concentrations. Similarly, the three-component system $BaCl_2-HCl-H_2O$ studied by Schreinemakers at 30°,[1] illustrates the use of hydrochloric acid to the same purpose. Indeed the method can, generally speaking, be recommended before the study of the two-component system whenever there is considerable tendency to formation of concentrated, viscous, aqueous solutions, provided of course that acid salts are not readily formed.

Finally it may be observed that the solubility of the anhydrous salt at 25° corresponds to those obtained by Bassett and Taylor at the higher temperatures and not with that obtained by D'Ans as previously mentioned.

PRINCETON, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF JOHNS HOPKINS UNIVERSITY.]

RADIOMETRIC MEASUREMENTS OF THE IONIZATION CONSTANTS OF INDICATORS.[2]

[SECOND COMMUNICATION.]

BY M. G. PAULUS, J. F. HUTCHINSON AND HARRY C. JONES.

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An investigation of the ionization constants of methyl orange and phenolphthalein has already been published in THIS JOURNAL by Shaeffer, Paulus and Jones.[3] In this paper a new method, based upon the absorption of light by solutions of indicators, was developed for the determination of the constants of indicators. It was shown that this method serves as well for a two-colored as for a one-colored indicator. The work recorded herein is to be regarded as a continuation of the original investigation, and the purpose is to test the applicability of the method to the determination of the ionization constant of rosolic acid. A description of the apparatus used has already been given in detail in the original paper.

Theoretical Discussion.—Considering, first of all, that rosolic acid is monobasic,[4] the ionization constant K_i, is expressed by the simple equilibrium equation

$$\frac{(H^+)(\bar{In})}{(HIn)} = K_i. \tag{1}$$

If, then, the hydrogen ion concentration of the indicator solution is fixed, the ratio $(\bar{In})/(HIn)$ at equilibrium can be determined. It has been shown in the original paper[5] that the percentage transmission of a solution, such as that of rosolic acid, containing two absorbing components is given by the equation

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[1] *Z. physik. Chem.*, **68**, 89 (1909).

[2] This investigation has been carried out with the aid of a grant from the Carnegie Institution of Washington to H. C. Jones.

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

[4] The behavior of rosolic acid as a dibasic acid will be discussed later.

[5] *Loc. cit.*

$$\ln (I/I_0) = -Kc - K'c_1, \tag{2}$$

where c and c_1 are the concentrations of the two absorbing components, and K and K′ are constants depending upon the nature of the absorbing components and the wave-length of light employed. Applying this equation to rosolic acid, let c represent the concentration of the red component, or $(\bar{In})$ in Equation 1, and let c_1 represent the concentration of the yellow component or (HIn). Equation 2, then, will represent the percentage transmission for some given depth of an incompletely transformed solution of rosolic acid. In a solution containing a large excess of acid $c = 0$, and Equation 2 becomes

$$\ln (I/I_0)' = -K'c_1 = -K'T. \tag{3}$$

If a large excess[1] of alkali is added to the indicator solution $c_1 = 0$, and Equation 2, reduces to

$$\ln (I/I_0)'' = -Kc = -KT, \tag{4}$$

where T equals the total concentration of the indicator in solution. If the percentage transmissions are determined for the same depth of solution and for the same wave-length of light, and if the total concentration of the indicator is the same in all solutions, then the values of the constants K and K′ given by Equations 3 and 4, can be substituted in Equation 2, whence

$$T \times \ln (I/I_0) = \ln (I/I_0)'' \times c + \ln (I/I_0)' \times c_1. \tag{5}$$

Since the total concentration of the indicator T is always equal to the sum of the two components, $T = c + c_1$, Equation 5 reduces to

$$c/c_1 = \frac{\ln (I/I_0)' - \ln (I/I_0)}{\ln (I/I_0) - \ln (I/I_0)''}. \tag{6}$$

The ratio $c/c_1 = (\bar{In})/(HIn)$ can be determined from Equation 6. (I/I_0) is the percentage transmission for some given depth of the incompletely transformed solution under investigation, for some wave-length of light; $(I/I_0)'$ the percentage transmission of the indicator solution completely transformed into the yellow component, for the same wave-length; and $(I/I_0)''$ the percentage transmission for the same depth of indicator solution completely transformed into the red component, for the same wave-length of light. The total concentration of the indicator in these three solutions must, of course, be the same, but the total concentration need not be known.

