TABLE VI

HEAT CONTENTS AND ENTROPIES OF MANGANESE AND MANGANOUS OXIDE ABOVE 298.1° K. AND THE FREE ENERGY OF FORMATION OF MANGANOUS OXIDE AT 100° INTERVALS

	Mn		MnO			MnSO₄	
T, ° K.	$H_T - H_{298.1}$. cal./g. f. w.	$S_T - S_{298.1}$, cal./deg. g. f. w.	$H_T - H_{298.1}$. cal./g. f. w.	$S_T - S_{298.1}$, cal./deg. g. f. w.	ΔF of formation. cal./g. f. w.	$H_T - H_{298.1}$. cal./g. f. w.	$S_T - S_{298.1}$, cal./deg. g. f. w.
298.1					−86,760		
400	660	1.89	1130	3.26	−84,970	2680	7.70
500	1364	3.46	2280	5.82	−83,240	5630	14.28
600	2100	4.80	3470	7.99	−81,520	8850	20.14
700	2874	5.99	4680	9.85	−79,820	12210	25.32
800	3668	7.05	5900	11.48	−78,120	15710	29.99
900	4480	8.00	7150	12.95	−76,430	19280	34.18
1000	5328	8.90	8430	14.30	−74,730	22970	38.07
1012α	5438	9.01					
1012β	6053	9.62					
1100	6750	10.26	9750	15.56	−73,000	26730	41.65
1200	7734	11.11	11100	16.73	−71,260		
1300	8672	11.86	12470	17.82	−69,500		
1340β	9040	12.14					
1340γ	(9220)	(12.28)					
1400	(9770)	(12.69)	13840	18.84	−67,740		
1500	(10690)	(13.33)	15210	19.79	−65,980		

given by Rossini.[9] The three lowest of Aoyama and Oka's points lie within a few hundred calories of values interpolated from Table VI, which may be said to be in good agreement. In general, however, their data give a larger ΔH and ΔS for the reaction than may be calculated from the third law.

Summary

The heat of formation of manganous oxide has been determined to be −92,040 ± 110 calories per g. f. w. and of manganous sulfate to be

−254,180 ± 250 calories per g. f. w. at 25°.

The heat contents of manganese, manganous oxide, and manganous sulfate from room temperature to temperatures between 811 and 1500° have been determined. These observations have disclosed a transition in manganese at 739°.

A table summarizing increments of heat contents, entropies and free energies at 100° intervals has been prepared from these data and others in the literature.

Isomers of Crystal Violet Ion. Their Absorption and Re-emission of Light

BY GILBERT N. LEWIS, THEODORE T. MAGEL AND DAVID LIPKIN

The possibility of a new type of isomerism in such substances as triphenylmethyl and its ions was pointed out recently.[1] An extensive investigation of the light absorption of the free radicals has not given us positive evidence of such isomerism.[2] On the other hand, in the derivatives

(1) Lewis and Calvin. *Chem. Rev.*, **25**, 273 (1939).

(2) The two absorption bands of triphenylmethyl in the visible which were obtained by Meyer and Wieland [*Ber.*, **44**, 2557 (1911)] and which were resolved into three bands by Anderson [THIS JOURNAL, **57**, 1673 (1935)] were shown by Dr. O. Goldschmid [Ph.D. Thesis, University of California (1939)] to be vibrational bands belonging to a single electronic band. This was shown by comparison of the absorption and fluorescence spectra of triphenylmethyl. We have further confirmed his results, but with a very high resolution we have found a much more intricate structure. This will be discussed in another place.

of triphenylmethyl ion we have sought, and believe to have found, these isomers.

It is often observed that the absorption curve of what is apparently a single substance, such as the ion of crystal violet (tris-(dimethyl-p-aminophenyl)-methyl ion, Fig. 6) as it exists in neutral or alkaline solution, has a shoulder as seen in Fig. 1. This shoulder suggests the superposition of two neighboring bands, which might result from (1) a partial resolution of the vibrational structure belonging to a single electronic level, which, according to the work of Dr. Goldschmid,[2] seems to be the explanation of a similar shoulder in the adsorption curve of methylene blue, or (2) two neigh-

boring electronic levels, or finally (3) two isomers in rapid equilibrium with one another. We shall find that it is the last of these theories which accounts for the crystal violet spectrum. In the experimental work that has led to this conclusion several perplexing phenomena have appeared which will be dealt with in their turn, and about 200 absorption curves have been obtained, of which only a few can be shown.

When we study the light absorption of crystal violet in a variety of solvents the curves fall roughly into three classes, exemplified by the solid curves in Figs. 1, 2 and 3. In each curve the ordinates (α) are proportional to the molar extinction coefficient, ϵ, the proportionality factor

Fig. 3.—Relative extinction coefficient of 10^{-6} M crystal violet (chloride) in toluene containing 0.1% β-naphthol at 293°K. Curve A is malachite green curve in same solvent, displaced. Curve B obtained as in Fig. 1. In this case the actual experimental points are shown.

being so chosen that in each case $\alpha_{max.}$ is unity.[3]

In order to show that in all three cases the absorption curve is a summation of two bands which differ in position and relative height, we may use a crude but apparently effective mode of analysis. We have noticed that the absorption curve of malachite green, which shows no pronounced shoulder, if displaced horizontally to bring the maximum into coincidence with that of the crystal violet curve, coincides with the latter in the whole left-hand portion. This is shown in Fig. 3 where the open circles represent experimental points for malachite green and the black circles those for crystal violet. If we assume now that this coincidence would continue all the way for the first (A) band of crystal violet, then we may construct the other (B) band by subtracting the dashed from the solid curve. When this is done we obtain the dotted curve which is marked B. Similarly, using the malachite green curve for the corresponding solvent we have obtained the A and B bands in Figs. 1 and 2.

