smoother set of first and second differences. Above 11.5 *M* the work of Shankman and Gordon is the only source of information of the necessary accuracy, and therefore the final values of Table III are arranged so as to join smoothly on to their values for more concentrated solutions.

Acknowledgments.—The writer wishes to thank Dr. R. A. Robinson for valuable help and encouragement in carrying out this work; also Messrs. Imperial Chemical Industries, Limited, for a substantial grant toward the cost of the apparatus, the Chemical Society (London) for a grant from their Research Fund and the the Dominion Laboratory of New Zealand for the loan of thermometers.

Summary

Measurements of the vapor pressures of sodium hydroxide solutions have been made by a method depending on vapor–phase equilibration of the solution at 25° with pure water at a lower temperature. The results are in fair agreement with those obtained by combining the isopiestic ratios of sodium hydroxide to sulfuric acid with the static vapor pressure measurements of Shankman and Gordon on sulfuric acid, and support the latter against electromotive force results. A set of standard values for the water activity in sulfuric acid solutions at 25°, for use in isopiestic measurements on concentrated solutions, is proposed.

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The Luminosity and Chromaticity of Indicators as a Function of *p*H

BY JUDSON J. VAN WYK AND W. MANSFIELD CLARK

In the visual method of using an indicator for the determination of *p*H there is obtained, ideally, a "match" between the tested solution and a standard, and to this end there must be fulfilled certain specifications which are so well known that they need not be reviewed here. In practice the precision attained depends upon the ability of the eye to discriminate between standard and tested solution when there is not a match. The requirements for discrimination may be resolved arbitrarily into the capabilities of individual eyes and those factors of chromaticity that have been developed for the standard observer. We shall confine attention to the properties of three indicators that can be described in terms of luminosity and the chromaticity diagram as developed for the standard observer. The indicators are phenol red, brom thymol blue and *p*-nitrophenol.

The treatment, as adopted by the International Commission on Illumination, provides a convenient method for specifying the three major characteristics of color: namely, luminosity, dominant wave length, and purity. The latter two are specified by chromaticity coördinates on the standard chromaticity diagram (Fig. 1). The method of obtaining these specifications may be briefly summarized.

The color of a solution when illuminated by a standard source is specified first in terms of the quantity of each of three standard primary colors, or basic stimuli, which would be required to synthesize an equivalent stimulus. To arrive at this specification the only experimental data required, in addition to those incorporated in tables,[1] are the spectral transmittances, **T**, of the particular solution at each 10 mμ interval throughout the visible spectrum. For the computations it is necessary to obtain from published tables[1,2] the spectral distribution of radiant power in a standard source at each of the selected intervals and trichromatic coefficients at the same intervals. These data are used in a simple, but lengthy, calculation to determine the total amounts of the primaries, X, Y and Z, which would be required to synthesize a stimulus matching that of the solution.

Because of the choice of basic stimuli the computed value of Y is a measure of the luminosity or "brightness"[1] of the solution.

For obtaining chromaticity coördinates, the relative amounts of the required primary stimuli rather than the absolute amounts are used. These values are obtained from the relations

$$x = \frac{X}{X + Y + Z} \quad y = \frac{Y}{X + Y + Z} \quad z = \frac{Z}{X + Y + Z}$$

and because $x + y + z$ equals 1, x and y are sufficient as coördinates on the chromaticity diagram (see Fig. 1). From enlarged diagrams published by Hardy,[1] the dominant wave length and purity are obtained.

On the chromaticity diagram (Fig. 1) the pure spectral colors fall on the peripheral curve and illuminant C at point C. The dominant wave length is the wave length at the intersection of the peripheral curve with a line drawn through the locus of the illuminant and that of the particular color. In the case of the non-spectral purples, the dominant wave length is that of the complementary color. The purity of a color is represented by the ratio of the distance between the locus of the particular color and the illuminant, to the distance between the locus of the illuminant and the periphery.

Determination of Transmittancy

In order to compute the luminosity values and chromaticity coördinates for the three indicators at a number of different *p*H values it was necessary to know accurately the transmittancies of each solution at 10 mμ intervals through the visible spectrum. The absorption coefficients of the un-ionized form of the indicator, and of the ionized form, were experimentally determined, and the transmittancies at intermediate values of α were calculated from these data on the assumption that at constant ionic strength the following relations hold

(1) A. C. Hardy, "Handbook of Colorimetry," Technology Press, Cambridge, Mass., 1936.

