the calomel electrode to determine "end points" and single potential differences in the analyses. For convenience the connections of this instrument are brought to the front of the panel, terminating in two binding posts.

The other two instruments have a range of 7.5 volts and 7.5 amperes respectively, and give the current and potential change through the analysis bath. The ammeter is connected through a modified "Jack" switch having four points; and the voltmeter, through a set of four double contact keys. Thus the voltage across and the current through any of the baths may be read by pressing plugs into the proper cavities. There is little sparking ordinarily, as the ammeter connection does not interrupt the current, and the voltmeter set across the bath only.

A double throw switch on the back of the panel allows the use of either 6 volt storage battery or 110 volt lighting current. To reduce the pressure of the latter, three key lamp sockets, wired in multiple, are placed in series with each analysis circuit, and two in each motor circuit. These sockets are set on a shelf attached to the rear of the panel. A neat effect is secured by employing extension keys, the handles of which only are visible on the face of the panel. When the storage battery is used, a fuse plug replaces one of the lamps in each circuit. The meter connections as noted above, are also on the rear of the panel.

Each circuit is further controlled by a nichrome rheostat set in porcelain. These rheostats are screwed to the rear of the panel, and are controlled by cheap typewriter twirlers on the front.

Artificial stirring is accomplished in the outer baths by the use of cheap battery motors with suitable stirrers of glass or platinum clutched (for PbO_2) or sealed on to the motor shafts. HENRY ZIEGEL.

BROOKLINE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE COLOR AND IONIZATION OF CRYSTAL-VIOLET.

BY ELLIOT Q. ADAMS AND LUDWIG ROSENSTEIN.

Received May 5, 1914.

Introduction.

The chromogens[1] derived from triphenylmethane[2] undergo, on the addition of strong acids to their aqueous solutions, a remarkable series of color transformations. The largest variety of color changes among these sub-

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[1] This term will be used to include both colored and colorless modifications.

[2] Kayser, *Handbuch d. Spekt.*, [5] 3, 87, 247, 534; H. W. Vogel, *Ber.*, 11, 622–624 (1878); *Ibid.*, 11, 913–920, 1363–1371 (1878); Berliner, *Ber.*, 1878, 409–431; Girard and Pabst, *Compt. rend.*, 101, 157–160 (1885). *J. Formánek. Unters. u. nachweis organ. Farbstoffe auf spekt. Wege.* (J. Springer, Berlin, 1908).

stances is shown by the dyes, N penta- and N hexa-methyl-*p*-trianilinomethyl chloride, respectively known as methyl and crystal-violet. Their color, in neutral solution, is blue-violet, changing on the gradual addition of strong acid, through violet-blue, blue, blue-green, green and yellow-green, to a pure yellow in concentrated acid. Accompanying these changes in hue another change takes place when the solutions are allowed to stand, the intensity of the color diminishing greatly in strongly acid or in alkaline solution. In weakly acid solution the fading is slower and less pronounced. Equivalent solutions of all strong acids produce identical effects, and, on neutralization, the original color is in every case restored, in hue at once, and in intensity on standing. Examination with a dark-field ultramicroscope of acidic, neutral and alkaline solutions of crystal-violet showed that only in the last case is this substance colloidal. It is clear from these observations that all these changes are brought about by reactions of the chromogens with hydrogen or hydroxyl ion (or with water), and that all these reactions are completely reversible. Rosaniline, para-rosaniline, malachite green and aniline blue show a series of changes similar in all respects (except that the variation in color is less) to those of methyl and crystal-violet. Solutions of either of the latter are well suited for spectroscopic observations, and at the same time the similarity in behavior and analogy in constitution almost certainly insures identity, in all these cases, of structure and reactions.

The rate of the *development* of color when *alkaline* solutions of triphenylmethane dyes are made acidic with strong or weak acids has been carefully studied by H. C. Biddle;[1] he has pointed out that these changes bear a close resemblance to the slow conversion of the cinchona alkaloids to their toxic isomers, in that the rate of both is greatly decreased by increase in the hydrogen ion concentration. He also called attention to the complexity of the equilibrium in the case of crystal-violet as a result of the possibility of the formation of mono-, di-, and tri-acid salts; and made reference to work bearing on this point already begun at his suggestion by the authors. We wish in this place to express our gratitude to Prof. Biddle for much helpful advice.

The accepted structures for the colorless carbinol (color-base) of crystal-violet and for the violet chloride are shown in the formulas on next page, and if, for convenience, the notation be adopted that the part of compound within the square be represented by **R,** these formulae become simply, **R**OH and $\overset{\mathrm{Cl}}{\mathbf{R}}$, whereas the true, (colored) base[2] would be represented by $\overset{\mathrm{OH}}{\mathbf{R}}$ Salt formation at the two remaining nitrogen atoms will be

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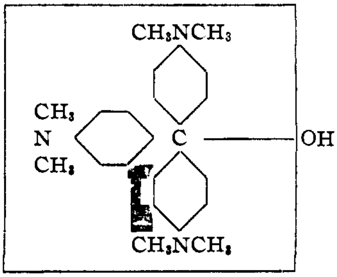
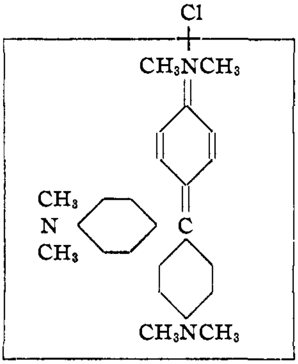
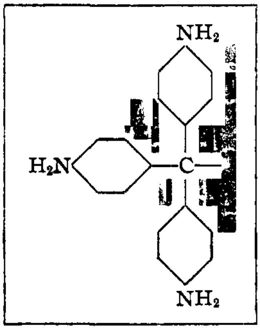
[1] Biddle, This Journal, **36**, 101, 103 (1914).

[2] Cf. Holleman, "Textbook of Organic Chemistry," p. 464 (1903).





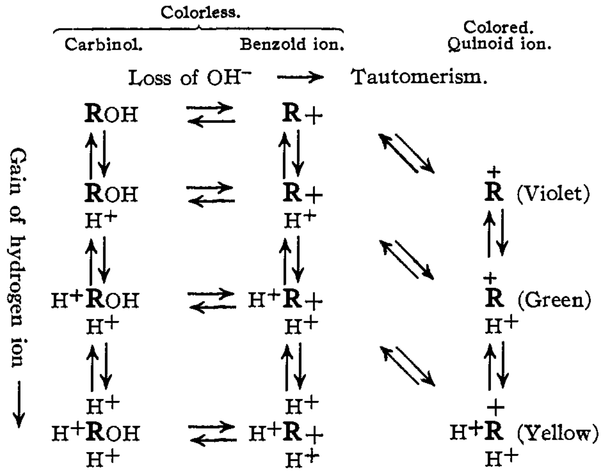
indicated by the addition of the symbol for hydrogen ion or for acid at the left or below the letter **R**. Thus a dichloride of crystal-violet would be represented by $\overset{\text{Cl}}{\text{ClH}\mathbf{R}}$; a color-base dichloride, which would be colorless, by $\overset{\text{Cl}}{\overset{\text{H}}{\text{ClH}\mathbf{R}\text{—OH}}}$ The ions of such chlorides can all be represented by replacing the chlorines by positive charges. In the case of para-rosaniline, the symbol **R** would represent



and for all the chromogens named above the same notation can be adopted.