It seems that in spite of the different appearance of the three solid curves of Figs. 1–3, they differ chiefly in the positions and the relative intensities of the A and B bands.

All of the solvents which we have studied can be classified roughly according to the resemblance of the absorption curves of crystal violet in the several solvents to the curves of Figs. 1, 2 and 3.
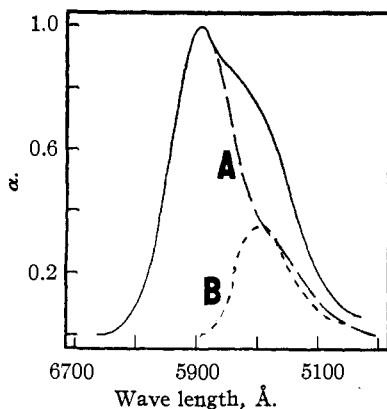

Fig. 1.—Relative extinction coefficient of 10^{-6} M crystal violet (chloride) in absolute ethanol at 293°K. (solid curve). Curve A (dashed line) is the curve of malachite green in ethanol, displaced horizontally to coincide with solid curve at maximum. This is also assumed to be the A band of crystal violet. Curve B (dotted) obtained from the two other curves by subtraction.
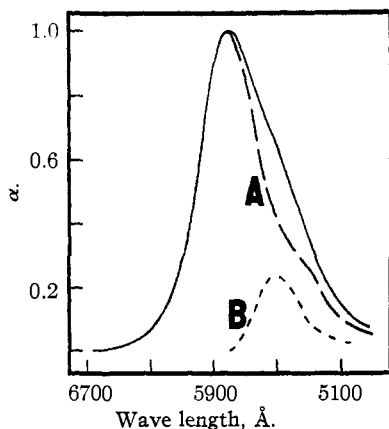

Fig. 2.—Relative extinction coefficient of 5 × 10^{-7} M crystal violet (chloride) in chloroform at 293°K. Curve A, malachite green curve in chloroform, displaced. Curve B obtained as in Fig. 1.
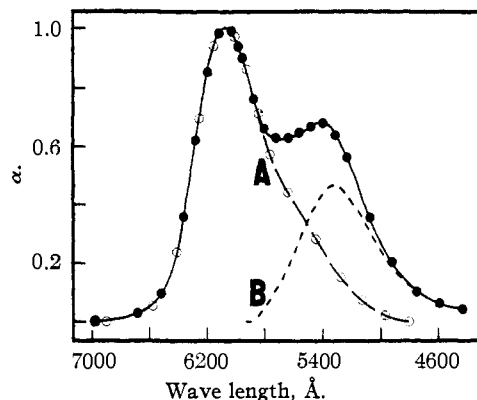
(3) We have chosen this method of representation best to display the shapes of the several curves. Furthermore, our determinations of relative extinction are far more accurate than our absolute values. The values of $\epsilon_{max.}$ that we actually obtained for these three curves were 8.1 × 10⁴ in absolute ethanol. 8.5 × 10⁴ in chloroform and about 7 × 10⁴ in toluene.

Class I comprises all the solvents that we have examined of high, or moderately high, dielectric constant: namely, ethanol, methanol, *t*-butanol, water, glycol, glycerol, glucose (supercooled), ethylene chlorohydrin, methyl cyanide, acetone, acetaldehyde, glacial acetic acid, pyridine, and aniline. In all of these λ_{max}. (A) lies between 5830 and 5940 Å., except that aniline gave 5990 Å.

Class II comprises chloroform,[4] *trans*-dichloroethylene, methyl iodide, chlorobenzene and a saturated solution of chloral hydrate in water. For all of these λ_{max}. (A) lies between 5780 and 5800 Å., except for chlorobenzene, 5940 Å. It will be noted that all of these solvents of Group II contain halogen and therefore have, if not for the molecule as a whole, at least for some part of it, a considerable dipole moment.

On the other hand, the tetrahedrally symmetrical carbon tetrachloride and the linearly symmetrical carbon bisulfide, both with high bond moments, fall into our third class, which also contains toluene, hexane, dioxane, isopentane, ether, methylal, carbon tetrachloride and carbon bisulfide. Here λ_{max}. (A) varies widely from 5930 Å. for methylal to 6140 Å. for carbon bisulfide. In all of these solvents small amounts of phenol, β-naphthol or ethanol were added to make the crystal violet chloride soluble. It seems to make no difference in the absorption curve which is used or at what concentration, provided that it does not exceed 1 or 2%.