(2) Report of the Committee on Colorimetry, *J. Optical Soc. Am.*, **34**, 245, 633 (1944).

$$p\mathrm{H} = pK' + \log \frac{\alpha}{1 - \alpha} \quad (1)$$

where α is the ratio of the concentration of the proton acceptor to the sum of the concentrations of proton acceptor and conjugate proton donor.

$$D_1 = \epsilon_1 lC(1 - \alpha) \quad (2)$$

$$D_2 = \epsilon_2 lC\alpha \quad (3)$$

D is optical density defined by $D = -\log \mathbf{T}$. D_1 (optical density) and ϵ_1 (absorption coefficient) pertain to proton donor, and D_2 and ϵ_2 pertain to the conjugate proton acceptor. C is the concentration of indicator in grams per 100 ml. In all cases cuvettes of 1 cm. length, l, were used. Accordingly the density D_x for any value of α is given by

$$D_x = D_1 + D_2 = \alpha C(\epsilon_2 - \epsilon_1) + C\epsilon_1 \quad (4)$$

D_1, and ϵ_1, were determined by using the indicator at a pH such that α approaches zero (Solution A). D_2 and ϵ_2 were determined by using the indicator at a pH such that α approaches 1 (solution B). Inasmuch as we are now concerned with factors that contribute to the ability to discriminate between solutions differing only slightly in pH we have used relation (1) to calculate the proportions of each species of indicator rather than resorting to actual measurements with their inevitable errors and for this purpose we have used the published values of pK'. Any mistakes in the assumption of the value of pK' will not appreciably affect the conclusions that pertain to small differences in pH and the related small differences in chromaticities.

The values of pK' assumed in the calculations and the solutions prepared for determining the various absorption coefficients are given below;

Indicator	pK'	Solution A pH	Solution A α	Solution B pH	Solution B α
p-Nitrophenol	7.0 [Clark (3)]	2.2	9×10^{-6}	9.8	0.998
Phenol red	7.81 [Kolthoff (4)]	3.34	0.0003	10.12	.995
Brom thymol blue	7.0 [Clark (3)]	2.2	9×10^{-6}	9.8	.998

Optical densities were determined for each of the above six solutions at wave lengths differing by 10 mμ between 380 and 740 mμ. All measurements were made at room temperature (20–25°) with a Beckman spectrophotometer and 1 cm. cuvettes. The buffer solutions served as blanks. Appropriate dilutions of the stock solutions were made so that the range of transmittancies fell between 0.25 and 0.80. The absorption coefficients obtained are given in Table I.

