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THE IONIZATION CONSTANT OF PHENOLPHTHALEIN AND THE EFFECT UPON IT OF NEUTRAL SALTS.

BY LUDWIG ROSENSTEIN.

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1. Outline of the Present and of Previous Investigations.

The systematic development of the quantitative theory of indicators by Noyes[1] has made it more than ever desirable to determin accurately the constants for a series of indicators. It is also desirable to determin the effect of the presence of neutral salts in the solution on these constants. The purpose of the present paper is to describe an investigation of these problems in the case of phenolphthalein.

The work here presented was begun under the guidance of Dr. M. S. Sherrill. It is my desire to express here my gratitude to him for his helpful advice and encouragement.

The general method of procedure has been to determin in the first place how the depth of color in a phenolphthalein solution depends on the concentration of hydrogen ion; and in the second place, how this depth of color depends on the amount of salt present in a solution of some fixed hydrogen ion concentration.

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[1] A. A. Noyes, THIS JOURNAL, 32, 7 (1910).

The ionization constant of phenolphthalein has been the subject of investigations by McCoy,[1] Salm,[2] Wegscheider,[3] Hildebrand,[4] and others. The values of the constant found in the literature are very diverse; in fact, they vary from about 0.8×10^{-10} to 8.0×10^{-10}. It was hoped that some clue might be found to the cause of so large a variation.

2. The General Principles Involved.

The constant with which we are here dealing is not the actual ionization constant as defined by the mass action law, but a combination of this quantity with another dependent on the existence of two tautomeric forms[5] of the indicator in equilibrium with each other. It is this "apparent" constant which is of significance in quantitative analysis, and it is likewise this "apparent" constant which we obtain through colorimetric determinations. It expresses the relation between the color change of the indicator and the concentration of hydrogen ion in the solution.

If the concentration of the hydrogen ion in any solution is fixed and the fraction of the indicator transformed to its colored form is determined in this solution, we have all the data necessary for calculating the apparent indicator constant. Indicators may be regarded as weak acids[6] and represented by the formula HIn.[7] The apparent constant K_I will then be equal to $\frac{(H^+) \times (In^-)}{(HIn)}$; or, if α is the fraction of the total indicator present that is transformed to its salt, *i. e.*, if $\alpha = \frac{(In^-)}{(HIn) + (In^-)}$, we have

$$K_I = (H^+) \gamma \alpha / 1 - \alpha, \qquad (1)$$

where γ is the degree of ionization of the indicator salt.

In the present investigation the concentration of hydrogen ion was fixed by means of solutions of ammonium hydroxide and ammonium chloride, keeping the concentration of neutral salt below 0.05 normal. The concentration of hydrogen ion in the solution was calculated from the formula

$$(H^+) = \frac{K_W (NH_4^+)}{K_B C_B} = \gamma \frac{K_W}{K_B} \frac{C_{AS}}{C_B}. \qquad (2)$$

In this equation K_W is the ionization constant for water, K_B the ionization constant for ammonia, (NH_4^+) the concentration of ammonium ion, and C_B the concentration of the total ammonia $(NH_3 + NH_4OH)$, C_{AS} the

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

[2] E. Salm, *Z. physik. Chem.*, **57**, 471 (1906–'07).

[3] R. Wegscheider, *Z. Elektrochem.*, **14**, 510 (1908).

[4] J. Hildebrand, *Ibid.*, 349 (1908).

[5] J. Stieglitz, THIS JOURNAL, **25**, 1112 (1903). Stieglitz and Acree, *Am. Chem. J.*, **39**, 528 (1908). Acree and Nagle, *Ibid.*, 789 (1908).