The observation by Lewis and Seaborg[5] that crystal violet can be made to dissolve freely in toluene by the addition of a small amount of a substance with labile hydrogen seemed to show "that crystal violet in toluene forms complexes with alcohols and acids, and the stability of these compounds reaches a maximum in the case of phenol." At first it seemed likely that such complexes, formed by hydrogen bonds at the nitrogen atoms, might account for the peculiarities in the absorption curve of Fig. 3. However, it was later found that other salts of crystal violet (perchlorate, iodide, acetate) are of themselves soluble in toluene, and in one experiment pure, dry crystal violet acetate was dissolved in very dry toluene. The absorption curve was identical with that of Fig. 3.

Absorption Spectra in Alcohol and Other Solvents of Class I.

Solutions in solvents of Class I are the only ones, as we shall see, in which we have the isolated ion of crystal violet. In these solvents the absorption curve proves extremely insensitive to any isothermal change.[6] In alcohol identical curves were obtained at 10^{-4} and 10^{-6} M, and in less exact measurements over a still wider range. Moreover, the curve was in no way affected by the nature of the anion (chloride, bromide, acetate or perchlorate). Even when large amounts of sodium chloride or bromide were added (10^{-2} M) the absorption curve was not altered.

Even the change from one to another solvent of Class I has, as we have seen, very little effect upon the absorption spectrum. The formation of complexes through hydrogen bonds,[7] which we have just shown to have no effect upon the spectrum in toluene, appears also to have very little effect in solvents of Class I. From cases where these complexes should be prominent, such as glacial acetic acid and ethanol containing considerable amounts of phenol, to cases such as acetone and pyridine, where such complexes must be absent, there is an increase in λ_{max}. of only about 50 Å.

When the temperature of the alcoholic solution is lowered, beginning at room temperature, there is a gradual but readily noticeable change in the character of the absorption curve. The shoulder (B band) becomes less marked and nearly disappears as we approach the temperature of liquid air. This phenomenon occurs in methanol and ethanol. We have studied most carefully ethanol containing 5% water,[8] the curves being shown in Fig. 4. Here again we have made α_{max}. = 1 for each curve. As we go to lower temperatures there is the usual slight steepening of the curve at the left. The value of ϵ_{max}., allowance having

(4) Mr. J. Biegeleisen, to whom we are indebted for several of our absorption curves, has measured the absorption of crystal violet in mixtures of chloroform and ethanol. The curves change continuously from one pure solvent to the other, the main difference being in the height of the B band which, relative to that of the A band, is 0.22, 0.35, 0.38, 0.40 and 0.40 with 0, 25, 50, 75, and 100% ethanol.

(5) Lewis and Seaborg, THIS JOURNAL, 61, 1894 (1939).

(6) It is true that in water at very high concentration (2×10^{-3} M) a new absorption band at about 5400 Å. was found by Holmes [*Ind. Eng. Chem.*, 16, 35 (1924)] which probably is due to a dimeric ion such as has recently been studied experimentally and theoretically in the case of the thionine dyes by Rabinowitch and Epstein [THIS JOURNAL, 63, 69 (1941)].

(7) It was noted by Lewis and Seaborg[5] that the trinitrotriphenylmethide ion seems to form complexes with substances like alcohol, phenol or acetic acid by attachment through hydrogen to the nitro groups, without causing any marked change in color. However, when hydrogen ion was similarly attached to a nitro group the color changed from blue to orange. In our present case the production of various solvates may be considered to produce slight shifts in the absorption band while the addition of hydrogen ion or other strong acid, such as stannic chloride [Lewis, *J. Franklin Institute*, 226, 293 (1938)], produces an altogether new absorption band. Evidently what has become known as the hydrogen bond differs not only in degree but in kind from a true chemical bond.

(8) It has been shown by Prietzschk [*Z. Physik*, 117, 482 (1941)] that a small amount of water greatly inhibits the crystallization of alcohol at low temperatures.
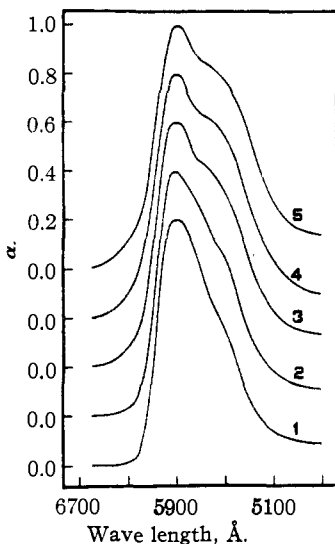
Fig. 4.—Relative extinction coefficient of 10^{-6} M crystal violet (chloride) in 95% ethanol at (1) 114°, (2) 162°, (3) 193°, (4) 240° and (5) 294°K.

been made for thermal contraction, increases 16 per cent. in going from 294° to 114°K. Some such increase is to be expected if we assume that much of the B isomer existing at room temperature has gone over to the A isomer at low temperature.

