

“On the Absorption Spectra of Dilute Solutions.” By THOS. EWAN, B.Sc., Ph.D., 1851 Exhibition Scholar in Chemistry in the Owens College. Communicated by Professor H. B. DIXON, F.R.S. Received April 7,—Read June 21, 1894.

The changes which occur in the colour of a solution when its concentration is changed, are closely connected with the simultaneous changes which occur in the molecular condition of the dissolved substance, and a study of these changes of colour may be expected therefore to furnish valuable information as to the molecular condition of the dissolved body. In a paper published in the ‘*Philosophical Magazine*’ for 1892, I described some experiments on the absorption spectra of solutions of copper salts, which were made from this point of view. It was found that with increasing dilution the spectra of the different salts examined tended to become the same. The solutions experimented with were, however, tolerably concentrated, which makes the interpretation of the results difficult, as, according to Kundt’s rule, the absorption spectrum of a substance varies to some extent with the dispersive power of the solvent in which it is dissolved, and, therefore, when working with strong solutions there is always the possibility that a change in the absorption, produced by changing the concentration of the solution, may be due to the alteration in dispersive power. In order to avoid this uncertainty, I have confined my attention almost exclusively to dilute aqueous solutions. In such solutions—differing very little from pure water—a change in colour can only be ascribed, according to our present knowledge, to some change in the nature of the dissolved substance, and therefore definite information as to the latter may be obtained.

A very large number of observations on the spectra of dilute solutions of salts of the same metal with different colourless acids and of the same acid with different colourless metals have been made by Ostwald (‘*Zeit. Phys. Chem.*,’ 9, 579, 1892). He measured the position of the absorption bands in the spectra, and also photographed them. Both methods of observation showed that the absorption spectra of all salts containing the same coloured metal or acid were identical. This is a necessary consequence of the electrolytic dissociation theory of Arrhenius. For at the concentrations employed, the salts being almost completely dissociated into their ions, the colour of all the salts containing the same coloured metal, for example, will be due to the same ion.

As, however, no photometric measurements of the absorption spectra of very dilute solutions have been made from this point of view, I thought it not superfluous to make a series of measurements

with solutions of copper salts. It was found that the solutions of copper bromide, chloride, nitrate, and sulphate possess—within the limits of experimental error—the same absorption spectrum, while that of copper acetate is different. The difference, however, diminishes with decreasing concentration.

The absorption spectrum of the dilute solutions of copper salts differs but little from those of concentrated solutions of copper sulphate and nitrate, although in the latter the salts are only partly dissociated into their ions, and in the former much more completely. Observations of a similar nature have led Magnanini\* to express the opinion that the absorption spectrum of a substance in solution is to be regarded as independent of the extent to which it is electrolytically dissociated. A more probable explanation is, as Ostwald has pointed out, that the absorption spectrum of the undissociated molecule is very nearly the same as that of the ions, and therefore a change in the degree of dissociation will produce little alteration in the spectrum.

A case in which the absorption of the undissociated molecule differs considerably from that of its ions was also investigated by Magnanini.† Solutions of the salts of violuric acid, in which the salt is almost completely dissociated, possess a violet colour; while Magnanini found the solutions of the free acid to be nearly colourless, although some 8 per cent. of the acid was dissociated into its ions. J. Wagner,‡ however, did not succeed in obtaining colourless solutions of the acid. He found that they had the same colour as the solutions of the salts, and a comparison of the intensity of colour in a solution of the free acid and in one of the sodium salt, showed that the intensity of the colour was nearly proportional to the number of ions present.

In dinitrophenol I have found another case of this sort. The solution containing only undissociated molecules is almost colourless, while solutions containing dissociated molecules are bright yellow. From the measurements of the absorption spectra of these solutions I have been able to calculate the fraction of the dinitrophenol dissociated into its ions at different concentrations, and the numbers so obtained are in very satisfactory agreement with those calculated from the electrical conductivity.

Besides the changes of colour which may be ascribed to the electrolytic dissociation of the dissolved substance, changes of colour occur in consequence of its hydrolysis by the water. As an example of this kind of change, I have studied the ferric salts, especially ferric chloride. The results are, however, more complicated than those obtained with

\* Magnanini, 'Rendic. Acc. Lincei,' (5), vol. 2, p. 17, 1893; Magnanini and Bentivoglio, 'Rendic. Acc. Lincei,' vol. 7, p. 356, 1891.

† 'Zeit. Phys. Chem.,' vol. 12, p. 56, 1893.

‡ Wagner, 'Zeit. Phys. Chem.,' vol. 12, p. 314, 1893.

bodies which are only electrolytically dissociated, and it will be better to consider them along with the experimental numbers. Changes of colour may also be due to the breaking up of polymeric molecules into smaller ones. It was found that solutions of colloid ferric hydroxide, obtained by dialysis, absorb less light than those obtained by the hydrolytic decomposition of ferric chloride, and in this case there is some reason to suppose that the dialysed hydroxide consists of larger molecular groups than that formed in the very dilute solution of ferric chloride.

#### *Apparatus Employed.*

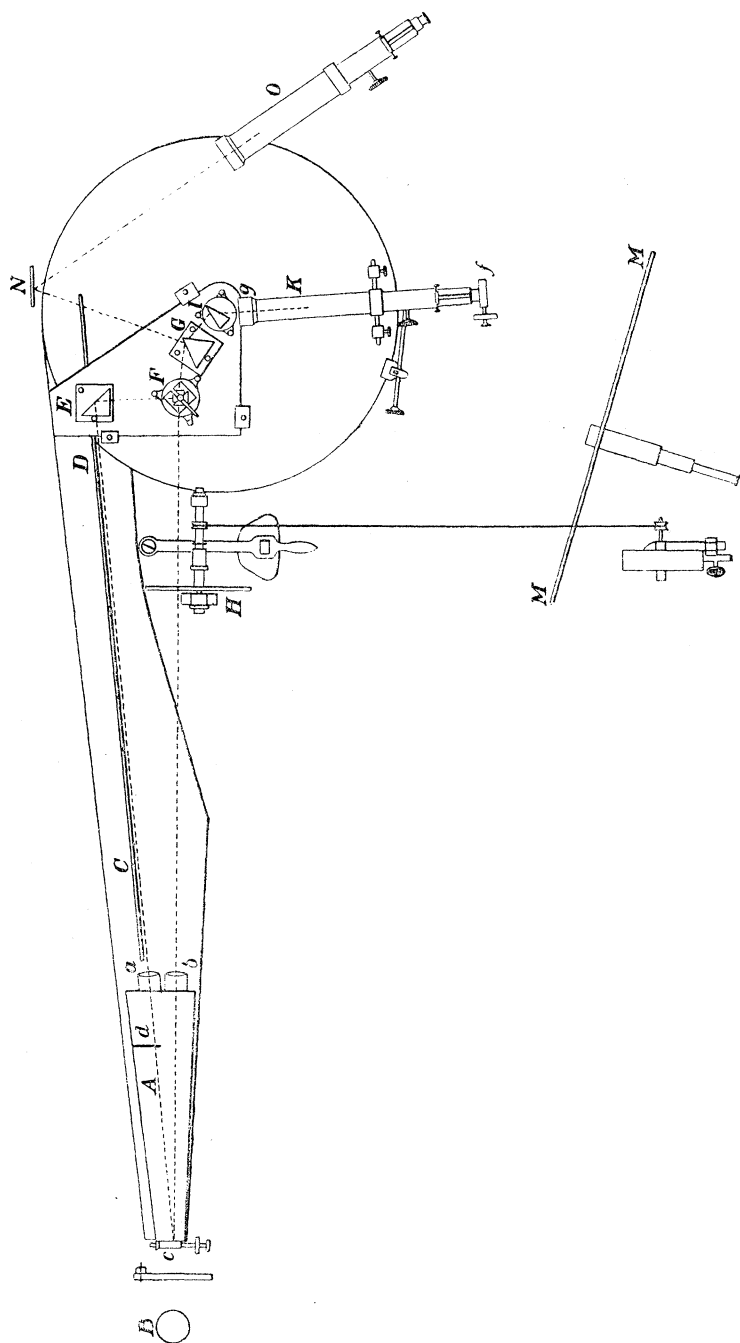
The measurement of the quantity of light of given wave-length which is absorbed by a substance in very dilute solution, is not very easy. In order to compensate for the small absorbing power of the solutions, it is necessary to employ long layers of them, and this makes it almost impossible to use a spectrophotometer such as that of Vierordt. The apparatus shown in fig. 1 was therefore put together.\* Both for advice and assistance in its construction, and for the loan of valuable apparatus, I am much indebted to Professor A. Schuster, F.R.S. My thanks are also due to the Government Grant Committee of the Royal Society, who provided me with the means of obtaining several pieces of apparatus.