As has been pointed out above, the changes in question are all to be attributed to reversible reactions of the chromogen with hydrogen ion, with hydroxyl ion, or with water. It will be well, at this point, to consider the constitution of the probable products of such reactions. Starting with the color-base of crystal-violet, **R**OH, which contains three nitrogens, there is the possibility of adding one, two, or three equivalents of hydrogen ion, to form the ions $\underset{\text{H}^+}{\mathbf{R}\text{OH}}$, $\underset{\text{H}^+}{\text{H}^+\mathbf{R}\text{OH}}$ and $\overset{\text{H}^+}{\underset{\text{H}^+}{\text{H}^+\mathbf{R}\text{OH}}}$. Each of the four substances may lose hydroxyl ion, forming the ions $\mathbf{R}+$, $\underset{H^+}{\mathbf{R}+}$, $\underset{H^+}{H^+\mathbf{R}+}$, and $\overset{H^+}{\underset{H^+}{H^+\mathbf{R}+}}$; the first three of these are in tautomeric equilibrium with the colored (quinoid) ions $\overset{+}{\mathbf{R}}$, $\underset{H^+}{\overset{+}{\mathbf{R}}}$, and $\underset{H^+}{H^+\overset{+}{\mathbf{R}}}$. Reactions with water will produce no changes which cannot be also brought about by reactions, successively, with hydrogen and hydroxyl ions. Owing to the symmetry of the crystal-violet molecule no isomers of these forms exist. The genetic relationship between these hypothetical substances is shown in Table I. In this table definite colors have been assigned to the three quinoid ions for reasons which will appear later.

TABLE I.



For a compound with one less amine nitrogen the substances in the bottom row of the table become impossible; with one amine nitrogen, only those in the first two rows remain; while triphenylcarbinol, having no nitrogen, is colorless under all conditions. On the other hand, molecular asymmetry, like that of rosaniline, increases the number of forms by the introduction of isomers.

Since the chromogens considered are amine carbinols, the relative speeds of the reactions postulated in Table I may be inferred from analogy with other amines and other carbinols. As is well known, salt formation from amines is instantaneous, whereas the reaction of carbinols with acids is invariably slow. Hence the reactions in Table I headed "loss of OH⁻" may be expected to be slow while all the others would be instantaneous.

The data needed for the establishment of the relative concentrations *of all* the substances present in acidic solutions of *N*-hexamethyl-*p*-trianilinomethyl chloride[1] fall naturally into two classes: the relative proportions of different colored substances in the solutions, and the variation of the proportions of colorless substances with the color of the solutions. The measurement of the proportions of substances of different colors involves comparisons of color intensities for many different shades lying between violet and yellow after equilibrium between all the different forms has established itself. On the other hand, since the hue of the solutions does not change on standing, the variation of the proportions of colorless substances in solutions of different colors involves only the measurement of the relation between original and equilibrium intensities.

The complete investigation is accordingly divided into three parts, the first to deal with the equilibrium between the colored forms; the second with the slow changes in color intensity toward equilibrium, and the third to comprise a discussion of the entire problem.

PART I.

Equilibrium between the Colored Forms of Crystal-Violet.

Acidic solutions of crystal-violet showed, on examination with a small spectroscope, well marked absorptions in the yellow, orange, and violet regions; the relative prominence of these absorptions changed in the order named above as the concentration of acid was increased. These facts were taken to mean that three substances, respectively violet, green, and yellow, produced the colors of all the solutions. This part of the present investigation was therefore undertaken to obtain quantitative proof of the truth or fallacy of the assumption of the presence of three, and only three, colored substances.

A 0.001 molal solution of crystal-violet (*N*-hexamethyl-*p*-trianilinomethyl chloride) was made in conductivity water and from this stock solution were made all the more dilute solutions used in the measurements. A 2 *N* solution of hydrochloric acid, standardized by titration against standard alkali, was used to obtain the desired concentrations of acid.

Since the color of freshly acidified crystal-violet solutions changes appreciably in the time required for a set of spectrophotometric measurements, it was necessary to make these measurements with solutions which had come to equilibrium. The ratios of initial to final color intensities in such solutions have been obtained from measurements[2] of the rate of

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[1] This substance was chosen rather than the pentamethyl derivative because it was available in (Kahlbaum's) pure form. Analysis gave N = 10.27%, 10.37%; theoretical, calculated for the hexamethyl derivative 10.33%; for the pentamethyl derivative, 10.70%.

[2] See Part II.

fading, and the absorption measurements at equilibrium have been combined with these ratios to obtain the initial absorption.

When monochromatic light of intensity I_0 passes through an absorbing medium, the intensity of the transmitted light, I_1 is given by the relation:

$$I_1 = I_0 \times 10^{-\epsilon d} \qquad (1)$$

where d is the depth of the absorbing layer and ϵ, the "extinction coefficient," is a constant which, for any wave length, is characteristic of the absorbing material. The value of the extinction coefficient for unit concentration of the absorbing substance is called the molecular extinction coefficient and is usually represented by A_λ. Then, in terms of this constant, equation (1) becomes

$$I_1 = I_0 \times 10^{-A_\lambda C d}$$

where C is the concentration in mols per liter of the absorbing substance, and the depth d, is measured in centimeters.

Equation (2) may also be written in the form,

$$\log I_1/I_0 = A_\lambda C d. \qquad (3)$$

The ratio of the intensity of the incident to that of the transmitted light was measured by means of a König, Martens and Grünbaum[1] spectrophotometer. In this instrument two beams of monochromatic light from the same source, which have passed respectively through the solution and through an equal column of the pure solvent, are polarized in mutually perpendicular planes and are compared by means of a Nicol in the rotating eye-piece of the instrument. If α be the angle at match between the analyzing Nicol and the polarizer in the beam from the pure solvent, then the ratio of the intensities is,

$$I_0/I_1 = \tan^2 \alpha, \qquad (4)$$

and combining with equation (3)

$$A_\lambda C d = 2 \log \tan \alpha. \qquad (5)$$

It will be well at this point to consider the accuracy attainable with this type of instrument. Under favorable conditions of illumination the accuracy of setting is considerably greater than that of reading the angle between the Nicol prisms. The absolute magnitude of the latter is obviously the same at all angles, hence the maximum of accuracy is reached when the specific extinction coefficient changes least rapidly with the angle, that is to say, when the logarithmic derivative of A_λ with respect to the angle is a minimum. From equation (5) this derivative is

$$\frac{d \ln A_\lambda}{d\alpha} = \frac{d \ln \tan \alpha}{\ln \tan \alpha \, d\alpha} = \frac{2}{\sin 2\alpha \quad \ln \tan \alpha} \qquad (6)$$

and will be a minimum when its denominator is a maximum;

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[1] Martens and Grünbaum, *Drude's Ann.*, 12, 984–1000 (1903).

$$\frac{d\ (\sin 2\alpha \ln \tan \alpha)}{d\alpha} = 2(\cos 2\alpha \ln \tan \alpha + 1) = 0. \qquad (7)$$

The solutions of this equation in the first quadrant are $\alpha = 16° 46'$; $\alpha = 73° 14'$. Substituting into equation (6), $\alpha = 16° 46'$, $d\alpha = 0.1°$ $= 0.0017$ radian; $d \ln A_\lambda = 1.2\%$; that is, the maximum accuracy is obtained if the concentration is so chosen that the instrument reading is $\alpha = 16° 46'$, and the error of a single reading, 0.1°, will then produce an error of 1.2% in A_λ.