That the two bands are actually to be ascribed to two isomers is made nearly certain by a simple analysis of the absorption curves.[9] If we subtract from the other curves of Fig. 4 the one obtained at 114°K. we obtain a set of curves given in Fig. 5 (the scale is twice that of Fig. 4). Although in this subtraction of curves the errors are exaggerated,
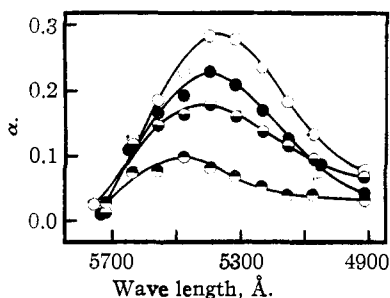

Fig. 5.—Curves obtained by subtracting successively Curve 1 from each of the other curves of Fig. 4. Since in this subtraction the experimental errors are greatly magnified the actual experimental data are shown.

(9) A previous detection of isomers by spectrophotometric methods occurred in the study of the infrared vibrational spectrum of o-chlorophenol. Two neighboring vibrational bands were found by Wulf and Liddel [THIS JOURNAL, **57**, 1464 (1935)] and attributed by Pauling [ibid., **58**, 94 (1936)] to cis and trans forms. This interpretation has been confirmed by Davies [Trans. Faraday Soc., **34**, 1427 (1938)] and more quantitatively by Zumwalt and Badger [THIS JOURNAL, **62**, 305 (1940)].

it is evident that the experimental points fall on curves which are essentially the same except for height. Even at 114°K. there must be some of the B isomer. Assuming the correctness of our calculation of the height of the B band at room temperature in Fig. 1, namely, $\alpha_{max.}$ (B) = 0.36, we obtain the following values for $\alpha_{max.}$ (B) at the several temperatures by adding 0.08 to the maximum values at the several temperatures shown in Fig. 5.

T, °K.	114	162	193	240	294
$\alpha_{max.}$ (B)	0.08	0.17	0.26	0.30	0.36

These values should be proportional to the ratio of the amount of B isomer to the amount of A isomer at each temperature. If we plot the logarithms of these values against $1/T$, all but the point at 193°K. lie on a straight line, from which we may conclude that we are dealing with an equilibrium between two substances. From the slope of the line we find that the B isomer has the greater energy by about 580 cal., while a similar but less exact set of measurements in pure ethanol gave 500 cal. On the other hand, the two isomers in their electronically excited states differ much more in energy. From $\lambda_{max.}$ (A) and $\lambda_{max.}$ (B) we find that the difference in energy is increased by 3300 cal.

The Nature of the A and B Isomers

We shall attempt to visualize the two isomers A and B with the aid of Fig. 6, which shows approximately the atomic distances in the crystal violet ion. Of the hydrogen atoms only the six in the ortho positions of the rings are shown. If the rings and the six ortho hydrogens were all to be in a plane, two adjacent hydrogens such as 2 and 6″ would be only about 0.5 Å. apart. Although the amount of repulsion of two such atoms is unknown, it must be considerable. The re-
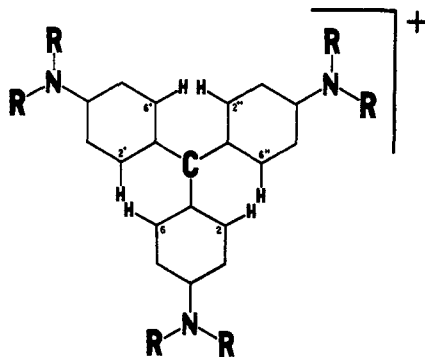

Fig. 6.—Representation of the crystal violet ion, the atomic distances being approximately to scale.

sulting strain can best be relieved by a small rotation of the benzene rings around their axes (the lines connecting the central carbon atom with an atom para to it). Such a rotation at the beginning meets no restoring forces, but these forces of restoration become large as the amount of rotation increases. The nature of these forces of restoration will best be understood if we ascribe to each bond from the central carbon atom one-third double bond character.

As a result of these rotations, we visualize the actual structure of the crystal violet ion as a non-planar one in which two adjacent ortho hydrogens have moved far enough from each other so that the force of repulsion is balanced by the force that opposes free rotation. If in the figure the atoms 2, 2' and 2" lie above the plane of the diagram and 6, 6' and 6" lie below, we have a model analogous to a windmill or propeller of three blades. It has complete screw or helical symmetry.[10] If in this model one pair of adjacent hydrogens such as 2 and 6" are forced by each other, or if one of the rings rotates through nearly 180°, we obtain a form like a propeller of three blades in which one blade is turned in the opposite sense from the other two. This distorted helical structure would presumably have more energy than the symmetrical one. Also, since the kind of resonance that favors light absorption would presumably be more inhibited, we should expect for it a lower value of $\lambda_{max.}$. On both these grounds we believe that our

Fig. 7.—Extinction of the same sample of malachite green in 95% ethanol, corrected for temperature expansion. (1) 114°K. and (2) 294°K.

isomer A is of the symmetrical helical type and isomer B is of the distorted helical type. The transition from one isomer to the other is apparently rapid in alcohol even at 114°K., so that presumably the heat of activation for isomerization is not more than 2 or 3 kcal. We cannot judge whether the actual process takes place chiefly through the rotation of one ring or the slipping by each other of two adjacent hydrogen atoms. The latter may occur only when the rings are momentarily separated by the vibrations of the molecule.

