5. Equations written in ionic form are offered in explanation of the facts observed in the reaction of sulfur with alkali and alkaline earth hydroxides in aqueous solution.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE DETERMINATION OF HYDROGEN-ION CONCENTRATION BY A SPECTROPHOTOMETRIC METHOD AND THE ABSORPTION SPECTRA OF CERTAIN INDICATORS[1]

BY WALLACE R. BRODE

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In the study of the absorption spectra of dyes and other colored organic substances in aqueous solutions, knowledge of the hydrogen-ion concentration of the solutions is quite essential, due to the variation of the absorption band in shape and intensity with various hydrogen-ion concentrations. Several methods have been suggested for the colorimetric determination of hydrogen-ion concentration of colored solutions, but all of them are more or less complicated and in most cases give only approximate results.[2]

All of these methods require the use of a colorimeter or other special apparatus, whereas the suggested spectrophotometric method employs no apparatus in addition to that necessary for the determination of the absorption band of the colored solution, and may be made in a comparatively short time after the completion of the determination of the absorption band.

It was observed in the spectrophotometric study of certain dyes at various hydrogen-ion concentrations,[3] that on the change of the hydrogen-ion concentration of the dye solution the absorption band did not shift gradually in wave length but merely changed in height. In the same manner the absorption bands of the indicators studied did not shift in wave length with a change in hydrogen-ion concentration but varied in intensity while, in most of the cases observed, another band proceeded in the opposite direction at the same time. By using the same concen-

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[1] This paper is the result of suggestions derived from a paper given by Buswell and Smith on "Color Standards in Water Analysis," at the 1923 Spring Meeting of the American Chemical Society, in which the absorption spectra curves of phenol red for various hydrogen-ion concentrations were determined in a manner somewhat similar to the method used in this paper, and a paper by Baker and Davidson (see Ref. 4d) on "Spectroscopic Measurements of the Hydrogen-ion Concentration Color Changes in Recent Indicators."

[2] (a) Gillespie, *J. Bact.*, **6**, 399 (1921). (b) Meyers, *J. Biol. Chem.*, **50** [Proc.] 22 (1922). (c) Everz, *Analyst*, **46**, 393 (1921). Other references as given in (d) Clark's "The Determination of Hydrogen Ions," Williams and Wilkins Co., **1922**, pp. 66–73.

[3] Brode with Adams, Forthcoming article in THIS JOURNAL, **46** (1924).

tration of indicator in all solutions the hydrogen-ion concentration of an unknown solution may be determined by comparing the height of its absorption band with those obtained from solutions of known hydrogen-ion concentrations. Any absorption due to the color of the original solution may be counteracted and its effect removed by using the original solution in the comparison cell. Since the height of the band varies, within certain ranges, with the hydrogen-ion concentration of the solution, it is necessary only to use a standard quantity of indicator solution to give a colored solution, the height of whose absorption band may be compared against the standard curves presented in this paper and the hydrogen-ion concentration determined.

The method proposed is not new or distinctive but very few data has been prepared on it and a large part of these data have been determined with a simple spectroscope, rather than by using a spectrophotometer, so that only the edge and not the peak of the band was determined.[4] A study of the series of curves presented in this paper will show that such a treatment does not lead to accurate or conclusive results in regard to the effect of hydrogen-ion concentration on the absorption spectra of these various indicators. Baker and Davidson have determined the absorption spectra of a number of the Clark and Lubs indicators at various Sörensen (*P*H) values, the curves being determined photographically and not photometrically. Their data, although not of the same degree of accuracy as attainable by a spectrophotometric method, confirm the fact that the band changes in intensity but not in frequency with a gradual change of the Sörensen value. The object of their work was to devise a new method to determine Sörensen values by spectrophotometric means. The determination of the dissociation constant of phenolphthalein by means of the change in height of the absorption band of that indicator[5] presents a method of determination which is quite similar to the proposed method for the determination of hydrogen-ion concentration. The measurement of the change in the amount of color content of one particular type in certain indicators with a change in *P*H is an approach at the same type of measurements as carried out in this paper.[6]

A number of indicators were tried so as to ascertain the best for the determination of certain hydrogen-ion concentrations and to obtain a range of curves that would cover a hydrogen-ion concentration of 1 to 10 *P*H, inclusive. The most suitable type of indicator for this purpose is one which has a narrow sharp band in the middle of the spectrum, whose

[4] (a) Ref. 2 d. (b) White and Acree, THIS JOURNAL, **40,** 1092 (1918). (c) Tingle, *J. Soc. Chem. Ind.*, 37, 117(t) (1918). (d) Baker and Davidson, *Phot. J.*, **62,** 375 (1922). (e) Holmes, THIS JOURNAL, **46,** 208 (1924).

[5] Hildebrand, *Z. Elektrochem.*, **14,** 349 (1908).

[6] Bjerrum, *Samml. Chem. Tech. Vortrage*, **21,** 30 (1914).

color change covers a fairly wide range of hydrogen-ion change, whose band at its maximum is quite intense, and the secondary band, which appears on the reduction of the primary band, is far enough removed from the latter so that it does not affect the determination of the height of the primary band. If possible, the secondary band should also be in the visible portion of the spectrum so that further continuous observations can be made on the indicator. An indicator satisfying all of these conditions might not necessarily be an ideal indicator, as it must have chemical properties which will cause it to resist certain reagents.

The indicator which comes nearest to satisfying this requirement is probably thymol blue, although the range that it covers is rather uncommon. The intermediate range within which thymol blue does not give any change can be covered by a mixed indicator of methyl red and bromothymol blue. This gives two indicator solutions capable of covering the entire range from 1.0 to 10.0 *P*H. The curves formed by these two solutions do not overlap to any great extent, and since the accuracy decreases as the maximum or minimum height of the curves is approached, other indicators were studied which covered these ranges, making it possible to obtain more accurate data at these values.

