

A SPECTROPHOTOMETRIC STUDY OF THE HYDROLYSIS OF DILUTE FERRIC CHLORIDE SOLUTIONS.

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I. GENERAL THEORY.

Suppose light of intensity  $i$  pass through a body of thickness  $x$ . Then the rate of change intensity is expressed by the simple formula  $di = -kidx$ , where  $i$  is the intensity at any point and  $k$  a constant of absorption depending only upon the wave-length. This gives us, for the intensity of the transmitted light the equation

$$i = i_0 \varepsilon^{-\kappa x}$$

where  $i_0$  is the intensity of the incident light. If the absorbing body be a solution of strength  $c$  and length  $l$ , we may express  $x$  as a function of  $c$  and  $l$ , or the equation may be written

$$i = i_0 \varepsilon^{-\kappa cl}$$

If the absorbing system has another component, its equations would likewise be

$$i_1 = i_0 \varepsilon^{-\kappa_1 c_1 l_1}$$

Since the total transmission is the product of the separate transmissions, we have generally

$$(1) \quad i = i_0 \varepsilon^{-\sum \kappa_i c_i l_i}$$

This equation involves Beer's law,<sup>1</sup> which says that decreasing the concentration will have the same effect upon the transmitted light as decreasing the thickness, or when the product of concentration and thickness is maintained constant the absorption spectra will also

<sup>1</sup> Pogg. Ann., 86, p. 78.

be constant. The formula also says that for a system of  $n$  components represented by  $\Sigma AB$  the absorption will vary according to the exponential law so long as the components change uniformly with the concentration. Probably very few experimenters, before the announcement of the dissociation theory, attributed deviations in the observed absorption to changes in the structure rather than to an untenable law.<sup>1</sup> However observations upon isotropic solids uniformly confirm the law. At present we may assume there is nothing wrong fundamentally with the formula, and that it gives us the means of testing the optical properties of solutions. If in our system  $\Sigma AB$ , two components  $A_1B_1$  and  $A_2B_2$  partly change so as to form new components  $A_1B_2$  and  $A_2B_1$  or if by dissociation  $\Sigma AB$  yields in part  $\Sigma A$  and  $\Sigma B$ , the solutions will show or will not show an apparent variation from Beer's law, according as a certain assumption which we may make is or is not true. If the absorption of a solution is an additive property of its elements, then the absorption of  $AB$  is the same as the absorption of  $A + B$  and the absorption of  $A_1B_1 + A_2B_2$  the same as  $A_1B_2 + A_2B_1$  and there could be no change in the simple statement of Beer's law. This would simply mean that the absorption phenomena can give us no information in regard to changes in solution. For changes take place through elements already present in the solution and are not introduced from without. This view of absorption is stated by Gladstone as follows: "From the general rule that a particular base (say  $B$ )<sup>2</sup> or acid (say  $A$ ) has the same effect on the rays of light with whatever it may be combined in aqueous solution, it may be inferred that when two bodies *combine*, each of which has a different effect on the rays of light, a solution of the salt itself will transmit only those rays not absorbed by either, or in other words transmitted by both. Thus if a red acid ( $A$ ) and blue base ( $B$ ) combine ( $AB$ ), the resulting salt will certainly not be purple, but it may present some color intermediate between red and blue." This means that it is impossible to have any apparent deviation from Beer's simple law. If we change Gladstone's statement so as to

<sup>1</sup> A comprehensive review of the literature upon this point is given by Ewan, *Phil. Mag.* (4), 33, p. 317, 1892. Also in the British Association Reports for 1882 by Dr. Schuster.

<sup>2</sup> Parentheses and italics are the writers.

read do not combine but *coexist* in solution, his statement will then cover very dilute solutions, and his result would be expected. This is a result obtained by Ostwald,<sup>1</sup> who interprets Gladstone's results with this limitation. That there is apparent deviation from Beer's law by chemical reaction is too evident to the unaided eye to need detailed observation. In fact, upon these changes depends the much-employed method of titration. Now it may be questioned whether we have even a right to expect, *a priori* that  $AB$  would absorb the same as  $A + B$ . From dynamical considerations, we may regard the spectral region of absorption of  $A$  and  $B$  to correspond to the periods of their respective free vibrations. To absorb the same amount in the same spectral region in combination, implies that the product  $AB$  is executing the vibrations of its original components, or in other words there is no bond of union between them. In general  $AB$  must have the characteristic vibration of an independent product, and characteristic absorption. This is not to say that the components do not determine the absorption of the molecule. For a combination in a particular way must affect the vibration in a particular way.

If a transparent radicle, one whose period of vibration lies outside of the visible spectrum, *combines* with a colored one, dynamically considered, such a system must execute a new vibration. Generally this will displace the absorption bands. The magnitude of the displacement would depend upon the relative importance of the radicles, and this importance at the outset can not be predicted. Observations show that the substitution of a heavier transparent radicle for a lighter transparent one in a colored molecule there is a displacement of the absorption toward the red.<sup>2</sup> The same thing

<sup>1</sup> Ostwald in *Zeit. für Phys. Chem.*, 9, p. 579, examined the position of the bands for some 300 solutions by aid of the eye and by photography. He concludes that the spectra of dilute solutions of different salts with a common colored ion are identical. Referring to Gladstone's investigations, he says Gladstone's experiments seem to confirm this view.

<sup>2</sup> C. Kruss (*Kalorimetrie und Quantitative Spectral Analyse*, p. 156, 1891—book not available to the present writer) says that variation in the molecule by replacing H or other element by a radical varies the absorption in a definite sense.

Stenger (*Wied. Ann.*, 33, p. 577), says that change in absorption is parallel to change in properties, *e. g.*, the absorption of rosalin is in the green and the substitution of methyl and phenyl for hydrogen displace the absorption toward the yellow and red respectively.

should happen in case of further addition of heavier radicles to the molecule or in the combination of molecules giving more complex molecules. Apparently the combination could displace the absorption so that it did not fall within the limits of the visible spectrum. In case of the coexistence of the components separately, *e. g.*, as ions, the observed absorption would arise from these components only, but the absorption in combination must not be confused with the absorption of such components. The displacement could begin suddenly when any sudden change in the grouping occurs. From dynamical considerations, therefore, color changes in solutions give us a means of testing the structure of solutions, and might in some cases reveal complex molecular aggregates<sup>1</sup> not suggested by other methods.