It should be further noted that the probable error in A_λ will be reduced nearly threefold by taking eight readings, as has been done in the measurements to follow. On the other hand, at the ends of the spectrum the lack of light makes the error in setting greater than that of reading α. The unavoidable inequality in illumination causes the value of α taken with the solution on the two sides of the instrument to differ, without introducing any error into their mean.

The Calibration of the Spectrophotometer.—The "wave length" scale of the spectrophotometer used being an entirely arbitrary one, it was necessary to calibrate it by means of some standard wave lengths. For this purpose were used the red lithium line, the sodium "D" line, and the yellow, yellow-green, blue-green and blue lines of mercury. All these lines appeared of appreciable width but had sharp edges, and therefore scale readings at both edges of the lines were made and their average was taken as the position of the line on the scale. No attempt has been made to correct for the slit width, since it was found that none of the slit widths used appreciably increased the apparent width of the lines. The results of the calibration measurements are given in Table II.

TABLE II.—THE CALIBRATION OF THE SPECTROPHOTOMETER.

Line.	Scale readings. a.	b.	Mean.	Slit width.	Wave length λ.	$\lambda^{-2} \times 10^8$.
Li red	3388	3249				
	3387	3247		15 µ	6708 Å	2.222
	3387	3253	3318			
Na D	3080	2957		10		
	3080	2955		30	5890	2.880
	3090	2947	3018	30	5896	
Hg yellow	3038	2897		5	5790	
	3038	2896	2967	5	5769	2.995
Hg green	2862	2730		5		
	2862	2730	2976	5	5460	3.355
Hg blue-green	2467	2338		5		
	2471	2344	2405	10	4916	4.140
Hg blue	1840	1709		5		
	1841	1711	1777	5	4358	5.265

A calibration curve was drawn plotting instrument readings against the square of the frequencies, and from this curve were obtained the intermediate wave lengths corresponding to instrument readings.

TABLE III.—WAVE LENGTHS AND CORRESPONDING INSTRUMENT READINGS.

Wave length λ.	Instrument readings.	Wave length λ.	Instrument readings.
4609 Å	2100	5955 Å	3050
4800	2300	6073	3100
5025	2500	6215	3150
5295	2700	6348	3200
5636	2900	6650	3300
5839	3000		

In Table III are given the wave lengths and the corresponding instrument readings at which all absorption coefficients were measured.

The Spectrophotometric Measurements.—The molecular extinction coefficient, A_λ, which has been defined in equation (2) is, according to Beer's law, a constant with respect to the concentration whenever dilution does not affect the chemical nature of the colored substances. That Beer's law holds for the solutions used in this work follows from the fact that the decrease in color intensity to an equilibrium value is unaccompanied by change of hue. Hence it is clear that comparison between the absorptions of solutions of different chromogen concentrations is possible through the use of the molecular extinction coefficient, and since the measurements gave the angle α of equation (5), this equation is directly applicable for the calculation of this characteristic constant. It may be pointed out again that the angle α was measured with a 10 cm. tube of the solution of chromogen on one side of the instrument and a 10 cm. tube of pure solvent on the other; and that after settings had been made in all four quadrants the tubes were interchanged and settings were again made in four quadrants. Thus any inequality in the illumination was eliminated from the average value of the angle. The method by which the calculation was made is illustrated, using a typical set of eight instrument readings, in Table IV.

TABLE IV.—INSTRUMENT READINGS AND CALCULATIONS ON THE BLUE SOLUTION FOR WAVE LENGTH 5955 Å.

Concentration of chromogen = 5.0×10^{-6} m.
Concentration of HCl = 0.016 *N*.

Quad.	I.	II.	III.	IV.		4α.	α.
L........	72.1°	105.9°	252.1°	285.8°	$360° + \text{I} - \text{II} + \text{III} - \text{IV}$	= 292.5°	73.12°
R.......	16.4°	161.6°	196.5°	341.4°	$- \text{I} + \text{II} - \text{III} + \text{IV}$	= 290.1°	72.52°
						Mean,	72.82°

$A_\lambda = 2 \log \tan 72.82° \div (10\ \text{cm.}) \div (5.0 \times 10^{-6}\ \text{m.}) = 20400.$

"L" and "R" signify respectively "chromogen solution on left side of instrument" and "chromogen solution on right side of instrument."

In the same way the values of α were obtained at the eleven wave lengths given in Table III for all six solutions, and these values of α, together with the concentrations of the solutions and the wave lengths to which they refer are given in Table V. From the mean values of α, A_λ has been calculated to obtain a measure for the concentrations of the colored substances; and Table VI gives these values of A_λ.

Dividing these figures by the ratio of equilibrium to initial color intensity (γ), found in Part II, we obtain the initial values of the molecular extinction coefficient. These values are given in Table VII.

TABLE V.—VALUE OF THE ANGLE α FOR SOLUTIONS OF THE CHROMOGEN IN PURE WATER AND IN ACID.

Color.	Violet.	Violet-blue.	Blue.	Blue-green.	Yellow-green.	Green-yellow.
Conc. HCl	None	0.004 *N*.	0.016 *N*.	0.040 *N*.	0.20 *N*.	1.00 *N*.
Conc. chromogen	1.5×10^{-6}	2.0×10^{-6}	5.0×10^{-6}	20×10^{-6}	50×10^{-6}	50×10^{-6}
Wave length.	α.					
6650 Å	46.80°	51.52°	56.30°	59.28°	50.38°	47.05°
	46.08°	51.55°	55.10°	59.20°	51.42°	48.15°
6348	52.15°	61.12°	70.25°	78.50°	59.92°	47.92°
	51.88°	61.65°	69.75°	78.58°	59.20°	49.10°
6215	60.50°	67.72°	71.95°	78.58°	59.52°	47.72°
	59.88°	68.12°	71.55°	79.00°	58.80°	48.78°
6073	70.82°	72.88°	72.72°	76.68°	55.35°	47.20°
	70.30°	73.38°	72.00°	76.70°	57.08°	48.10°
5955	77.18°	77.38°	73.12°	74.60°	53.25°	46.90°
	77.12°	77.20°	72.52°	74.92°	55.12°	47.82°
5830	77.58°	77.52°	71.88°	72.10°	52.05°	46.32°
	77.22°	77.08°	71.08°	73.18°	53.78°	47.05°
5636	72.78°	72.82°	65.65°	65.00°	49.00°	46.68°
	73.18°	72.52°	65.10°	66.28°	51.38°	47.10°
5295	66.80°	65.50°	57.78°	55.58°	46.50°	47.00°
	67.18°	65.15°	57.25°	57.70°	49.65°	46.95°
5025	56.10°	55.32°	51.05°	49.88°	46.28°	48.58°
	56.25°	55.02°	50.22°	52.58°	50.48°	48.32°
4800	51.20°	49.62°	48.28°	48.52°	46.95°	50.85°
	51.70°	49.18°	47.52°	51.10°	51.82°	50.90°
4609	47.80°	47.08°	47.20°	48.82°	49.70°	54.45°
	49.65°	47.22°	46.55°	51.35°	53.98°	53.85°

The set of values of the molecular extinction coefficient at various wave lengths for a single chemical species of the chromogen will be called a "fundamental." The absorption of a solution containing several chemical species will be the sum of the products of the fundamentals by the fractions of chromogen present in the respective colored forms. To prove that three colored forms are present we must show that three fundamentals

TABLE VI.—EQUILIBRIUM VALUES OF THE MOLECULAR EXTINCTION COEFFICIENT, A_λ AT 20.0°.