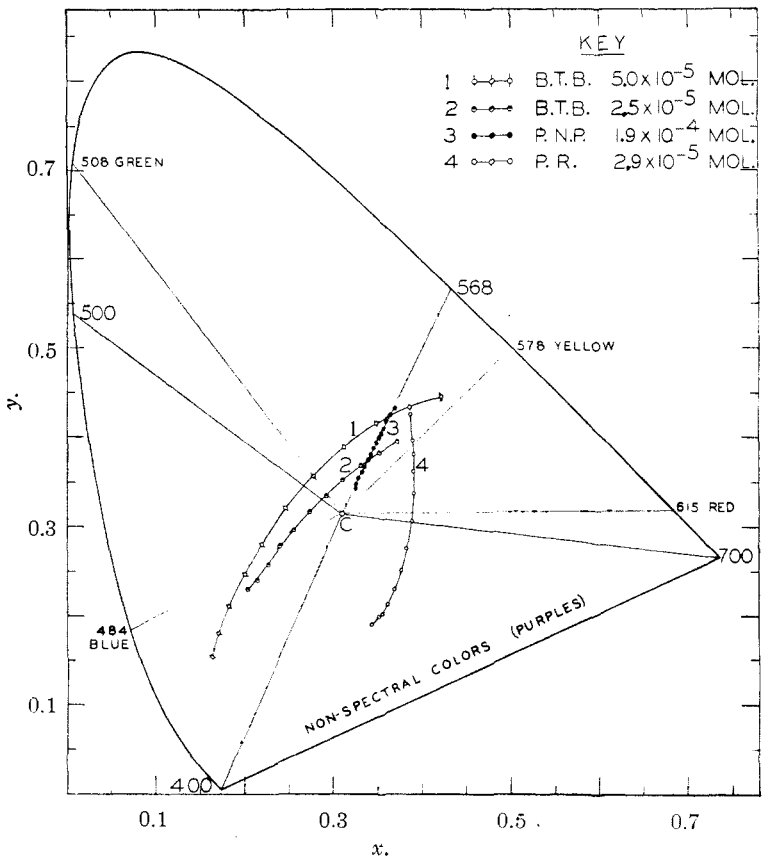

Fig. 1.—I. C. I. standard chromaticity diagram: the pH values of each indicator plotted in order from the lower left extremity of each curve are as follows: brom thymol blue (both concentrations), 9.8, 7.95, 7.60, 7.37, 7.18, 7.00, 6.82, 6.63, 6.40, 6.05 and 2.2; p-nitrophenol, 6.1, 6.2, 6.3, 6.4, 6.5, 6.6, 6.7, 6.8, 6.9, 7.0, 7.1, 7.2, 7.4, 7.7 and 9.8; phenol red, 10.11, 8.8, 8.6, 8.4, 8.2, 8.0, 7.89, 7.6, 7.4, 7.2, 7.0, 6.8 and 3.24.

In the development of formula (4) it is implied that there are no more than two species of each indicator. Presumptive evidence that a given indicator has only two absorbing forms is the occurrence of an isosbestic point[5] where all isohydric curves cross. At such a point $\epsilon_1 = \epsilon_2$, and consequently D_x must equal $C\epsilon_1$ and is independent of α at all pH values if formula (4) holds. That there is a sharp isosbestic point for brom thymol blue was demonstrated by Buch[6] and by Brode.[7] The curves for phenol red obtained by Brode and pub-

(3) W. M. Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 1928.

(4) I. M. Kolthoff and C. Rosenblum, "Acid Base Indicators," Macmillan Co., New York, N. Y., 1937.

(5) A. Thiel, A. Dassler and F. Wülfken, "Über Azo-Indikatoren von Typus des Methylgelb, Methylorange, and Methylrot," in *Forschr. Chem. Physik physik. Chem.*, **18**, H. 3 (1924).

(6) K. Buch, "Spectrophotometric Investigation of Color Indicators," *Soc. Sci. Fennica, Commentationes Phys. Math.*, **2**, 26 (1926).

(7) W. R. Brode, "The Determination of Hydrogen Ion Concentration by a Spectrophotometric Method, and the Absorption Spectra of Certain Indicators," THIS JOURNAL, **46**, 581 (1924).

lished by Prideaux[8] show few common intersections. Therefore we reexamined this case with a specially purified sample supplied by Dr. Fitzgerald Dunning of Hynson, Westcott and Dunning, Inc. A stock solution of the indicator was prepared and diluted with Clark and Lubs buffer solutions at seven pH values. The final ionic strength for each solution was 0.1. Density readings were made at 5 mμ intervals from 350–740 mμ. A sharp isosbestic point was found at 481 mμ, and a second one at 364–370 mμ (Fig. 2). The latter was not sharply defined as was the first, but the experimental errors were much larger at the lower wave lengths. We have assumed but two species and have used formulas (1) and (4) to calculate the optical densities of intermediate pH values from the values of ϵ_1 and ϵ_2 given in Table I.

TABLE I

ABSORPTION COEFFICIENTS MEASURED SPECTROPHOTOMETRICALLY

l = 1 cm. c = 1 g. per 100 ml.

Wave length, mμ	p-Nitrophenol ϵ_1	p-Nitrophenol ϵ_2	Phenol red ϵ_1	Phenol red ϵ_2	Brom thymol blue ϵ_1	Brom thymol blue ϵ_2
380	4.97	105	312	99	153	123
390	1.50	123	396	41	180	132
400	0	131	468	28	208	129
410	0	124	541	32	237	112
420	..	104	601	45	255	83
430	..	75	630	65	266	56
440	..	49	622	88	264	38
450	..	28	586	120	252	34
460	..	13	501	167	229	36
470	..	4.8	402	225	197	45
480	..	1.3	311	302	162	58
490	..	0.4	227	407	129	74
500	..	0.1	152	511	99	94
510	..	.0	100	668	72	118
520	..	...	54	857	50	146
530	..	...	31	1037	35	181
540	..	...	13	1263	23	219
550	..	...	10	1617	14	268
560	..	...	9.5	1819	9.5	315
570	..	...	6.3	1402	6.0	368
580	..	...	4.7	649	4.5	426
590	..	...	0.7	254	3.2	478
600	..	...	.0	81	2.0	539
610	..	...	...	27	1.0	580
620	..	...	...	10	0.8	582
630	..	...	...	5.5	.0	517
640	..	...	...	2.4	...	407
650	..	...	...	0.8	...	282
660	..	...	...	.0	...	173
670	..	...	...	....	...	102
680	..	...	...	....	...	52
690	..	...	...	....	...	28
700	..	...	...	....	...	15
710	..	...	...	....	...	7
720	..	...	...	....	...	4
730	..	...	...	....	...	2
740	..	...	...	....	...	1