[6] Noyes, *Loc. cit.*

[7] In the first instance phenolphthalein will be regarded as monobasic. The probability that it behaves as a dibasic acid will be discussed later.

concentration of the ammonium salt and γ its ionization[1] at this concentration. Combining equations (1) and (2) we get

$$K_{\mathrm{I}} = \frac{K_{\mathrm{W}}}{K_{\mathrm{B}}} \frac{C_{\mathrm{AS}}}{C_{\mathrm{B}}} \frac{\gamma^2 \alpha}{(1 - \alpha)}. \tag{3}$$

3. The Experimental Method.

The fraction α of the indicator transformed was determined by comparing the color of the solution in which α is unknown with that of a completely transformed solution of indicator having the same total indicator concentration. The actual concentration of indicator in the solution need not be known.

The instrument used in making the color comparisons was a colorimeter of the Duboscq type, constructed as shown in the accompanying sketch. The mirror "E" reflects light through the solutions contained in the cups D, D′, and through the glass plungers C, C′, to the prisms B. These bring the beam of light to the same eyepiece A, so that through A is seen a divided field half illuminated by light coming through the solution in D, and the other half by light coming through D′. The heights of the solutions in the two cups may be varied by changing the positions of the plungers. The relative heights of these are read on a scale on the back of the instrument.

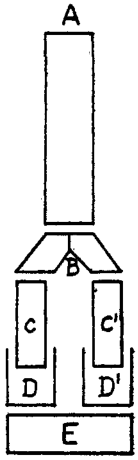

Fig. 1.

The calculation of the fraction $\alpha/(1-\alpha)$ may best be explained by an illustration. In one experiment the solution in cup D had the composition, 15 cc. standard NH_4OH, 20 cc. standard NH_4Cl, and 15 cc. indicator solution. The solution in D′ consisted of 6 cc. of the indicator solution completely transformed by the addition of a few drops of 0.1 normal KOH and made up to the same volume as the first solution, namely, 50 cc. The height of the plunger in the latter solution was fixed at 40 on the scale, and the following settings for the height of the plunger in the unknown solution were obtained:

38.5, 38.2, 39.0, 37.5, 39.0, 38.0; average, 38.4.

Assuming that the concentrations of the colored substances are inversely proportional to the heights of the plungers, or of the respective liquids, it follows that $6/15 \times 40/38.4 = 0.417$ is the fraction of the indicator, transformed and therefore that $\alpha/1-\alpha = 0.417/0.583 = 0.715$. It will be noticed that the actual strength of the indicator standard does not enter into the calculation.

In order to test the accuracy of this method, 31.6 cc. of the indicator solution were completely transformed and made up to a volume of 50 cc.

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[1] The ionization values γ, in equations (1) and (2), may be considered equal, since they refer to solutions with the same salt concentration.

This solution was then compared with solutions made by completely transforming 30, 35, and 40 cc. of the standard and diluting to 50 cc. in each case. The results of these measurements are as follows:

Plunger in unknown soln.[1]	Plunger in known soln.	Cc. found.	Percentage error.
28.65	35	32.8	+3.8
32.0	40.0	32.0	+1.3
32.1	40.0	32.1	+1.6
32.7	40.0	32.7	+3.4
32.4	40.0	32.4	+2.5
35.9	30.0	33.4	+5.6
37.2	30.0	32.2	+1.9

In another set of experiments four solutions were made by completely transforming measured volumes of the standard indicator solution, diluting to 50 cc., and comparing with known quantities of the standard treated in the same way.

Cc. standard taken.	Cc. standard found.	Percentage error.
3.80	3.85	+1.3
7.40	7.51	+1.5
10.90	10.35	—5.0
14.85	14.85	0.0

These results show that the error in the determination of α, the fraction of the indicator transformed, is not likely to be greater than 5%. This error will, however, be somewhat increased in calculating the indicator constant, because the ratio $\alpha/(1-\alpha)$ occurs in the calculation.

4. Preparation of the Solutions.

Pure phenolphthalein was prepared from the usual commercial product, which contains resinous matter, by washing with methyl alcohol and recrystallizing from this solvent until a product of constant melting point was obtained. For the last three fractions thus crystallized the melting points were 255°, 254°, and 254°, respectively. The crystals were pure white and left no residue when heated on platinum. From them the standard indicator solution was made by boiling 0.0272 g. with one liter of conductivity water. This quantity of indicator did not dissolve completely; but, as shown above, it is unnecessary to know the exact strength of the standard solution.