We have observed that the shoulder on the absorption band, indicating two isomers, is nearly always found in dyes of the triaminotriphenyl-methyl group. On the other hand, we know of no case in which it has been reported in the diaminotriphenylmethyl dyes such as malachite green (phenyl - bis - (dimethyl-p-aminophenyl) - methyl chloride). In these dyes the unsubstituted phenyl group does not participate in the main resonance of the molecule. It should, therefore, be nearly free to occupy various positions of rotation about its axis. We should expect, however, two positions to be of somewhat lower energy than the rest, corresponding to the A and B forms of crystal violet. In fact, we have found that at low temperatures the absorption curve of malachite green is resolved into two narrower bands A and B as shown in Fig. 7. The great increase in $\alpha_{max.}$ of 35% (correction having been made for temperature contraction of the solvent) and the appearance of the two narrow bands indicate pretty clearly that the molecules with varying positions of rotation that exist at room temperature, and each of which has a different $\lambda_{max.}$, have at the low temperature been largely converted into the A and B forms. Our experiments at several low temperatures show that the difference in energy between these two forms is too small to measure.

Absorption Spectra in Solvents of Classes II and III.—In solvents of low dielectric constant it has been shown by the work of Kraus and his associates[11] that the number of free ions is extremely small. While we have reason to believe that the number of free ions is greater in our case than in theirs, most of the dissolved salt must be present as ion pairs and larger ion clusters. It is the absorption spectra of such aggregates that we obtain in Figs. 2 and 3 and it is surprising, therefore, that these curves show as little difference as
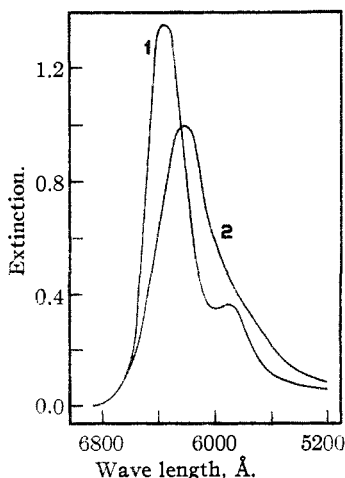
(10) The term symmetry is not used in the same sense as in discussing optical isomerism. Indeed, each of the two isomers here discussed must represent a pair of optical isomers, which may ultimately be resolved.

(11) For example, Fuoss and Kraus, THIS JOURNAL, 55, 3614 (1933), and Batson and Kraus, ibid., 56, 2017 (1934).

they do from the absorption curve of the free ion. Even this difference can be made to disappear in part.

The absorption curve in chloroform at 5×10^{-7} M is given again as Curve 1 of Fig. 8. As the concentration of the crystal violet is increased, at first there is little change in the curve except a slight broadening, but by the time we reach 1×10^{-4} M (Fig. 8, Curve 3) a shoulder appears at the position of the B band. This phenomenon, which looks at first like an ordinary case of polymerization, proves to be a real enhancement of the B band through a salt effect. Identical results may be obtained by adding foreign salts to the very dilute solution. Thus, Fig. 8, Curve 2 shows the absorption of 5×10^{-7} crystal violet in the presence of 10^{-2} M tetra-n-butylammonium iodide, and in this solution the absorption curve is independent of the crystal violet concentration. While the addition of the tetra-n-butylammonium iodide produces the same result as an increase in the concentration of the crystal violet chloride, its effectiveness is far less. When the solution contains only 10^{-4} M tetra-n-butylammonium iodide the absorption curve hardly differs from Curve 1.[12]

The salt effect is much less noticeable in solvents of Class III than in those of Class II, but a careful examination of many absorption curves

(12) We are thus led, merely by a careful inspection of absorption curves, to suspect the existence of a salt effect, in electrolytes such as crystal violet chloride, at concentrations far below those in which similar effects have been obtained with other electrolytes. Preliminary experiments fully justify this suspicion. While Vernon, Luder and Giella [THIS JOURNAL, **63**, 862 (1941)] found that the solubility of tetrabutylammonium iodide in benzene is about doubled in the presence of tetrabutylammonium picrate or nitrate at 10^{-3} M, we find similar and indeed greater effects with salts of crystal violet at concentrations as low as 10^{-6} M.

Vernon, Luder and Giella postponed a theoretical consideration but state that "it seems likely that association is the primary factor," and this is certainly correct. When a very dilute solution of a salt consists chiefly of the species X^+Y^-, $X_2^+Y_2^-$, $X_3^+Y_3^-$, ..., and we add a second salt which consists chiefly of the species X^+Z^-, $X_2^+Z_2^-$, $X_3^+Z_3^-$, ..., the species of one set will not sensibly affect the activities of the other species as such. However, new species are now possible, since we have what may formally be written as the two new species $X_3^+Y^-Z^-$ and $X_2^+Z^-Y^-$ for the quadruplet and $X_3^+Y_2^-Z^-$, $X_3^+Z^-Y_1^-$, $X_3^+Y^-Z_2^-$ and $X_3^+Z_2^-Y^-$ for the sextuplet. In the special case that Y^- and Z^- are sufficiently similar so that their interchange in the clusters produces little change in energy or entropy, but not similar enough so that the solid salts form solid solutions, the mutual solubility effect, when the equilibrium between species of each set is known, could be calculated from probability considerations alone.