Fig. 1 is a diagrammatic representation of the arrangement of the parts of the apparatus as seen from above.

It consists of a collimator A, with two lenses, *a* and *b*, of 20 in. focal length, which are both filled with light from the slit *c*. The source of light was an incandescent "Auer" lamp; and in order to distribute the light more evenly a plate of ground glass was introduced between the lamp and the slit. When it was desirable (as in the violet and extreme red ends of the spectrum) to obtain a stronger illumination this was removed. The parallel beam of light from the lens *a* passes through the solution; that from *b* was used as the standard of comparison; the object of using only one source of light being to keep the ratio between the brightness of these two beams constant. The solutions were contained in tubes which rested on Y-shaped supports capable of sliding along the bar C, D, which was clamped to the board on which the apparatus rested, and which allowed of a horizontal adjustment of the position of the tube. The Y-supports allowed of a vertical adjustment. The ends of the tubes were ground as nearly as possible parallel to each other, and closed by plates of glass which were simply pressed against the ground ends, no cement or washer being necessary. The tubes were 34—5 mm.

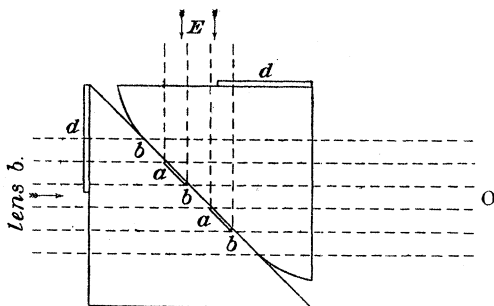
\* A description of a very similar instrument by Lummer and Brodhun appeared in the 'Zeitschrift für Instrumentenkunde,' 1892, p. 133, when my apparatus was nearly completed.

FIG. 1.



internal diameter, and the longest (length = 1 metre) was provided with five rings of ebonite (2—3 mm. wide), distributed at equal distances along its inside in order to prevent reflexion from the walls. The shorter tubes were provided with black paper rings at their ends for this purpose. After passing through the solution, the light is reflected internally by a right-angled flint-glass prism E, and falls on the Lummer and Brodhun prism F.\* The construction of this photometric prism has been described minutely by Lummer and Brodhun (*'Zeitschrift für Instrumentenkunde,'* 1889, p. 461; and 1892, p. 46). It consists of two right-angled prisms, ground and polished together on their hypotenuse surfaces, and held together as shown in fig. 2. Certain parts of the surface of one prism are removed, at *a, a* for example, so that the light coming from E is totally reflected at the surfaces *a*, but transmitted at *b*. The light from lens *b* is only transmitted at the surfaces *b*. Consequently, an eye placed at O sees the surface *b, b, b, a, a*, illuminated on the parts marked *a* by light from E, and on the parts *b* by light from the lens *b*. The measurement then consists in varying the brightness of the light coming from lens *b*, until the brightness of the different surfaces is the same. By means of glass plates at *d, d* (fig. 2), a reading by equal contrast

FIG. 2.



between two pairs of surfaces of somewhat different brightness, can also be made at the same time. For the details of this arrangement, however, I must refer to Lummer and Brodhun's original papers.

The variation of the intensity of the light from lens *b* was produced by means of the rotating sector described by Abney (*'Phil. Mag.,'* vol. 27, p. 62, 1889). The sector was made by Mr. A. Hilger.

After passing through the prism F, the two beams of light follow the same path through the two colourless flint-glass prisms G and I (one of 60°, the other 45°). The lens *g* then throws the spectrum thus pro-

\* It was made by Messrs. Schmidt and Haensch, of Berlin.

duced on to the slit,  $f$ . The tube K can be rotated round the centre of the iron table (represented in the figure by a circle; it was part of a large Steinheil spectroscope), and thus the slit  $f$  can be made to cut out portions of any desired wave-length from the spectrum. The eye placed behind the slit then sees the surface of the photometer prism in the colour of the part of the spectrum which is allowed to pass by the slit. Both slits were provided with micrometer screws, the heads of which were divided into 100 parts, and one whole turn of which opened the slit 0.5 mm. The axle round which the telescope, K, turns ended below the table in a small mirror, which turned with the telescope, and which served for reading its position by means of the millimetre scale and telescope, MM. The wave-lengths of the light passing through the slit,  $f$ , were measured by means of a small spectroscope with graduated arc, the readings of which were converted into wave-lengths by means of a curve drawn from readings of the positions of the principal Fraunhofer lines. The lamp was enclosed in a blackened box, and all the parts of the apparatus covered as much as possible by blackened screens. In the later measurements the lamp was connected with a gas pressure regulator, as variations in the gas pressure are apt to cause changes in the ratio of the brightness of the two beams of light.

A difficulty which was encountered at first was due to the ends of the glass tubes containing the solutions not being exactly parallel. They act as prisms of very small angle, and deflect the light which passes through them to some extent; so that, after adjusting the two images of the slit,  $c$ , which are formed by the two lenses,  $a$  and  $b$ , to fall together at  $f$ , and putting in the tube of solution, the two images no longer coincide. The light coming from the lens,  $b$ , is unchanged, while that from  $a$  has a colour differing from that which it had at first. It was therefore necessary to have some method of adjusting quickly and accurately the two images to fall together. This was done by allowing the light reflected from the front surface of the prism, G, to fall on a mirror, N, from which it was reflected into the telescope, O. This was an ordinary telescope, in which the two images of the slit,  $c$ , were seen, side by side, as two bright lines, which could easily be brought to coincidence by rotating somewhat the prism, F. A glance at fig. 2 will show that, by a small rotation of this prism, the direction of the light from the lens,  $b$ , is unchanged, while that of the light from  $a$  is changed by twice the angle through which the prism is rotated.

The careful adjustment of the apparatus was also necessary in order to obtain good results. This was done briefly as follows:—

The collimator lenses were placed at their focal distance from the slit,  $c$ , and the lamp arranged (the ground glass plate being removed) so that they were both just filled with light. The triangular ground

glass plate on which the prisms stand was then placed as nearly as possible horizontal, and the prisms adjusted with their refracting edges vertical by reflecting the light from the slit, *c*, first from one surface and then from the other into the telescope, K (the slit of this telescope being replaced by an eye-piece with cross threads) until the images reflected from the two surfaces were seen in the same position. The telescope, K, was then placed horizontal, and the collimator levelled, so that the images of the slit, *c*, seen in the telescope were in the centre of the field of view.

The right-angled prism, E, was then put in position and levelled, so that the light underwent no vertical displacement on passing through it. The Lummer and Brodhun prism is next treated in the same way, and finally the two refracting prisms are put in position and adjusted to minimum deviation. The angle at which the light was internally reflected in the right-angled prism was in my apparatus  $43^{\circ} 30'$ . As the critical angle for flint glass is  $37^{\circ} 19'$  there was no danger of the internal reflexion being incomplete. Finally it was found to be of great importance that the light should pass centrally through the tube of solution. To adjust the tube, cross threads were attached to the lens, *a*. This was conveniently done by means of a brass ring which just slipped over the tube carrying the lens to which the threads were attached. A card with a pin-hole in it was set up at a distance of about a metre and half from the lens in such a position that the prolongation of the line joining the centre of the slit, *c*, and the intersection of the cross threads passed through the pin-hole. The tube of solution, also provided with cross threads at each end, was then placed in position and adjusted, so that, on placing the eye behind the little hole in the card, the intersections of all three cross threads fell together. It was found that a perfectly satisfactory adjustment could be got in this way.

#### *Method of making the Readings.*

The sector being open to its full extent, the brightness of the two lights was arranged by putting a smoke-glass plate in the collimator at *d*, so that the comparison light was a little brighter than the other. The width of the slits was taken as small as was consistent with having sufficient light. Five readings were then made of the ratio between the intensities of the two beams. The tube of solution was then put in position, the two images adjusted to coincide, and five more readings made. Then the readings were repeated, the tube being, however, the second time placed in such a position that the deflection of the light was in the opposite direction; consequently the tube rotated  $180^{\circ}$  round its long axis.

When the means of these sets of readings did not agree, the ad-

justment was generally defective, and was repeated. As the apparatus was not very rigid, owing to its size, the adjustments had to be repeated every two or three weeks. That of the tube of solution was done before each set of measurements, and the wave-lengths of the light were read after each day's work. The following readings were made on a solution of  $\text{CuSO}_4$  in the tube 1 meter long; they are readings of average goodness, and will serve to show the sort of differences which occurred between the single readings. The numbers given are the openings of the sector.