On account of their brilliancy, permanence, the shapes of their absorption bands, and the positions of the bands in the spectrum, the Clark and Lubs indicators[7] seem quite superior to almost all of the common indicators, with the possible exception of phenolphthalein which is a phthalein dye like the Clark indicators. Methyl red, which is not a phthalein dye, is not as satisfactory as the other indicators of this series, but must be used as it covers a range that is not covered by any other of these indicators.[8]

Apparatus

The spectrophotometer was a Keuffel and Esser Model C direct reading color analyzer, with a lamp housing containing the standard magnesium carbonate block holders in a direct line with the solution tubes, rotating sector discs and constant deviation spectroscope. The light source consisted of two 400-watt projection Mazda lamps. The tubes supplied with the instrument proved unsatisfactory for the purpose of this research, as they were made of copper alloy and were affected by the alkali or acid in the solutions to be tested. A much simpler tube was used in this work which gave quite satisfactory results. It was so constructed that the only surface in contact with the solution was glass and it was possible to empty, wash and refill the tube in a very short time. For the experiments described in this paper, tubes 5 cm. in length were used. The

[7] Ref. 2 d, p. 74.

[8] Recently some new sulfonephthalein indicators have been prepared, among which is bromocresol green, which almost perfectly covers the hydrogen-ion concentration of methyl red. (a) B. Cohen, *Public Health Repts.*, **38**, 199 (1923).

rubber caps on the tubes have a decided advantage over metal in that they prevent to a large degree the warming up of the solutions due to conduction of heat.

Inasmuch as the curves which were being studied were sharp and pronounced, it was found much more satisfactory to set the transmission for certain definite values and adjust the wave length until the two halves of the field matched, rather than set the wave length at a definite value and adjust the transmission. Values for the transmission settings were so chosen as to give direct values for the "—log." of the transmittancy or the extinction coefficient, at intervals of 0.10 from 0.00 to 2.00.[9] In this way twenty different settings were made of the transmission discs and the position of the band noted for both sides of it throughout this series of settings, or as far as the band extended. In the case of a substance which gave a broad flat band this method was not as satisfactory or did not give as many readings as one which required the setting of the wave length at definite intervals and the adjusting of the transmittancy to obtain the necessary data.

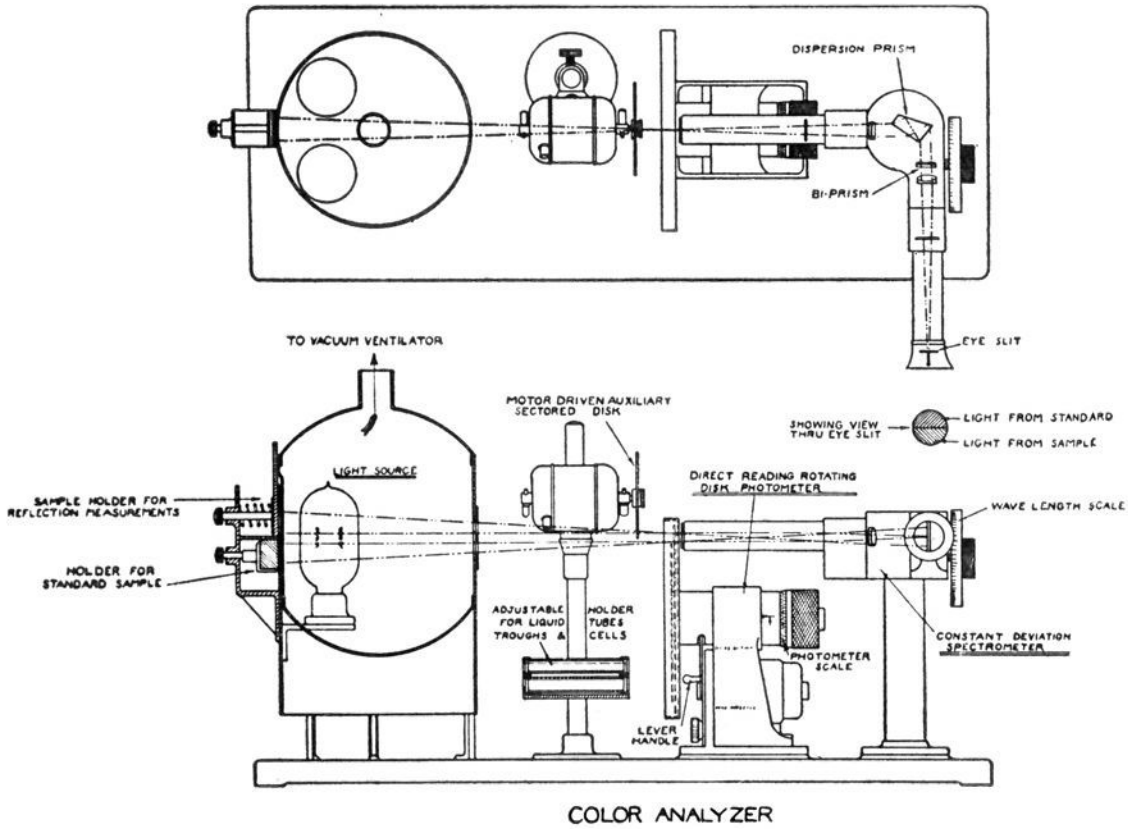

Fig. 1.—Optical system.

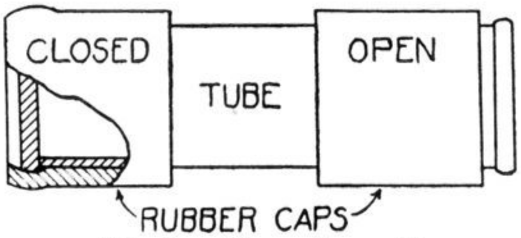

Fig. 2.—Absorption cell.

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[9] Gibson and others, *Bur. Standards (Sci. Paper,* **440**) **18,** 124 (1922).

