

THE ABSORPTION SPECTRUM OF COLLOID  
FERRIC HYDRATE.

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IN a recent article upon "A Spectrophotometric Study of the Hydrolysis of Ferric Chloride,"<sup>1</sup> I have pointed out that the probable final product of hydrolysis,  $x(\text{FeO}_3\text{H}_3)$ , could be advantageously compared with Graham's colloid ferric hydrate. For, if two solutions of the same base should have identical absorption spectra, it would be natural to assume the same structure of the molecule.

A solution of colloid ferric hydrate was prepared according to Graham's direction. After dialyzing for five weeks, the solution was kindly tested by Mr. R. W. Thatcher who found it to be .1116 normal with respect to iron and that 90.4 per cent. of the chlorine had been removed. From a sample of this solution I prepared a dilute solution, .002462 normal, and another solution of the same concentration from the stock of ferric chloride made twelve months previous. These solutions were placed in two absorption cells of identical absorption coefficients. One cell was placed before each slit,<sup>2</sup> and ten readings of the slit were taken at a definite point in the spectrum. The cells were then interchanged, and ten new readings taken. Similar readings were taken at other points in the spectrum. A comparison of these sets of readings gives double the relative difference of absorption. This method was particularly good at points in the spectrum where absorption differences were small. When the absorption differences were large, in one position the slit must be opened very wide, which necessitated its abandonment. However, the absorption spectra of each could be determined separately as in the previous contribution. This method was also adopted at all

<sup>1</sup> PHYSICAL REVIEW, Vol. 12, p. 151.<sup>2</sup> PHYSICAL REVIEW, Vol. 12, p. 160.

points in the spectrum as a check. The ferric chloride solution had been hydrolizing for eight days at room temperature and a comparison of its absorption spectrum with the curve for the same concentration in the previous article shows that the hydrolysis would proceed a little farther. However, the general character of the two spectra is the same. But there is a marked difference between the

TABLE.

*Transmission in per cent.*

	Colloid Ferric Hydrate.			Hydrated Ferric Chloride.
	$n = .002462.$	$n = .001231.$		
	Observed.	Observed.	Calcu. <sup>1</sup>	
6500	89.3	93.6	94.5	82.1
6000	87.6	92.5	93.6	75.2
5750	82.5	89.3	90.8	61.5
5500	71.5	82.	84.5	40.5
5250	41.3	66.8	64.3	19.8
5000	13.25	34.1	36.4	9.4

absorption spectra of these solutions and the absorption spectrum of colloid ferric hydrate, as is shown by the following table of data

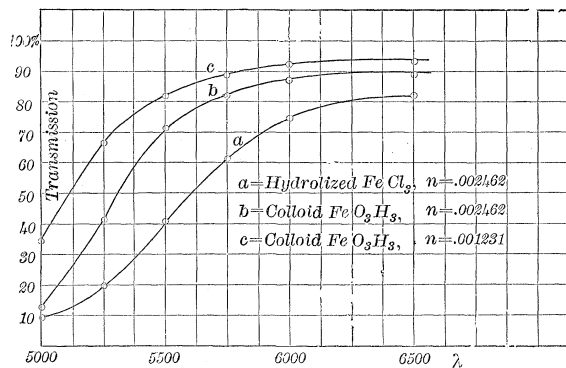


Fig. 8.

and curves. The character of the curves is not the same. The ferric chloride solution absorbs more throughout the spectrum, but

<sup>1</sup> Calculated from formula  $\text{colog } i_2 = -\frac{\text{colog } i_1}{2}$ , where the intensities,  $i_1$  for  $n = .002462$  are assumed correct.

relatively more in the red. The curve for the colloid absorption is much steeper as it approaches the region of strong absorption so that it would intersect several of the previous curves<sup>1</sup> for solutions of the hydrolized ferric chloride. This fact excludes the assumption of the same product but diluter solution. It leaves us two other assumptions. We may assume with Antoni and Giglio, that in the process of transformation there is a combination of iron, chlorine and hydroxyl; or we may assume there is present an appreciable amount of crystalloid ferric hydrate in the colloid hydrate prepared by dialysis. Small quantities of the crystalloid are expected to be present in the colloid solution but the difference in the absorption spectra would necessitate the assumption of larger quantities of the crystalloid than I had anticipated. However, for reasons previously given, I think the latter view more tenable than the first assumption. The nine per cent. chlorine is not responsible for the difference, since in the hydrolized ferric chloride there may be as much as thirteen per cent. of the ferric chloride not transformed.

I now prepared a dilute solution of colloid ferric hydrate and replaced 5 cu. cm. of 90 cu. cm. of water with 5 cu. cm. of strong chlorine water, and compared this solution at different points in the spectrum with the previously prepared solution of colloid ferric hydrate. Tests made at different times during two weeks' interval showed no difference whatsoever. A solution of hydrochloric acid whose density was 1.163 at 25° C. was diluted 100 fold and 5 cu. cm. of this diluted acid replaced 5 cu. cm. of water as before. At different times for two weeks, this solution was compared with the two previous ones and at no time was there a difference observed which could not be attributed to working conditions. That is, neither the chlorine caused the formation of any chlorine products nor the hydrogen effected any transformation of the possible crystalloids. The introduction of 5 cu. cm. of Graham's colloid ferric hydrate into a fresh prepared solution of ferric chloride accelerated the hydrolysis<sup>2</sup> so that in two hours the solution was as dark as the older solution of the same concentration had become upon standing for four hours. Next, 5 cu. cm. of an old solution of

<sup>1</sup> Previous contribution, Fig. 5, p. 175.

<sup>2</sup> Goodwin, *PHYS. REV.*, Vol. II, p. 193.

hydrolized ferric chloride was added to a new solution and at the end of two hours, the mixed solution was as dark as the old solution had become at the end of 5.5 hours. All the solutions in this test were of the same concentration, viz. : .002462 normal. The action indicates that the accelerators are the same in the two cases but that there is a larger quantity of it present in the hydrolized ferric chloride than there is in the dialyzed ferric hydrate. The two were of the same concentration as to iron and the slower acceleration of the Graham's colloid ferric hydrate can be readily explained upon the assumption previously made of appreciable quantities of inactive crystalloid hydrate. The absorption curves then suggest that the colloid absorption spectrum lies between the hydrolized ferric hydrate and the ferric chloride spectra.

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