A solution of ammonium hydroxide, free from carbon dioxide, was prepared by distilling pure ammonium chloride with barium hydroxide and condensing the gas in conductivity water. Later on in the work Merck's guaranteed pure ammonia was used to make up the solution. The solution was standardized by titrating with 0.1 normal hydrochloric acid and methyl-red.

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[1] In these and all the subsequent measurements the mean of six settings of the plunger was taken.

A solution of pure ammonium chloride in conductivity water was made and was standardized by precipitation with silver nitrate.

5. Fraction of the Indicator Transformed and Calculated Ionization Constant at Various Hydrogen Ion Concentrations.

In Table I are given the results of the measurements. The temperature was always about 23.5°. Column 1 gives the number of the experiment, columns 2 and 3 the final concentrations C_B and C_{AS} in equivalents per liter of NH_4OH. and NH_4Cl respectively, column 4 the ionization of NH_4Cl at these concentrations, column 5 the concentration of H^+ ion calculated according to equation (2), column 6 the experimentally determined ratio $\alpha/(1-\alpha)$, and column 7 the corresponding values of the indicator constant K_I calculated according to equation (3). The values of the other constants used in calculating K_I are: $K_W = 0.72 \times 10^{-14}$, and K_B[1] $= 17.7 \times 10^{-6}$.

TABLE I.—OBSERVED VALUES OF THE FRACTION (α) OF THE INDICATOR TRANSFORMED AND THE IONIZATION CONSTANTS (K_I) CALCULATED FROM THEM.

1 Expt. No.	2 C_B.	3 C_{AS}.	4 γ.	5 $(H^+) \times 10^{10}$.	6 $\alpha/1-\alpha$.	7 $K_I \times 10^{10}$.
1	0.0168	0.0510	0.89	10.9	0.113	1.08
2	0.0168	0.0408	0.90	8.82	0.174	1.38
3	0.0077	0.0163	0.95	8.06	0.172	1.32
4	0.0168	0.0306	0.91	6.70	0.250	1.52
5	0.0116	0.0143	0.94	4.65	0.356	1.55
6	0.0333	0.0408	0.90	4.41	0.452	1.79
7	0.0333	0.0306	0.91	3.42	0.622	1.94
8	0.0154	0.0122	0.93	2.96	0.603	1.66
9	0.0500	0.0408	0.90	2.93	0.705	1.86
10	0.0333	0.0204	0.92	2.26	0.868	1.81
11	0.0667	0.0204	0.92	1.13	1.86	1.94
12	0.0667	0.0204	0.92	1.13	2.00	2.06

As will be shown in Section 8 of this paper the effect of neutral salts on the color obtained in a given solution is considerable; and so the constants determined must first be reduced to the same concentration of neutral salt. This reduction may be made by means of equation (6) proposed in Section 8. Since in practice titrations are most frequently made in solutions about 0.05 normal with respect to neutral salt at the end-point, the relation between the hydrogen ion concentration and the fraction $\alpha/(1-\alpha)$ in a 0.05 normal salt solution has been calculated; and new ionization constants have been calculated from these values by equation (3), taking the ionization γ as 0.89. The results are given in Table II.

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[1] Sosman, *Carnegie Institution Publ.*, 63, 228 (1907).

TABLE II.—VALUES OF THE FRACTION TRANSFORMED AND OF THE INDICATOR CONSTANT CORRECTED TO A SALT CONCENTRATION OF 0.05 NORMAL.