The readings were all made within 15 minutes of the time that the indicator was introduced into the solution and in most of the cases observed, the curves were completed within ten minutes. Data for the entire curve were obtained for each solution and the points obtained recorded directly on special graph paper so that any discrepancy caused by misreading a number on either of the two discs could be rectified before the solution was discarded. In practice, however, for the determination of the hydrogen-ion concentration in solutions, it would not be necessary to determine the entire curve but merely the peak of the curve, so that the determination could be done in a much shorter time.

Experimental Part

The buffer solutions used with the indicator solutions to give definite values of hydrogen-ion concentration were for the most part made up according to the Clark and McIlvain buffer standards.[10] By this means buffer solutions were obtained covering a range of 1 to 10 *P*H at intervals of 0.2 *P*H and in some cases two different buffers were obtained which covered the same values, so that a check reading could be made on them.

The following strengths of indicator solutions[11] were made up after first determining the maximum height of the band produced when 1 cc. of the initial indicator solution, made according to the directions of Clark and Lubs, was added to 50 cc. of solvent, and then this indicator solution was diluted to a final strength which would give an absorption band that approached an extinction coefficient of 2.00 at its maximum.

Table I

Strengths of Indicator Solutions

Indicator	Initial g. per 100 cc.	Final g. per 100 cc.	Ratio of final to initial	*P*H range of indicator
Thymol blue	0.04	0.04	1.0	1.2– 3.4
Bromophenol blue	.04	.02	0.5	2.4– 5.6
Methyl red	.02	.015	.75	3.4– 7.0
Bromocresol purple	.04	.032	.8	4.8– 7.6
Neutral red	.02	.0266	1.33	5.6– 8.4
Bromothymol blue	.04	.04	1.0	5.8– 8.4
Phenol red	.02	.0133	0.66	6.2– 9.2
Cresol red	.02	.016	.4	6.8– 9.6
Thymol blue	.04	.032	.8	7.4–10.2
Phenolphthalein	.02	.01	.5	8.0–10.6

Other indicators, such as congo red, methyl orange, benzopurpurin 4B, methyl violet, etc., were tried, but the band was too broad, the secondary band too near the primary, or the indicator so unstable that the change in the height of the band was small or difficult to determine. For the solutions mentioned above, water was used as a solvent except in the cases

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[10] Ref. 2 d, pp. 111–116.

[11] Ref. 2 d, p. 80.

of methyl red, phenolphthalein and neutral red. In the first two of these 95% alcohol was used, and in the latter 50% alcohol.

To 50 cc. of the buffer solution of known hydrogen-ion value, 1 cc. of the prepared indicator solution was added, the solution thoroughly shaken and the absorption spectra immediately determined. This process was repeated for each indicator covered by that particular hydrogen-ion value and for all hydrogen-ion values at intervals of 0.2 *Ph* from 1.2 to 10.0 *Ph*. From these series of curves, obtained by the determination of the absorption spectra of each of these solutions, another set of curves was derived; by plotting the height of the absorption band in terms of the extinction coefficient, against the hydrogen-ion values for each of these bands. These curves which correspond to dissociation curves[5,6] are similar for all of the indicators tried and afford a more condensed form for comparison of the heights of the bands, and a quicker method for determining the hydrogen-ion concentration of an unknown solution by the spectrophotometric method.

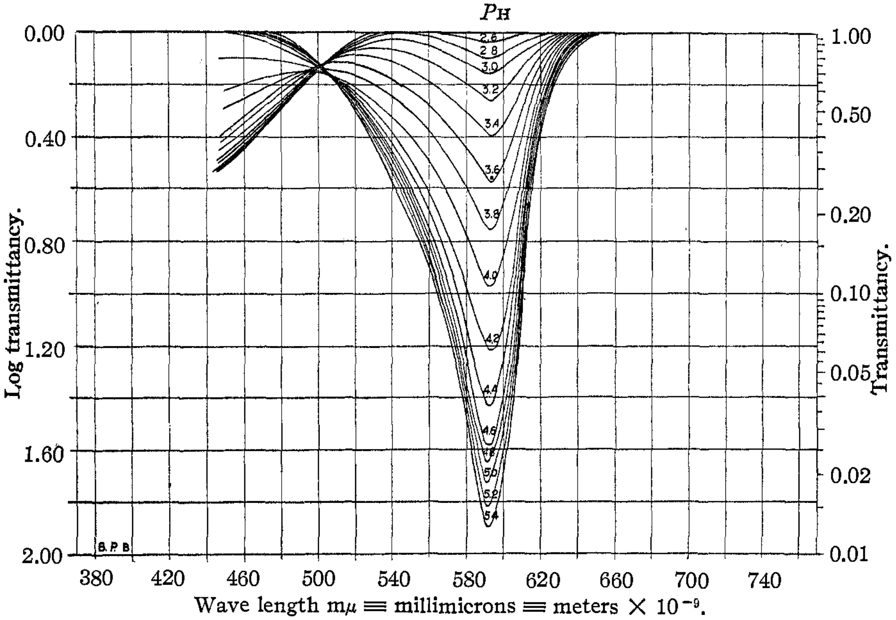

Fig. 3.—Transmittancy curves for bromophenol blue from 2.2 to 5.4 *Ph*: cell thickness (b) = 5 cm.; concentration (c) = 0.04 g. per 100 cc.

The curves for phenolphthalein were similar to the primary band only of bromophenol blue (there being no secondary band); maximum at 553 mμ, range (8.4 – 10.0 *Ph*) b = 5 cm.; c = 0.01 g.

In using the condensed graph for this determination, it is not necessary to determine the entire curve of the absorption band, but simply the peak of the curve. For this reason it is convenient to know the wave length of the absorption bands for the indicators used, the values given being determined from the curves described in this paper.