Returning now to Equation 1, the method of obtaining all the data necessary for calculating the ionization constant is known, except that for determining the concentration of the hydrogen ion. This was fixed by solutions of disodium phosphate containing varying amounts of hydro-

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[1] By "a large excess" is meant sufficient alkali to convert the indicator entirely into its red component.

chloric acid. The addition of hydrochloric acid converts the hydrophosphate ion almost quantitatively into the dihydrophosphate ion. The hydrogen ion concentration is given in such a solution by

$$H^+ = \frac{1.95 \times 10^{-7}\ (H_2\bar{P}O_4)}{(H\bar{\bar{P}}O_4)} \qquad (7)$$[1]

If we represent by *a*, the concentration of the added hydrochloric acid, and by *b*, the concentration of the disodium phosphate, then Equation 7 becomes

$$H^+ = \frac{1.95 \times 10^{-7} \times a\alpha_1}{(b - a)\alpha_2}, \qquad (8)$$

where α_1 and α_2 represent, respectively, the dissociations of the mono- and disodium phosphates present at equilibrium.

If the quantity of disodium phosphate in the solutions investigated is always kept the same, the hydrogen ion concentration can be varied simply by the addition of different amounts of hydrochloric acid. In this case the total salt concentration is constant. This is extremely desirable, as it has been shown by Rosenstein,[2] that neutral salts have a great effect upon the fraction of the indicator transformed. The value of the ionization constant in the case of phenolphthalein is doubled by increasing the total salt concentration from 0.03 to 0.40 *N*.

Preliminary Work on Rosolic Acid.—Three stock solutions were prepared, all solutions being made up at 20° with conductivity water. The stock solution of disodium phosphate was prepared from a pure sample of standard make. Its concentration was 0.1036 g. molecules per liter, the concentration being determined gravimetrically as magnesium pyrophosphate. The concentration of the stock solution of hydrochloric acid was 0.08085 *N*. The stock indicator solution was prepared by dissolving about 0.4 g. of an excellent sample of rosolic acid in two liters of conductivity water. The total quantity of the indicator did not dissolve, but as has been previously explained, it is not necessary to know the concentration of the indicator employed.

The incompletely transformed solutions to be tested were prepared from the stock solutions, so that all contained the same amounts of indicator and disodium phosphate, but different amounts of hydrochloric acid. This procedure was followed to keep the total salt concentration the same in all solutions. The volume of each solution was 100 cc. The percentage transmissions (I/I_0) were taken with a 20 mm. depth of each solution, and for the same five wave-lengths of light. As explained in the original article,[3] the percentage transmissions were determined by a

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[1] The value of the constant was taken from the work of Abbott and Bray, THIS JOURNAL, 31, 760 (1909).

[2] THIS JOURNAL, 34, 1128 (1912); see also *Ibid.*, 37, 804 (1915).

[3] *Loc. cit.*

differential method, which avoided the necessity of introducing certain correction factors due to the glass ends with which the cells were provided.

A consideration of Equation 6 will show that the method of calculating the ratio of the red to the yellow component of any incompletely transformed indicator solution, not only depends upon the transmission of the solution under investigation, but also upon the transmission of an indicator solution containing a large excess of acid in which the indicator is totally transformed into its yellow constituent; and also upon the transmission of an indicator solution containing a large excess of alkali in which the indicator is totally transformed into its red component. Table I gives the results of a series of measurements made upon the indicator solution containing an excess of alkali. All solutions contain 50 cc. of the stock solution of rosolic acid, plus the amount of *N* NaOH indicated in the table, the solutions being in all cases diluted to 100 cc. The percentage transmissions are given for five wave-lengths of light between $\lambda = 0.56\mu$ and $\lambda = 0.58\mu$, which is the region of the spectrum employed throughout this investigation. In certain cases, the results of duplicate measurements are given, which indicate in a general way the accuracy of the results.

TABLE I.

(I/I_0) — depth of solution equals 20 mm.