Expt. No.	$(H^+) \times 10^{10}$.	$\alpha/1-\alpha$ (corr.).	$K_I \times 10^{10}$.
1	10.9	0.111	1.08
2	8.82	0.184	1.44
3	8.06	0.218	1.56
4	6.70	0.277	1.66
5	4.65	0.449	1.86
6	4.41	0.474	1.86
7	3.42	0.691	2.10
8	2.96	0.766	2.02
9	2.93	0.744	1.94
10	2.26	1.03	2.08
11	1.13	2.22	2.23
12	1.13	2.36	2.37

The values of K_I show a steady increase from 1.1×10^{-10} to 2.4×10^{-10}, as the solution becomes more alkalin.[1] The average of these values of K_I is 1.8×10^{-10}; but, since they steadily increase with decrease in the hydrogen ion concentration, we have to look for the cause of this variation.

If the principle that $(H^+)\,\alpha/1-\alpha = K_I$ holds true, a straight line should be obtained when the hydrogen ion concentration is plotted against

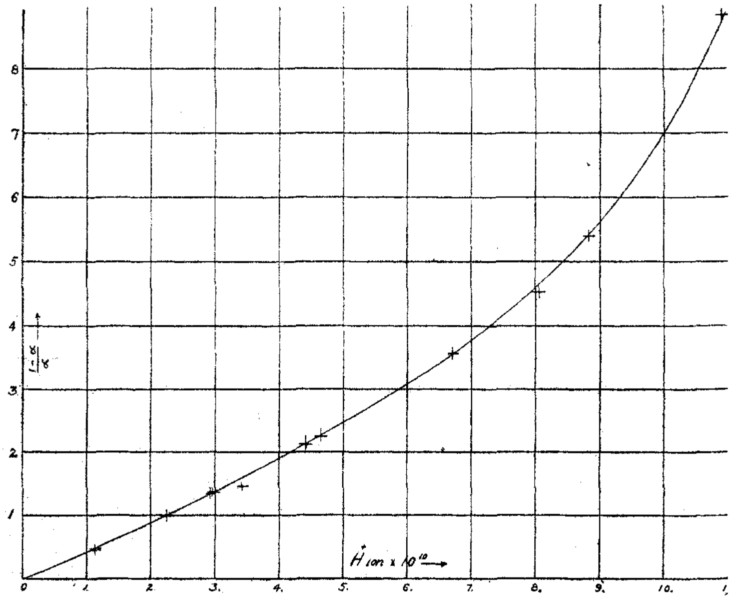

Fig. 2.

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[1] The average value of the results for K_I obtained by Hildebrand is 1.70×10^{-10}; by Wegscheider, 1.76×10^{-10}. These values lie between the limits of the values here reported. McCoy, who worked in exceedingly dilute salt solutions, obtained 0.75×10^{-10}; and Salm, who worked in strong salt solutions, obtained 8×10^{-10}.

$(1-\alpha)/\alpha$. In Fig. 2 this graph is shown. It is evident that the function is not a linear one, and therefore that this simple relation does not hold. The fact should be emphasized, however, that Fig. 2 represents the actual relation between the hydrogen ion concentration and the fraction $(1-\alpha)/\alpha$, in solutions 0.05 normal with respect to neutral salt. The plot may therefore be used directly in the quantitative interpretation of the behavior of the indicator, without reference to its theoretical significance.

6. The Hypothesis that Phenolphthalein Acts as a Dibasic Acid.

Wegscheider[1] has pointed out that the values of the ionization constant obtained by Hildebrand, McCoy, and Schugowitsch show considerable variation with the concentration of hydroxide ion, in the solution; that this variation is always in the same direction; that it is largest when the hydroxide ion concentration is small; and that the values became very nearly constant in the more alkalin solutions. Wegscheider concludes that the variation may be accounted for by regarding phenolphthalein as a dibasic acid[2] which dissociates in two stages, according to the equations $H_2In = H^+ + HIn^-$ and $HIn^- = H^+ + In^=$.