TABLE II

WAVE LENGTHS OF ABSORPTION BANDS

Indicator	Wave length mμ	Indicator	Wave length mμ
Thymol blue (acid)	544	Cresol red	572
Bromophenol blue	592	Phenol red	558
Methyl red	530	Thymol blue (alk.)	596
Bromocresol purple	591	Neutral red	533
Bromothymol blue	617	Phenolphthalein	553
		Thymolphthalein	598

For work involving a limited range of hydrogen-ion change or where the hydrogen-ion concentration of the solution to be tested is approximately known, the proper indicator may be selected for that range so that the change in the absorption band will be between extinction coefficient values of 0.50 and 1.50, in which range the greatest change in the band takes place and also the greatest accuracy is attained in measuring the height of the band. Where the hydrogen-ion concentration is unknown or where a wide range is to be compared, the best indicators are thymol blue (with a range of 1.0 to 3.5 and 7.5 to 10.0 P_H) and a mixed indicator consisting of methyl red and bromothymol blue, in the same concentrations as in the separate solutions of each of them. This indicator will cover a range of 3.5 to 8.3 P_H although in the middle of this range the accuracy is not as great as might be desired. Values obtained in this part of the curve may be checked by the use of bromocresol purple.

To determine the hydrogen-ion concentration of an unknown solution 2 cc. of the indicator solution is added to 100 cc. of the unknown solution, the mixture shaken thoroughly, and the height of the absorption band in a 5cm. cell determined. The hydrogen-ion value is then determined by comparing the height of this curve against the standard curves given here. In using cells of other lengths than 5 cm. it may be assumed that Beer's law holds for these solutions and the values obtained may, therefore, be reduced to the equivalent of a 5cm. cell. With the help of a color chart[12] or standard samples it is possible to determine the approximate hydrogen-ion concentration and whether the correct indicator has been used. In the case of colored dye solutions the 2 cc. of the indicator solution are added to the 100 cc. of the colored solution and the absorption band determined in the usual manner, except that in place of a colorless solvent in the standard or compensating cell of the spectrophotometer, there will be the dye solution of unknown hydrogen-ion concentration, without the

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[12] Ref. 2 d, p. 52.

indicator solution. For extreme accuracy, the standard solution should be diluted with 2 cc. of the original colorless solvent for each 100 cc. so as to compensate for the dilution of the dye solution by the indicator solution.

Discussion of Results

The curves obtained in the investigation of the effect of hydrogen-ion concentration on the absorption spectra of these indicators are of interest from a theoretical as well as a practical point of view. They show clearly that for at least two classes of dyes, namely, phthalein and azo dyes, the absorption band does not shift in wave length but simply changes in intensity with a change of hydrogen-ion concentration. This rule does not hold for all classes of dyes; for example, the absorption band of methyl violet, a triphenylmethane dye, changes in wave length with only a slight change of intensity, upon a change of hydrogen-ion concentration. This effect is being further investigated and agrees with the data of Holmes[13] and with unpublished observations by Appel and Brode of the United States Bureau of Standards on the fact that the triphenylmethane dyes do not necessarily obey Beer's law and that their color production appears to be of a different type from that of the azo dyes. The curves presented

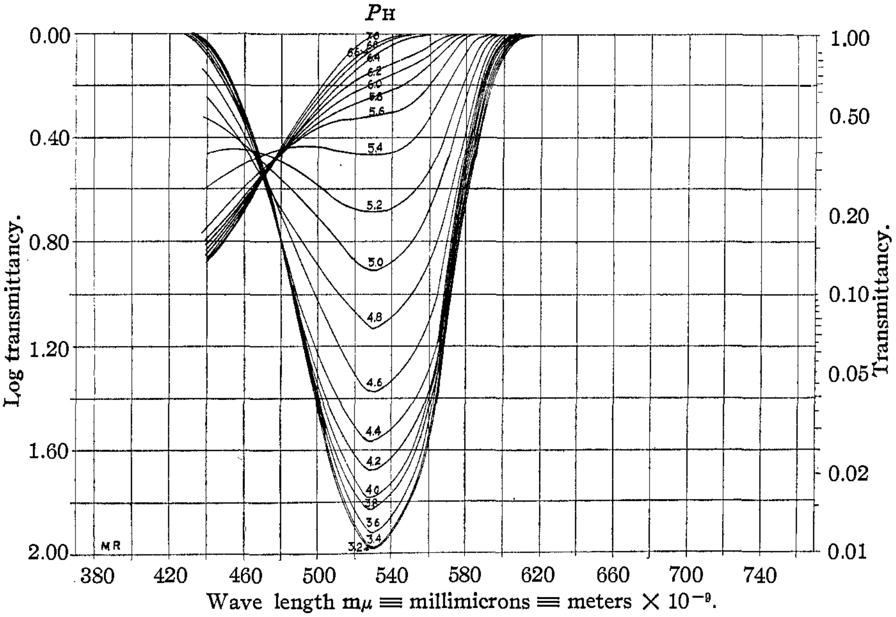

Fig. 4.—Methyl red (3.2 – 5.4 PH); b = 5 cm.; c = 0.015 g.

The curves for neutral red were similar to those for methyl red; maximum 533 $m\mu$; intersection of curves at 480 $m\mu$; 0.10 transmittancy; range (5.8 – 8.6 PH) b = 5 cm.; c = 0.0266.

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[13] Holmes, *Ind. Eng. Chem.*, **16**, 35 (1924).

here also show that a secondary band appears on the disappearance of the primary band and that at certain hydrogen-ion concentrations there is an equilibrium between the heights of the two bands.