Wave-length.	Single readings.	Mean.
621—613·5	59·0, 57·8, 57·2, 58·9, 56·8	57·94 solution out.
	11·8, 11·5, 11·8	11·73 } solution in.
	11·2, 11·5, 12·0	11·53 }
	57·2, 59·1, 58·4, 58·0, 57·9	58·12 solution out.
516—510·5	69·8, 71·3, 73·4, 72·0, 69·9	71·30 solution out.
	61·8, 60·9, 62·5, 57·0, 60·1	60·46 } solution in.
	58·9, 59·3, 61·0, 58·0, 63·0	60·04 }
	72·0, 70·9, 71·0, 71·4, 72·3	71·52 solution out.

### *Reduction of Results.*

The quantity which is directly measured is the amount of light which is lost by passing through a system consisting of two glass plates with a layer of aqueous solution between them. In order to calculate from these numbers the part of the light absorbed by the dissolved substance, it is necessary to allow for the light reflected or absorbed by the glass plates and the water. To obtain the necessary formulæ, I have applied the equations given by Stokes ('Roy. Soc. Proc.,' vol. 11, p. 545) to this special case as follows:—

Call the fraction of the light incident on the glass plate from air, which is reflected  $\rho = \left( \frac{\mu - 1}{\mu + 1} \right)^2$ , and the same quantity when the

light is incident from the liquid on the glass plate  $\rho' = \left( \frac{\mu' - 1}{\mu' + 1} \right)^2$ .

$\mu$  and  $\mu'$  are the refractive indices for air to glass and water to glass respectively. And suppose that a fraction  $(1 - a)$  of the light is absorbed by passing once through the glass plate. Then, allowing for the repeated reflections between the two surfaces of the plate, the quantity of light (calling its original intensity = 1) which will pass into the liquid is

$$t = \frac{(1 - \rho)(1 - \rho')a}{1 - a^2\rho\rho'},$$



and the part reflected will be

$$r = \rho + \frac{(1-\rho)^2 \rho' a^2}{1-a^2 \rho \rho'}.$$

If the light is incident on the plate from the liquid instead of from air, the part transmitted will be the same, while that reflected will be

$$r' = \rho' + \frac{(1-\rho')^2 \rho a^2}{1-a^2 \rho \rho'}.$$

Now consider in the same way the layer of liquid as being a plate, the end surfaces of which have the property of transmitting a fraction  $t$  of the light incident upon them, and of reflecting parts  $r$  or  $r'$ , according as the light is incident externally or internally, and which further transmits a part,  $b$  or  $c$ , of the light which passes through its whole length once. Take  $b$  to be the transmission coefficient for the solvent, and  $c$  that for the dissolved substance. Then the part of the light transmitted by the whole system is

$$T = \frac{t^2 b c}{1 - (b c)^2 r'^2} \dots \dots \dots (1).$$

$T$  is the quantity which is directly determined; from it we have to calculate  $c$ .  $b$ ,  $t$ , and  $r'$  are determined by preliminary experiments. The values of  $t$  and  $r'$  depend on the refractive indices of the glass plates and of the solutions. The solutions used were all so dilute that no appreciable error is made by using the same values for  $t$  and  $r'$  as are found for pure water.

Having found the value of  $c$ , the extinction coefficient  $\epsilon_1$ , for the dissolved body, is obtained by means of the relation  $-\log c = \epsilon_1$ .

The calculation of  $c$  from equation (1) may be much simplified in the following way. We may write equation (1):—

$$bc = \frac{T}{t^2} (1 - (bc)^2 r'^2).$$

For the glass plates used the greatest possible value of  $(bc)^2 r'^2$  was 0.0023. So that approximately  $(bc)^2 = \frac{T^2}{t^4}$ , from which

$$c = \frac{T}{t^2 b} \left( 1 - \frac{T^2}{t^4} r'^2 \right),$$

$$\text{or} \quad \epsilon_1 = -\log c = \log t^2 b - \log T - \log \left( 1 - \frac{T^2}{t^4} r'^2 \right) \dots (2).$$

$\log t^2 b$  only depends on the wave-length of the light used, and is most conveniently obtained from a curve drawn once for all. Also  $\frac{r'^2}{t^4}$  is

almost independent of the wave-length, and may be regarded as a constant, and the values of  $\log \left(1 - \frac{T^2}{t^4} r'^2\right)$ , read from a curve in which the values of  $\log T$  are taken for abscissæ. The wave-lengths and value of  $\log T$  being then directly determined, the calculation of  $\epsilon_1$  is extremely simple.

*Transmission Coefficients of the Glass Plates.*

The plates were of crown-glass 3·4 mm. thick, and of specific gravity 2·480. Their refractive index for sodium light determined by the method of De Chaulnes was 1·525. The refractive index was assumed to vary with the wave-length in the same way as that of a specimen of crown-glass examined by Fraunhofer.\*

Measurements were made of the light transmitted by two of these plates placed one behind the other, with the results contained in the following table. In it  $T$  is the light transmitted by the two plates, and  $\alpha$  the transmission coefficient for 3·4 mm. of the glass:—

Table I.

Wave-lengths.	Mean $\lambda$ .	$T$ .	$\alpha$ .
744 — 698·3	721·1	0·8561	1·0040
697·5—673	685·2	0·8578	1·0006
676 — 652	664·0	0·8542	0·9999
653 — 625·7	639·3	0·8465	0·9993
595·5—574·3	584·9	0·8451	0·9989
551·5—538·5	545·0	0·8476	1·0009
519·0—507	513·0	0·8436	0·9991
483·3—473	478·1	0·8374	0·9959
454·2—446·8	450·5	0·8266	0·9900
433·5—426·4	429·9	0·8248	0·9896
418·0—411·0	414·5	0·8214	0·9879

It will be seen that to a wave-length of about 513 the glass was completely transparent, the loss of light on passing through the plates being entirely accounted for by the reflections at their surfaces. A small absorption of light appears to take place in the violet.

*Absorption of Light by Water.*

As is well known, the presence of dust in water greatly diminishes its transparency. In order, therefore, to get the water as free as

\* Its specific gravity was 2·535 and its refractive index for the line D = 1·529 (see Wüllner, 'Experimental-Physik,' II, p. 157).

possible from dust, ordinary distilled water was taken and distilled a second time from a metal can with black-tin condenser, the first third of the distillate being rejected. This water, filled immediately into the tube, was almost free from visible dust in a layer 1 m. long. It was just visibly blue. I found afterwards that water filtered through a "Chamberland Pasteur candle" was even more devoid of dust than that which had been freshly distilled, and some measurements were made with such filtered water. There was, however, no noticeable difference in the numbers.

The actual measurements of the light transmitted by a tube of water 100.1 cm. long are given in the Appendix Table I. A curve smoothed as little as possible was drawn from these numbers, and the values of  $T$  in Table II interpolated from it. From them the values of the extinction coefficient for 1 cm. of water ( $\epsilon = -\frac{\log b}{100.1}$ ) were calculated.

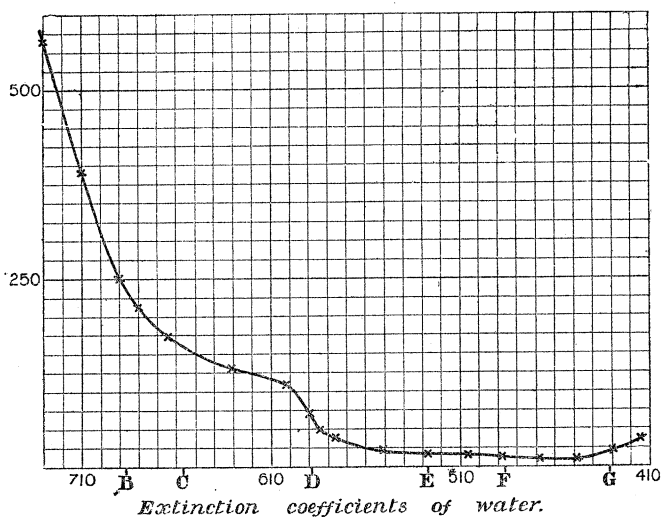
Table II.

Mean $\lambda$ .	$T$ (from curve).	$\epsilon$ .	$\epsilon$ (Hüfner and Albrecht).
730	0.246	0.00567	
710	0.37	0.00390	
690	0.51	0.00251	
680	0.5595	0.00210	
664.5	0.6105	0.00173	0.00171
631	0.6732	0.00130	0.00122
602	0.7075	0.00109	0.00109
590	0.765	0.00070	
584	0.814	0.00048	
576.5	0.8315	0.00039	0.00049
551.5	0.861	0.00023	0.00033
527	0.869	0.00019	0.00019
506	0.8728	0.00016	0.00018
487	0.8737	0.00014	0.00016
468	0.8727	0.00012	0.00012
449	0.868	0.00012	0.00012
430	0.8425	0.00023	
415	0.815	0.00035	

The numbers obtained by Hüfner and Albrecht ('Wied. Ann.,' vol. 42, p. 10, 1891) are also included in the table. The agreement is satisfactory except at wave-lengths 576.5 and 551.5. Owing to this lack of agreement I repeated the measurements in this part of the spectrum several times, but never found such large absorptions as Hüfner and Albrecht.