(8) E. B. R. Prideaux, "The Spectrophotometric Examination of Dyes and Indicators," *J. Soc. Chem. Ind.*, **45**, 664, 678, 697 (1926).

The chromaticity coördinates and luminosity values were computed from the transmittancies by the method referred to in the introduction. We have assumed the use of I. C. I. Illuminant C which is comparable to noon daylight. The results are summarized in Tables II and III, and the chromaticity coördinates are plotted in Fig. 1. Since the luminosity of each indicator is highest at the lowest value of α, we have in each case assigned the arbitrary value of 10 to this form and scaled the other luminosities accordingly. These values are plotted in Fig. 3.

TABLE II

CHROMATICITY AND LUMINOSITY DATA ON PHENOL RED AND p-NITROPHENOL

pH	α	Chromaticity: x	y	Dominant wave length, mμ	Purity, %	Y	Lumin. rel. to 10 at α=0
Phenol Red, 0.001%, 2.9 × 10^{-6} M							
3.336	0.0003	0.3876	0.4271	572	50	981.4	10.000
6.80	.089	.3897	.3975	577	43	830.8	8.465
7.00	.134	.3901	.3820	581	38.5	769.0	7.834
7.20	.197	.3902	.3639	585	34	698.5	7.117
7.40	.280	.3904	.3381	595	24	613.2	6.247
7.60	.381	.3886	.3077	700	19	536.7	5.469
7.81	.500	.3832	.2769	497 C[a]	28	470.5	4.794
8.00	.607	.3762	.2521	498.5 C[a]	38	425.1	4.331
8.20	.710	.3688	.2304	510 C[a]	46	391.3	3.987
8.40	.796	.3612	.2136	517 C[a]	51	368.5	3.754
8.60	.860	.3555	.2027	524 C[a]	54	354.2	3.608
8.80	.907	.3511	.1949	529 C[a]	57	344.9	3.514
10.106	.995	.3426	.1799	535 C[a]	61	329.0	3.352
p-Nitrophenol, 0.0264%, 1.9 × 10^{-4} M							
6.1	0.112	0.3235	0.3437	568	11	1060.84	10.000
6.2	.137	.3260	.3489	568	13	1060.12	9.993
6.3	.166	.3289	.3548	568	15.5	1059.28	9.985
6.4	.201	.3321	.3611	568	18	1058.42	9.979
6.5	.240	.3354	.3678	568	20.5	1057.39	9.968
6.6	.285	.3389	.3746	568	23.5	1056.44	9.958
6.7	.334	.3424	.3815	568	26	1055.37	9.949
6.8	.387	.3458	.3882	568	29.5	1054.32	9.939
6.9	.443	.3491	.3945	568	31.5	1053.31	9.929
7.0	.500	.3521	.4004	568	34	1052.53	9.922
7.1	.557	.3549	.4056	568	36	1051.40	9.911
7.2	.613	.3574	.4102	568	38	1050.54	9.903
7.3	.666	.3598	.4142	568	40	1049.75	9.895
7.4	.715	.3614	.4176	568	41	1049.30	9.891
7.5	.710	.3620	.4205	568	42	1048.67	9.885
7.7	.834	.3654	.4247	568	44	1047.63	9.876
9.8	.998	.3700	.4333	568	48	1046.10	9.861

[a] C = complement.