In interpreting the results by this hypothesis, it seems essential to take into account the tautomeric relations involved. To do this, let us represent by H_2In, HIn^-, and $In^=$ the colorless forms of the indicator, and by H_2In', HIn'^-, and $In'^=$ the red forms. With respect to these six substances the only definit knowledge we have is that, since acid solutions are colorless, the concentration of H_2In' is negligible in comparison with that of H_2In. We should therefore have to assume in a complete treatment of the subject that the four other substances, HIn^-, HIn'^-, $In^=$, $In'^=$, as well as the H_2In, might all be present in appreciable quantity. Such a treatment would be, however, rather complicated. It seems therefore best for our present purposes to consider the two limiting cases, between which all possible cases must lie.[3]

The first limiting case assumes that the substance H_2In is so very weak an acid that the concentrations of the colorless forms HIn^- and $In^=$ are negligible in comparison with those of the red forms HIn'^- and $In'^=$. In this case, we may write for the ratio of the red to the colorless substance in any solution

$$\frac{\alpha}{1-\alpha} = \frac{(HIn'^-) + (In'^=)}{(H_2In)}.$$

We have in addition the three following equilibrium equations:

$$K_T = \frac{(H_2In')}{(H_2In)},\quad K'_1 = \frac{(HIn'^-)(H^+)}{(H_2In')},\text{ and } K'_2 = \frac{(In'^=)(H^+)}{(HIn'^-)}.$$

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[1] *Loc. cit.*

[2] The salts $C_{20}H_{12}O_4Na_2$ and $C_{20}H_{12}O_4K_2$ have, in fact, been prepared.

[3] I am indebted to Prof. A. A. Noyes for this discussion of the tautomeric relations involved.

Combining these four equations we get

$$\frac{\alpha}{1-\alpha} = \frac{K_{\mathrm{T}}K_1'}{(\mathrm{H}^+)}\left[1 + \frac{K_2'}{(\mathrm{H}^+)}\right]. \tag{4}$$

The second limiting case assumes that the red substance $\mathrm{HI}n'^-$ is negligible in comparison with the colorless substance $\mathrm{HI}n^-$, and that only when the second hydrogen of the acid is displaced an appreciable concentration of the red form (as the substance $\mathrm{I}n'^=$) results. In this case we may write[1]

$$\frac{\alpha}{1-\alpha} = \frac{(\mathrm{In}'^=) + (\mathrm{In}^=)}{(\mathrm{HIn}^-) + (\mathrm{H_2In})}.$$

For $(\mathrm{I}n'^=) + (\mathrm{I}n^=)$ we may write $k(\mathrm{I}n'^=)$, in virtue of the mass-action relation $(\mathrm{I}n'^=) = K_{\mathrm{T}}(\mathrm{I}n^=)$, k being written for $(1 + 1/K_{\mathrm{T}_2})$. We have, in addition, the equilibrium equations:

$$\frac{(\mathrm{H_2In'})}{(\mathrm{H_2In})} = K_{\mathrm{T}},\quad \frac{(\mathrm{H}^+)^2(\mathrm{In}'^=)}{(\mathrm{H_2In'})} = K_1'K_2',\ \text{and}\ \frac{(\mathrm{H}^+)(\mathrm{HIn}^-)}{(\mathrm{H_2In})} K_1.$$

Combining these equations we get

$$\frac{\alpha}{1-\alpha} = \frac{kK_1'K_2'K_{\mathrm{T}}}{(\mathrm{H}^+)(\mathrm{H}^+ + K_1)}. \tag{5}$$

The application of these equations to the experimental data has been tested by calculating the values of the constants occurring in them from two observed values of $\alpha/(1-\alpha)$ near the ends of the experimental series (Expt. No. 2 and the mean of Expts. 11 and 12 of Table II being used), and then calculating from these constants by means of the equations the

TABLE III.—BEHAVIOR OF PHENOLPHTHALEIN AS A DIBASIC ACID.