One method of attacking this problem consists in diluting the solution and increasing the length of the column so as to keep the amount of the solute in the path of light constant and then to observe if there is any shifting of the absorption bands.<sup>2</sup>

Such a difference could only arise from a difference between  $\Sigma AB$  and  $\Sigma A + \Sigma B$ . The more frequent method is to determine  $z$  for each concentration in the general formula. We have then, making  $c$  equal to unity,

$$z = -\frac{1}{l} \log_e \frac{l}{l_0}.$$

If  $i$  is measured as percentage of  $i_0$ , then

$$z = -\frac{1}{l} \log_e i$$

or if common logarithms are used  $z$  is the reciprocal of that length which will reduce the intensity of the transmitted light to one-tenth of its original value. The value of  $z$  so found throughout the spectrum divided by the concentration of the solution is a constant,

<sup>1</sup> B. Walter (Wied. Ann., 36, p. 523) says the width of the penumbra round an absorption band is closely connected with the presence of more complex molecular aggregates in solution.

<sup>2</sup> Lippisch (Sill. Journ. (3), 13, p. 304); Russel (Proc. Roy. Soc., 32, p. 258, 1881) found no parallelism between  $c$  and  $l$ , by this method; and Knoblauch (Wied. Ann., 43, p. 748) observed deviations.

$$\frac{x_1}{c_1} = \frac{x_2}{c_2} = \dots = \frac{x_n}{c_n}.$$

This constant  $x$  has been designated the extinction coefficient,<sup>1</sup> and on account of the convenience in calculating it, it has been extensively used by observers. In both these methods, the *general condition* would indicate a system of absorption curves intersecting each other. For it is clear that each component must have its own extinction coefficient, and on account of selective and overlapping absorption these coefficients not only change from wave-length to wave-length, but also some increase while others decrease. It is also possible, for example, in case of transparent ions to have two systems of absorption curves failing to touch each other at any point. It is further clear that the possibility of observing such a system of absorption spectra depends upon two things, viz: firstly upon a sufficiently sensitive optical system of measurement and secondly upon an appreciable magnitude for the extinction coefficients and an appreciable difference in those magnitudes. It may happen that an extinction coefficient is zero, *i. e.*, its corresponding component is transparent. It may happen that the coefficients are nearly equal. In the system  $AB$  yielding in part  $A + B$ , which occurs upon diluting water solutions, Gladstone's theory requires that the coefficient of the first should exactly equal the sum of the coefficients of the latter two components. The variation in the extinction coefficients is frequently not large, and sometimes within the limits of error of the observations. More generally the fault lies in the ability to command a sufficiently sensitive optical system.<sup>2</sup>

When solutions are studied spectrophotometrically it is not possible to test the optical laws completely and comprehensively in a few months. In the present paper the writer has had time to study but one solution. However, the solution was chosen with reference to its wide range of optical variation. The study of the optical behavior of solutions of ferric chloride was suggested to

<sup>1</sup> Bunsen & Roscoe, Pogg., Ann., 101, p. 242.

<sup>2</sup> The Vierordt double slit is the most sensitive arrangement previously used. It does not make use of the Lummer Brodhum principle of the vanishing line. It is further necessary to calibrate the slit, an error generally overlooked.

me by an article by Goodwin upon "The Hydrolysis of Ferric Chloride," studied electrolytically.<sup>1</sup> It was thought that the well-known color phenomena might be followed spectrophotometrically, that there might be a possibility of getting further information either to confirm or refute the hydrolytic theory; that the rate of formation of the final product could possibly be measured; and that some evidence relating to the above dynamical considerations could be obtained. That the presence of hydrolysis and dissociation would complicate the condition was apparent.<sup>2</sup> However, it was thought the phenomena could possibly be separated.<sup>3</sup> How well I have succeeded in this must be judged by the results.

## 2. THEORY APPLIED TO EXPERIMENTAL CONDITIONS.

To study absorption experimentally it is desirable to isolate the components and study each separately. This we certainly can do in the case of isotropic solids, *e. g.*, glass plates. In dealing with solutions, the components in a few cases, *e. g.*, very dilute solutions, can be isolated. Just here, however, the great dilution makes quantitative measurements difficult. Seldom can the components be reduced to one and the phenomenon is necessarily complicated. Solutions must be placed in containing vessels, isotropic solids, which have absorption. Then if the absorption of the solute is desired, we have never less than three components—cell, solvent and solute—over which the summation sign in the general equation extends. Fortunately the cell and solvent may be eliminated. To do this there are several methods of procedure. We may, firstly, take measurements through the empty cell, and then through the cell

<sup>1</sup>Zeit. Phys. Chem., 21, p. 1, 1896. Another article continuing this investigation has appeared in the PHYSICAL REVIEW, 11, p. 193, since the present experiments were completed.

<sup>2</sup>Knoblauch, l. c., says, "To test the Arrhenius law, solutions which hydrolyze are to be excluded, since the color changes are produced not only by progressive dissociation, but by *chemical variation of the solution.*" The italics are the authors and seem practically self evident. Knoblauch would probably accept the further qualification, hydrolyzing solutions must be excluded from the test of the Arrhenius law unless measurements are made before hydrolysis begins.

<sup>3</sup>Antony and Giglio (*Gazette Chemica*, 25, 1, 1895) studied, colorimetrically, the intensity of the blue color, at the beginning and at the end of the colloid reaction, produced by addition of potassium ferrocyanide (quoted from Goodwin as all efforts to obtain this paper were fruitless).

filled with solution. Corrections according to the Fresnel theory for difference in refraction of glass, air and solution are necessary. Then the ratio of the light transmitted by solution and cell to the light transmitted by the cell alone, gives the light transmitted by the solution.<sup>1</sup> If the absorption of the solute is desired, this value must be divided by the absorption of the solvent. We may, secondly, pass light through a cell of thickness  $l_1$ , and then through another another cell of thickness  $l_2$ , containing end glasses of identical material. Then the ratio of the readings through the latter solution to those through the former solution give the absorption for a solution of thickness  $l_2 - l_1$ .<sup>2</sup> If the absorption of the solute is desired, we may proceed as before. This method requires no Fresnel correction. We may, thirdly, use two identical cells, fill one with water and another with solution. Then the ratio of the readings through the solution to the readings through the water give at once the absorption of the solute, when the solution is dilute. When the solution is not dilute two corrections are necessary. One correction due to the difference in the index of refraction of water and solution and another correction due to the fact that the solute displaces an appreciable part of the solvent, whose equivalent thickness is thereby reduced. In the study of the dilute solutions, the third method has been employed. In the study of the more concentrated but thin solutions, the third and second methods were used.