Treatment of Results.—A linear chromaticity difference, ΔC, between adjacent points x_1y_1 and x_2y_2 on Fig. 1 was calculated by $\Delta C = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2}$. The successive values of ΔC were added cumulatively and plotted against the values of α at the midpoint of each pH interval. The additive change in chromaticity was found to be practically a linear function of α, and by graphic interpolation the chromaticity changes per 0.1 pH unit were obtained. These values are plotted in Figs. 4, 5 and 6 in relation to the respective pK' values. The luminosity values at 0.1 pH increments were likewise obtained by

TABLE III

CHROMATICITY AND LUMINOSITY DATA ON BROM THYMOL BLUE

		Chromaticity				Luminosity	
*p*H	α	x	y	Dominant wave length. $m\mu$	Purity. %	Y	Lumin. relative to acid form = 10
Brom Thymol Blue, 0.0032% 5×10^{-5} *M*							
2.2	0.000	0.4211	0.4467	576	66	891.15	10.000
6.046	.100	.3859	.4352	571.5	52	711.82	7.988
6.398	.200	.3492	.4161	565	36.2	577.80	6.484
6.632	.300	.3125	.3895	552	20.5	476.4	5.346
6.824	.400	.2778	.3567	507	10.3	400.0	4.488
7.000	.500	.2463	.3205	492	23.5	340.5	3.821
7.176	.600	.2208	.2813	486.2	30.6	295.0	3.309
7.368	.700	.2003	.2463	483	47.5	262.4	2.944
7.602	.800	.1835	.2107	480.1	50.8	223.6	2.639
7.954	.900	.1724	.1802	478	65.5	213.2	2.392
9.80	.998	.1640	.1540	476.6	72.0	197.2	2.213
0.0016%. 2.5×10^{-5} *M*							
2.2	.000	.3723	.3965	574.1	38	964.7	10.000
6.046	.100	.3519	.3838	571.0	29	866.2	8.978
6.398	.200	.3317	.3692	566.0	20	781.0	8.098
6.632	.300	.3117	.3531	558	6.0	707.8	7.337
6.824	.400	.2926	.3354	504	6.0	643.9	6.675
6.948	.470	.2797	.3225	493	10.8	604.6	6.266
7.00	.500	.2744	.3168	491	13.5	588.7	6.108
7.176	.600	.2574	.2977	486.5	21	541.0	5.608
7.368	.700	.2419	.2782	484	29	499.1	5.174
7.602	.800	.2279	.2589	482	36	462.9	4.798
7.954	.900	.2154	.2399	480.5	43	431.2	4.470
9.8	.998	.2044	.2219	479	49	403.4	4.181
0.0004%. 6.41×10^{-6} *M*							
2.2	.000	.3264	.3388	572	10.5	1036.56	10.000
6.046	.100	.3208	.3348	570.5	7.7	1009.76	9.741
6.398	.200	.3158	.3300	570	5.8	984.56	9.498
6.632	.300	.3107	.3256	555	2.4	960.13	9.263
6.824	.400	.3056	.3210	505	1.75	936.36	9.033
7.000	.500	.3005	.3163	491	3.5	913.64	8.814
7.176	.600	.2954	.3114	487	5.9	891.51	8.601
7.368	.700	.2905	.3068	485	8.1	870.38	8.397
7.602	.800	.2856	.3018	483	10.5	849.73	8.198
7.954	.900	.2808	.2971	482.5	12.75	830.50	8.012
9.8	.998	.2761	.2923	422	15	811.84	7.832

graphic interpolations, and the changes in relative luminosity per 0.1 *p*H are plotted in Figs. 5 and 7.

As is well demonstrated in Fig. 1 and in Table II, the one color indicator *p*-nitrophenol owes its "color-change" solely to its changing purity. Between *p*H 6.1 and 7.7 there is better than a four fold increase in purity, while there is less than a two per cent. change in luminosity, and the dominant wave length remains constant at 568 mμ. This may be correlated with the notoriously poor "virage" of this indicator. It may be seen in Fig. 4 that the maximum chromaticity increments occur on the acid side of the pK' value. This is in agreement with the range of usefulness of this indicator which is given by Michaelis as *p*H 4.7 to 7.9 (quoted by Clark[3]).