Expt. No.	$10^{10}(\mathrm{H}^+)$.	Value of $\alpha/(1-\alpha)$. Observed (corr.).	Calc. by (4).	Calc. by (5).
1	10.9	0.111	0.146	0.133
2	8.82	0.184	0.184	0.182
3	8.06	0.218	0.203	0.207
4	6.70	0.277	0.247	0.266
5	4.65	0.45	0.37	0.43
6	4.41	0.47	0.40	0.46
7	3.42	0.69	0.54	0.64
8	2.96	0.77	0.64	0.76
9	2.93	0.74	0.65	0.77
10	2.26	1.03	0.90	1.03
11	1.13	2.22	2.29	2.28
12	1.13	2.36	2.29	2.28

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[1] The intensity of color is in this case a measure of the sum $(\mathrm{In}'^=) + (\mathrm{In}^=)$, even though the $\mathrm{In}^=$ is colorless; for when the indicator is completely transformed into its salt $\mathrm{B_2In}$ by an excess of base, $\mathrm{In}'^=$ and $\mathrm{In}^=$ are present in some definit proportion; and this proportion, in virtue of the mass-action relation $(\mathrm{In}'^=) = K_{\mathrm{T}_2}(\mathrm{In}^=)$, is the same in every other solution, whose color may be compared with that of the completely transformed standard.

values of $\alpha/(1-\alpha)$ which correspond to the other H^+ concentrations. The constants of equation (4) were found to be $K_TK_1' = 1.47 \times 10^{-10}$ and $K_2' = 0.86 \times 10^{-10}$. The constants of equation (5) were found to be $(kK_1'K_2'K_T) = 32.5 \times 10^{-10}$ and $K_1 = 11.5 \times 10^{-10}$. The results of the calculations are given in Table III, beside the observed corrected values taken from Table II.

It will be seen that the intermediate values calculated by equation (4) do not agree at all well with the observed values; but that those calculated by equation (5) agree with these satisfactorily. This confirms the conclusion of Wegscheider that phenolphthalein acts as a dibasic acid. It shows, furthermore, that the colored form of the indicator is produced in appreciable quantity only when the *second* hydrogen of the indicator acid has been replaced by the base.

7. Measurements on the Effect of Neutral Salts on the Fraction Transformed.

Various investigators[1] have observed that the color change of an indicator is affected by the amount of neutral salt in the solution, the effect being in general to hasten the appearance of the color or to intensify color already partially developed. In studying this effect of neutral salts on phenolphthalein the method pursued was to keep the hydrogen ion concentration nearly constant in a series of solutions, while varying the quantities of neutral salt. The ratio of ammonium chloride to ammonium hydroxide was kept 2 to 1, and potassium chloride was added to the solutions in such quantities as to vary the total salt concentration from 0.03 to 0.80 normal. The color comparisons were made as described in Section 3. The results of these determinations are given in Table IV. In columns 1, 2 and 3 are given the concentrations of ammonium chloride, of potassium

TABLE IV.—CHANGE OF THE FRACTION OF THE INDICATOR TRANSFORMED WITH THE CONCENTRATION OF NEUTRAL SALT IN THE SOLUTION.

Expt. No.	1 NH_4Cl.	2 KCl.	3 Total salt.	4 NH_4OH.	5 $\alpha/1-\alpha$.	6 γ.	7 $\gamma^2\alpha/1-\alpha$.	8 $10^{10}Ki$.
1	0.03	0.00	0.03	0.015	0.155	0.90	0.126	1.02
2	0.03	0.03	0.06	0.015	0.172	0.88	0.133	1.08
3	0.03	0.10	0.13	0.015	0.269	0.84	0.190	1.54
4	0.03	0.50	0.53	0.015	0.406	0.78	0.247	2.01
5	0.10	0.00	0.10	0.05	0.246	0.85	0.178	1.44
6	0.10	0.03	0.13	0.05	0.261	0.84	0.184	1.50
7	0.10	0.10	0.20	0.05	0.310	0.82	0.208	1.69
8	0.10	0.50	0.60	0.05	0.469	0.77	0.278	2.26
9	0.30	0.00	0.30	0.15	0.356	0.80	0.228	1.85
10	0.30	0.03	0.33	0.15	0.394	0.79	0.246	2.00
11	0.30	0.10	0.40	0.15	0.416	0.78	0.253	2.06
12	0.30	0.50	0.80	0.15	0.556	0.76	0.321	2.61