1.	2.	3.	4.	5.	6.	7.	8.		9.		10.
	0.5 cc. *N* NaOH.										
λ = Å. U.		After 5 min.	After 10 min.	After 20 min.	After 30 min.	After 55 min.	After 5 hrs.		After 24 hrs.		3.0 cc. after 24 hrs.
5598	22.6	16.1	12.5	10.7	9.08	7.55	6.25	6.37	6.53	6.53	9.16
5648	36.1	30.6	27.4	22.6	20.0	20.0	17.0	16.7	17.6	16.7	19.1
5698	52.3	44.8	44.2	38.8	37.9	37.0	34.5	34.5	32.2	32.2	35.6
5748	64.8	60.6	58.3	55.6	52.8	51.4	52.4	50.7	49.3	48.7	50.7
5798	77.0	73.3	71.1	68.4	64.1	64.8	66.6	66.2	63.5	63.7	66.3

Column 2, Table I, gives the percentage transmissions of an indicator solution containing 0.5 cc. *N* NaOH, the transmissions being determined within a short time after the solution was prepared. Columns 3 to 7, inclusive, give the percentage transmissions after the same solution had stood for various intervals of time up to 55 minutes. Columns 8 and 9 give the percentage transmissions of new indicator solutions containing the same amount of indicator and alkali, after these solutions had stood, respectively, for 5 to 24 hours. It will be observed that the percentage transmissions for any given wave-length of light become constant after the solutions have stood between 1 and 5 hours.

The fact that solutions of rosolic acid containing an excess of alkali become less and less transparent to yellow light on standing, clearly indicates that the concentration of the red component (In) present is becoming greater and greater, with a resulting decrease in the concentration of the yellow component (HIn), since the greater the concentration of the red component the more opaque the solution becomes to yellow light.

According to the most recent views[1] concerning the cause of color production of indicators of the aurine type, the color is not due simply to the presence of a quinoid group as such, but to an inter- or intramolecular combination of the metallic phenolate with the quinoid complex. It is very probably true, in the case of rosolic acid, that this combination between the metallic phenolate and the quinoid complex takes place rather slowly, with a corresponding intensification of the red color.

It will be observed that the transmission values recorded in Column 10, Table I, of an indicator solution containing 3 cc. *N* NaOH are considerably higher than those recorded in Columns 8 and 9, for a solution containing 0.5 cc. *N* NaOH. In both cases the solutions have come to equilibrium, since it has been shown that equilibrium is established after the solutions have stood between 1 and 5 hours. When very much larger amounts of alkali are added (say 10 cc.), a very perceptible bleaching takes place. In solutions, then, containing an excess of sodium hydroxide two opposing reactions take place: first, a gradual intensification of the red color brought about very probably by a time reaction between the metallic phenolate and the quinoid complex; and second, a bleaching of the red color which is greater the larger the amount of the alkali added. Since it is necessary to know the true percentage transmission $(I/I_0)''$ of a solution completely transformed into the red component, in order to determine the ratio c/c_1 (see page 1695), it follows that the bleaching must be avoided. This result can be obtained by keeping the concentration of the alkali as small as possible, only adding sufficient to transform completely the indicator. The obvious method was to increase gradually the hydroxyl ion concentration, until the solutions were shown to be completely transformed. Table II gives the results of such a determination. All solutions contain 50 cc. of the stock solution of indicator, plus the amount of disodium phosphate and hydrochloric acid indicated in the table. All solutions were allowed to stand a sufficient length of time for equilibrium to be established.

TABLE II.

(I/I_0'') — depth of solution equals 20 mm.

λ = Å. U.	1. 25 cc. Na_2HPO_4. 1 cc. HCl. After 24 hrs.		2. 25 cc. Na_2HPO_4. 0.5 cc. HCl. After 48 hrs.	3. 25 cc. Na_2HPO_4. 0 cc. HCl. After 48 hrs.		4. 25 cc. Na_2HPO_4. 0 cc. HCl. After 96 hrs.
5598	4.44	4.35	4.68	4.68	4.76	5.00
5648	13.7	14.0	11.1	10.8	11.0	9.6
5698	22.8	22.8	19.4	19.4	18.8	19.0
5748	40.0	40.0	33.3	34.1	34.9	34.5
5798	51.6	51.0	48.4	48.4	49.4	48.8

Solution 1, Table II, in which the hydrogen ion concentration is 0.8266×10^{-8}, gives higher values for the percentage transmissions than solu-

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[1] *Am. Chem. J.*, 39, 537, 650, and 651 (1908).

tions 2 and 3, in which the hydrogen ion concentrations are, respectively, $0.4157, \times 10^{-8}$ and 0.043×10^{-8}. This shows that Solution 1 is not completely transformed, since an increase in the red component and a corresponding decrease in the yellow component make the solution more opaque to yellow light. Solution 2 must, however, be completely transformed since, when the hydrogen ion concentration is still further decreased as is the case in Solution 3, the transmission values remain the same. The values of the percentage transmissions recorded in Columns 2, 3 and 4 are the values to be substituted for $(I/I_0)''$ in Equation 6.