The sulfonphthalein indicators illustrate the situation which exists when all three color characteristics change with *p*H. Figs. 5 and 6 show that the maximum change of chromaticity occurs at pK'. This may be predicted, because at this point $\Delta\alpha/\Delta p\text{H}$ is maximal. However, it is well known that the useful range of each of these indicators is centered to the acid side of pK'. Figures 5 and 7 demonstrate that the maximal change in luminosity occurs on the acid side of pK'. These maximal points are given in Table IV along with the useful ranges of these indicators as given by Clark and Lubs[9] and by Saunders.[10] From these data it is evident that it is the "brightness" com-

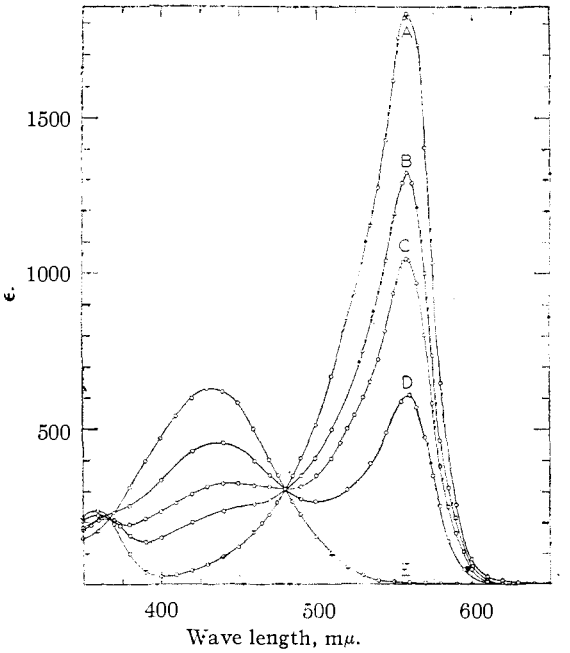

Fig. 2.—Isohydric absorption curves for phenol red showing a sharp isosbestic point at 481 mμ and a second isosbestic point at 364–370 mμ. Ordinate, ϵ, is absorption coefficient for 1 cm. and 1 g. per 100 ml.: A, *p*H 10.11; B, *p*H 8.22; C, *p*H 7.89; D, *p*H 7.45; E, *p*H 3.56.

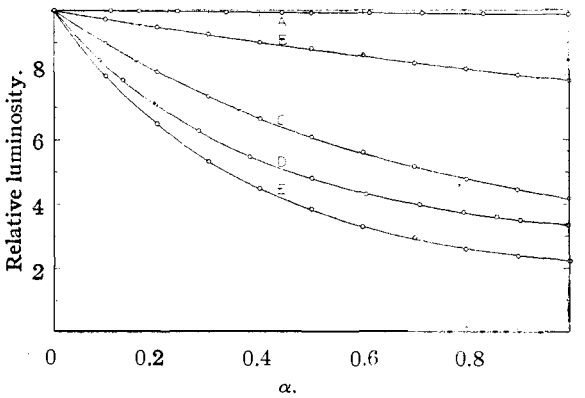

Fig. 3.—Luminosity as a function of *p*H. The luminosities are scaled relative to the luminosity at $\alpha = 0$, which in each case is given the arbitrary value of 10: A, *p*-nitrophenol, 1.9×10^{-4} molar; B, brom thymol blue, 6.41×10^{-6} molar; C, brom thymol blue, 2.5×10^{-5} molar; D, phenol red, 2.9×10^{-5} molar; E, brom thymol blue, 5×10^{-5} molar.

(9) W. M. Clark and H. A. Lubs, *J. Bact.*, **2**, 1, 109, 191 (1917).
(10) J. T. Saunders, *Proc. Cambridge Phil. Soc.*, **1**, 30 (1925).

TABLE IV

Indicator	pK'	Useful range, pH	Center of useful range	Displacement from pK'	Maximum change of luminosity: Concn., %	Maximum change of luminosity: pH	Maximum change of luminosity: Displacement from pK'[c]
Phenol red	7.8	6.7–8.3 (Clark and Lubs)[a]	7.5	−0.3	0.001	7.35	−0.45
		7.2–8.0 (Saunders)[b]	7.6	− .2			
Brom thymol blue	7.0	6.0–7.6 (Clark and Lubs)[a]	6.8	− .2	0.0004	6.85	− .15
		6.4–7.2 (Saunders)[b]	6.8	− .2			

[a] Ability of observer to distinguish intervals of 0.2 pH at concentration of 0.0004%. [b] Ability of observer to discriminate "changes of tint" at 0.02 pH unit. Concentration not stated. [c] The displacement of the peak in the luminosity gradient increases with an increase in concentration. See Fig. 7.

ponent of color sensation which is responsible for the shifting of the range of usefulness to the acid side of pK'. It is evident that the utility of these indicators is governed by changes in "brightness" as well as by changes in "hue."