### 3. THEORY APPLIED TO DILUTE FERRIC CHLORIDE SOLUTIONS.

When we come to apply the theory to the study of dilute solutions of ferric chloride, Goodwin's electrolytic investigations of this solution throw some light upon what may be expected. We have, according to Goodwin, at the outset  $\alpha$  ions of  $\text{Fe}^{+++}$  and  $3 \text{Cl}'$ , and  $\beta$  ions of  $\text{FeOH}''$ ,  $\text{H}'$  and  $3 \text{Cl}'$ . At some instant,  $t$ , after dilution  $\delta$  ions of  $\text{FeOH}''$  have disappeared, forming with water colloid hydrate  $(\text{FeO}_3\text{H}_3)_x$ . We then have at any instant four components  $\text{FeCl}_3$ ,  $\text{Fe}^{+++}$ ,  $\text{FeOH}''$ , and  $(\text{FeO}_3\text{H}_3)_x$  from which we might anticipate absorption. To the unaided eye the very dilute solution appears transparent. This would be prima facie evidence for regarding the

<sup>1</sup> Ewan, l. c., p. 327, illustrates the inconvenience of such processes.

<sup>2</sup> Hesse, Wied. Ann., II, p. 876.

components  $\text{Fe}^{++}$  and  $\text{FeOH}^{+}$  transparent. The apparent transparency of the dilute solutions also indicate there is too little of the original product  $\text{FeCl}_3$  to give an appreciable absorption. (The experimental evidence indicates these components are not as near transparent as is desirable for convenient calculation.) Any color later would then arise from the  $(\text{FeO}_3\text{H}_3)_x$  component and the amount of absorption would be proportional to its rate of formation. Formula (1) then becomes

$$i = i_0 \epsilon^{-\kappa \lambda c}$$

where the concentration,  $c$ , is the only variable. If we take  $i_0$  as unity and measure  $i$  in per cent., we have

$$(2) \quad c = -a \log_{\epsilon} i$$

where  $a$  is a constant and equals  $\frac{1}{\kappa \lambda l}$ , and the cologarithms of the observed transmission are proportional to the product formed. If a solution of known concentration,  $n_1$ , is supposed to be  $A$  per cent., transformed we have  $An_1 = -a \log_{\epsilon} i$ , where  $a$  is the only unknown. If  $c$  is  $B$  per cent. of a solution of concentration  $n_2$ , we have

$$(3) \quad B = \frac{n_1 A}{n_2} \log \frac{i_2}{i_1}.$$

By sufficiently diluting the solution  $A$  can be made to approach 100 per cent. and hence  $B$  can be calculated with a fair degree of reliability, provided the solutions  $n_1$  and  $n_2$  are similar in composition and their ratio is not so large as to change the relation of the components. By the electrolytic method  $B$  can not be directly measured since the product is not an ion, however, it is formed at the expense of ions, and can therefore be approximated sufficiently well to indicate the general process. To repeat a little from Goodwin's article, if we designate the relative mobility of the  $\text{Fe}^{++}$ ,  $\text{H}^+$ ,  $\text{FeOH}^+$ , and  $\text{Cl}^-$  ions by  $u$ ,  $u'$ ,  $u''$ , and  $v$  respectively, we have

$$(4) \quad \mu_{t=0} = a(u + v) + \frac{\beta}{3}(2u'' + u' + 3v)$$

where  $\mu_{t=0}$  is the molecular conductivity for infinite dilute solutions.



This formula of Goodwin we may extend to the colloid reaction when we have any instant  $t$ ,

$$(5) \quad \mu_t = a(u + v) + \frac{(\beta - \delta)2u'' + (\beta + 2\delta)u' + 3\beta v}{3}.$$

If  $a$  decreased no farther during the formation of a colloid, (5) could be written in the form

$$(5a) \quad \mu_t = \mu_{t=0} + \frac{2}{3}(u' - u'')\delta.$$

Then if  $\beta$  ions are entirely transformed into the colloid we have finally

$$(6) \quad \mu_{t=\infty} = a(u + v) + \delta(u' + v)$$

unless the transformation involves further hydrolysis of the  $a$  ions and ultimate change of the entire product into FeOH and free ions of HCl. In which case we have

$$(7) \quad \mu_{t=\infty} = u' + v.$$

The product,  $\delta$ , in equations (5), (5a) and (6) corresponds to the product,  $B$ , in equation (3). Unfortunately the steps required to obtain  $\delta$ , and the assumptions made, do not leave the value as accurate as desirable. In the first place, some of the mobility constants must be assumed; secondly the solutions are not infinitely dilute; thirdly we do not know that  $a$  remains constant as given in formula (5a) and (6); and fourthly the method which I have adopted to obtain  $\mu$  from the equivalent conductivities is not free from error. We have a certain equivalent conductivity,  $x$ , before the colloid formation. This value will have a certain ratio to  $\mu_{t=0}$  which we may express by the equation

$$\mu_{t=0} = mx$$

where  $m$  is a constant. We may further assume that this constant relation maintains during the colloid formation. If we then multiply the observed equivalent conductivities in Goodwin's tables by the value of this constant,  $m$ , we have values for  $\mu_t$  during the process of the colloid formation. From these values of  $\mu_t$  substituted in (5a) we may calculate  $\delta$  for different intervals during the change.

## 4. USE OF THE APPARATUS AND ERRORS INVOLVED.

The spectrophotometric measurements were made with the Brace spectrophotometer.<sup>1</sup> The arrangement finally adopted was slightly different from the methods previously described. The light all comes from a single source. The light from one side of a broad thin acetylene flame falls upon one slit. The other side of the same flame falls upon the other slit, so that any fluctuation of the light would cause an equal fluctuation of the intensity before each slit.

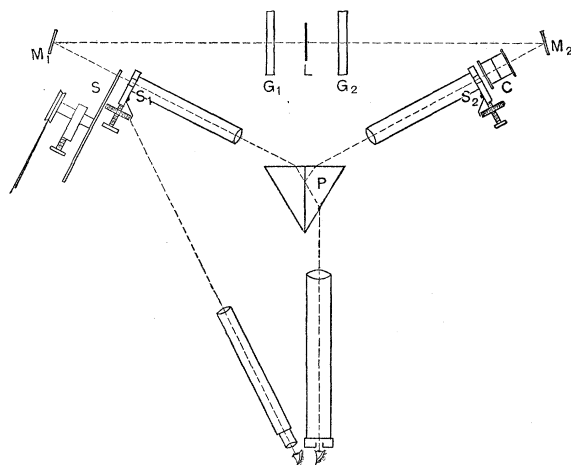


Fig. 1.