In fig. 3 the values of  $\epsilon$  are plotted against the wave-lengths. The absorption diminishes very rapidly between the solar lines A and B,

FIG. 3.



and again in the neighbourhood of D, corresponding to the two absorption bands which have been described by several authors.\* It is also noticeable that the absorption slightly increases in the violet near G.

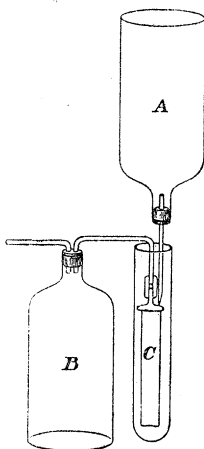
#### *Solutions of Cupric Salts.*

The salts used were cupric sulphate, nitrate, chloride, bromide, and acetate. They were purified carefully, notwithstanding which the solutions made by dissolving them in water were not sufficiently clear to be measured. Filtration through fine Swedish filter paper only improved them a little. The desired freedom from suspended particles was, however, easily obtained by filtration through porous earthenware. The apparatus shown in fig. 4 was found to be very convenient, as it allowed of two or three litres of a solution being filtered without requiring any attention. A and B are ordinary Winchester quart bottles, C is the "Chamberland Pasteur candle." The solution to be filtered is contained in A. B is evacuated, and the apparatus left to itself till the solution has filtered. Two litres could be filtered in an hour, or less if a good vacuum was kept up.

The solutions measured were always analysed as the filtration changes their concentration somewhat. Two methods of analysis were used, and the mean result taken.

\* Schönn, 'Pogg. Ann. Ergz.,' 8, p. 670, 1878; Russel and Saprak, 'Nature,' 22, p. 368, 1880; and Soret and Sarasin, 'Arch. de Sc. Phys. et Nat.,' vol. 11, p. 327, 1884.

FIG. 4.



(1.) From 0.5 to 1 litre of the solution was evaporated to dryness (with a little hydrochloric or acetic acid) on the water bath, the residue dissolved in a small quantity of water, excess of potassium iodide added, and the liberated iodine titrated with sodium thio-sulphate solution. In order to obtain accurate results by this method the cupric solution must be concentrated, otherwise the reaction with potassium iodide is incomplete, and the thiosulphate solution must be standardised by means of pure  $\text{CuSO}_4$  in exactly the same way as it is subsequently to be used in the analyses.

(2.) The solutions, without evaporation, were titrated with potassium cyanide solution in presence of ammonia. Here also the KCN solution was always standardised by means of a solution of  $\text{CuSO}_4$  of known strength before using it, as its strength changes on keeping. The results of the two methods agreed satisfactorily.

The results of the photometric measurements are contained in Table II Appendix. In order to be able to compare the absorption spectra of the different solutions, the extinction coefficients  $\epsilon$  for the dissolved substance for 1 cm. layer, and for a concentration of 1 gram molecule per litre, have been calculated from the values of  $\epsilon_1$  given by equation 2 (p. 125). The extinction coefficient is proportional to the length of layer ( $l$ ), and to the concentration ( $c$ ), so that  $\epsilon = \frac{\epsilon_1}{c.l.}$ . From these values of

$\epsilon$  curves were drawn (not smoothed), and from them the numbers contained in the following table (Table III) were interpolated.

The Roman numerals at the head of each column indicate that the figures are derived from the experiment similarly numbered in the Appendix.

Table III.

Mean $\lambda$ .	$\epsilon$ CuSO <sub>4</sub> .			$\epsilon$ CuCl <sub>2</sub> .		$\epsilon$ Cu(NO <sub>3</sub> ) <sub>2</sub> .			$\epsilon$ CuBr <sub>2</sub> .		$\epsilon$ Cu(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> . X and XI.
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.		
660	—	—	—	—	—	—	—	—	—	3.200	
650	2.615	2.939	2.939	2.790	2.730	—	—	—	—	2.737	
640	2.141	2.362	2.362	2.272	2.282	—	—	—	—	2.284	
630	1.748	1.892	1.892	1.879	1.862	—	—	—	—	1.911	
613.5	—	1.305	1.305	1.305	1.253	2.055	1.830	2.034	1.350	4.359	
586.8	—	0.623	0.623	0.623	0.587	1.342	1.110	1.385	0.640	3.119	
562.9	—	0.310	0.310	0.310	0.279	0.695	0.538	0.640	0.291	1.535	
542.8	—	0.158	0.158	0.158	0.110	0.334	0.293	0.291	0.158	0.712	
526.2	—	0.080	0.080	0.080	0.048	0.175	0.138	0.158	0.083	0.327	
510.3	—	0.045	0.045	0.045	0.020	0.105	0.067	0.083	0.039	0.161	
495.3	—	0.021	0.021	0.021	0.005	0.062	0.026	0.039	0.020	0.061	
481.5	—	0.005	0.005	0.005	—	0.037	—	0.020	0.009	0.035	
						0.019	—	0.009		0.020	

In some cases the numbers given by two different sets of measurements were so nearly the same that they were united to one curve. This was the case with  $\text{CuSO}_4$  III and II and part of the numbers for  $\text{CuCl}_2$ ; and also with the two solutions of  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$  X and XI. Leaving for the present the numbers for  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$  out of account, it is evident that the differences which occur between the numbers obtained with different solutions of the same salt are as great as those which are found between solutions of different salts. The absorption spectra of the four salts  $\text{CuSO}_4$ ,  $\text{CuCl}_2$ ,  $\text{Cu}(\text{NO}_3)_2$ , and  $\text{CuBr}_2$  must accordingly, in the concentrations used, be regarded as the same.

In the following table (p. 132) the means of the above numbers are compared with the numbers which I formerly obtained ('Phil. Mag.' [5], vol. 33, p. 317, 1892).

These numbers show that the absorptions change very little when the solutions are diluted. The electrolytic dissociation, however, changes considerably. For  $\text{CuSO}_4$  the fraction of the salt electrolytically dissociated increases from 0.317 in the stronger solution to 0.494 in the more dilute. For  $\text{CuCl}_2$  the increase is from 0.634 to 0.920. That the change in dissociation produces very little change in the absorption is most simply explained by supposing that the Cu existing in chemical combination with other atoms in the solution has the same absorption spectrum as the copper ion. In the case of  $\text{CuCl}_2$  this leads to a result of some interest. For the concentrated aqueous solution of cupric chloride and also its alcoholic and ethereal solutions are brownish-green in colour, and as these solutions doubtless contain the molecule  $\text{CuCl}_2$  we cannot ascribe to it the same absorption spectrum as to the Cu ion. In the dilute solutions of  $\text{CuCl}_2$  examined, therefore, the combined part of the copper probably exists in the form of the ion  $\text{CuCl}$ . This is also in good agreement with the observation which I made formerly ('Phil. Mag.', 1892): that the rapid change in the absorption spectrum which accompanies the dilution of a concentrated solution of  $\text{CuCl}_2$  ceases when the concentration reaches a value lying between 0.5 and 0.2 gram molecules per litre. The fractions of the salt dissociated in these concentrations, calculated from the electrical conductivities of the solutions, are 0.41 and 0.634 respectively. It would appear thus that on diluting a strong solution of cupric chloride the  $\text{CuCl}_2$  molecules first dissociate into the ions  $\text{CuCl}$  and  $\text{Cl}$ , and that the dissociation of the  $\text{CuCl}$  ions only takes place to any considerable extent after this process is tolerably complete, that is, after the dissociation of the salt has reached 50 per cent. This behaviour is very common in the case of dibasic acids, of which a large number have been examined by Ostwald ('Zeitschrift für Phys. Chem.', vol. 3, pp. 186 and 280, 1889).

It will be seen from Table III that the extinction coefficients of

Table IV.