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[1] Szyszkowski, *Z. physik. Chem.*, **58,** 420 (1907); Sörensen and Palitzsch, *Biochem. Z.*, **24,** 387; Michaelis and Rona, *Z. Elektrochem.*, **14,** 251–3 (1908).

chloride, and of total salt in equivalents per liter; in column 4 is given the concentration of NH_4OH; in column 5, the ratio $\alpha/(1-\alpha)$ as determined from the color change; in column 6, the ionization of the salts in the solution; in column 7, the values of the quantity $\gamma^2\alpha/(1-\alpha)$, which as shown by equation (3) should be constant, if the mass-action principles involved hold true; and in column 8 the corresponding values of $10^{10}K_{\mathrm{I}}$.[1]

From column 5 it will be seen that there is a large increase in the fraction of the indicator transformed and that, correspondingly, the color of a solution containing the same ratio of ammonium chloride to ammonium hydroxide becomes much more intense when the neutral salt concentration is considerably increased. This doubtless explains the discrepancies in the results of previous investigators who have left this factor out of account.

8. Discussion of the Effect of Neutral Salts.

The large variation of the values given in the seventh and eighth columns of Table IV shows that the theoretical mass action principles do not apply even approximately to the equilibrium in question. Let us consider the significance of this variation. For this purpose equation (3) may be written in terms of the corresponding concentrations, as follows:

$$\frac{(\mathrm{In}^-)(\mathrm{NH_4}^+)}{(\mathrm{HIn})(\mathrm{NH_3})} = \frac{(\mathrm{H}^+)(\mathrm{In}^-)}{(\mathrm{HIn})} \cdot \frac{(\mathrm{NH_4}^+)}{(\mathrm{H}^+)(\mathrm{NH_3})} = \text{const.}$$

Since, contrary to the mass action requirements, this expression does not have a constant value, some of the substances involved in it must have an abnormal activity, that is, an activity which is not proportional to the concentration. We may, however, assume with much probability that any abnormality of the NH_4^+ is largely compensated by a corresponding abnormality of the H^+, since these two ions are present in the same salt solution. We can furthermore eliminate any abnormal activity of the NH_3 by calculating from the measurements of its partial vapor pressure above salt solutions containing it how the ratio of its activity to its concentration varies with the salt concentration in the solution. Thus it follows from the measurements of Abegg and Riesenfeld[2] that this ratio increases with the salt concentration C_S in the proportion $1/(1-0.077C_S)$. New values (corrected for this deviation) of the quantity $(H^+)(In^-)/(HIn)$, or of the indicator constant K_{I}, may therefore be obtained by multiplying by $(1-0.077C_S)$ the values of K_{I} originally calculated by equation (3) and recorded in Table IV. These new values are recorded in Table V in the column headed K_{I} (corr.).

In order to express the variation of these values with the salt concen-

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[1] Throughout this section and the following one phenolphthalein is for greater simplicity regarded as a monobasic acid. As the H^+ concentration was nearly the same in all the experiments, this cannot affect the interpretation of the results.

[2] *Z. physik. Chem.*, 40, 84.

tration, it is natural to try to employ a function of the form $K_I = K[1 + k(C_S\gamma)^m]$, since this function has recently been shown by Kraus and Bray[1] to be of almost universal applicability. In this case the numerical equation is

$$10^{10}K_I = 0.77[1 + 2.8(C_s\gamma)^{1/2}]. \qquad (6)$$

That the results are satisfactorily expressed by it[2] may be seen from a comparison of the values calculated by it, which are given in Table V in the column headed $10^{10}K_I$ (calc.), with the values in the column headed $10^{10}K_I$ (corr.) taken from Table IV.

TABLE V.—CORRECTED VALUES OF THE INDICATOR CONSTANT AND THEIR VARIATION WITH THE SALT CONCENTRATION.