In order to ascertain if this same decrease in the transmissions, corresponding to an increase in the red component, would take place on standing with solutions of indicators which are incompletely transformed, four solutions were prepared containing in 100 cc.–50 cc. rosolic acid, 25 cc. Na_2HPO_4 and 1 cc., 5 cc., 10 cc. and 15 cc. of HCl, respectively.

In Table III, are given the percentage transmissions for a depth equal to 20 mm. of the above series of solutions. The transmissions were determined after the solutions had stood for intervals of 5, 16 and 24 hours. The transmission values recorded in Columns 1 and 3 were determined with the same series of solutions. A new series of solutions were prepared for the 16-hour determination, the results of which are recorded in Column 2. Solution 1 was not made up for this determination. Duplicate measurements are given in every case.

TABLE III.

(I/I_0) — depth of solution equals 20 mm.

Solution.	λ = Å. U.	1. After 5 hrs.		2. After 16 hrs.		3. After 24 hrs.	
No. 1 containing 1 cc. HCl Plus 25 cc. Na_2HPO_4	5598	16.7	16.3	..	..	4.44	4.35
	5648	32.7	30.2	..	..	13.7	14.0
	5698	42.8	43.2	..	..	22.8	22.8
	5748	59.1	57.4	..	..	40.0	40.0
	5798	69.7	70.3	..	..	51.6	51.6
No. 2 containing 5 cc. HCl Plus 25 cc. Na_2HPO_4	5598	30.8	30.8	25.7	25.0	26.4	26.4
	5648	39.3	39.6	35.4	35.9	37.5	35.7
	5698	52.6	51.7	48.3	40.0	50.0	49.3
	5748	66.1	64.5	60.8	60.7	60.3	59.4
	5798	72.7	74.3	71.0	71.0	70.7	70.6
No. 3 containing 10 cc. HCl Plus 25 cc. Na_2HPO_4	5598	49.0	49.0	50.7	50.7	49.0	49.1
	5648	57.8	57.8	60.0	59.3	60.0	58.8
	5698	66.7	68.3	68.7	68.7	70.6	70.6
	5748	73.8	73.4	78.5	77.7	76.2	77.4
	5798	83.3	83.6	84.2	84.2	84.4	83.0
No. 4 containing 15 cc. HCl Plus 25 cc. Na_2HPO_4	5598	66.1	67.3	68.0	67.2	67.3	67.8
	5648	72.4	74.1	74.9	74.3	76.4	76.4
	5698	81.6	80.3	81.3	80.4	81.0	79.5
	5748	83.2	83.2	87.2	87.2	85.5	85.5
	5798	88.2	89.4	90.2	90.2	87.7	87.8

An examination of the transmission values recorded for Solutions 1 and 2, Table III, show that a decrease in the transmissions of incompletely transformed solutions of rosolic acid also takes place on standing. Solution 2, in which the hydrogen ion concentration[1] is 4.484×10^{-8}, has come to equilibrium between 5 and 16 hours, as is shown by the fact that the transmission values become constant after 16 hours. In Solutions 3 and 4, in which the hydrogen ion concentrations are, respectively, 10.53×10^{-8} and 19.52×10^{-8}, equilibrium was established before standing 5 hours. This points to the conclusion that in the incompletely transformed solutions of the indicator, the more alkaline the solution the greater the time before equilibrium is established.

Results with Rosolic Acid.—For the first determination of the indicator constant K_i, solutions were used containing in 100 cc., 50 cc. rosolic acid, 25 cc. Na_2HPO_4 and 5, 10 and 15 cc. HCl, respectively.