Color.	Violet.	Violet-blue.	Blue.	Blue-green.	Yellow-green.	Green-yellow.
Conc. HCl	None	0.004 *N.*	0.016 *N.*	0.040 *N.*	0.20 *N.*	1.00 *N.*
Conc. chromogen	1.5×10^{-6}	2.0×10^{-6}	5.0×10^{-6}	20×10^{-6}	50×10^{-6}	50×10^{-6}
Wave length.	$A_\lambda \times 10^{-3}$.					
6650 Å	2.90	9.99	6.64	2.25	0.390	0.158
6348	14.51	26.31	17.56	6.93	0.964	0.214
6215	32.22	39.18	19.27	7.09	1.00	0.198
6073	60.19	52.06	19.91	6.26	0.709	0.161
5955	85.60	64.65	20.41	5.65	0.585	0.144
5830	86.79	64.71	18.99	5.05	0.493	0.097
5636	68.55	50.57	13.55	3.43	0.316	0.114
5295	49.62	33.76	7.83	1.81	0.186	0.120
5025	23.20	15.75	3.54	0.950	0.204	0.210
4800	13.14	6.70	1.76	0.734	0.268	0.398
4609	7.53	3.26	1.13	0.777	0.418	0.564

TABLE VII.—INITIAL VALUES OF THE MOLECULAR EXTINCTION COEFFICIENT, A_λ, AT 20.0°.

Wave length.	$A_\lambda \times 10^{-4}$.					
6650 Å	0.29	1.20	2.80	1.88	1.12	0.35
6348	1.45	3.16	5.84	5.78	2.79	0.47
6215	3.22	4.70	6.40	5.91	2.87	0.44
6073	6.02	6.25	6.62	5.22	2.04	0.36
5955	8.56	7.76	6.79	4.71	1.68	0.32
5830	8.68	7.77	6.43	4.21	1.42	0.22
5636	6.86	6.06	4.50	2.86	0.91	0.25
5295	4.96	4.05	2.60	1.51	0.54	0.27
5025	2.32	1.89	1.18	0.79	0.59	0.46
4800	1.31	0.80	0.58	0.61	0.77	0.88
4609	0.75	0.39	0.38	0.65	1.20	1.25

are necessary and sufficient. The calculation of the fundamentals from the absorptions of mixtures of forms is *algebraically* impossible. However, if we impose the restrictions that the concentration of total chromogen is fixed, and that neither the concentration of any of the forms not their absorptions at any wave length can become less than zero, the fundamentals are restricted within very narrow limits.

It was at first attempted to assume that the sum of the fractions of chromogen in the several colored forms added up to unity, but this was found impossible, indicating that even initially a part of the chromogen is present is some colorless form. However, this sum cannot exceed unity and this condition was imposed.

The fundamentals were found by trial, and are given in Table VIII and Fig. 1.

The fractions of chromogen present in the different forms are given in Table IX.

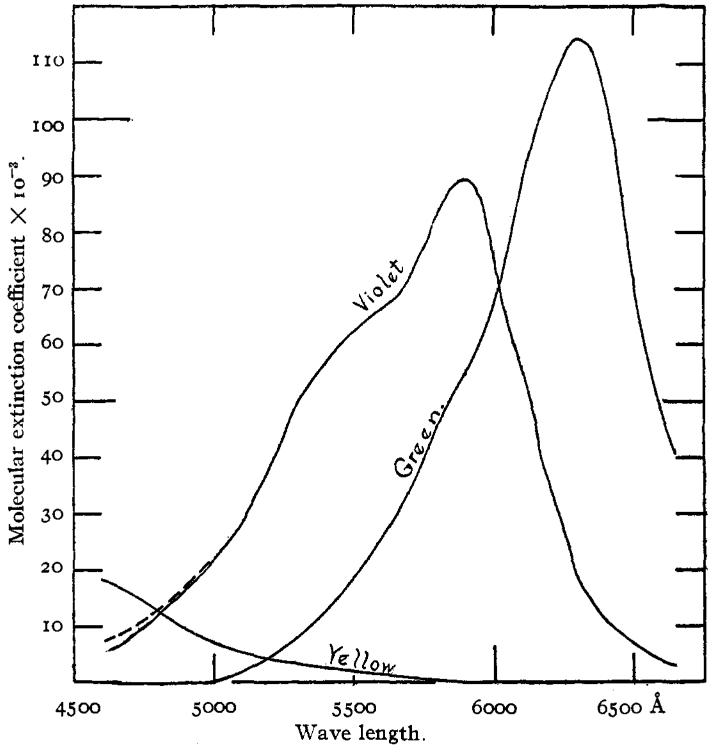

Fig. 1.—Fundamental absorption curves of crystal-violet.

Table VIII.—Fundamental Molecular Extinction Coefficients.

Wave length.	Violet.	Green.	Yellow.
6650 Å	3000	40800	...
6348	14500	112500	...
6215	32200	107200	...
6073	60200	82500	...
5955	85600	61000	...
5830	86800	49200	200
5636	68400	28400	1300
5295	49600	8000	3500
5025	23200	800	6700
4800	12000	..	12800
4609	5000	..	18300

Table IX.—Calculated Fractional Concentrations of Colored Forms.

Color of solution.	Acid.	Violet.	Green.	Yellow.	C by diff.
Violet	None	1.000	...	...	..
Violet-blue	0.004 *N*	0.779	0.195	0.011	..
Blue	0.016 *N*	0.462	0.466	0.090	..
Blue-green	0.040 *N*	0.206	0.490	0.298	..
Yellow-green	0.20 *N*	0.019	0.250	0.690	0.04
Green-yellow	1.00 *N*	0.003	0.042	0.685	0.27

The comparison with the experimental results is given in Figs. 2 and 3, on which the lines represent the calculated absorptions, while the experimental points are marked by crosses. The completeness of the agreement establishes that three absorbing substances are necessary and sufficient to

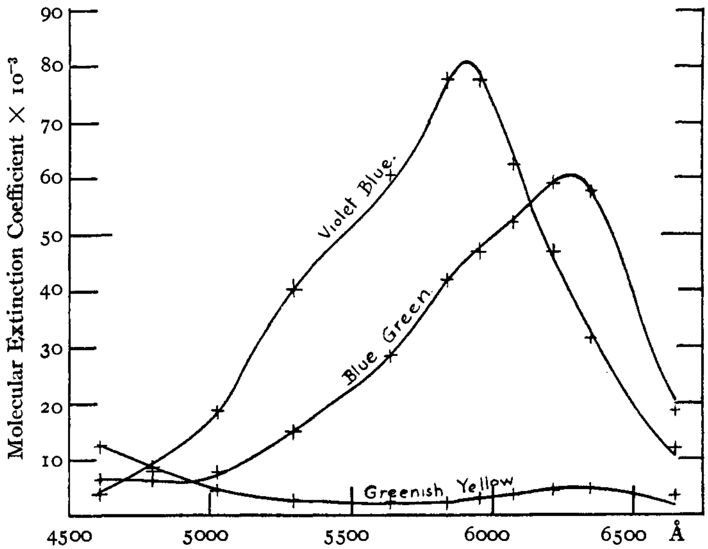

Fig. 2.—Absorption curves for crystal-violet.