The existence of absorption bands of definite wave lengths and of an equilibrium between two types of color-producing molecules, is in accordance with recent color theories[14] that a definite configuration and frequency of vibration exists for each color of a certain substance. The way in which the fading of the band takes place fails to confirm theories that intermediate colored products exist between any two principal colored modifications,[15] as the curve retains the same general continuity and does not change on one side of the center of absorption more rapidly than on the other. Another interesting point is that in practically all of the curves studied, there was one point at which all curves of various Sörensen values crossed in changing from one colored form to the other, this point being about midway between the centers of the two bands. It is hoped that it will be possible to study the ultraviolet absorption spectra of these indicators with special

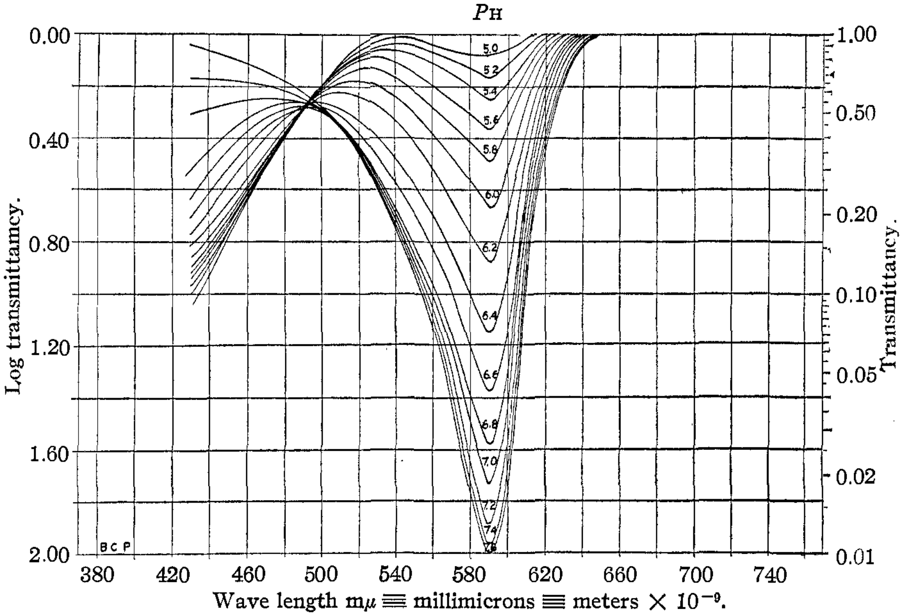

Fig. 5.—Bromocresol purple (4.8 – 7.6 *P*H); b = 5 cm.; c = 0.016 g.

The curves for thymol blue (acid) were not completed within the range of Sörensen values studied. They were similar in shape to the bromocresol purple curve but had a maximum at 544 mμ and an intersection of the curves at 485 mμ and 0.30 transmittancy; range (1.2 – 3.4 *P*H); b = 5 cm.; c = 0.04 g.

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[14] Moir, *J. Chem. Soc.*, **121,** 1555 (1922). Hantzsch, *Ber.*, **48,** 158 (1915). Watson, "Color in Relation to Chemical Constitution," Longmans, 1918. Ref. 2 d, p. 54.

[15] Moir, *J. Chem. Soc.*, **123,** 2792 (1923), and Ref. 14.

reference to the relation between the structure of the dyes, the number, shape and order of appearance of the various bands and the hydrogen-ion concentrations required to produce or diminish the various bands.

The determination of acidity or alkalinity by spectroscopic means was suggested by Tingle[4c] in which the lateral shifting of the band was measured by a simple spectroscope. The conclusion was drawn that "the absorption bands of colored solutions in most cases, shifted in wave length rather than the substitution of one band for another" with a change of hydrogen-ion concentration. By using a simple spectroscope and a cell of constant thickness, one obtains the same effect as that which results from the following of the curves here presented at one definite extinction coefficient. The apparent effect thus obtained is a lateral shift in the band, due of course to the simultaneous change of the height of the peak. This effect is especially true with azo dyes (Tingle used methyl orange) where the secondary band is near the primary and the bands are quite broad. The same conclusions were reached by Smith and Boord,[16] in regard to the position of the peak of the absorption band of certain azo dyes in solutions of various bases and different strengths of solutions

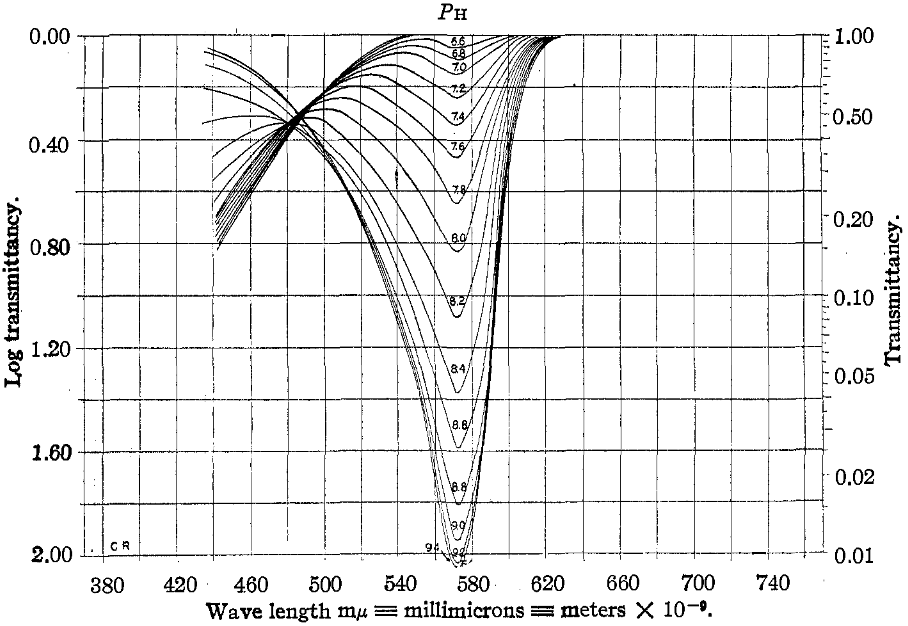

Fig. 6.—Cresol red (6.4 – 9.4 PH); b = 5 cm.; c = 0.016 g.