In Fig. 1,  $L$  is the light,  $G_1$  and  $G_2$  are ground-glass plates,  $M_1$  and  $M_2$  are reflecting mirrors,  $C$  is an absorption cell,  $S$  is a rotating sector,  $s_1$  and  $s_2$  are slits at the ends of the collimator tubes,  $P$  is the Brace prism, and  $T$  the observing telescope. Mr. Capps in using this instrument had placed the lights where the mirrors  $M_1$  and  $M_2$  are now located.<sup>2</sup> It is at once seen that any fluctuation in the intensity of one light would produce an error in the readings. Several sources of illumination were tried and none found to be as satisfactory as the incandescent light. However, the light from this source could not be made to cover the solid angle of the slit without the use of the ground-glass plates. This reduced the

<sup>1</sup> Phil. Mag. (5), 48, p. 420. Astrophysical Journal, II, p. 1.

<sup>2</sup> Astrophysical Journal, II, p. 29.

intensity of his field so much that it became difficult to take readings in the ends of the spectrum. Mr. Capps set about to make incandescent lights which would give large enough solid and uniform illumination to fill the solid angle of the field. After long and patient labor his mechanical ingenuity was rewarded with a satisfactory light. The present writer had neither time nor inclination to learn to make these lights. However, efforts were made to get different lamp factories to make them. Some companies would not furnish them in a small order and other companies forwarded lamps which did not fill the requirements. After wasting some months with these lights, acetylene was finally tried in the positions where the mirrors  $M_1$  and  $M_2$  are placed in the present figure. Obviously any lights burning in an open atmosphere will be subjected to some fluctuations, protected as much as possible. A trial showed that these lights would give all that was desirable in intensity. In fact the field was so bright that one could work with a slit as small as one tenth millimeter. These flames would also fill the field with exceptionally uniform light. Still there was a constant "pumping" amounting to at least one half per cent. The lights were then tried in the position used throughout the experiment. The light was placed in a position  $L$  without any ground glasses  $G_1$  and  $G_2$ . To cover the entire field the broad side of three acetylene flames were turned together. The mirrors  $M_1$  and  $M_2$  were then adjusted so that corresponding parts of the flame appeared along the vanishing line of the field. Any fluctuating of the flame will now cause a variation in both parts of the field of view and will not interfere with the observations within narrow limits. The light then covers the entire field but not uniformly. To secure uniformity it was necessary to introduce the ground glasses  $G_1$  and  $G_2$ . Unfortunately these glasses cut out 98 per cent. of the light which made readings difficult in the ends of the spectrum. Between  $4750\lambda$  and  $6500\lambda$  results could be obtained which are reliable to within one half per cent., at least so far as the optical measurements were concerned. Farther out in the violet the accuracy diminished rapidly. At  $4250\lambda$  the vanishing line disappeared and it became necessary to match intensities as in many other photometers. By removing the ground-glass plates, this difficulty could be

somewhat overcome as far as  $4000\lambda$ . This, however, left the present light unsatisfactorily distributed in the field. Frequently sets of ten readings have been taken which showed a probable error no greater than one tenth per cent. Then with the plates  $G_1$  and  $G_2$  slightly shifted so as to change nothing but the variable slit readings another set of readings sometimes as accurate as the previous one could be obtained, but the mean result would often differ from the previous result by as much as three fourths of one per cent. This fact seems to indicate that outside the optical measurements personal errors arise. Possibly even in working with the vanishing line, personal judgments in regard to matching intensity are not entirely overcome.

The solution to be studied was placed in a cell,  $c$ , before the slit  $s_2$ . The slit  $s_1$  was then adjusted until the line between the fields vanished, *i. e.*, until the fields matched. A sector,  $S$ , was also used as well as this slit  $s_1$ . By cutting out part of the light with the sector and making the final adjustment with the slit  $s_1$ , we can avoid the calibration of the slit, provided we use the sector in such a way as to keep the slit  $s_1$  as near as possible to its original width. It is of course possible to avoid the use of the slit  $s_1$  if we have an adjustable sector of the Lummer Brodhum type. In the present experiments I made use of an inexpensive sector cut into eight sections, used by Mr. Capps in his calibration of the slit.<sup>1</sup> By the use of the sector alone the difference between the two fields could be reduced to one sixteenth, and only this value need be compensated with the slit. Then with a one half millimeter slit, the error in observations arising from the slit can be reduced to one twentieth per cent. This value is certainly negligible in comparison to the errors of the results.

Two cells of the same thickness and having faces of the same kind of glass were used. One cell was used for water, the other for the solution. The water cell was first placed before the slit and readings taken. Then readings were taken through the solution cell and then again through the water to avoid any possibility of fluctuation due to a change in the intensity of the light. Except when studying velocity changes five readings were taken through

<sup>1</sup> Loc. cit.

the water, then ten through solutions and finally five through water. The ratio of the mean readings gives at once the per cent. of the original light transmitted by the solute. The only source of error in this method arose from the fact that the solution persisted in tarnishing the faces of the solution cell and only with the most scrupulous care in cleaning the cell could the absorption be made equal when the two were filled with water.

In the study of the time rate of change of solutions the position in the spectrum was not varied for several days. So that by keeping the ground glasses in the same position, and by keeping the burners clean, practically constant readings through water could be obtained. Readings through water could be taken just before the solution was prepared and then again later as a check when the rate of change in the solution would permit. Sometimes appreciable changes in the water readings occurred when it became necessary to stop the readings of the solution and prepare a new solution. In some solutions the changes were so rapid that only one reading could be taken, but a great number could be taken at short intervals. On account of these changes these solutions were studied for at least three samples for each concentration. Below .0012 normal these solutions show a variation for a given time during the first few minutes changes, as large as two per cent. The first few sets showed values much larger. It was thought that the light had an actinic action upon the solutions and that the difference arose from the length of time the light fell upon the cell. A simple test disproved this. It was known that a small change in temperature influenced the rate of change and a test showed that the trouble in part arose from this source. The solutions were prepared at 25° C. and maintained at that temperature in a constant temperature bath. This bath contained over one hundred and twenty liters of water, was double-walled, and wrapped with asbestos. With a temperature difference between the bath and the room of 5° C. the temperature of the bath would change about one degree in twelve hours, so that it was quite easy to regulate the bath by hand within .05° C. of the required temperature. No attempt was made to regulate the temperature of solutions while before the slit. At the outset some readings were taken and solutions returned to the stock. Although

the difference in temperature between the cell and the room during the summer months was very small, it was found that the trouble was at least in part here. Accordingly, the sample used before the slit was thrown away after a few minutes' use, and a fresh sample taken from the stock. This gave more uniform results, but not as uniform as the optical measurements would indicate one might expect. Just what the acting force or source of error may be is to me quite uncertain. Many of the solutions prepared identically, with absorption changes of the same relative magnitude, maintained at the same temperature during the experiment, and subjected only to the fluctuations of the bath after the experiment, were found to be quite different after six weeks. In some cases the more recently prepared solution of a given concentration had entirely precipitated the product and became as transparent as water, while the older solution showed its original color. Some of the stronger solutions (.0016 *n* and .0024 *n*) sometimes showed plainly a marked turbidity before the change had completely ended and at other times they did not. Though the latter solution would not reach the limit of transformation and sometimes began to precipitate at 25° C., a fresh solution heated, could be forced to change completely without any sign of turbidity. These facts lead me to believe that the solutions are very unstable, and that the errors do not arise from optical measurements and temperature changes alone.

