very recently Lubs and Clark, in coöperation with us in this field, have calculated the affinity constants derived from a few measurements along the same lines. Taking the P_H values given in the following table as a rough approximation of the hydrogen-ion concentration at which the indicator is half transformed, the "total" or "apparent" affinity constant, K *aff.*, given is calculated at once from the equations derived earlier for such tautomeric acids. The more accurate work by Professor Guy and the new measurements planned will be published later in detail.

Substance.	P_H.	K aff.
Phenolsulfonphthalein	7.5	3.1×10^{-8}
Tetrabromphenolsulfonphthalein	4.0	1.0×10^{-4}
Tetranitrophenolsulfonphthalein	Probably <2	Probably $<10^{-2}$
o-Cresolsulfonphthalein	8	1.0×10^{-8}
Thymolsulfonphthalein	8.8	1.6×10^{-9}
Dibromthymolsulfonphthalein	6.6	2.5×10^{-7}
Thymolnitrosulfonphthalein	8.9	1.2×10^{-9}

By the use of these values and the solutions transformed 25, 50, 75 per cent., etc., as standards, it is easy to ascertain by comparison the P_H values of solutions covering a wide range of hydrogen-ion concentrations. Our chief reason for choosing this field of sulfonphthaleins for our indicator studies was the possibility of preparing this large series of sulfonphthalein derivatives giving brilliant color changes over a wide range of P_H values and hence enabling us to test the quinone-phenolate theory in this new field. The wisdom of this choice has been very happily justified not only by our own work but by that of Lubs and Clark and of Guy. For example, it is seen in the above tables that different groups substituted in the phenol residue cause a variation of from 10^5 to 10^7 in the apparent affinity constants. All of these equilibrium and affinity constants will be discussed in detail in another article.

We shall investigate a series of bromo- and nitrophenolsulfonic acids and analogous compounds and of the phenolsulfonphthaleins by the use of conductivity, hydrogen-electrode and catalytic methods in order to correlate the affinity constants and colors of these series.

[1] Lubs and Acree, THIS JOURNAL, 38, 2777 (1916).
[2] See especially Lubs and Clark, *Jour. Wash. Acad. Sci.*, 5, 609 (1915); 6, 483 (1916).

Conclusions.

(1) The molecular conductivities and colors of approximately 0.001 N solutions of phenol-, tetrabromophenol-, and tetranitrophenolsulfonphthalein show that these indicators are at least 60% in the quinoidal form. The *yellow* color is dependent upon the quinone group and not appreciably on the *primary ionization*, that of the sulfonic acid group.

(2) A comparison of the colors, conductivities, and P_H values of the phenol- and tetrabromophenolsulfonphthalein with those of the tetranitrophenolsulfonphthalein show that the *intense red or blue* colors of these indicators develop simultaneously with the *secondary ionization*, that of the phenol groups, and thus with the formation of quinone phenolate ions.

THE PREPARATION OF ALKYLHYDROXYUREA CHLORIDES AND THEIR RELATION TO ESTERS OF CARBON DIOXIDE OXIME, R — O — N = C = O.

BY LAUDER WILLIAM JONES AND LEONORA NEUFFER.[1]

In the course of investigations with nitroparaffins and fulminates, Nef believed that he had prepared the first derivative of the oxime of carbon dioxide.[2] By the action of mercuric chloride on sodium isonitromethane, a yellow salt was obtained to which Nef assigned the formula

$$Hg\diagdown\!\!\!\!\!\!\!\!\!\diagup\!\!\!\!\!\!C\!=\!N\!-\!Ohg.$$

He supposed it to be a basic mercury salt[3]

of carbon dioxide oxime, H—O—N = C = O, but attempts to prepare the alkyl esters of this acid by the action of alkyl iodides on the yellow mercury salt proved unsuccessful. Later Jones[4] showed that Nef's salt was probably a basic mercury salt of formhydroximic acid,

$$H-C\diagdown\substack{O-Hg-OH\\N-O-hg}$$. Attempts were then made by Jones[5] to

prepare the derivatives of carbon dioxide oxime by removing alcohol from the salts and esters of hydroxyurethane. The work was based on the assumption that Lossen's formula for the hydroxamic acids,[6]

[1] The material presented here is used by Leonora Neuffer in her dissertation in part fulfillment of the requirements for the Ph.D. degree of the University of Cincinnati.

[2] *Ann.,* **280,** 279 (1894).

[3] Hg represents a half atom of bivalent mercury.

[4] *Am. Chem. J.,* **20,** 1 (1898).

[5] *Loc. cit.*

[6] *Ann.,* **287,** 295 (1898).