The curves for phenol red were similar to those for cresol red; maximum 558 mμ; intersection of curves at 481 mμ; 0.45 transmittancy; range (6.2 – 9.2 PH); b = 5 cm.; c = 0.0133 g.

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[16] Smith and Boord, This Journal, 44, 1449 (1922).

Although they used a spectrophotometer they did not measure the peak of the band, but simply the side of the band near the base and from that concluded that the addition of alkali (or acid) caused a "decrease in the frequency of the center of the vibration producing the absorption band," and that the band varied in wave length rather than in intensity. Baker and Davidson[4d] have measured photographically the absorption spectra of a number of the Clark indicators at various hydrogen-ion concentrations and found that the ratio between the two different color components of the indicator is dependent solely on the hydrogen-ion concentration of the solution and not on the amount of indicator present. Their data also confirm the fact that the absorption bands of these indicators change in intensity rather than in wave length with a change of hydrogen-ion concentration.

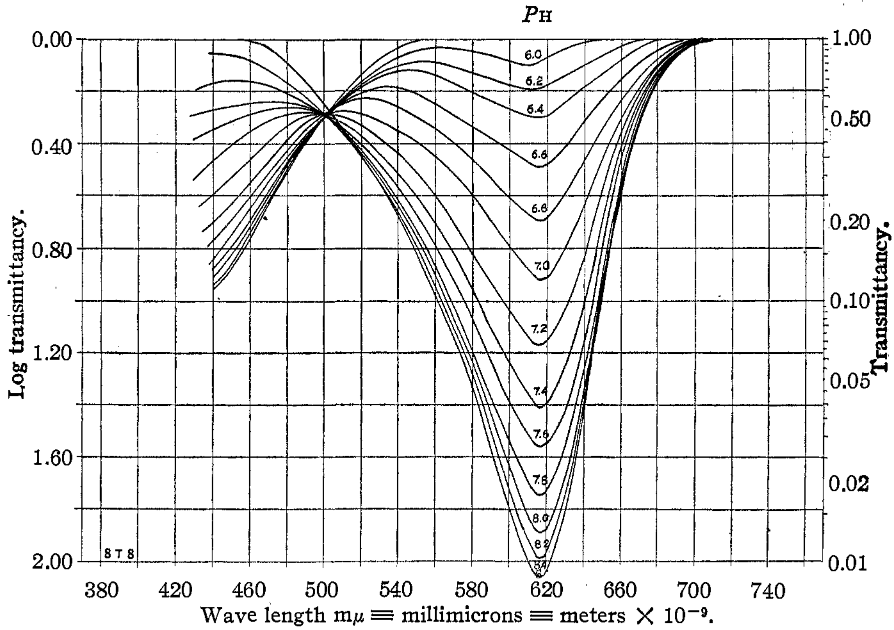

Fig. 7.—Bromothymol blue (5.8 – 8.4 PH); b = 5 cm.; c = 0.04 g.

The curves for thymol blue (alkaline) were similar to those for bromothymol blue; maximum at 596 mμ; intersection of curves at 500 mμ; 0.47 transmittancy; range (7.4 – 10.0 PH); b = 5 cm.; c = 0.032 g.

It is noticeable that the band after reaching a certain hydrogen-ion value which gives it a maximum height, remains constant at this value over a considerable range of hydrogen-ion concentration and then in certain cases, on further treatment with alkali or acid, as the case may be, it again begins to drop and a different band appears. The shape of the phthalein and sulfonephthalein curves particularly adapts them to use as indicators, as they are narrow, sharp and show a relatively large change in the position of the absorption-band maximum in relation to the change in the hydrogen-ion concentration of the solution. The azo dyes, on the other hand, have broad curves with a secondary band so near the primary that it adds to the effect of the primary and reduces the amount of possible change in the transmissive index, with a change in the hydrogen-ion value of the solution. The use of methyl red, however, was necessary, due to the fact that in this investigation there were no phthalein dyes available which covered the particular hydrogen-ion range covered by methyl red.[8a]

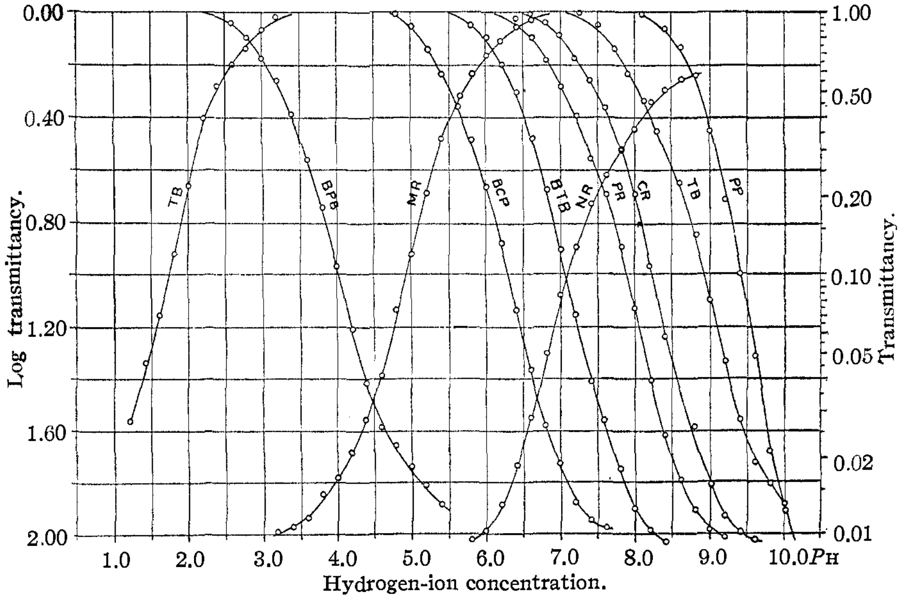

Fig. 8.—Condensed graph showing the relation between the extinction coefficient of the peak of the bands (—log transmittancy) and the hydrogen-ion concentration of the indicator solutions.