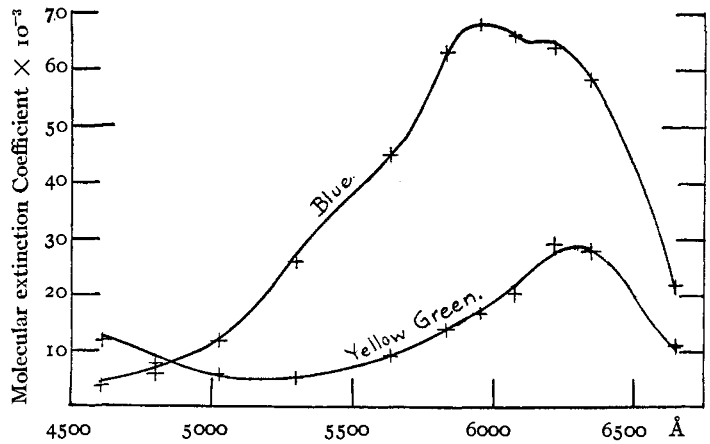

Fig. 3.—Absorption curves for crystal-violet.

produce the observed absorption of all the solutions. The presence of other colored substances would be possible only if their absorption were a linear function of that of two or all three of the fundamentals given above—a condition so improbable as to merit practically no consideration.

Such conclusions as are possible will now be drawn regarding the nature of the substances *initially* present in acidic solutions of crystal-violet. It is well known that the color of strong electrolytes is almost completely independent of the degree of ionization. The work of Hantzsch and others has shown that pseudo-bases, such as crystal-violet, *are* strong electrolytes in acid solution; hence the concentrations of colored forms found by colorimetric means are the sums of ionized and unionized forms. The researches of A. A. Noyes and his co-workers have shown that if γ_1 be the degree of ionization of a uni-univalent strong electrolyte in a solution of total ion-concentration C_1, then the degree of ionization, γ_{mn}, of a salt of valence product *mn* is equal to γ_1^{mn}. If now the ions of two chlorides ACl_p and BCl_q combine to form a $(p+q)$-valent ion the equilibrium constant for the reaction $AB^{[p+q]+} = A^{p+} + B^{q+}$ is

$$K = \frac{(A^{p+})(B^{q+})}{(AB^{[p+q]+})} = \frac{(\Sigma A)\gamma_1^{p}(\Sigma B)\gamma_1^{q}}{(\Sigma AB)\gamma_1^{p+q}} = \frac{(\Sigma A)(\Sigma B)}{(\Sigma AB)}$$

where (ΣA), (ΣB) and (ΣAB) are the total concentrations of ionized or un-ionized ACl_p, BCl_q and $ABCl_{p+q}$. Hence the equilibrium constant for the ions is identical with that for the total reagents, and mass-law considerations can be applied to the total concentrations in such reactions, of which those of crystal-violet with hydrochloric acid are typical cases. The solid violet substance is known to be $C_{25}H_{30}N_3Cl$, which, for brevity may be written **RCl**, hence it may be concluded that the violet fundamental is due to $\mathbf{RCl} \rightleftarrows \mathbf{R}^+ + Cl^-$, while the increase in the concentrations, relative to it, of the other colored forms with increasing acid concentration proves that they are formed from it by combination with acid. The amount of acid can be found by application of the mass law. In Table X are given values of the ratios $K_1 = \frac{(\Sigma V)(\Sigma H)}{(\Sigma G)}$, $K_2 = \frac{(\Sigma G)(\Sigma H)}{(\Sigma Y)}$, $K_3 = \frac{(\Sigma Y)(\Sigma H)}{(\Sigma C)}$, where (ΣV), (ΣG), (ΣY) and (ΣC) are the respective total concentrations of violet, green, yellow and initial colorless forms, and (ΣH) is the total acid concentration.

TABLE X.—MASS LAW CONSTANTS.

Color of solution.	Acid.	K_1.	K_2.	K_3.
Violet-blue	0.004 *N*	0.0160	...	...
Blue	0.016 *N*	0.0159	0.083	...
Blue-green	0.040 *N*	0.0168	0.066	...
Yellow-green	0.200 *N*	0.0152	0.072	3.4
Green-yellow	1.000 *N*	....	0.061	2.5

The substantial constancy of the first two ratios establishes the composition of the green and yellow forms as $\mathbf{RHCl_2} \rightleftarrows \mathbf{RH}^{++} + 2Cl^-$ and $\mathbf{RH_2Cl_3} \rightleftarrows \mathbf{RH_2}^{+++} + 3Cl^-$, respectively. There is also evidence, not entirely conclusive, that the "initial colorless" form is $RH_3Cl \rightleftarrows RH_2^{++++} + 4Cl^-$.

PART II.

Measurements of the Rate of Fading of Crystal-Violet in Acid Solution.

The slow changes in color intensity mentioned in the introduction take place at a rate and to an extent which increase with increasing acid concentration. With acid concentrations less than 0.0001 *N* no measurable fading occurs, while in normal acid the color fades rapidly and nearly disappears in the course of an hour. Miss A. Morse and Miss L. Vance, at the suggestion of Prof. H. C. Biddle, carried on an investigation of this fading, using a Stammer colorimeter. They demonstrated that the reactions involved are monomolecular in both directions and also found a much greater dependence on temperature than had been anticipated. The measurements were therefore repeated at 20.0°, using the instrument and concentrations of solutions employed in Part I of this investigation.

Constancy of temperature during the measurements was maintained by setting up the spectrophotometer in an air thermostat which was maintained at 20° ± 0.1° by means of an electric lamp. The entire equipment was placed directly over a large water thermostat constant at 20° ± 0.01, in which all solutions, tubes, etc., were permitted to come to constant temperature before the beginning of an experiment. The large heat capacity of the solutions must have prevented their following to any great extent the small and rapid fluctuations in the temperature of the air thermostat.

The reactions which produce colorless modifications of the chromogen from colored ones all take place in solutions extremely dilute with respect to chromogen, and so the only concentrations which can be changed appreciably are those of the colored and colorless substances. The reaction may therefore be represented as "colored $\leftrightarrows$ colorless;" and if, now, it be assumed that this reaction is monomolecular in both directions, the rate of the transformation of colored to colorless chromogen is expressed by the differential equation

$$-dC/dt = K_1C - K_2L, \tag{8}$$

where C and L are the concentrations at the time "*t*" of the colored and of the colorless substances, and K_1 and K_2 are the specific reaction rates of the direct and reverse reactions. Representing the initial concentration of chromogen by C_0, the values of C and L become $C_0\gamma$, and $C_0(1-\gamma)$, and equation (8) then reads

$$-d\gamma/dt = K_1\gamma - K_2(1-\gamma), \tag{9}$$

an equation giving the rate of change of γ, the fraction of chromogen which is colored. On integration this last equation becomes

$$\ln (\gamma/\gamma_\infty - 1) = -(K_1 + K_2)t + \ln (1 - \gamma_\infty) \qquad (10)$$

or

$$\ln (C - C_\infty) = -(K_1 + K_2)t + \ln (C_o - C_\infty). \qquad (11)$$

Changing to common logarithms and combining with equation (5) gives the two equations

$$\log (\log \tan \alpha - \log \tan \alpha_\infty) = \frac{-K_1 + K_2}{2.303} t + \log (\log \tan \alpha_o - \log \tan \alpha_\infty). \qquad (12)$$

$$\gamma_\infty = \frac{\log \tan \alpha_\infty}{\log \tan \alpha_o}. \qquad (13)$$

At equilibrum equation (9) becomes, $K_1\gamma_\infty - K_2(1 - \gamma_\infty) = 0$, whence

$$K_2 = \gamma_\infty (K_1 + K_2), \qquad (14)$$

an equation by which the separate specific reaction rates may be calculated.