In the crystal violet ion the positive charge may be considered to be shared equally by the three amino groups, and when a negative ion comes as close as possible to one of these groups, even allowing for induction, the resulting dipole moment must be at least 50% greater than in any of the ion pairs studied by Kraus. The ion pair should therefore be far less stable in our case, but on the other hand the higher multiplets, especially the sextuplet, should be extremely stable even at dilutions where other types of salts would show no appreciable association.
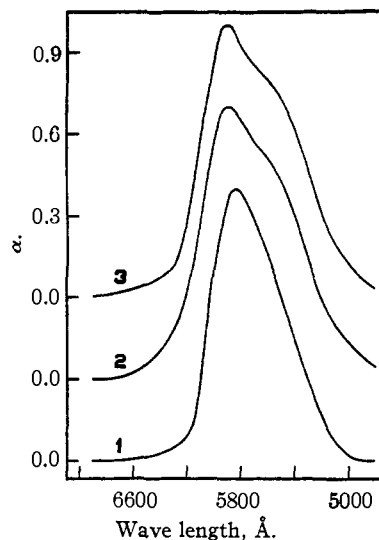

Fig. 8.—Relative extinction coefficient of crystal violet (chloride) in chloroform at 293°K.: (1) dye at 5×10^{-7} M; (2) dye at 5×10^{-7} M, but 10^{-2} M in tetra-n-butylammonium iodide; (3) dye at 1×10^{-4} M.

shows that the effect exists and, in this case also, increasing salt concentration brings the curve nearer to the curve in alcohol. In the solutions in toluene (plus β-naphthol) in going from 5×10^{-6} to $2 \times 10^{-4}M$, $\lambda_{max.}$ (A) remains unchanged but $\lambda_{max.}$ (B) becomes about 50 Å. greater and the B band appears to be a little broader. These changes in the B band may be reproduced and enhanced in the very dilute solutions in benzene or toluene by the addition of tetra-n-butylammonium iodide or silver perchlorate.[12]

For the difference between the absorption curves of Classes II and III we have no definite explanation. It appears not to be due to differences in dielectric constant and we may surmise that it depends upon the extent and the manner in which the solvent itself goes into the polyionic clusters, as it sometimes enters into crystals as "solvent of crystallization."

The Phosphorescent States of Crystal Violet.

—In studying the absorption curve of crystal violet in glycerol, we encountered a phenomenon so strange that it was not understood until we had turned aside to make a thorough study of the phosphorescent state.[13] The phenomenon is illustrated in Fig. 9 where Curves 1 and 2 show the measured extinction of a given sample of crystal violet in glycerol at 228° and 178°K., respectively. As we cool the solution from room temperature, there is a gradual increase in the ab-

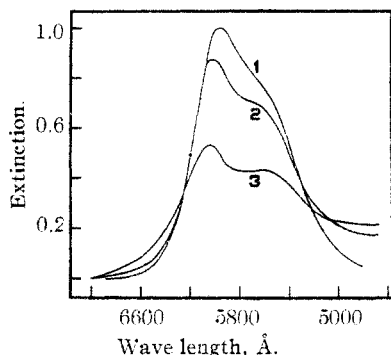(13) Lewis, Lipkin and Magel, THIS JOURNAL, **63**, 3005 (1941).

Fig. 9.—Extinction of a single sample of crystal violet (chloride) in glycerol: (1) at 233°K., with or without illumination by mercury arc; (2) at 178°K., no illumination except that used in measurements; and (3) at 178°K.. illuminated also by mercury arc.

sorption corresponding to the contraction of the medium. However, at about 200°K. the apparent absorption begins to diminish rapidly and the absorption curve becomes broader. The whole phenomenon occurs in the same range of temperature where Gibson and Giauque[14] found the specific heat of glycerol to diminish about one-half. It is in this range that glycerol changes from a very viscous liquid to a rigid glass, and it is in this same region that the solution of crystal violet in glycerol begins to phosphoresce. A similar diminution in the apparent absorption coefficient of crystal violet in alcohol appears when the temperature is so low that the alcohol is rigid.

We have shown that when fluorescein in a rigid solvent is exposed to intense illumination, the greater part of the molecules go over into the isomer that is characteristic of the phosphorescent state. In that case the phosphorescent molecules had an absorption in a different part of the spectrum from that in which the normal molecules absorbed. Unfortunately in the case of crystal violet the molecules in the phosphorescent state have an absorption of smaller intensity and lying in the same region as the normal absorption. It has not been possible, therefore, to obtain the pure spectrum of the isomeric phosphorescent state, but it probably is not far different from that shown in Curve 3 of Fig. 9, which is obtained when the sample is exposed to illumination of high intensity from a high-pressure mercury arc. The difference between Curves 1 and 2 was found to be due to illumination by the light used in the measurements. At 228°K., where there is no phosphorescence, Curve 1 was obtained regardless of the

(14) Gibson and Giauque. THIS JOURNAL. 45. 93 (1923)

intensity of the light to which the sample was exposed. At 178°K. the extinction at 5960 Å. fell off with increasing intensity of illumination in a way entirely parallel to that shown for fluorescein in Curve 2, Fig. 8, of our preceding paper.[13] The resemblance between Curves 2 and 3, the former being obtained with light containing almost no ultraviolet, indicates that the phenomenon is not connected with the green phosphorescence to be described later.