The dissociation or ionization constants of the indicators studied may be determined in a manner similar to the method applied to phenolphthalein, methyl orange, etc.,[17,5,6] the constant being taken as the middle point on the condensed curve between the maximum and minimum heights of the band, or approximately on the line representing an extinction coefficient of 1.00. The values obtained agree closely with those obtained by Clark.[18]

Application and Limitation of Method

Unknown solutions were made up from various buffer solutions and the hydrogen-ion concentrations determined both by this method and by the

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[17] Prideaux, "Theory and Use of Indicators," Constable, 1917, p. 127.

[18] Ref. 2 d, p. 55.

TABLE III

DISSOCIATION CONSTANTS OF INDICATORS

Indicator	Spectrophotometric value	Clark's value	Indicator	Spectrophotometric value	Clark's value
Thymol blue (acid)	1.75	1.7	Bromothymol blue	7.10	7.0
Bromophenol blue	4.05	4.1	Phenol red	7.90	7.9
Methyl red	4.95	5.1	Cresol red	8.20	8.3
Bromocresol purple	6.30	6.3	Thymol blue (alkaline)	8.90	8.9

electrometric method. The electrometric determinations were made with a palladized electrode in a special type of quartz hydrogen electrode developed by Dr. T. E. Phipps.

TABLE IV

DETERMINATIONS BY THE SPECTROPHOTOMETRIC METHOD, AND ERRORS INVOLVED

Soln. no.	*P*H (elec.)	*P*H (spectra)	Error	Indicator used
1	1.62	1.59	—0.03	T. B.
2	3.42	3.42	.00	B. P. B.
3	3.44	3.43	− .01	B. P. B.
4	4.40	4.42	+ .02	B. P. B.
4	4.40	4.48	+ .08	M. R.
5	6.60	6.57	− .03	B. C. P.
5	6.60	6.58	− .02	N. R.
5	6.60	6.57	− .03	B. T. B.
6	7.58	7.53	− .05	N. R.
6	7.58	7.59	+ .01	B. T. B.
6	7.58	7.58	.00	P. R.
6	7.58	7.66	+ .08	C. R.
7	7.85	7.92	+ .07	P. R.
7	7.85	7.87	+ .02	C. R.
8	8.19	8.29	+ .10	P. R.
8	8.19	8.29	+ .10	C. R.
9	8.44	8.50	+ .06	P. R.
9	8.44	8.42	− .02	C. R.
10	8.67	8.61	− .06	T. B.
11	8.80	8.76	− .04	C. R,
12	9.20	9.15	− .05	P. P.
12	9.20	9.22	+ .02	T. B.
13	9.39	9.36	− .03	P. P.
13	9.39	9.32	− .07	T. B.
		Av. error	0.042 *P*H	
		Mean error	±0.0054 *P*H	

The method may be applied somewhat better to cloudy or milky solutions than to colored solutions. Intensely colored solutions cannot be determined by this method, but dye solutions of the strength usually employed in spectrophotometric analysis, where the peak of the band is to be determined, can be used. A suitable concentration for the determination of their absorption bands and one which permits the use of this method is about 0.2 to 0.25 cg. of dye per liter of solution. In using cells of other thickness this concentration may be varied accordingly. The error involved in the determination of the hydrogen-ion concentration of a colored solution is somewhat greater than the above, due to the reduction of the intensity of the light transmitted through the cell, especially if the absorption band of the colored substance is near that of the indicator. The error, however, is not as great as that which would probably be incurred in measuring the small amount of indicator solution. In the determination of hydrogen-ion concentration by this method it is suggested that check observations be made on buffer solutions or on other solutions of known hydrogen-ion concentration, in order to eliminate any possibility of error in the preparation of the indicator solutions or other mechanical errors in the spectrophotometer.

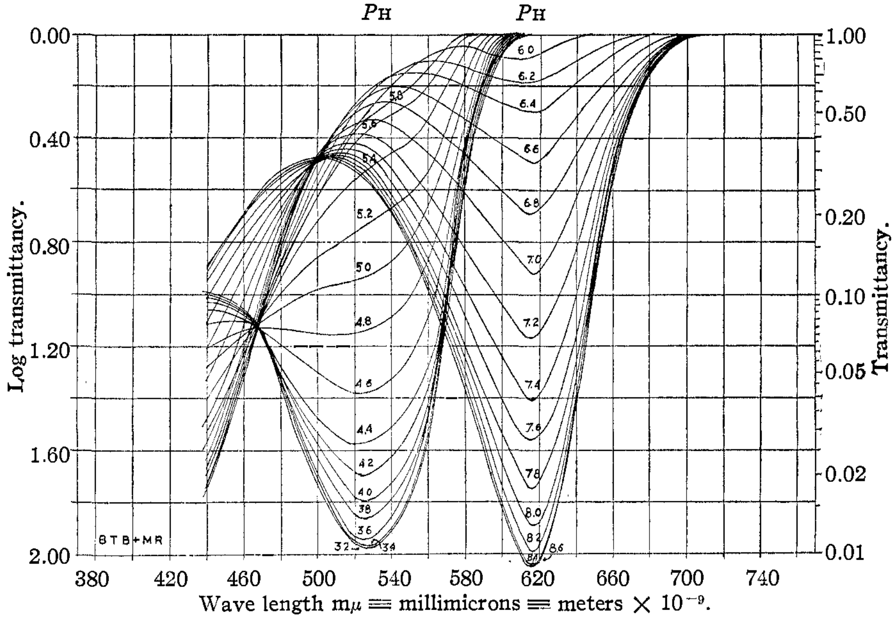

Fig. 9.—Transmittancy curves for the mixed indicator of methyl red and bromothymol blue (3.2 – 8.6 *P*H); b = 5 cm.; c of M. R. = 0.015 g.; c of B. T. B. = 0.04 g.