These solutions were prepared from the stock solutions, and solutions were allowed to stand for 24 hours, which time, according to the results of the preliminary work, was amply sufficient for equilibrium to be established. In Table IV are given the percentage transmissions for a depth equal to 20 mm. of each of these solutions, the values being in every case the average of two measurements. These are the values to be substituted for (I/I_0) in Equation 6. As has previously been explained, the ratio c/c_1 also depends upon the percentage transmission $(I/I_0)''$ of an indicator solution completely transformed into the red component, and also upon the percentage transmission $(I/I_0)'$ of an indicator solution completely transformed into the yellow constituent. The transmissions $(I/I_0)''$ used are the averages of those recorded in Columns 2, 3 and 4, Table II. It was found that solutions containing 50 cc. of the stock solution of the indicator, plus the necessary amount of hydrochloric acid to convert the indicator entirely into the yellow component, were completely transparent to the five wave-lengths of light used. The transmissions $(I/I_0)'$ are therefore in every case 100%.

In Table IV the ratios $c/c_1 = (In)/(HIn)$ were calculated from Equation 6, and the constants K_i from Equation 1. The hydrogen ion concentrations were calculated by means of Equation 7, α_1, and α_2 being interpolated from the percentage ionizations of monosodium and disodium phosphates at various dilutions given by Abbot and Bray.[2]

Another series of solutions, similar to the preceding with the amounts of acid indicated in Table V, were prepared, and allowed to stand 16 hours, in which time all of them had come to equilibrium. The percentage transmissions,[3] calculated ratios, c/c_1, and the constants K_i, are given in

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[1] See page 1696.

[2] THIS JOURNAL, 31, 729 (1909).

[3] The average values of two determinations are given.

Table V. The same values for $(I/I_o)'$ and $(I/I_o)''$ were used as for the preceding determination.

TABLE IV.

Solutions.	λ = Å. U.	$H^+ \times 10^8$.	Average percentage transmissions.	c/c_1.	$K_i \times 10^8$.
1 (5 cc. HCl)......... (25 cc. Na_2HPO_4)	5598	4.484	26.4	0.803	3.60
	5648		36.6	0.811	3.64
	5698		49.6	0.734	3.29
	5748		59.8	0.920	4.13
	5798		70.6	0.937	4.20
2 (10 cc. HCl)........ (25 cc. Na_2HPO_4)	5598	10.53	49.0	0.306	3.23
	5648		59.4	0.302	3.19
	5698		70.6	0.266	2.81
	5748		76.8	0.326	3.44
	5798		83.7	0.329	3.48
3 (15 cc. HCl)........ (25 cc. Na_2HPO_4)	5598	19.52	67.5	0.148	2.89
	5648		76.4	0.136	2.66
	5698		80.2	0.154	3.05
	5748		85.5	0.171	3.34
	5798		87.7	(0.223)	(4.35)

TABLE V.

Solutions.	λ = Å. U.	$H^+ \times 10^8$.	Average percentage transmissions.	c/c_1.	$K_i \times 10^8$.
1 (3 cc. HCl)......... (25 cc. Na_2HPO_4)	5598	2.533	12.1	2.28	5.77
	5648		20.8	2.33	5.89
	5698		32.0	2.20	5.56
	5748		48.1	2.14	5.42
	5798		60.9	2.22	5.63
2 (5 cc. HCl)......... (25 cc. Na_2HPO_4)	5598	4.484	25.4	0.822	3.69
	5648		35.7	0.847	3.81
	5698		48.3	0.785	3.53
	5748		60.8	0.849	3.82
	5798		71.0	0.906	4.07
3 (10 cc. HCl)........ (25 cc. Na_2HPO_4)	5598	10.53	50.7	0.288	3.03
	5648		59.7	0.298	3.14
	5698		68.7	0.293	3.08
	5748		78.1	0.298	3.14
	5798		84.2	0.314	3.30
4 (15 cc. HCl)........ (25 cc. Na_2HPO_4)	5598	19.52	67.6	0.148	2.89
	5648		74.6	0.150	2.93
	5698		80.8	0.146	2.89
	5748		87.2	0.146	2.85
	5798		(90.2)	(0.167)	(3.26)

The values of K_i, Table V, show a steady decrease from 5.65×10^{-8} to 2.89×10^{-8}, as the solution becomes less alkaline. The average constant is 3.91×10^{-8}.[1] It is to be remembered that the constants were determined on the assumption that rosolic acid is monobasic. As is

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[1] The value given by Salm, *Z. physik. Chem.*, **57**, 496 (1907), is 1.1×10^{-8}.

well known the indicator is dibasic, and the decrease in the constants with decreasing alkalinity was expected. Rosolic acid actually dissociates in two stages according to the equations, $\mathrm{H_2In} = \mathrm{HI\bar{n}} + \mathrm{H^+}$, and $\mathrm{HI\bar{n}} = \mathrm{I\bar{\bar{n}}} + \mathrm{H^+}$.