##### 5. OBSERVATIONS AND THEIR DISCUSSION.

The ferric chloride was prepared by sublimation. The solution was kindly tested by Mr. R. S. Hiltner and found to have .28 per cent. excess of iron. The concentration, mean of iron and chlorine, with respect to  $\text{FeCl}_3$  was 3.0779 normal. While a solution prepared from resublimed ferric chloride which was purchased from a reliable firm, Mr. M. E. Hiltner found to have 1.7 per cent. excess of iron. All solutions studied were made from a sample of the former solution of one-tenth the concentration, namely, .30779 *n*. The concentrations of the solutions studied were .0003078 *n*, .0006156 *n*, .000821 *n*, .001026 *n*, .0012312 *n*, .0016416 *n* and .002462 *n* with reference to  $\text{FeCl}_3$ . However, in the tables, these concentrations are designated, for convenience, by their significant

figures. The absorption cell in which these solutions were placed was four centimeters long. A layer of the triple normal solution .0032 cm. in thickness contains the same amount of iron as the strongest of the above solutions. We could then for convenience designate both of these solutions by .0024  $n$ . Their spectra would be identical if there is no change in the components of the system upon dilution. The thinner layer of the concentrated solution was placed between two plates of clear glass in the form of a wedge. This wedge could be driven at right angles to the slit to the position of desired thickness by means of a micrometer. This method of measuring thickness is certainly not as accurate as an optical method, but is certainly within the limits of the present measurements. These measurements were made upon the thin layer by the second and third methods described in the theory. The readings by the third method were used because the method obviated errors due to changes in intensity of the light. In the study of the diluted .0024  $n$  it was however necessary to reprepare five solutions on account of time changes before a complete determination of its absorption spectra could be made, similar readings were made for .0008  $n$  in the form of a film and .0008  $n$  in dilution. For the latter the values are no more than a rough approximation of the transmission of a fresh prepared solution. The solution cannot be prepared, shaken, and a rough reading taken inside of one minute. During the next minute, in the violet one can see changes that amount to as great as 20 per cent. It was only possible therefore to make a setting, then to set the slit for a little larger transmission and to prepare a fresh solution. After about five trials one could find a setting which did not seem too small when a reading was taken as quickly as possible after the solution was prepared. Similar preparations were required for other points in the spectrum. The values obtained are not therefore the actual transparencies of this solution fresh prepared, but values which the transparencies possibly exceed by several per cent. in the blue. The transparencies certainly do not fall below these values and are therefore significant.

Table I. gives the values by this process for .0024  $n$  and .0008  $n$  in thin films and in fresh diluted solutions. Columns  $a$  and  $a'$  give

TABLE I.

$\lambda$	$n = .0024$		$n = .0008$	
	$a$	$b$	$a$	$b$
5750	99.3	100	100	100
5500	97.9	99.1	100	100
5250	95.8	97.9	99.1	100
5000	92.9	94.8	97.2	100
4750	87.4	90.9	95.7	98.9
4500	70	80.5	84.	94.3
4375	10.9	70.5	51.	90
4250		57.5		83.5
4125				
4000		23		61

transmissions for the films and dilute solutions respectively. It is of interest to compare these values with the transmissions of the same solutions after the colloid formation in Table II. The results are shown graphically in Fig. 5 where the same numbers correspond to the same amounts of ferric chloride before the slit and the letters  $a, b, c$ , correspond to concentrated, dilute, and colloid condition respectively. It is evident that diluting the solution makes it relatively more transparent. At  $5000 \lambda$  the  $.0024 n$  in the concentrated form gives a transmission of 93 per cent. In the fresh diluted condition the transmission is 94.6 per cent. From Table X. of Goodwin's results we can infer the degree of ionization of this solution, and therefore also the amount of the original product present. If the ions were transparent this solution should show a transmission of 99.7 per cent. or an absorption of .3 per cent., whereas the absorption observed is 5.4 per cent. This leads to the inevitable conclusion that the ions are not transparent but that their absorption constant is smaller than the constant for the original product. The same conclusion is also drawn from the other concentration and from the other points in the spectrum. Goodwin's results indicate the presence of two positive ions for this dilution and it is apparent that we can not separate the absorption of these ions. However there are seven times as many of the  $\text{FeOH}^+$  ions as of the  $\text{Fe}^{++}$  ions, and it would seem reasonable to attribute a large part of the absorption to the larger product. Otherwise the



Fe<sup>+++</sup> ions would require a much larger coefficient of absorption than the original component. However, diluting the solution further apparently *decreases* the absorption of these ions more rapidly than the dilution. During such a process according to Goodwin, the relative amount of FeOH<sup>++</sup> with respect to Fe<sup>+++</sup> is *increasing*. This would indicate greater relative absorption for the Fe<sup>+++</sup> ion. This action is the only evidence from the present observations to indicate the presence of both Fe<sup>+++</sup> and FeOH<sup>++</sup> ions, but the observations are not conclusive upon this point.

Table II. contains a spectra study of the solutions after the colloid formation has practically ceased. Fig. 5 shows the results graphically. To obtain the calculated values it is assumed by exter-

TABLE II.

λ	n=.002462			n=.001231			n=.000821			n=.000615			n=.000308
	obs.	cal.	dif.	obs.	cal.	dif.	obs.	cal.	dif.	obs.	cal.	dif.	obs.
7000	85.5			88.5			93.2			94.4			97.
6500	80.9	81.1	-.2	87.4	88.5	-1.1	91.6	92.3	-.7	93.8	94.1	-.3	97.
6000	73.1	72.7	+.4	82.9	83.5	-.6	87.6	88.6	-1.0	90.8	91.3	-.5	95.5
5750	56.	56.1	-.1	73.3	72.1	+1.2	79.6	79.9	-.3	85.2	84.8	+.4	92.
5500	37.	35.3	+1.8	54.8	55.3	-.5	65.9	67.2	-1.3	74.2	74.2	0	86.
5250	16.9	15.3	+1.6	34.2	34.6	-.3	47.8	49.	-1.2	57.8	58.5	-1.0	76.3
5000	5.2	5.2	0	19.2	19.2	0	32.5	32.5	0	42.4	43.2	-.8	65.5
4750				7.7	9.1	-1.4	18.3	20.9	-2.6	30.4	30.2	+.2	55.2
4500							9.	13.3	-4.3	22.8	22.	+.8	46.5

polarization from Goodwin's Table X. that the .0003 *n* is 99.2 per cent. hydrolyzed at the outset. The assumption of 100 per cent. hydrolysis would not materially affect the calculation. The per cent. transmission of the colloid formation for other solutions is calculated for 5000 λ, since more observations were taken at this wavelength than in other parts of the spectrum. Formula (3) then becomes

$$(3a) \quad B = -\frac{\log i}{618n_2}$$

and very similar expressions for other points in the spectrum. This gives for .0024 *n*, 86.7 per cent; for .0016 *n*, 90.6 per cent; for .0012 *n*, 98 per cent; and for .0008 *n*, 98.7 per cent; for .0006