The Fluorescence and Phosphorescence Spectra.—We have already[13] mentioned and discussed the fact that crystal violet shows appreciable fluorescence only when the solvent is nearly in a rigid state; as in alcohol a little above the temperature of liquid air, in glycerol at about 215°K., and in supercooled glucose at room temperature. At these or slightly lower temperatures phosphorescence also appears.

When a solution of crystal violet, for example in glycerol, is illuminated at various temperatures with a mercury arc, and the phosphorescence observed, an apparently anomalous result is obtained. At 160°K. a bright red phosphorescence is seen, but at 90°K. the phosphorescence is green. It was found, however, that the green phosphorescence is due to an entirely distinct phosphorescent state which is excited only at wave lengths less than 4000 Å. When excited by visible light there is a strong red phosphorescence at the higher temperature (sufficiently intense to mask the green in the preceding experiment) which nearly disappears at the lower temperature. The visible red phosphorescence is nearly all due to an alpha band, the intensity of which diminishes as the temperature is lowered, but there is also a beta band that lies chiefly below the visible.

We have studied photographically the phosphorescence and fluorescence of crystal violet in glycerol at 178°K. From the spectrograms, together with suitable calibrations described later, we have obtained the Curves 1 and 2 of Fig. 10. The ordinates of each curve are proportional to the absolute emission at each wave length, but the ordinates of one curve are not comparable with those of the other. Curve 2 shows the spectrum of fluorescence accompanied by a small amount of phosphorescence. Curve 1 shows the pure phosphorescence spectrum as excited by visible light. For reference we give also Curve 3, the absorption spectrum, (Curve 1 of Fig. 9), as well as Curve 4, which is a rough determination of

the spectrum of the green phosphorescence. In both curves the ordinates involve an arbitrary factor. It will be seen that as in other cases the alpha band is identical with the band of fluorescence. This band diminishes as the temperature is lowered and nearly disappears at the temperature of liquid air.

The lifetime of the phosphorescent state is much less than that of fluorescein, being of the order of 10^{-1} second for the green phosphorescence and 10^{-2} second for the red and infrared phosphorescence. We have not, therefore, measured the heat of activation corresponding to the alpha process, but we may obtain it by the principle of Jablonski.[15] From the positions of the emission maxima of Fig. 9 we find that the fluorescent state is 43.8 kcal. and the phosphorescent state 38.0 kcal. above the ground state. The difference, which represents the heat of activation from the phosphorescent to the fluorescent state, is 5.8 kcal. When we compare this with the 9 kcal. similarly obtained for fluorescein in boric acid we understand why the alpha band of fluorescein disappears at only a little below room temperature, while the alpha band of crystal violet is still prominent at 178°K.

We believe that all of the observed fluorescence and phosphorescence of crystal violet are due to the A isomer alone. If we correct Curve 2 for the small contribution of phosphorescence (say 10% of Curve 1 as drawn) the fluorescence spectrum looks very like a mirror image of one of our A bands of absorption. If there were any contribution of isomer B to the fluorescence we should have an emission band to the right of Curve 2, and such a band is certainly missing. The situation seems to be analogous to that of *cis-* and *trans-*stilbene where we have shown[16] that *trans-*stilbene fluoresces strongly while *cis-*stilbene, the isomer of

greater steric strain, gives no observable fluorescence.

The green phosphorescence of crystal violet[17] which is stimulated by ultraviolet shows that the molecule is capable of existence in a second
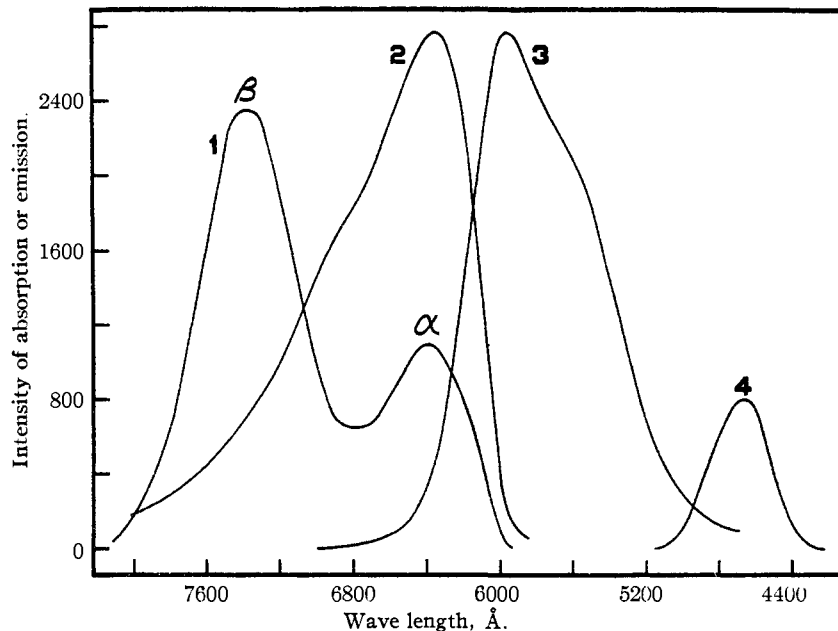