In this experimental work no attempt has been made to correct for any "salt effect." The work of Acree[19] has shown, however, that in the case of buffer solutions of the concentrations of the Clark solutions, the salt effect is small; for example, the correction for a 0.04 *N* phosphate mixture was 0.02 *P*H and this concentration was greater than those of nearly all of the solutions used in these experiments. Inasmuch as this method is

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[19] Brightman, Meacham and Acree, *J. Bact.*, **5**, 169 (1920), and other articles by Acree and co-workers in the *Am. Chem. J.*, and THIS JOURNAL.

intended for the determination of the hydrogen-ion concentration in solutions containing only 0.25 cg. or less of dye per liter, it would be permissible to neglect the salt effect, providing the buffer solvent for the dye did not contain a salt concentration greater than that in the Clark buffer standards.

The author wishes to express his appreciation of the suggestions given by Professor Roger Adams of the University of Illinois, and Dr. C. E. Waters and Dr. W. D. Appel of the United States Bureau of Standards, during the progress of this work.

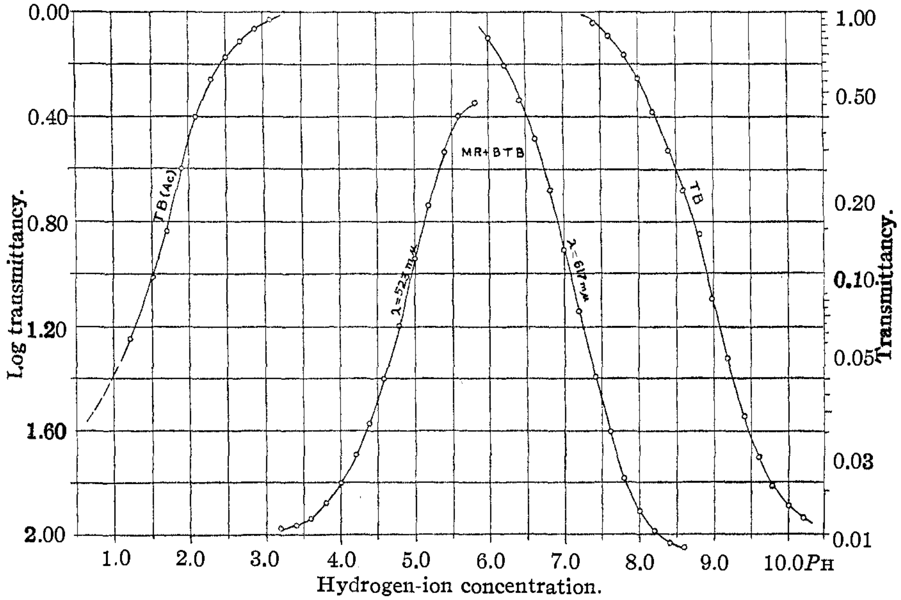

Fig. 10.—Condensed graph showing the relation between the extinction coefficient of the peak of the bands and the hydrogen-ion concentration of the indicator solutions of thymol blue and methyl red-bromothymol blue; b = 5 cm.; c of T. B. = 0.0266; c of M. R. = 0.015; c of B. T. B. = 0.04. Data on M. R. taken at 523 mμ.

Summary

A new method has been proposed for the rapid determination of the hydrogen-ion concentration of dye solutions and other solutions which are being studied spectrophotometrically.

Data are included, showing the effect of the change of hydrogen-ion concentration on a number of common indicators and that the height of the absorption band of these indicators is, within certain limits, a function of the hydrogen-ion concentration of the solution.

From the curves obtained it has been shown that on the change of the hydrogen-ion concentration the center of the absorption band (the peak) does not change in wave length, but rather in intensity.

A secondary band is in equilibrium with the primary band and on the decrease of one of the bands the other increases in height.

The dissociation constant for the indicators studied was determined by a photometric method.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ADSORPTION OF VAPORS BY CHARCOAL

BY ALBERT SPRAGUE COOLIDGE

RECEIVED NOVEMBER 26, 1923

In a previous paper[1] in collaboration with Professor A. B. Lamb, have been reported the results of some measurements of the heats of adsorption of the vapors of various liquids on activated coconut charcoal. As stated in that paper, our original object was to study both heats of adsorption and equilibrium pressures, but the measurements of pressure were found to be beset with so many difficulties and uncertainties that it seemed best to postpone this part of the problem until the passing of the war emergency should allow more leisure. Work was resumed in the summer of 1921, and is still in progress; but as the technical difficulties appear to have been overcome and a fair body of reliable data accumulated, it seems desirable to publish the results so far attained without waiting for the completion of the proposed program. Additional results, together with a critical discussion, will be given in a later paper.

Most of the work was done in my laboratory on South Mountain, Pittsfield, Massachusetts, the remainder in the laboratories of Harvard University.

Variables Influencing Results

A charcoal-vapor system is most conveniently treated as consisting of two components and two phases, and accordingly enjoying two degrees of freedom. If p, the pressure, be the dependent variable, the independent variables may be chosen as the temperature, t, and the concentration of the condensed phase, q; that is, the quantity of vapor adsorbed by one gram of gas-free charcoal, the vapor being measured by volume under standard conditions. If the phase rule holds, then the pressure observed when quantities of charcoal and vapor are isolated in a closed system will be completely determined by (*a*) the kind of charcoal used (source, method of activation, etc.); (*b*) the vapor used; (*c*) the concentration of the condensed phase; (*d*) the temperature. Actually, however, other observers have found that the following additional variables have or may have an influence on the result: (*e*) temperature of previous outgassing of charcoal; (*f*) time of outgassing; (*g*) efficiency of outgassing

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[1] Lamb and Coolidge, THIS JOURNAL, **42,** 1146 (1920).