$n$  the value is assumed to be 99 per cent., which lies between the value for .0003  $n$  and .0008  $n$ . Now assuming these per cents. and taking the values of  $i_1$  from .0003  $n$  column, formula (3) can be used to determine  $i_2$ . This gives the calculated values recorded in Table II. In Fig. 5 the observed values are plotted in continuous lines and the calculated values in broken lines. These curves seem to agree as well as could possibly be expected except where the absorption is large in the blue and at 7000  $\lambda$ . There is however a preponderance of negative differences in the difference columns. Table III.

TABLE III.

$\lambda$	$n = .0024.$	$n = .0012.$	$n = .0008.$	$n = .0006.$	$n = .0003.$
6500	86.5	110.	107.5	104.5	99.2
6000	84.8	100.4	107.	104.	99.2
5750	86.3	92.4	101.8	95.4	99.2
5500	81.7	98.9	102.7	98.7	99.2
5250	81.4	102.4	106.	105.	99.2
5000	86.7	98.7	98.7	100.5	99.2
4750		107.	106.3	99.4	99.2
4500			114.	92.8	99.2
Mean.	84.57				99.2

interprets the same readings in another way. Formula (3) is again used.  $A$ , in that formula, is again assumed to be 99.2 per cent. for .0003  $n$  and the readings for this solution are assumed correct. From the observed intensities the per cents. of hydrolysis are calculated for the different concentrations. The variations here appear quite large although in the previous set of observations the differences appeared very natural. But these very differences account for this variation in per cent., since the observed differences are a larger per cent. of the low transmissions than they are of the high transmissions. These results also show that I might have obtained greater uniformity by taking some other solution for standard of reference.

Tables IV. and V. and Fig. 2 show the transmissions of the various solutions during the progress of the transformation. This study was made at 5000  $\lambda$ , and has been repeated at least three times for each solution. The transmissions in Table IV. are taken to represent the transmissions of the colloid formation. For reasons given

TABLE IV.

Time.		$n=.0003$		$n=.0006$		$n=.0008$		$n=.0010$	
hr.	min.	Intens.	$-\log i$	I	$-\log i$	I	$-\log i$	I	$-\log i$
	2	92.0	.0362						
	4	85.5	.0680			95.6	.0195		
	5	82.2	.0851					95.	.0223
	7			87.2	.0595				
	8	80.0	.0969			90.8	.0419	93.	.0315
	12	77.6	.1101	81.2	.0904	87.0	.0605	90.0	.0458
	16	76.0	.1192			84.0	.0757	87.8	.0565
	20			76.7	.1152	80.2	.0958	85.0	.0706
	26	72.8	.1379						
	30					75.5	.1221	79.0	.1024
	40	69.8	.1561	68.8	.1624	71.7	.1445	74.5	.1278
1	00	67.5	.1701	63.6	.1965	65.0	.1871	68.0	.1675
1	20			60.2	.2204	60.4	.2190	62.5	.2041
1	40			57.2	.2426	57.2	.2426	58.0	.2366
2	00			55.0	.2596	54.8	.2612	54.6	.2628
2	40			51.0	.2924	50.2	.2992	49.3	.3072
4	00			48.0	.3188	45.0	.3468	43.7	.3595
6	00					40.5	.3925	38.7	.4123
6	40			46.8	.3298				
8	00					37.8	.4225	35.7	.4473
19 days		65.5	.1838						
16	“ 2 hours			42.4	.3726				
18	“					32.5	.4881		
8	“ 3 “							25.	.6021

in discussing Table I., the transmissions of the stronger solutions need some correction before they can be taken to represent the formation of a colloid hydrate. Evidently when  $i_1$  and  $i_2$  are the transmissions of components  $A$  and  $B$  respectively, and  $i$  the transmissions of the two,  $i = i_1 i_2$ . At the outset we have no colloid or  $i = i_1$ . Then the observed transparency at the outset divided into the transparency at any other instant would give the transparency of a new product, provided, the original product remains constant. However the colloid forms at the expense of the other product. We may then assume that the absorption of this product decreases at the same rate the other forms. Then by successive approximations, we may obtain the transmission of a colloid alone. We observe, *e. g.*,  $i_1$ , at the outset, and later  $i$ , and  $i_2 = i/i_1$ , for the first approximation. Then  $(100 - i_1) i_2$  is the approximate absorption

of the original product remaining. Then  $100 - (100 - i_1) i_2$  would be the corrected value for  $i_1$ , which divided into  $i$  gives the second approximation for  $i_2$ . Further approximation is scarcely necessary.

As noted in discussion, Table I., the absorption at the outset may arise from both the iron ions rather than from one and a small per cent., never greater than .3 per cent., may arise from the original product. In this change one of these products, the Fe-OH ion is certainly active and if the other components are active it will make but a trifle difference, and scarcely affect the values obtained by the second approximation. In fact so far as the general course of the formation of the final product is concerned, it is not necessary to assume here any intermediate ion whatsoever. In Tables IV. and V. are also tabulated cologarithms of the colloid transmission. From formula (1) it is evident that these values are proportional to the

TABLE V.

*A* = Observed transmission. *B* = Transmission calculated for the hydrolyzed product.