Fig. 10.—Curve 1: absolute intensity (except for an arbitrary constant) of the phosphorescent emission of crystal violet in glycerol at 178°K., showing the alpha and beta bands. Curve 2: similar absolute intensity of fluorescent emission (plus 5–10% phosphorescence), at 178°K. Curve 3: for reference. the absorption spectrum. Curve 4: intensity of green phosphorescence band (not corrected for plate characteristics).

phosphorescent state. That this green phosphorescence is due to a beta process is certain, since we have observed it down to 20°K. From the frequency of the emission maximum we find that the energy of the corresponding phosphorescent state is 60 kcal. above the ground state, while the phosphorescent state corresponding to the infrared beta emission we have seen to be 38 kcal. above the normal state. It would be interesting to find whether any dye has a still greater number of phosphorescent states. Such observations might clarify our ideas as to the exact nature of the phosphorescent state itself.

Evidence for Another Isomeric State.—In addition to the two stereoisomers A and B, and the two fleeting isomers or electromers produced from the former when it goes into its phosphorescent states, we have found some evidence of still another isomeric condition of the crystal violet ion in rigid media. When a colorless compound of

(15) Jablonski. Z. Physik. **94**, 38 (1935).

(16) Lewis. Magel and Lipkin. THIS JOURNAL. **62**. 2973 (1940).

(17) Nearly half a century ago in a similar dye. methyl violet. a green phosphorescence was observed by Schmidt [Ann. Physik. **58**, 103 (1896)].

crystal violet ion with a strongly basic anion such as cyanide, borate or sulfide is ionized, the crystal violet ion would initially have a pyramidal structure and in a rigid solvent might have difficulty in going over to one of the nearly planar forms which are strongly colored. In fact, we sometimes find that, when one of these compounds, in a rigid solvent at liquid air temperature, is illuminated by ultraviolet light, the solution remains colorless or nearly so, but after the illumination has ceased and the solution is slowly warmed the characteristic absorption of crystal violet appears, although the color may disappear at a still higher temperature. This phenomenon is being further investigated.

Experimental

Many of our experiments were made with commercial crystal violet but for all crucial cases the dye was purified as follows. To a large volume of nearly saturated crystal violet chloride in water a small amount of sodium hydroxide was added. After the lapse of sufficient time for the formation of the carbinol, the latter was extracted by shaking several times with benzene and discarded. To the remaining aqueous solution a larger amount of sodium hydroxide was added to convert about one-half of the chloride into carbinol. This was shaken into benzene and kept. This last solution was shaken several times with water containing a little hydrochloric acid, and finally with water containing hydrochloric acid equivalent to one-half the remaining carbinol. From the aqueous solution thus obtained, after washing with benzene, the final product was obtained by crystallization. Other salts of crystal violet were obtained in a similar way.

The absorption and emission of light were measured by methods which we have already described.[13] In the present case the fluorescence and phosphorescence spectra shown in Fig. 10 were obtained as absolute values, except for a constant factor attending each curve, in the following way. On the same plates as the emission spectrograms, photographs were taken, through wire screens of varying transparency, of the light from a tungsten lamp operating at a color temperature of 2430°K. From the photometric tracings of all the plates, and from the known spectral distribution of the lamp, the absolute emission spectra were obtained by familiar methods.

Summary

The absorption of light by crystal violet has been studied under varying conditions and in numerous solvents. With respect to the appearance of the absorption curves solvents may be roughly placed in three classes, of which the first is typified by ethanol, the second by chloroform, and the third by toluene. All three types of curves show on analysis two absorption bands called A and B. The curve in ethanol is entirely independent of every isothermal change. With diminishing temperature the relative height of the B band in alcohol decreases and the two bands are thus shown to belong to two isomers of crystal violet ion, A and B, of which B has the higher energy by 580 cal. A theory as to the nature of these stereoisomers is given and is supported by experiments on the absorption curve of malachite green at low temperatures.

In solvents of Classes II and III (all of low dielectric constant) there is no appreciable number of free ions, but rather ion clusters of the sort described by Fuoss and Kraus. Small changes in the curves of Class III and a remarkable change in the chloroform curve, with increasing concentration of dye, are shown to be due to a salt effect and can be duplicated by adding other salts. That such salt effects exist, and in much higher degree than in any other known cases, is shown by other experiments.

The fluorescent and phosphorescent emission from crystal violet has been studied quantitatively. As in the previously described case of fluorescein, visible light of high intensity converts most of the dye into the phosphorescent state, so as to change greatly the absorption spectrum. The phosphorescent state gives rise to alpha and beta bands in the red and infrared, respectively. In this case the heat of activation from the phosphorescent to the fluorescent state is only 5.8 kcal. With ultraviolet light a new phosphorescent state is produced giving a green emission band. All the phosphorescence and fluorescence are attributed to isomer A.

There is evidence of still another isomeric condition of crystal violet ion, when produced from a leuco compound by illumination in a rigid solvent. This condition persists in the dark until the solvent is melted.