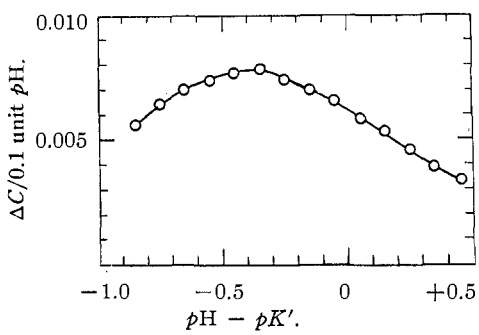

Fig. 4.—p-Nitrophenol, 1.9×10^{-4} molar: chromaticity gradient as ordinate, expressed as change in chromaticity per 0.1 pH unit. The change in luminosity is negligible.

We have further studied the effect of concentration upon the chromaticity and luminosity of brom thymol blue. The results are seen in Table III and in Figs. 3, 6 and 7. From Fig. 6 it is immediately evident that decreasing the concentration lowers the magnitude of the chromaticity increments, but the maximal change remains at pK'. Figure 7 shows, however, that lowering the concentration not only decreases the luminosity changes, but it also shifts the peak of Δl (increment of luminosity) toward pK'. Thus with a concentration of 0.0004%, the maximal Δl is at $p\mathrm{H} - pK' = -0.15$. Reference to Fig. 3, however, shows that the over-all luminosity change is so small that it would not be expected to exert much effect on the range of usefulness at this concentration. It is expected that some further decrease in concentration would make the peak of Δl occur at pK', but the errors involved in interpolating luminosity changes of this small magnitude make further calculations with these small concentrations impractical.

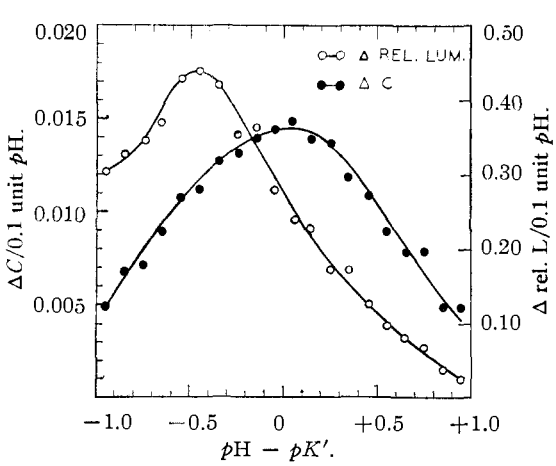

Fig. 5.—Phenol red, 2.9×10^{-5} molar: gradients of luminosity and chromaticity: ordinate on left, ●-●-●, change in chromaticity per 0.1 pH unit; ordinate on right, O-O-O, change in relative luminosity per 0.1 pH unit.

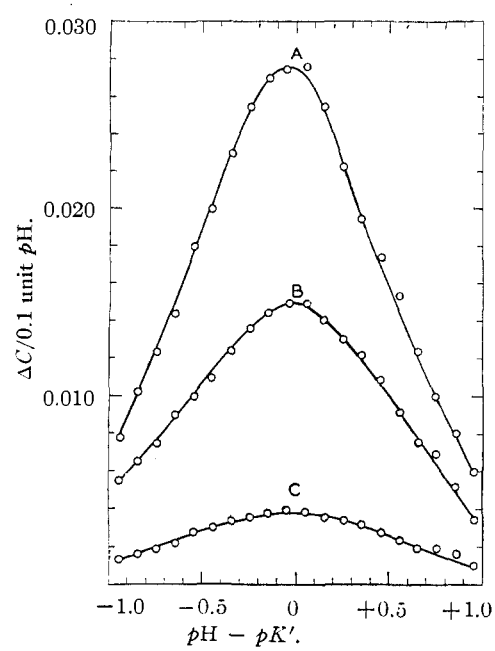

Fig. 6.—Brom thymol blue—chromaticity gradients at various concentrations, ordinate is change in chromaticity per 0.1 pH unit: A, 5×10^{-5} molar; B, 2.5×10^{-5} molar; C, 6.41×10^{-6} molar.