Behavior of Rosolic Acid as a Dibasic Acid.—With regard to the two ions $\mathrm{HI\bar{n}}$ and $\mathrm{I\bar{\bar{n}}}$, three assumptions can be made: (1) that the intermediate ion $\mathrm{HI\bar{n}}$ is yellow and the secondary ion $\mathrm{I\bar{\bar{n}}}$ is red; (2) that the ion $\mathrm{HI\bar{n}}$ is red and the ion $\mathrm{I\bar{\bar{n}}}$ is yellow; (3) that both the ions $\mathrm{HI\bar{n}}$ and $\mathrm{I\bar{\bar{n}}}$ are red. In the first case the ratio of the red to the yellow component will be given by

$$c/c_1 = \frac{\mathrm{I\bar{\bar{n}}}}{\mathrm{HI\bar{n}} + \mathrm{H_2In}}. \tag{9}$$

In addition, the equilibrium equations given below have to be considered.

$$\frac{(\mathrm{H^+})(\mathrm{HI\bar{n}})}{(\mathrm{H_2In})} = \mathrm{K_1} \qquad \frac{(\mathrm{H^+})(\mathrm{I\bar{\bar{n}}})}{(\mathrm{HI\bar{n}})} = \mathrm{K_2}. \tag{10}$$

By combining these three equations we obtain

$$c/c_1 = \frac{\mathrm{K_1K_2}}{\mathrm{H^+(H^+ + K_1)}}. \tag{11}$$

In the second case, when the ion $\mathrm{HI\bar{n}}$ is red and the ion $\mathrm{I\bar{\bar{n}}}$ is yellow, the ratio becomes

$$c/c_1 = \frac{\mathrm{HI\bar{n}}}{\mathrm{H_2In} + \mathrm{I\bar{\bar{n}}}} \tag{12}$$

and from Equations 10

$$c/c_1 = \frac{\mathrm{H^+K_1}}{\mathrm{H^2 + K_1K_2}}. \tag{13}$$

In the third case, *i. e.*, when both ions $\mathrm{HI\bar{n}}$ and $\mathrm{I\bar{\bar{n}}}$ are red, the ratio is given by

$$c/c_1 = \frac{\mathrm{HI\bar{n}} + \mathrm{I\bar{\bar{n}}}}{\mathrm{H_2In}} \tag{14}$$

whence, $c/c_1 = \dfrac{\mathrm{H^+K_1 + K_1K_2}}{\mathrm{H^{+2}}}$.[1] (15)

Equations 11, 13, and 15 were tested by substituting the experimental values of the ratios c/c_1 and the hydrogen ion concentrations given for Solutions 1 and 4, Table V, in the equations, and solving for the constants $\mathrm{K_1}$ and $\mathrm{K_2}$. The constants were then used to calculate the ratios for Solutions 2 and 3. In Table VI, are given the values of the ratios c/c_1 calculated from the various equations, and also the observed experimental ratios which are the averages of those given in Table V.

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[1] The development is essentially the same as given by Rosenstein for phenolphthalein. THIS JOURNAL, 36, 1124 (1912).

TABLE VI.

		Values of c/c_1.			
Solution.	$H^+ \times 10^8$.	Observed.	Calc. by 11.	Calc. by 13.	Calc. by 15.
1............	2.533	2.23	2.23	2.23	2.23
2............	4.484	0.842	1.12	...	0.953
3............	10.53	0.298	0.371	...	0.308
4............	19.52	0.148	0.148	0.148	0.148