It follows that if log (log tan α — log tan α_∞) be plotted against the time there should result a straight line whose slope is $(K_1 + K_2)/2.303$ and from whose intercept γ_∞ may be calculated by equation (13).

From equation (7) it may be inferred that the accuracy of the measurements suffers if α varies too widely from 74° (or the corresponding angle in the other half quadrants). The wave lengths at which rate measurements were made were so chosen as to give as high an accuracy as possible, hence in the more acid solutions a change to another wave length was made when the absorption of the solution became too small. The observed values of α are given in Table XI.

The mode of calculating the average value of α used in Part I automatically eliminates two sources of error of single measurements: that due to the angle between the zero of the scale and the position of crossing of the Nicol prisms (found to be 1.1°), and that due to inequality of illumination of the two sides of the spectrophotometer. To make the first correction, 1.1° was added to all the observed angles before taking the logarithmic tangent; to make the second, 0.1° has been added to left-hand readings and subtracted from right-hand readings in the case of the violet-blue solution. In the other cases the correction has been made either by averaging equal numbers of right-hand and left-hand observations or by drawing the best representative line of the plot midway between those determined by the two sets of readings.

Since in the more slowly changing solutions several minutes are required to produce a change of 0.1° in α, in these cases two or more readings have been reduced to the same half quadrant and averaged before taking logarithmic tangents, and the times of readings likewise averaged.

TABLE XI.—AVERAGE VALUE OF α REDUCED TO SECOND HALF-QUADRANT.

Color.	Violet-blue.		Blue.		Blue-green.		Yellow-green.		Green-yellow.	
Conc. HCl	0.004 *N*.		0.016 *N*.		0.040 *N*.		0.20 *N*.		1.00 *N*.	
Conc. chromogen	2.0×10^{-6} m.		5.0×10^{-6} m.		20×10^{-6} m.		50×10^{-6} m.		50×10^{-6} m.	
	Mean Time.	Mean α.	Mean Time.	Mean α.	Mean Time.	Mean α.	Mean Time.	Mean α.	Mean Time.	Mean α.
	λ 5839.		λ 5295.		λ 5025.		λ 5295.		λ 5839.	
	Min. Sec.		Min. Sec.		Min. Sec.		Min. Sec.		Min. Sec.	
	5	80.4°	5	76.6°	3	79.5°	3^{30}	84.1	3	70.4°
	8	80.3	7	76.6	4	78.6	4	83.6	4	68.2
	10	80.1	9	76.2	6	77.7	5	82.5	5	67.8
	37	79.4	13	75.7	8	77.5	6	81.1	6	65.7
	41	79.5	17	75.4	29	70.6	7	80.8	7	65.2
	70	78.8	21	74.8	32	69.7	8	79.5	8	63.0
	71^{30}	78.9	25	74.0	35	69.2	9	78.3	9	62.9
	105	78.3	29	73.4	43	66.2	10	76.7	10	61.4
	106^{30}	78.3	33	72.9	45	66.1	11	75.7	∞	46.60
	120^{30}	77.9	39	72.0	46^{30}	65.8	12	75.0	..	...
	122^{30}	78.1	47	71.4	∞	51.22	13	74.1	λ 6348	
	124^{30}	78.0	55	70.5	..	...	14^{15}	72.6	12^{30}	71.5
	126	78.0	63	69.6	λ 5295		15	71.0	13	70.6
	∞	77.18	73	68.5	38^{30}	81.1°	16	70.0	14^{30}	67.9
			81	67.8	40^{30}	80.7	17	68.1	15	67.7
			91	67.0	41^{30}	80.3	18	67.9	16	66.4
			∞	57.50	48	78.9	∞	48.07	17	65.0
					49^{30}	78.3	..	...	18	64.5
					68	73.8	λ 5636		19	62.0
					69^{30}	72.9	16^{40}	82.7	20	61.0
					72^{30}	72.1	17^{30}	81.8	22	59.1
					75	72.3	18^{30}	80.9	27	55.8
					∞	56.63	19	80.9	28	56.2
							20	79.6	∞	47.65
							21	78.1		
							22	77.0		
							29	69.2		
							30	69.0		
							38	62.1		
							39	61.6		
							∞	50.19		
							λ 6073			
							37	78.2		
							38^{30}	76.4		
							39^{30}	75.2		
							40^{30}	74.4		
							41^{30}	73.7		
							42	73.1		
							56	63.8		
							58	62.8		
							60	61.8		
							∞	56.20		

Table XII.—Calculations from Rate Data on Blue-Violet Solution (taken at $\lambda = 5839$ Å).

No. of readings.	Mean time.	Mean α.	log. tan α.	$lt\alpha - lt\alpha_\infty$.	log Δ.
7	5	80.4	0.7718	0.1247	9.0959
4	8	80.3	0.7672	0.1201	9.0795
4	10	80.1	0.7581	0.1110	9.0453
4	37	79.4	0.7278	0.0807	8.9069
4	41	79.5	0.7320	0.0849	8.9289
4	70	78.8	0.7033	0.0562	8.7497
4	71^{30}	78.9	0.7073	0.0602	8.7796
4	105	78.3	0.6838	0.0367	8.5647
4	106^{30}	78.3	0.6838	0.0367	8.5647
4	120^{30}	77.9	0.6688	0.0217	8.3365
4	122^{30}	78.1	0.6763	0.0292	8.4654
4	124^{30}	78.0	0.6725	0.0254	8.4048
4	126	78.0	0.6725	0.0254	8.4048
	∞	77.18	0.6471	..	..

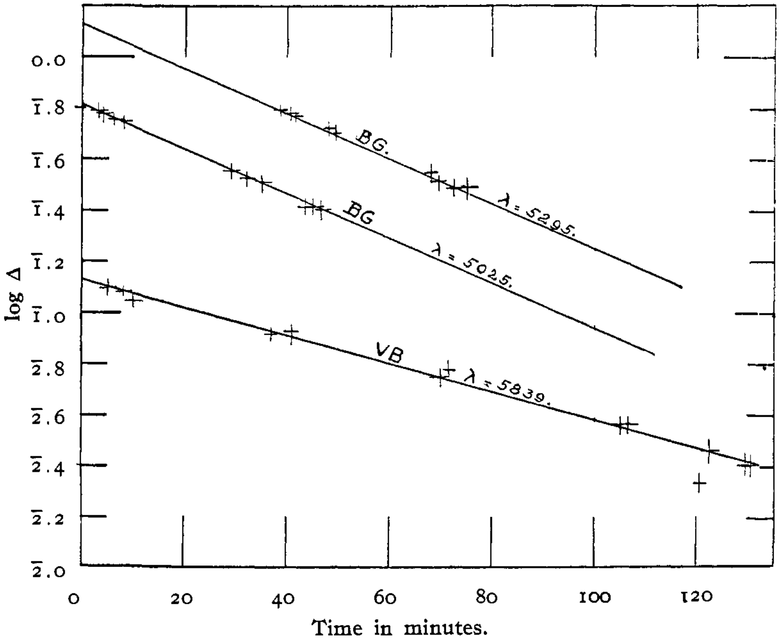

Fig. 4.