Mean $\lambda$ .	$\epsilon$ for $\text{CuSO}_4$ , $c = 0.00373$ .	Old numbers. $c = 0.14$ .	$\epsilon$ for $\text{CuCl}_2$ , $c = 0.00397$ .	Old numbers. $c = 0.2$ .	$\epsilon$ for $\text{Cu}(\text{NO}_3)_2$ , $c = 0.00447$ .	Old numbers. $c = 0.175$ .	$\epsilon$ for $\text{CuBr}_2$ , $c = 0.00445$ .
660	—	—	—	—	—	—	3.200
650	2.831	—	2.790	—	2.730	—	2.737
640	2.288	—	2.272	—	2.282	—	2.284
630	1.844	—	1.879	—	1.915	—	1.972
613.5	1.305	1.117	1.305	1.042	1.235	1.020	1.367
586.8	0.623	0.586	0.623	0.535	0.607	0.531	0.640
562.9	0.310	0.294	0.310	0.291	0.302	0.328	0.291
542.8	0.158	0.158	0.158	0.152	0.141	0.167	0.158
526.2	0.080	0.091	0.080	0.083	0.073	0.085	0.083
510.3	0.045	0.049	0.045	0.047	0.086	0.043	0.039
495.3	0.021	0.024	0.021	0.026	0.021	0.022	0.020
481.5	0.005	0.014	0.005	0.015	0.009	—	0.009

The concentration,  $c$ , is given in gram molecules per litre.



solutions of copper acetate are much larger than those of the other salts. The concentrations of the two solutions, the measurements on which are there given, were 0·003748 and 0·004203 gram molecules per litre respectively. The following numbers (Table V) show that the extinction coefficients diminish rapidly when the concentration becomes smaller. The most dilute solution used still gives larger extinction coefficients than those found for the other copper salts, but it was unfortunately not possible with my apparatus to make accurate measurements with still smaller concentrations, so that I was unable to find out whether the absorption spectrum of copper acetate becomes ultimately identical with that of the others or not; it appears, however, to tend to do so.\*

Table V.—Copper Acetate (c).

Conc. ....	0·003748	0·0007144	Mean $\epsilon$ for other salts of copper.
$\lambda$ .	X.	XII.	
650	—	4·412	2·772
640	—	3·625	2·281
630	4·359	2·785	1·902
613·5	3·119	1·450	1·303
586·8	1·535	0·735	0·623
562·9	0·712	0·470	0·303

Two explanations of the abnormal behaviour of copper acetate solutions offer themselves: (1) The electrolytic dissociation into Cu ions may be incomplete, and the still undissociated part of the salt may have a different colour from the Cu ion; (2) the salt may be partially hydrolysed, acetic acid being a so much weaker acid than the others used. In the latter case, however, one would expect the difference between the spectrum of copper acetate and that of the other salts to become greater with increasing dilution, as in the more dilute solutions the hydrolytic decomposition would be most advanced. The opposite, however, is the case. The addition of acetic acid to the solutions should, by diminishing the amount of hydrolysis, bring the copper acetate spectrum nearer to that of the others, if the

\* The uncertainty of observations of absorption spectra made without the help of photometric measurements is illustrated by the following remark of Knoblauch ('Wied. Ann.' vol. 43, p. 754). He says: "Ebensowenig wie bei Kupfersulfat zeigte sich bei Kupferacetat mit der Verdünnung eine Veränderung im Character des Spectrums. Die Beobachtung der Absorptions-Grenze im Roth war auch bei diesem Salze für verdünnte Lösungen durch die Absorption des Wassers beeinträchtigt." Table V shows that a not very considerable dilution (about one to five) reduced the absorbing power of a copper acetate solution by about one-half.

difference were due to hydrolytic decomposition. The following measurements of  $\epsilon$  show that again the opposite to this really occurs.

Table VI.

Conc. $\left\{ \begin{array}{l} \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \\ \text{Acetic acid.} \end{array} \right.$	0·0007144 —	0·0007395 0·00155	0·00289 0·0088	0·00479 0·136	0·004203 —
$\lambda$ .	XII.	XV.	XIII.	XIV.	XI.
650	4·412	4·515			
640	3·625	3·730			
630	2·785	2·931	—	—	4·359
613·5	1·450	1·745	2·720	3·321	3·119
586·8	0·735	0·818	1·287	1·760	1·535
562·9	0·470	—	0·681	0·958	0·712
542·8	—	—	—	0·470	0·327

That some very small amount of hydrolytic dissociation takes place is, however, probable. Dibbitts\* found that a solution of copper acetate in the cold is very weakly acid towards litmus, and that on warming it basic salts separate out, and on boiling the decomposition into acetic acid and basic salt reaches about 50 per cent. The most dilute solutions which I used did not deposit any visible quantity of copper hydroxide on the porous vessel through which they were filtered, and, even after standing for three days, the filtered solution remained perfectly clear. The behaviour of the solutions of copper acetate is, on the other hand, qualitatively at any rate, in agreement with the hypothesis that the substance is dissociated into ions. Professor J. H. van't Hoff was so kind as to place the results of an unpublished set of determinations made by him of the electrical conductivity of solutions of copper acetate at my disposal, for which I take this opportunity of again expressing my indebtedness to him. The numbers are given in Table VII.

$\mu_\infty$  for copper acetate is calculated from Kohlrausch's numbers as follows:— $\mu_\infty$  for  $\frac{1}{2}\text{CuSO}_4$  at  $14^\circ\text{C} = 100\cdot2$ .

The difference between  $\mu_\infty \frac{1}{2}(\text{K}_2\text{SO}_4)$  and  $\mu_\infty \text{KC}_2\text{H}_3\text{O}_2$  at  $14^\circ\text{C} = 30\cdot4$ ,

So that we get  $\mu_\infty \frac{1}{2}\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$  at  $14^\circ\text{C} = 69\cdot8$ .

It will be noticed that  $k$  remains constant till  $0\cdot35$  of the salt is dissociated, after which it diminishes. This behaviour reminds one strongly of that of the dibasic acids studied by Ostwald ('Zeitschrift für Phys. Chem.,' vol. 3, p. 170, 1889); the only difference is that with the acids  $k$  finally increases instead of diminishing. It

\* 'Maandblad voor Natuurwetenschappen,' vol. 3, p. 80, 1873, and vol. 4, p. 104, 1874.

Table VII.—Electrical Conductivity of Copper Acetate Solutions.  
At 14.1°.

V.	$\mu$ .	$a$ .	$k$ .
4.06	19.8	0.1418	0.0058
$4.06 \times 2$	26.9	0.1927	0.0057
$4.06 \times 2^2$	37.1	0.2658	0.0059
$4.06 \times 2^3$	48.1	0.3446	0.0057
$4.06 \times 2^4$	60.7	0.4348	0.0052
$4.06 \times 2^5$	74.7	0.5351	0.0047
$4.06 \times 2^6$	90	0.6447	0.0045
$4.06 \times 2^7$	101.3	0.7257	0.0037

$$\mu_{\infty} = 139.6.$$

V = vol. in litres in which 1 gram molecule  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$  is dissolved.

$\mu$  = molecular conductivity.

$$k = \frac{a^2}{(1-a)V}.$$

$a = \frac{\mu}{\mu_{\infty}}$  = fraction of the copper acetate dissociated into ions.

seems probable then that just as the dibasic acid first split off one hydrogen atom as an ion and then the second, so the copper acetate splits up first into the ions  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)$  and  $(\text{C}_2\text{H}_3\text{O}_2)$ , and then the ion  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)$  breaks up, after the first process is fairly complete, into the ions Cu and  $(\text{C}_2\text{H}_3\text{O}_2)$ . Calculated from the numbers for the electrolytic conductivity given above the quantities of the salt dissociated in the two solutions in Table V are—

Conc. .... 0.003748 = 65 per cent.

0.0007144 = 85 „ (extrapolated).

These two solutions will accordingly contain the ions Cu and  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)$ , the greater the quantity of the latter the more will the colour of the solution differ from the normal. The addition of acetic acid to the solution diminishes the dissociation of the copper salt, and so increases the difference of the colour from the normal.

#### *Salts of Dinitrophenol, $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{OH}$ (2.4.1).*

The dinitrophenol used was the ordinary one; the specimen obtained from Kahlbaum melted at 114—115°. The potassium and ammonium salts were prepared from it. They both crystallise very well, the former in orange, the latter in bright yellow needles, and are therefore easily obtained pure.

The potassium salt lost on prolonged heating  
to 100° ..... 3.95 per cent.  $\text{H}_2\text{O}$ . }  
Calculated for  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{OK} + \frac{1}{2}\text{H}_2\text{O}$  ..... 3.9 „ }

The ammonium salt volatilises on heating. The ammonia was therefore determined.

NH <sub>3</sub> found .....	7.69 per cent. }
NH <sub>3</sub> calculated for C <sub>6</sub> H <sub>3</sub> (NO <sub>2</sub> ) <sub>2</sub> ONH <sub>4</sub> .....	7.76 „ }

As I could find no satisfactory way of analysing the dilute solutions of these salts, I made them by dissolving a weighed quantity of the carefully purified salt in water. The solutions so obtained were fairly clear. The values of  $\epsilon$  (the extinction coefficient for the dissolved body for 1 cm. layer and 1 gram molecule per litre concentration) are given in the following table. The experimental numbers are given in the same way as before in the Appendix Table III.

The numbers given in Table VIII are obtained from the numbers in Table III of the Appendix by graphical interpolation. The concentrations are in gram molecules per litre.