Expt. No.	NH_3 conc.	Total salt conc. (C_S).	Total ion conc. ($C_S\gamma$).	$10^{10}K_I$ (corr.).	$10^{10}K_I$ (calc.).
1	0.015	0.030	0.027	1.02	1.02
2	0.015	0.060	0.053	1.08	1.26
3	0.015	0.130	0.11	1.52	1.50
4	0.015	0.53	0.41	1.93	2.15
5	0.050	0.10	0.085	1.43	1.39
6	0.050	0.13	0.11	1.48	1.50
7	0.050	0.20	0.16	1.66	1.63
8	0.050	0.60	0.46	2.16	2.23
9	0.15	0.30	0.24	1.81	1.82
10	0.15	0.33	0.26	1.95	1.87
11	0.15	0.40	0.31	2.00	1.98
12	0.15	0.80	0.60	2.45	2.45

9. Summary.

1. The fraction of phenolphthalein transformed from the colorless to the colored form has been determined colorimetrically in solutions of various hydrogen ion concentrations and of various neutral salt concentrations.

2. The value of the ionization constant of phenolphthalein, as calculated from the fraction transformed to the colored form under the assumption that this indicator is a monobasic acid, has been found to increase with the alkalinity of the solution, even when the amount of neutral salt is kept constant. Thus, when the hydrogen ion concentration is varied from 10.9×10^{-10} to 1.1×10^{-10}, the constant varies from 1.1×10^{-10} to 2.3×10^{-10}.

3. It is shown, as has previously been done by Wegscheider, that this variation can be explained by considering that the phenolphthalein acts as a dibasic acid. A consideration of the tautomeric relations involved

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[1] *Science*, **35**, 433 (1912).

[2] This is true at any rate of the last two groups of experiments (Nos. 5–8 and 9–12). There seem to be large experimental errors in Expts. Nos. 2 and 4 of the first group.

shows that it is then necessary to assume that the colored form of the indicator is produced in appreciable quantity only when the second hydrogen of the indicator acid has been replaced by the base.

4. Neutral salts are shown to have a great effect on the fraction of the indicator transformed (as determined by its color) and correspondingly on its ionization constant; thus the value of the constant is doubled by increasing the salt concentration from 0.03 to 0.40 normal. The change of the constant K_I (regarding the indicator as a monobasic acid) with the total salt concentration C_S can be expressed by the equation $K_I = 0.77 \times 10^{-10}[1 + 2.8(C_S\gamma)^{0.5}]$, in analogy with the expression for the deviations shown by strong electrolytes.

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A SUMMARY OF THE SPECIFIC HEATS OF GASES.

By Gilbert N. Lewis and Merle Randall.

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In free energy calculations over a wide range of temperature, the specific heats play a very important role. Most of the important chemical equilibria which have been studied at high temperatures involve gaseous substances. It is therefore necessary to consider with care what values are to be attributed to the specific heats of those common gases which enter into many important chemical reactions. Professor Haber[1] has given an admirable treatment of this whole subject, but since the publication of his book several important experimental investigations in this field have appeared. It is therefore desirable to review the whole subject of gaseous specific heats, and to select for further reference formulas which will represent the most probable values of the specific heats of the more important gases over a considerable range of temperature.

The methods which have been employed in determining the specific heats of gases may be divided into three groups: The first comprises what we may call the direct methods in which a hot gas is led directly into a calorimeter. The second includes a number of methods such as the one used in the celebrated experiments of Kundt and Warburg, the method of Clément and Desormes, and the method of Lummer and Pringsheim. This group of methods we will call the adiabatic, since they all involve the change of pressure, volume and temperature when a gas is compressed or expanded adiabatically. The calculation of the specific heat by any of these adiabatic methods requires the assumption of the complete validity of the gas law.

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[1] "Thermodynamics of Technical Gas Reactions." English Translation by Lamb; Longmans, Green & Co., 1908.