The calculation of the left-hand member of equation (12) is given for the violet-blue solution in Table XII, in which the first column gives the number of readings averaged, the second and third columns the average time and average α, the fourth column gives log tan α, the fifth log tan α—log tan α_∞ and the sixth log (log tan α — log tan α_∞), which has been called log Δ. The values of α_∞ are taken from Part I, Table V. The calculations from the other solutions were made in the same way. The results of these calculations are shown graphically on Figs. 4 to 7.

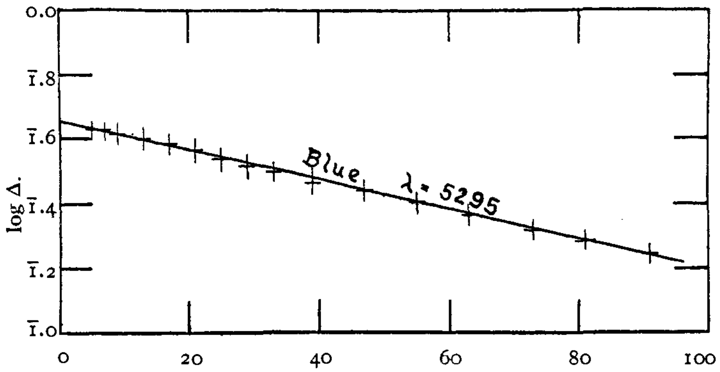

Fig. 5.

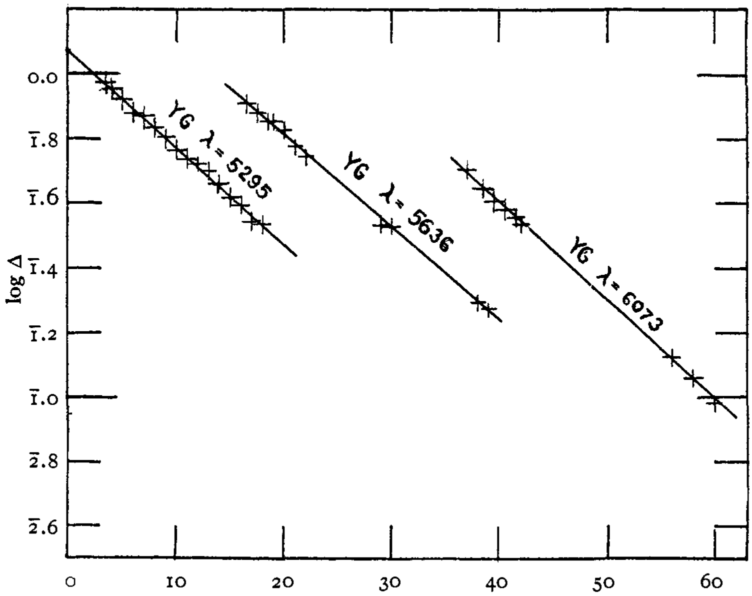

Fig. 6.

Table XIII gives in the first two columns the intercept and slope of the lines of these plots, in Column three the values of γ_∞ calculated by equations (12) and (13), and in Column five the value of K_2 from equation (14). K_1 is obtained by difference and is given in Column four.

The effect of increasing acid concentration on the rates of the reactions "colored $\rightleftarrows$ colorless" is to cause the rate of the direct reaction to increase continuously although not proportionately, and the rate of the reverse reaction to pass through a minimum.

Table XIII.

Color.	$(K_1+K_2)/2.303$. Mean slope.	Intercept.	γ_∞.	K_1.	K_2.
Violet-blue	0.00525	$\bar{1}.113$	0.838	0.00202	0.0101
Blue	0.00456	$\bar{1}.657$	0.301	0.0073	0.00316
Blue-green	0.00874	$\bar{1}.817$ 0.124[1]	0.120	0.0177	0.00241
Yellow-green	0.0295	0.072 0.384[2]	0.0348	0.0656	0.00237
Green-yellow	0.0350	$\bar{1}.716$[3]	0.0452	0.0768	0.00364

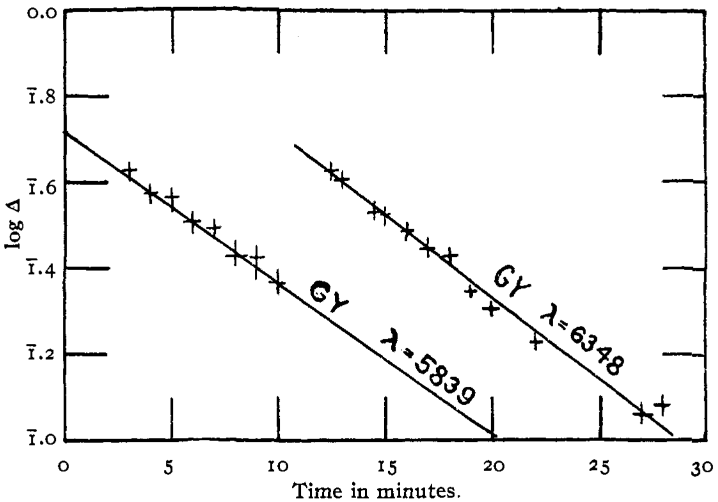

Fig. 7.

PART III.

Discussion.

The composition of the colored ions has been definitely established in Part I. Comparison with Table I shows that they are to be identified with the three quinoid ions there given, and since they are in rapid tautomeric equilibrium with three of the benzoid ions the concentrations given in Table IX are the sum of the concentrations of the two tautomers, and there appears to be no way of ascertaining the separate concentrations.

The carbinol forms, like the benzoid ions above, are colorless, hence the measurement of their concentrations must of necessity be indirect. The

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[1] γ_∞ has been calculated from this intercept ($\lambda = 5295$) since readings at the shorter wave length ($\lambda = 5025$) were less reliable.

[2] γ_∞ has been calculated using both intercepts ($\lambda 5295$, $\lambda 5636$).

[3] $\lambda = 5839$.

study by Hantzsch and others of the equilibrium between carbinol, violet ion and hydroxyl ion in alkaline solutions, shows that the concentration of carbinol becomes very small in neutral solution; it is *a fortiori* negligible in acidic solutions. The concentration of the ion $\underset{H^+}{ROH}$ may be inferred from the rates of reaction in neutral solution in the two directions. The rate of fading, K_1, from Table XIII, is 0.002 min.$^{-1}$ in 0.004 *N* acid and is presumably still less in neutral solution, whereas Biddle[1] has found the rate of the *reverse* reaction in neutral solution too great to measure. It may therefore be concluded that at equilibrium the carbinol ion concentration is certainly less than 0.1% and probably less than 0.01%, and when the violet ion concentration is diminished by acidification will decrease in the same ratio. From the definition of γ_∞ (see equation (10)) it follows that $(1/\gamma_\infty - 1)/(Y)$ is the ratio of *total* carbinol concentration to the concentration of yellow ion (plus its tautometer); the values of this ratio are given in Table XIV.