The two most concentrated solutions used give somewhat smaller numbers than the others, which may probably be attributed to the electrolytic dissociation being incomplete in the stronger solutions. The numbers obtained with the other solutions vary irregularly; by taking their mean the following numbers are obtained.

$\lambda$ .	K salt.	NH <sub>4</sub> salt.
530	—	2.195
520	4.19	3.995
510	10.82	10.85
500	26.26	25.1
490	67.23	74.5
480	194.3	173.4
470	398.5	368.0

The absorption increases so extremely rapidly between the wavelengths 470 and 500 that a small error in the measurement of the wave-length can make a great difference in the value of  $\epsilon$  obtained. Taking this into account the absorption spectra of the potassium and ammonium salts may be regarded as the same. These salts dissociate electrolytically into the ions K<sup>+</sup> or NH<sub>4</sub><sup>+</sup> and C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>O—. The mean of the above numbers may therefore be taken as representing the absorption spectrum of the ion C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>O.

#### *Dinitrophenol.*

The behaviour of the solutions of the free dinitrophenol is of some interest. The solutions in benzene or ether are brownish-yellow, but the colour is faint, and unless they are fairly concentrated they appear colourless. An alcoholic solution is much more strongly

Table VIII.

$c =$	Potassium salt of dinitrophenol.				Ammonium salt of dinitrophenol.			
	0.001646	0.0004107	0.0001027	0.0001027	0.00009861	0.004739	0.001185	0.001185
$\lambda$	XVI.	XVII.	XIX.	XVIII.	XX.	XXI.	XXII.	XXIII.
670	0.121	—	—	—	—	0.319	0.939	—
680	0.270	—	—	—	—	0.409	1.278	1.48
590	0.181	—	—	—	—	0.715	2.15	2.04
560	0.305	—	—	—	—	1.614	4.25	3.74
550	0.488	—	—	—	—	—	—	10.85
540	0.823	—	—	—	—	—	—	25.1
530	1.995	—	—	—	—	—	—	—
520	—	4.19	—	—	10.8	—	—	—
510	—	10.85	—	—	27.0	—	—	—
500	—	25.01	26.8	—	63.5	—	—	—
490	—	—	62.1	76.1	186.5	—	—	—
482.5	—	—	124.94	151.8	—	—	—	—
480	—	—	—	194.3	—	—	—	—
470	—	—	—	398.5	—	—	—	—
								74.5
								173.4
								368.0

yellow, and a saturated aqueous solution is bright yellow. A drop of potash solution added to either the alcoholic or aqueous solutions increases the depth of colour. The addition of hydrochloric acid diminishes it, till, with some excess of acid, it disappears almost entirely. The fact that the solutions of dinitrophenol in benzene or ether are only faintly coloured, suggests that the undissociated dinitrophenol molecule is devoid of any great absorbing power in the visible spectrum. The action of the hydrochloric acid in decolorising the solutions of dinitrophenol is also due to its converting the dissociated molecules into undissociated molecules.\* In order to obtain the spectrum of the undissociated dinitrophenol a solution of dinitrophenol to which excess of hydrochloric acid had been added was used.

The dinitrophenol had been recrystallised from water, notwithstanding which the solutions obtained from it were never sufficiently clear. They had, therefore, to be filtered through the porous earthenware and analysed. The analysis was made by titration with a dilute ammonia solution, using litmus as indicator. The change of colour not being very sharp, standard hydrochloric acid was added till the liquid was acid, and then ammonia till alkaline, and so on several times. Tests with solutions of known concentration showed that accurate results could be obtained in this way. The following table contains the extinction coefficients of the solution containing excess of hydrochloric acid, and also for comparison, the mean of the numbers obtained with the potassium and ammonium salts.

Table IX.

$\lambda$ .	$c = \begin{cases} 0.001202 \text{ dinitrophenol} \\ + 0.2132 \text{ gr. mol. HCl.} \end{cases}$	Mean $\epsilon$ for K and $\text{NH}_4$ salts.
520	0.321	4.09
510	0.355	10.83
500	0.397	25.68
490	0.456	70.86
480	0.553	183.85
470	0.600	383.25
460	0.974	
450	2.284	

It is evident that the absorption of the acid solution is almost negligible compared with that of the solutions of the salts.

With the help of these numbers it is possible to calculate the frac-

\* Arrhenius, 'Zeitschrift Phys. Chem.,' vol. 2, p. 284, 1888, and vol. 5, p. 1, 1890.

tion of the dinitrophenol which is electrolytically dissociated in a solution, a measurement of its extinction coefficient for any one wave-length having been made. If  $x$  is the part which is dissociated into its ions, the extinction coefficient of the solution (calculated for unit concentration and 1 cm. layer) will be

$$\epsilon_{(\text{sol.})} = x\epsilon_{(\text{ion})} + (1-x)\epsilon_{(\text{undiss.})}.$$

Table X contains the results of the measurements of a number of solutions of dinitrophenol of different concentrations. For the experimental details see Appendix, Table V. In Table X,  $\epsilon_s$ ,  $\epsilon_i$ , and  $\epsilon_u$ , are the extinction coefficients for the solution actually measured, for the ion,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{O}$ , and for the undissociated molecule of dinitrophenol respectively. The values of  $\epsilon_i$ , as remarked above, are taken as the mean of the measurements made with dilute solutions of the potassium and ammonium salts.

$x$  the fraction dissociated is calculated from the equation given above.

Table X.

$\lambda$ .	$c$ = concentration.	$\epsilon_s$ .	$\epsilon_i$ .	$\epsilon_u$ .	$x$ .	Mean $x$ .	$x$ (cal.).
480.2	0.001581	46.69	181.2	0.550	0.2554		
496	—	9.44	36.23	0.419	0.2519		
497.5	—	7.829	32.47	0.410	0.2314		
497.7	—	6.421	31.76	0.409	0.1915		
487.2	—	20.8	91.1	0.480	0.2242	0.2309	0.2010
479.2	0.0007905	61.58	198.5	0.564	0.3083		
493.3	—	11.52	46.2	0.432	0.2423		
480.8	—	36.93	172.2	0.544	0.2120	0.2509	0.2715
493.6	0.000395	17.11	44.84	0.431	0.3756		
476.8	—	83.07	241.8	0.597	0.3419	0.3588	0.3600
472.1	0.0001581	163.9	332.3	0.663	0.4923		
493.2	—	23.83	46.7	0.433	0.4017	0.4470	0.5018
496.2	0.00001581	32.3	35.67	0.418	0.9044		
473.8	—	278.5	298.5	0.641	0.9329	0.9187	0.8539
480.1	0.002886	32.86	182.2	0.551	0.1779		
479	—	33.37	202	0.568	0.1629	0.1709	0.1532

The numbers under  $x$  calculated are the fractions of the substance electrolytically dissociated calculated from the determinations of the electrical conductivity of solutions of dinitrophenol made by Bader. ('Zeit. Phys. Chem.,' vol. 6, p. 298, 1890). He found the dissociation constant of dinitrophenol  $K = 0.008$ . This is connected with  $x$  by the formula  $K = \frac{100x^2}{(1-x)V}$ .

$V$ , the volume in litres in which 1 gram molecule is dissolved, may be replaced by  $\frac{1}{c}$ , which gives

$$x = \frac{1}{200c} [\sqrt{3.2c + 0.000064} - 0.008].$$

The agreement found between the numbers obtained from two so very different properties as the absorption of light and electric conductivity, is so striking, taking into account the very considerable experimental error, that little doubt can be felt as to the substantial accuracy of the hypothesis on which the whole calculation is based.

### *Ferric Salts.*

The changes of colour which take place when the aqueous solution of a ferric salt is diluted are so considerable that they appear to offer a very suitable means of determining the amount and nature of the decomposition which the salt undergoes.

In 1856, Péan de St. Gilles,\* made a study of the decomposition which ferric salts undergo on heating their aqueous solutions. He noticed the peculiar appearance of the solutions containing ferric hydroxide, they being clear by transmitted, but apparently turbid by reflected light. He was aware that the hydrate exists in the liquid in a state of pseudo solution and uncombined with the acid present, as the following remark shows:—"Il semblerait plutôt que l'acide acétique exerce sur l'hydrate une action purement mécanique en divisant à l'extrême les particules insolubles et simulant ainsi une dissolution véritable."

In 1861, Graham† showed how the colloidal ferric hydroxide can be prepared by dialysis, and described its principal properties. He regarded it as being different from the soluble hydroxide obtained by Péan de St. Gilles, by heating the solution of ferric acetate.