Discussion.—A color can be specified in terms of luminosity and chromaticity, but there has been devised no three dimensional model in which equal distances in space represent equally noticeable color differences involving both luminosity and chromaticity. It is for this reason that we have analyzed our data separately in these two categories.

Our luminosity data cannot be too rigidly correlated with the optimal concentrations for obtaining the best virage. This follows from the fact that the eye is unequally sensitive to unit luminosity differences in different parts of the luminosity scale. Furthermore, one cannot interpret linear changes of chromaticity per unit pH change with the assumption that the visual sensitivity to unit chromaticity differences is equal on all parts of the I. C. I. diagram. This was pointed out by MacAdam,[11,12] who showed that the standard deviations of visual matching of colors of equal luminance could be plotted as an ellipse about any given point on the diagram, and furthermore that the magnitude and major axis of the ellipse vary greatly in different regions of the diagram.

The ellipses of MacAdam were compared with the chromaticity differences between adjacent pH's on Fig. 1 to determine the smallest increment of pH which could be discriminated on the basis of chromaticity change. It was found that those major axes of the ellipses which lie within the area of the sulfonphthalein indicators are of the order of magnitude of 0.02 pH. A difference of 0.02 pH has been found to be the limit of discrimination attained by the ordinary method with visual observation. See for example Saunders[10] and Hastings and Sendroy.[13] It should be emphasized that these standard deviations of error in matching chromaticities were obtained with constant luminosity, a condition that does not hold for our data.

Summary

The method of the International Committee on Illumination has been used to characterize the indicators phenol red, brom thymol blue and p-nitrophenol.

In the course of the investigation a sharp isosbestic point for phenol red was demonstrated.

The "one-color" indicator p-nitrophenol has a dominant wave length of 568 mμ independent of pH. At the concentration used this indicator exhibits only about two per cent. change of luminosity between pH 6.1 and 7.7 but a four-fold change of spectral purity. Thus, discrimination between solutions of different pH is based almost exclusively on the change of spectral purity.

In contrast with p-nitrophenol the two sulfonphthalein indicators show distinct changes in luminosity, dominant wave length and purity. While it is impractical to weight these factors, as applied to discrimination between solutions of different pH, the following points were developed. Since the change of ionization per unit increment of pH is maximal at the pH corresponding to pK' it may be predicted that the maximal change of position on the chromaticity diagram (change of chromaticity) per unit increment of pH is also maximal at pH = pK'. This was confirmed. The maximal change of luminosity per unit increment of pH is at pH less than pK' and corresponds roughly with the center of the "useful pH-range" estimated on the basis of experience. This suggests that luminosity, or the "brightness" component of color sensation, plays a dominant role in the use of these sulfonphthalein indicators.

There are given some details regarding the shift of the luminosity maxima relative to pH–pK' as a function of the concentration of a sulfonphthalein indicator.

The present state of analysis of factors concerned in the discrimination between small color differences does not permit the weighting of the effects of changes in luminosity and changes of chromaticity. However, MacAdam's data, obtained with constant luminosity, indicates certain minimal differences in chromaticity which can be discriminated. These we find to be of the order of magnitude of chromaticity differences of the sulfonphthalein indicators corresponding to the least difference of pH detectable by eye.

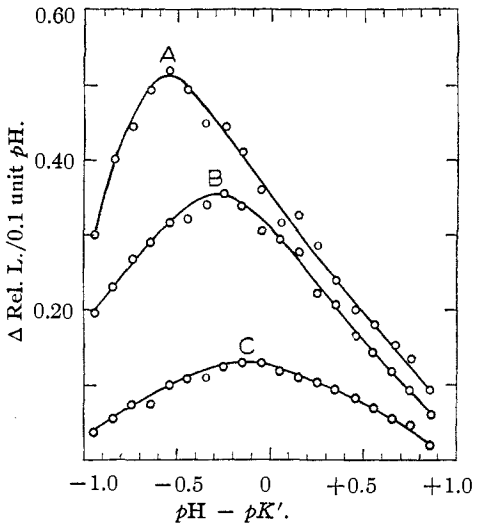

Fig. 7.—Brom thymol blue—luminosity gradients at various concentrations, ordinate is change in relative luminosity per 0.1 pH unit: A, 5×10^{-5} molar; B, 2.5×10^{-5} molar; C, 6.41×10^{-6} molar.

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