TABLE XIV.

Color of solution.	(HCl)	(Y)	$(1/\gamma_\infty - 1)/(Y)$	$K_1/(Y)$
Violet-blue	0.004 *N*.	0.011	18	[0.184]
Blue	0.016	0.090	25.8	0.081
Blue-green	0.040	0.298	24.6	0.060
Yellow-green	0.20	0.690	41.6	0.097
Green-yellow	1.00	0.685	32.3	0.112

The ratio will be seen to be fairly constant, increasing slightly[2] with increase in acid concentration. This is evidence that the carbinol $\underset{H^+}{\overset{H^+}{H^+\mathbf{R}OH}}$ is the principal colorless form in strongly acidic solutions. As for the compound $\underset{H^+}{H^+\mathbf{R}OH}$ we know only that its concentration at equilibrium is never large, although it may constitute, in some solutions, a large part of the total carbinol.

It is also possible to draw some conclusions as to the rates of the various reactions. The reaction $\mathbf{R}OH \longrightarrow \mathbf{R}^+ + OH^-$ is very rapid, as has been mentioned above; the reverse reaction takes place rapidly is strong alkali. The observation of Biddle[1] that the rate of development of color in solutions of the carbinol between neutrality and 0.01 *N* acid is given by the formula $A + B/(\Sigma H)^2$ indicates that the reaction proceeds at a rate, A, unaffected by the acid concentration, increased by a rate $B/(\Sigma H)H^2$ where

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[1] *Loc. cit.*

[2] If any importance is to be attached to this increase it is evidence that compounds exist containing more H^+ than the carbinol $\underset{H^+}{\overset{H^+}{H^+\mathbf{R}OH}}$.

(ΣH) is the acid concentration. The second term is to be attributed to the reaction $\mathbf{R}\mathrm{OH} \longrightarrow \mathbf{R}^+ + \mathrm{OH^-}$; for the formula holds in a region where the rate of reaction due to the carbinol is considerable, and so must be one of the terms, and this term must also diminish with increasing concentration of hydrogen ion since the carbinol concentration does so. Then the first term in the formula must be identified with the rate of the reaction $\underset{\mathrm{H}+}{\mathrm{H^+}}\mathbf{R}\mathrm{OH} \longrightarrow \underset{\mathrm{H^+}}{\mathrm{H^+}}\mathbf{R}{+} + \mathrm{OH^-}$, in order to account for the presence of the inverse square of the acid concentration in the second term. It is also necessary that the ion $\underset{\mathrm{H^+}}{\mathrm{H^+}}\mathbf{R}\mathrm{OH}$ constitute the largest part of the total carbinol concentration, for otherwise the first term would also be a function of the acid concentration. Since the rate of the reverse reaction, K_2 (see Table XIII) continues to increase after the concentration of green, and therefore of $\underset{\mathrm{H^+}}{\mathrm{H^+}}\mathbf{R}\mathrm{OH}$, has reached a maximum it must be concluded that the reaction $\overset{\mathrm{H^+}}{\underset{\mathrm{H^+}}{\mathrm{H^+}}}\mathbf{R}\mathrm{OH} \longrightarrow \overset{\mathrm{H^+}}{\underset{\mathrm{H^+}}{\mathrm{H^+}}}\mathbf{R}{+} + \mathrm{OH^-}$ is also taking place. The last column of Table XIV gives the ratio of K_1 to the concentration of yellow. The approximate constancy of this ratio shows that the reaction $\overset{\mathrm{H^+}}{\underset{\mathrm{H^+}}{\mathrm{H^+}}}\mathbf{R}{+} + \mathrm{OH^-} \longrightarrow \overset{\mathrm{H^+}}{\underset{\mathrm{H^+}}{\mathrm{H^+}}}\mathbf{R}\mathrm{OH}$ (or the equivalent $\underset{\mathrm{H^+}}{\mathrm{H^+}}\mathbf{R}{+} + \mathrm{H_2O} \longrightarrow \overset{\mathrm{H^+}}{\underset{\mathrm{H^+}}{\mathrm{H^+}}}\mathbf{R}\mathrm{OH}$) is the principal one taking place in acidic solutions.

In conclusion, a few words as to the relation between the color and constitution of crystal-violet will not be out of place. From the electromagnetic theory, absorption of light can result only from the sympathetic vibration of charged particles. These particles may be either electrons or ions, and the study of the ultraviolet and infra-red absorptions of such substances as quartz, rock salt, water and carbon dioxide, has shown that resonance periods in the former region are in general due to electrons, in the latter to charged radicals. Resonance periods in the visible spectrum may therefore be due either to ions vibrating at a frequency unusually high or to electrons of unusually low frequency. The latter condition might be expected in an ion in which tautomeric shift would involve the virtual passage of an electron from one end of the ionic structure to the other. Thus phenolphthalein, which Wegscheider[1] and Rosenstein[2] have

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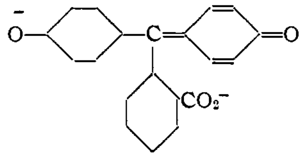
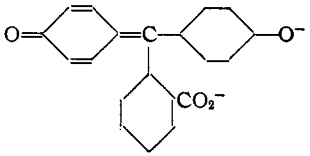
[1] R. Wegscheider, *Z. Electrochem.*, 14, 510 (1908).

[2] L. Rosenstein, THIS JOURNAL, 34, 1117 (1912); L. Rosenstein and E. Q. Adams, *Ibid.*, 35, 1883 (1913).

shown to assume color only when the dibasic ion is formed, has then the structure



which can become



by the type of transformation just mentioned. Continuous alternation between the two forms is equivalent to the oscillation of a single electron between the positions. The frequency of such an oscillation might be expected to be less than that of an electron limited in its motion to the dimensions of a single atom, and therefore to give an absorption band in the visible rather than in the ultraviolet. In the case of crystal-violet a similar relation exists between the ions $\overset{+}{\mathbf{R}}$, $+\mathbf{R}$ and $\underset{+}{\mathbf{R}}$, and between $\underset{H^+}{\overset{+}{\mathbf{R}}}$ and $\underset{H^+}{+\mathbf{R}}$, and both these forms, as has been experimentally shown, have great absorbing power. The much weaker color of the yellow ion can be accounted for by its quinoid structure, which is capable of producing a yellow color even where no electronic shift beyond a single benzene ring seems possible.

Rosaniline and para-rosaniline give ions which are similar to those of crystal-violet and may be represented by the same symbols. It is therefore to be expected that the rosanilines would have the same number of absorption bands as crystal-violet and the relative position of the three is indeed found to be the same. The first two absorption bands are, however, much closer together, so that on casual observation the first two colors are hardly distinguishable. In the case of malachite green (which has two amine nitrogens) only the ions $\overset{+}{\mathbf{R}}$ and $+\mathbf{R}$ are related as indicated above; it therefore should have only the two last colors of crystal-violet, and such is again the case. The interesting and important problem remains to apply similar considerations to other derivatives of triphenyl methane and related substances.

BERKELEY, CAL.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

CERTAIN DERIVATIVES OF IODOANIL.[1]

BY C. LORING JACKSON AND E. K. BOLTON.

Received April 23, 1914.

This paper contains a description of the conclusion of our work upon

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[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Elmer Keiser Bolton.