Time.		<i>n</i> = .0012.			<i>n</i> = .0016.			<i>n</i> = .0024.		
hr.	min.	<i>A.</i>	<i>B.</i>	$-\log i.$	<i>A.</i>	<i>B.</i>	$-\log i.$	<i>A.</i>	<i>B.</i>	$-\log i.$
	2	97.	99.5	.0022	95.7	99.9	.0004	94.6	100.	.0000
	4	96.5	99.	.0044	95.3	99.5	.0022	94.5	99.9	.0004
	8	94.8	97.3	.0119	94.8	99.	.0044	94.3	99.7	.0013
	12				94.1	98.3	.0074			
	14	92.2	94.3	.0255						
	20	89.8	91.9	.0367	93.1	97.2	.0123	94.	99.4	.0026
	30	84.8	86.5	.0630	91.2	95.2	.0214			
	40	80.	81.6	.0883	89.7	92.5	.0339	93.	98.3	.0073
1		71.	77.2	.1415	84.8	88.4	.0535	91.8	97.2	.0123
1	20	64.5	65.5	.1838	78.2	81.4	.0894	89.5	94.5	.0246
1	40	59.1	60.0	.2218	70.8	73.4	.1343	86.5	91.4	.0391
2		54.9	55.6	.2549	63.8	66.	.1805	81.9	85.7	.0670
2	40	48.3	48.9	.3107	57.	52.5	.2798	71.8	74.2	.1296
3					46.	47.4	.3242	66.8	69.	.1612
3	20				43.	44.4	.3526	61.	62.8	.2020
3	40				40.5	41.7	.3788	56.2	58.1	.2358
4		40.4	40.8	.3893	39.	40.2	.3958			
6		34.9	35.1	.4546	31.4	32.3	.4908	34.8	35.1	.4547
8		31.	31.2	.5058	26.7	27.5	.5607	26.2	26.3	.5800
10		26.6	26.7	.5735	24.9	25.7	.5901	21.2	21.3	.6716
14 days.		19.1	19.2	.7167						
22	"				12.5	12.7	.8962			
32	"							5.2	5.2	1.2840

total amount of the product formed. Therefore these values have been plotted here directly and are found in Fig. 3. By dividing

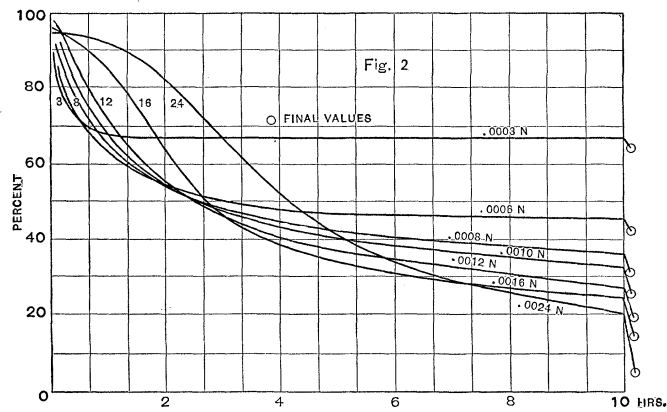


Fig. 2.

these values by the thickness of the cell 4 cm., we obtain the extinction coefficient, the latter divided by the concentration gives the absorption ratio. However these values give no additional infor-

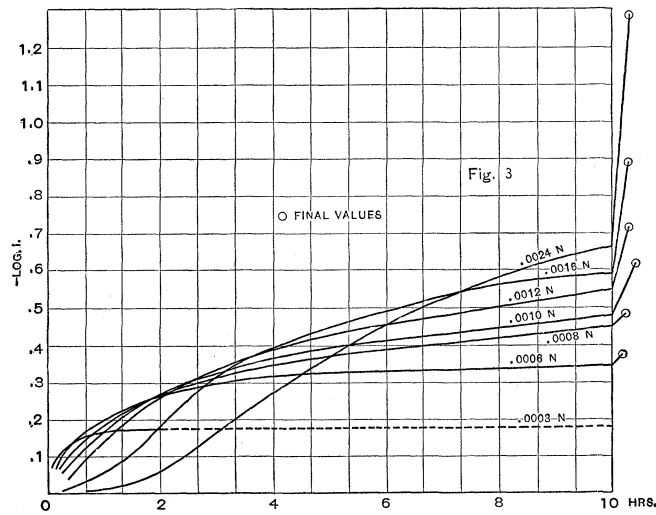


Fig. 3.

mation upon the rate of formation. Again the final values of cologarithms  $i$  in the .0003  $n$  are taken to represent 99.2 per cent.

transformation and by aid of formula (2) the per cents. transformed for all other values of cologarithms  $i$ , both for .0003  $n$  and other concentrations are calculated. The values of  $\delta$  are calculated, as indicated in the theory, from Goodwin's data by use of formulæ (5) and (5a). The values so obtained for  $\delta$  and  $B$  are given in Table (VI.) under the names of Goodwin and Moore. The concentrations

TABLE VI.

$G$  = Goodwin.  $M$  = Moore.

Time. hrs. min.	$n=.00303$		$n=.000606$		$n=.000802$		$n=.001211$		$n=.0016$	$n=.00242^2$	
	$G.$	$M.$	$G.$	$M.$	$G.$	$M.$	$G.$	$M.$	$M.$	$G.$	$M.$
1	3.	10.	0.		0.	3.9					
4	24.6	36.7	.3					.6	.22		
10	44.2	56.	2.0	20.8	1.3	10.3		2.2	.6		
20	59.7	68.4	9.	31.1		19.4	.04	5.	1.24		.18
35	70.5	80.8			10.1	27.			2.85	.6	
45			30.5	45.8	21.3		4.2	13.7		1.0	
1 00		91.9	39.	53.		37.8	7.8	19.1	5.4		.83
1 15	84.3										
1 30			52.	61.8	38.4	46.7	18.3	27.4	11.3	2.4	2.37
2 00				70.	46.4	52.8	26.3	34.4	18.3	5.9	4.53
2 30			63.1				32.2	39.4	25.8	9.1	7.63
3 00			66.9	80.8	56.6		37.8		32.6	13.5	10.9
3 30							41.7		37.	17.6	14.8
4 00	94.3			86.	62.8	71.8	45.	52.5	40.	21.5	
5 00			74.		65.		50.2			30.3	
6 00					79.4		55.	61.3	56.6 <sup>1</sup>		30.7
									59.6 <sup>2</sup>		
Final	103.6	99.2	104.	100.5	98.	98.7	103.	97.9	90.6	80.4	86.7

are according to Goodwin. The values are shown graphically in Fig. 4. This system of curves shows the same general character and indicates approximately the same final condition. The wide gap between the curves at some points I can hardly attribute to the errors in the data of either observer or to the method of calculation. There is a marked tendency, except for the .0024  $n$ , for the writer's solutions to begin the reaction sooner than Goodwin's solutions. They behave as if they were warmer. However, I rather anticipate a difference in the solutions, possibly due to a difference in internal condition rather than due to a concentration difference.

<sup>1</sup> 8 hrs.      <sup>2</sup> 10 hrs.

The observed concentration difference of 1.7 per cent. would cause a difference of opposite kind.