Gunning,‡ in 1869, Tichborne,§ in 1871, and Berthelot,|| in 1873, made studies of the decompositions which occur both on heating the solutions and on diluting them with water. Their results, however, do not lend themselves to a calculation of the amount of decomposition which has taken place. In 1871, Krecke¶ made a number of determinations of the quantity of ferric hydroxide formed in solutions of ferric chloride of different concentrations, and at various temperatures. The amount of ferric hydroxide present was determined by precipitating it with sodium chloride. He found that the precipitate formed by heating solutions of ferric chloride containing more than 4 per cent. of the salt contained a variable amount of chlorine. The more

\* 'Ann. Chim. Phys.,' (3), vol. 46, p. 47, 1856.

† 'Phil. Trans.,' 1861, p. 209.

‡ 'Aanteekeningen, etc., Prov. Utrechtsche Genootschap, 1869, p. 14.

§ 'Roy. Irish Acad. Proc.,' 1871, p. 169.

|| 'Ann. Chim. Phys.,' (4), vol. 30, p. 145, 1873.

¶ 'J. prakt. Chem.,' (2), vol. 3, p. 286, 1871.



dilute solutions deposit only ferric hydroxide. He found also that the amount of decomposition increases with rising temperature and increasing dilution.

Finally, G. Wiedemann,\* in 1878, published an investigation on the hydrolysis of ferric salts, the determinations of the amount of hydrolysis which had taken place being made by means of the molecular magnetism of the solutions. The molecular magnetism of iron in the form of hydroxide being 0.16 of its value in a strongly acid solution, a measurement of the magnetism of a solution of known strength allows the ratio in which the iron is divided between the two forms to be calculated.

The fact that, as Krecke observed, the precipitate formed by heating solutions of ferric chloride contains chlorine, and also an observation made by Picton and Linder,† that on filtering a solution of colloid ferric hydroxide containing chlorine through a porous cell the filtrate contained neither iron nor chlorine, led me in the first place to attempt to decide whether the hydroxide formed in dilute solutions of ferric chloride contained chlorine or not.

For this purpose solutions of known concentration were filtered through a porous cell. The cell was first well washed with distilled water, and then a quantity of the solution filtered through it to remove the water from its pores. The next portion of the filtered solution was collected and analysed. The difference between the composition of the original solution and that of the filtrate gives the composition of the substance held back by the porous cell. The filtration apparently removed the hydroxide completely from the solution. The yellow-brown coloured solutions were, after filtration, either completely colourless or very faintly yellow, according to their concentration. This method of analysis has the drawback that the solution changes its concentration to some extent during the filtration partly owing to evaporation in the vacuous vessel into which it is filtered, partly owing to the difficulty in removing the water which has served for washing the cell from its pores. A direct analysis of the precipitate is hardly possible as it cannot be collected on a filter, nor can it be washed by decantation, as it refuses to settle. Further, to wash it with water is not allowable, as it would tend to change its composition. The ferric chloride used was purified by repeated recrystallisation of the hydrate,  $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ ;‡ an analysis of its solution showed that it contained iron and chlorine in the ratio represented by its formula.

\* 'Wied. Ann.,' vol. 5, p. 45, 1878.

† 'Journ. Chem. Soc.,' 1892, p. 152.

‡ Bakhuis Roozeboom, 'Zeit. Phys. Chem.,' vol. 10, p. 477, 1892.

250 c.c. of a solution of the salt gave  $\begin{cases} 0.1042 \text{ gram Fe}_2\text{O}_3. \\ 0.5639 \text{ ,, AgCl.} \end{cases}$

From which ratio  $\frac{\text{Cl}}{\text{Fe}} = 1.913.$

Ratio calculated for  $\text{Fe}_2\text{Cl}_6 = 1.903.$

Two other solutions which were subsequently analysed, contained

1.882 grams eqs. Fe per litre to 1.864 grams eqs. Cl.

and 0.0303 ,, ,, 0.0296 ,,

The dilute solutions made by diluting a concentrated solution of known concentration, were allowed to stand for some weeks at the ordinary temperature ( $15-16^\circ$ ), so that a condition of equilibrium was almost certainly reached.

The following table contains the results of the filtration experiments. The concentrations are here (as elsewhere in the paper) given in gram molecules per litre, the molecule of the ferric salts being always taken, for convenience, as the quantity containing one atom of iron.

Table XI.

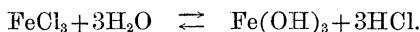
Concentration of unfiltered solution.		Concentration of filtered solution.		Loss per cent.		$k_1.$	$k_2.$
Fe.	Cl.	Fe.	Cl.	Fe.	Cl.		
0.00505	0.0148	0.00319	0.01453	36.83	1.93	922	346
0.002525	0.0074	0.00126	0.00728	50.10	1.75	787	394
0.001263	0.0037	0.000445	0.00376	64.77	-1.48	664	430
0.000505	0.00148	0.000095	0.00143	81.19	3.51	565	459

The decrease in the concentration of chlorine in the solutions, caused by filtration, is so small (in one case there was even an increase), that it appears probable that the substance separated from the solutions is really a hydroxide of iron, and contains no chlorine. The changes of concentration of the chlorine are probably sufficiently explained by the errors inherent in the method used, which have been already mentioned. On the other hand the loss of iron increases as the solutions become more dilute.

Walker\* found, in an investigation on the hydrolysis of the salts of some weak bases, that the decomposition took place in agreement

\* 'Zeitschrift f. Phys. Chem.,' vol. 4, p. 319, 1889.

with the law of Guldberg and Waage. This is, however, here not the case. The equilibrium which takes place in dilute solutions of ferric chloride may be most simply represented by the equation



Suppose that to begin with one gram molecule of  $\text{FeCl}_3$  was dissolved in  $n$  molecules of water, neither hydrochloric acid nor ferric hydroxide being present. When the equilibrium is reached, suppose that a fraction  $x$  of the ferric chloride molecules have been decomposed. Then we have  $(1-x)$  molecules  $\text{FeCl}_3$ ,  $x$  molecules  $\text{Fe}(\text{OH})_3$ ,  $3x$  molecules  $\text{HCl}$ , and  $(n-3x)$  molecules of water. As  $n$  is large compared with  $3x$ , this may be taken as the same as  $n$ .

According to Guldberg and Waage these quantities should be connected together by the equation

$$\frac{(1-x)n}{x^3} = 3K \dots\dots\dots (3).$$

$x$  is identical with the loss of iron given in Table XI divided by 100, and, calling the concentration of the original unfiltered solution (with regard to Fe) =  $c$ , we have 1 gram molecule  $\text{FeCl}_3$  in  $1/c$  litres, or, as 1 litre of water contains 55.5 gram molecules, we have 1 gram molecule  $\text{FeCl}_3$  in  $55.5/c = n$  gram molecules  $\text{H}_2\text{O}$ . Putting these values in the above equation we get

$$\frac{(1-x)}{x^3 \cdot c} = \frac{3}{55.5} K = k_1.$$

The values of  $k_1$ , calculated from the different values of  $x$ , are given in Table XI, and are evidently very far from being constant, as is required by the law of Guldberg and Waage.

The agreement is hardly improved by regarding the ferric hydroxide as an insoluble body and putting its active mass constant. The equation then becomes

$$\frac{(1-x)}{xc} = \text{const.} = k_2.$$

The values of  $k_2$  also vary considerably, as Table XI shows.

According to the equation for the equilibrium of four electrolytes given by Arrhenius,\* however,  $K$ , on the right-hand side of equation (3), is not a constant. For Arrhenius regards only those parts of the electrolytes which are dissociated into their ions as the active masses, so that if  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$ , and  $\alpha_4$  are the fractions of the electrolytes  $\text{FeCl}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{Fe}(\text{OH})_3$ , and  $\text{HCl}$  respectively, which are dissociated, we must substitute for the equation of Guldberg and Waage the expression

\* 'Bihang k. Svensk. Vet.-Ak. Hand.,' vol. 8, No. 14, 1884.

$$(1-x) \alpha_1 \times \frac{n}{3} \alpha_2 = x \alpha_3 \times x \alpha_4.$$

As Arrhenius\* has shown, the values of  $\alpha_1$ ,  $\alpha_2$ , &c., are to be obtained from equations of the form

$$\frac{\alpha_1 n}{n(1-\alpha_1)} = K_1 \dots\dots\dots (5).$$

$n$  is the whole number of dissociated molecules of all kinds in the solution, and  $K_1$ ,  $K_2$ , &c., are the characteristic dissociation constants for the four electrolytes. The values of  $\alpha_2$  and  $\alpha_3$  are very small, so that we have

$$\alpha_2 = K_2 \frac{n}{m} \quad \text{and} \quad \alpha_3 = K_3 \frac{n}{m}.$$

$\alpha_4$ , the fraction of the hydrochloric acid dissociated, may be put = 1, so that the equation becomes, putting  $n = 55.5/c$ ,

$$\frac{(1-x)}{x^2 c} = \frac{3}{55.5} \frac{K_3}{K_2} \frac{1}{\alpha_1} \dots\dots\dots (6).$$

Neglecting small quantities, we have

$$m = (1-x) \alpha_1 + x.$$

Substituting which in (5),

$$\frac{\alpha_1 ((1-x) \alpha_1 + x)}{1-\alpha_1} = n K_1 \dots\dots\dots (7).$$

The values of  $\alpha_1$ , the dissociation coefficients of ferric chloride, are unknown. I have attempted to test the agreement of the experiments with the Equations 6 and 7, thus:—Each experiment gives a value for  $\frac{3}{55.5} \cdot \frac{K_3}{K_2} \cdot \frac{1}{\alpha_1} = \frac{1}{b}$  (say), or, writing the constant part  $\frac{3}{55.5} \cdot \frac{K_3}{K_2} = \frac{1}{d}$ , we get  $\alpha_1 = \frac{b}{d}$ .