On the first assumption, namely, that the ion $\mathrm{HI\bar{n}}$ is yellow and the ion $\mathrm{I\bar{\bar{n}}}$ is red, the ratios calculated by Equation 11, for Solutions 2 and 3, do not at all agree with the experimentally determined values. On the assumption that the intermediate ion $\mathrm{HI\bar{n}}$ is red and the secondary ion $\mathrm{I\bar{\bar{n}}}$ is yellow, the constant K_2, Equation 13, was found to be a negative quantity. This, in itself, proves the absurdity of the assumption; consequently, no ratios for Solutions 2 and 3 were calculated. On the assumption, however, that both the ions $\mathrm{HI\bar{n}}$ and $\mathrm{I\bar{\bar{n}}}$ are red, the ratios calculated by Equation 15, agree fairly closely with the experimentally determined values. The agreement is as close as might be expected considering that in work of this character so many different sources of error are possible. The results lead to the conclusion, therefore, that rosolic acid acts as a dibasic acid, and furthermore, show that both the primary and secondary ions are intensely colored.

In the case of phenolphthalein, it has been shown by Rosenstein[1] that the colored form of the indicator is only produced in appreciable quantity when the second hydrogen of the indicator acid is replaced by the base. This is in accord with the theory already referred to,[1] that the cause of the color production is due to a combination between the metallic phenolate and the quinoid complex: since it is only where the second hydrogen is replaced that the formation of the quinoid phenolate complex is possible. In the case of rosolic acid, however, the quinoid phenolate complex can be found when the first hydrogen of the indicator acid is replaced by the base. The experimental fact, then, that the intensely colored form of the indicator is produced when the first hydrogen is replaced by the base is perfectly in accord with the theories advanced.

Summary.

1. An intensification of the red color of rosolic acid solutions incompletely transformed by the addition of alkali was found to take place when such solutions were allowed to stand, the time reaction being in all probability due to a slow union of the metallic phenolate with the quinoid complex.

2. In rosolic acid solutions containing a large excess of alkali a perceptible bleaching of the red color was also indicated.

3. The ratio (c/c_1) of the red to the yellow component has been de-

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[1] *Loc. cit.*

termined for indicator solutions of various hydrogen ion concentrations using the radiometric method developed in the original article.[1]

4. The values of the ionization constant of rosolic acid calculated from the ratio c/c_1, on the assumption that the indicator acid is monobasic, were found to decrease with decreasing alkalinity. When the hydrogen ion concentration was increased from 2.533×10^{-8} to 19.52×10^{-8}, the total salt concentration being 0.0259 N, the value of the ionization constant K_i was found to decrease from 5.65×10^{-8} to 2.89×10^{-8}.

5. It was found that this variation in the constants could be explained by regarding the indicator as a dibasic acid, and it was shown, furthermore, that the intensely colored form of the indicator is formed when the first hydrogen of the indicator acid is replaced by the base.

BALTIMORE, MD.
April, 1915.

THE SOLUBILITY OF MAGNESIUM CARBONATE IN NATURAL WATERS.[2]

BY ROGER C. WELLS.

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Treadwell and Reuter,[3] who determined the solubility of magnesium carbonate in water under given partial pressures of carbon dioxide, found for a partial pressure of "0 mm." of carbon dioxide at 15°, 0.6410 g. magnesium carbonate and 1.9540 g. magnesium bicarbonate per liter. This is equivalent to 0.51 g. magnesium and 2.09 g. carbon dioxide per liter. Cameron and Briggs,[4] however, found only 0.18 g. magnesium and 0.543 g. carbon dioxide per liter at room temperature after passing a current of air through the solution for a very long period. Feeling that more attention should be paid to the nature of the solid phase, I have carried out experiments that show a difference in the behavior of magnesite, the simplest natural variety of magnesium carbonate, and nesquehonite, the trihydrate $MgCO_3.3H_2O$ and, furthermore, find solutions in equilibrium with the latter substance under atmospheric conditions at 20° to contain 0.36 g. magnesium and 1.01 g. carbon dioxide per liter.

As the object of the experiments was to imitate natural conditions, the solutions were exposed to the action of outdoor air over long intervals, in order that they might come into equilibrium with the small amount of carbon dioxide in the atmosphere. The air was filtered through cotton, washed by distilled water and bubbled through the solutions contained in Jena flasks immersed in a thermostat. The thermostat was

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[1] *Loc. cit.*

[2] Published by permission of the Director of the United States Geological Survey.

[3] *Z. anorg. Chem.*, 17, 202 (1898).

[4] *J. Physic. Chem.*, 5, 553 (1901).