It is desirable also to follow these transformations at other points in the spectra. Other wave-lengths will not be so favorable as this one since we can in this position begin with large transmissions, obtain large absorption for small changes and finally large absorption when the product is entirely formed. However, some tests were made at  $6000 \lambda$  where the absorption seems to form a penumbra. If the absorption at the two points arises from the same molecules, the extinction coefficients should be in a constant ratio to each other. This seems to be true for the final products in Table II.

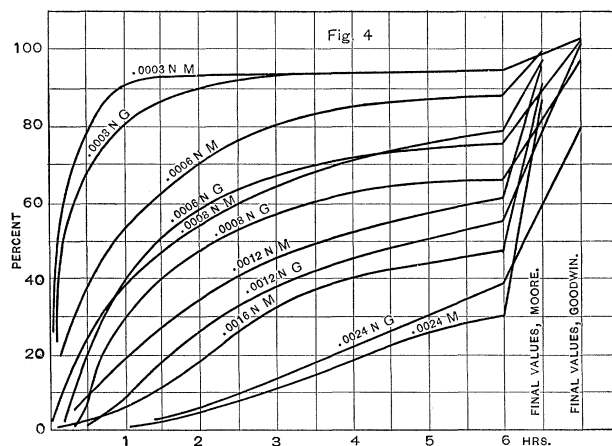


Fig. 4.

The extinction coefficients were so small, however, for the more dilute solutions that the observations, though giving a slight curve could have nearly coincided with previous curves by magnifying them or could have approached a straight line and in either case have been within the limits of error of the observations. It was thought more might be accomplished with the .0024 normal. I tried four solutions of this concentration. The transmissions of these solutions when plotted spread over a field 1.5 per cent. wide. In the early part of the reaction the total absorption after the transformation is practically ended, is only 26.9 per cent. So that a difference of 1.5 per cent. in the early readings makes consider-

able error in the rate of formation. These readings indicate transformations 10 per cent. larger for .0024  $n$  after one and two hours change than at 5000  $\lambda$ . Plotted as a curve in Fig. 4 they would cross the .0024  $n$  curve between 4.5 and 6 hours, but ultimately reach as high a value. If the colloid molecules  $(\text{FeO}_3\text{H}_3)_x$ , were not all alike, but if, for some molecules  $x$  had one value, and for other molecules another value; and if one set were formed early, in the transformation and another set later, just such action as here observed would take place. Antony and Giglio<sup>1</sup> assumed the presence of  $\text{FeCl}_2(\text{OH})$  and  $\text{FeCl}(\text{OH})_2$  in varying proportion depending upon the dilution. Now if we modify this statement and say one product appears early and another later, the selected absorption of the assumed products would produce the observed optical phenomena. Since, however, the final curves show at all points absorption in proportion to the concentrations, it is evident that the ratio of the possible different components is finally the same for all concentrations. The absorption spectra observed could, of course, arise from products of the form  $\text{FeCl}(\text{OH})_2$ . However, from the present standpoint of the theory of solutions and the observations of Goodwin the product  $(\text{FeO}_3\text{H}_3)_x$  may be regarded as practically demonstrated if the final product in solution is  $\text{FeO}_3\text{H}_3$ , we could prepare this solution independent of  $\text{FeCl}_3$  and test it for identical absorption spectra.<sup>2</sup> The writer may make such an examination later.

In Fig. 5 we find the thin films of a triple normal solution represented .0024  $n$  and .0008  $n$  to have large absorption bands beginning very suddenly and falling nearly perpendicularly. These absorption bands recede toward the violet when the film is made thinner. From the sharply defined character of the absorption it appears that the molecules have an equally well-defined period of vibration and probably are quite uniform in structure. The presence of well-defined anomalous dispersion in this solution is at once suggested. However, for the colloid formation, the range of molecular vibration is not so uniform. The umbra shades off slowly

<sup>1</sup> Antony & Giglio (reference Zeit. Phys. Chem., 19, p. 191).

<sup>2</sup> Goodwin's recent paper (PHYS. REV., 11, p. 193) makes a very similar test, viz.: The accelerating effect of  $\text{FeOH}$  upon the hydrolizing process.



into a penumbra. Hence again the suggestion of less regularity in the structure of this product. The final curves for the colloid (Fig. 5) are, as previously shown, proportional to the product at all

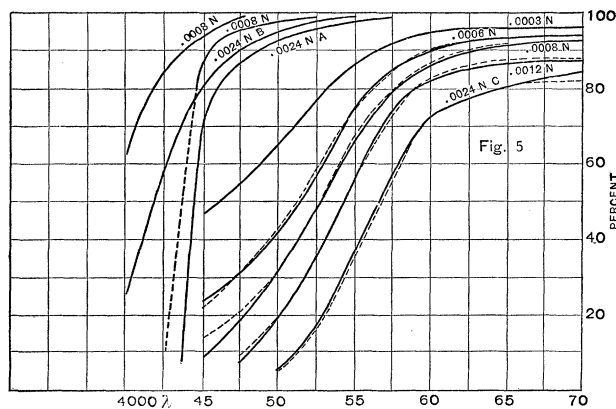


Fig. 5.

points. This shows that for final examination any mixed red or yellow light could be used in the study instead of spectral lines or the color could be compared with another absorption red.

#### 6. CONCLUSIONS.

1. A study of the absorption spectra has proved to be a good method for following the progressive changes in the colloid formation, and will be serviceable whenever any color changes take place.
2. The presence of ionization is detected and the fact that the ions are not completely transparent is shown.
3. A quantitative determination of the rate of ionization is impossible in the present case, but it is indicated that it is quite possible with some solutions.
4. There is but slight direct evidence for the presence of two iron ions so clearly shown by the electrical method. However, the general agreement of the optical with the electrical methods of finding the rate of formation of the final products gives us further, through indirect, reason for accepting Goodwin's theory of the reaction.
5. There is some, but rather slight, evidence for thinking that the molecules of the final product are not all of the same magni-

tude, *i. e.*,  $x$  in the formula  $(\text{FeO}_3\text{H}_3)_x$  may have more than one value for different molecules.

6. The clearing of the solution and the displacement of the absorption bands toward the violet upon dilution ; and the subsequent formation of a much greater absorption band displaced toward the red upon the formation of a more complex molecule, confirm the dynamical considerations.

7. *General Conclusion.*—The optical study of absorption spectra on account of both the optical theory of the relation of absorption to dispersion and the relation of absorption to the molecular structure of solutions should be more general. The method is not as easy to manipulate as the raising of the boiling point, lowering of the freezing point, osmotic pressure or electrical methods ; and by reason of the transparency and general overlapping of the absorption spectra has nowhere near their range of application. However, there is a possibility that the method will show complexity of structure in some cases not brought out by other methods. Further confirmation of results by the other methods is also desirable.

UNIVERSITY OF NEBRASKA, January, 1901.