Substituting this in Equation 7,

$$\frac{cb^2}{d-b} + cd x = 55.5 K_1 d.$$

From these equations  $d$  and  $K_1$  can be found. The following numbers were obtained:—

\* 'Zeit. Phys. Chem.' vol. 5, p. 1, 1890. Cf. J. J. van Laar, 'Die Thermodynamik in der Chemie,' 1893, where a convenient collection of the formulæ is to be found.

$$\begin{array}{rcl}
 d = 0.00163 & \} & 55.5 K_1 d = 0.0000085 \\
 0.00196 & & 0.0000072 \\
 0.00205 & \} & 0.0000069 \\
 & & 0.0000075
 \end{array}$$

Mean used = 0.002

Mean = 0.0000075

The numbers now found are approximately constant. As  $d = 18.5 \frac{K_2}{K_3}$ , we get  $\frac{K_3}{K_2} = 9250$ .

That is, the dissociation constant of ferric hydroxide is about 9000 times that of water. Ferric hydroxide is thus an extremely weak base. From  $55 K_1 d = 0.0000075$  we get also  $K_1 = 0.000068$ . For comparison,\* the dissociation constants of  $KCl = 0.00958$ , that of  $CuSO_4 = 0.0001898$ , so that ferric chloride must be regarded as one of the exceptionally slightly dissociated salts.

A number of photometric measurements were made of the absorption spectra of solutions of ferric chloride, but their peculiar properties make it rather difficult to obtain accurate results. The solutions were made by diluting a concentrated solution of ferric chloride, which had been made as clear as possible by filtration through paper. They were then allowed to stand till no further change took place in their colour; if they were then without visible turbidity, they were used for measurement, but, owing to the peculiar fluorescent appearance of solutions containing colloid ferric hydroxide, it was not easy to see whether they were really free from solid suspended particles or not.

The numbers which are contained in Table VI of the Appendix, and from which the following table is calculated, give results which agree approximately with the results of the filtration experiments given above. The calculation of the amount of ferric hydroxide in the solutions was made as follows:—The most dilute solution of  $FeCl_3$  which was used (XXV, Table XII), and another one to which a small quantity of ammonia had been added (XXVI, Table XII), gave nearly the same numbers. The decomposition in these solutions appeared to be complete, as neither of them gave a red colour on addition of excess of ammonium sulphocyanide. Solutions of colloid ferric hydroxide, obtained by dialysis, also give no red colour with sulphocyanide. I took the absorptions of these solutions as corresponding to complete hydrolysis. The smaller absorptions of the other solutions will then correspond to a proportionately smaller decomposition, if we assume that the whole absorption is due to the ferric hydroxide, an assumption which is quite allowable, as the filtration

\* The numbers are from van Laar, *loc. cit.*, p. 154. To convert them into the units used by Ostwald they must be divided by 0.018.

Table XII.

$\lambda$	$c = 0.00002525$	0.000332 + 0.000407NH <sub>3</sub>	Mean of XXV and XXVI.	0.000101		0.000101		0.00036		0.000505	
				Per cent. hydroxide.		Per cent. hydroxide.		Per cent. hydr- oxide.		Per cent. hydroxide.	
				$\epsilon$ .	Per cent. hydroxide.	$\epsilon$ .	Per cent. hydroxide.	$\epsilon$ .	Per cent. hydr- oxide.	$\epsilon$ .	Per cent. hydroxide.
	XXV.	XXVI.		XXVII.		XXVIII.		XXIX.		XXX.	
580	39.3	—	39.3	31.8	80.9	—	—	49.2	86.9	36.9	65.2
560	57.3	55.9	56.6	47.0	83.0	—	—	68.6	80.7	72.1	84.8
540	84.8	85.2	85.0	75.6	86.9	—	—	112.3	88.0	113.1	88.8
520	124.0	131.4	127.7	115.0	90.1	117.6	92.1	157.6	86.8	167.0	91.9
500	168.0	195.5	181.7	152.4	83.9	143.8	79.2	—	—	—	—
480	221.7	—	222.0	203.3	91.7	180.3	81.3	—	—	—	—
460	308.1	—	308.0	—	—	183.3	91.6	—	85.6	—	82.7
			Mean per cent. decomposed = 86.1				86.0	—	86.0	—	81.0
							95.0				

Per cent. decomposed, by interpolation from filtration experiments

experiments show, the removal of the hydroxide from the solutions leaving them nearly colourless.

All the solutions in which the hydrolysis was incomplete gave the red colour with ammonium sulphocyanide.

The measurements which G. Wiedemann made of the amount of hydrolysis in the more concentrated solutions of ferric chloride appear to be in harmony with the results given in Table XI. The numbers, when plotted against concentrations, give two curves, which appear to be parts of the same curve.

*Colloid Ferric Hydroxide.*—A solution was prepared by dialysing a solution of ferric chloride in which a quantity of ferric hydroxide had been dissolved. It was clear red-brown by transmitted but apparently turbid by reflected light; it gave no deposit on standing for three months, and passed through filter paper without leaving any residue. A solution of  $\text{NH}_4\text{SCN}$  coagulated it, but gave no red colour. Analysis showed that it contained 12.4 per cent. of the amount of chlorine corresponding to the formula  $\text{FeCl}_3$ . The extinction coefficients obtained for different solutions, made by diluting this solution, are given in Table XIII; they are obtained by graphic interpolation from the experimental numbers given in the Appendix, Table VII.

Table XIII.

$c =$	0.09855	0.02531	0.000568	0.000568	0.0001254	Mean for dil. $\text{FeCl}_3$ solutions.
$\lambda$ .						
660	6.52	5.94				
640	7.98	7.46				
620	9.91	9.40				
600	12.61	12.02	12.35			
580	16.85	16.38	17.20	—		39.3
560	26.64	25.42	26.45	—	30.5	56.6
540	44.95	43.50	46.30	46.5	51.2	85.0
520	—	—	80.10	82.9	84.4	127.7
500	—	—	—	136.9	139.2	181.7
480	—	—	—	197.4	200.9	221.7
460	—	—	—	218.0	219.7	308.1
440	—	—	—	285.2	277.5	
430	—	—	—	—	354.0	

The numbers, on the whole, show some tendency to increase as the dilution increases. A comparison with the numbers obtained for the completely hydrolysed solutions of ferric chloride (last column, Table XIII) shows that the spectra are entirely different. There can be little doubt that both the solutions contain colloid ferric hydroxide. The filtration experiments show that this is the case in

the ferric chloride solution, and one would imagine that if all the iron exists as hydroxide in a solution containing an equivalent quantity of chlorine this should be certainly the case in one containing only some 12 per cent. of that quantity of chlorine. An explanation is, I think, suggested by an observation made by Picton.\* He noticed that a solution of antimony hydrosulphide, obtained by pouring a solution of tartar emetic into one of sulphuretted hydrogen, possessed only a faint fluorescence, and, under the microscope, no particles were visible in it. On dialysing the solution the fluorescence increased, and gradually minute particles became visible under the microscope; finally the solution coagulated. Picton and Linder ('J. Chem. Soc.,' 1892, 154) found also that silicic acid behaves in quite a similar way. In a colloid solution of silicic acid containing hydrochloric acid the particles were too small to reflect light, while after dialysis they were large enough to do so. Krecke (*loc. cit.*) also found that, on dialysing a concentrated ferric chloride solution, it finally coagulated. It would appear as though the dialysis always favoured the formation of larger molecular aggregates. A possible reason for this, in the case of ferric hydroxide, at any rate, is not difficult to see. In the solutions containing hydrochloric acid the hydroxide must be regarded as constantly being acted upon by the acid with formation of ferric chloride, which is at once decomposed again. Consequently the hydroxide never has the opportunity of forming large molecular groups.

*Solutions containing excess of Hydrochloric Acid.*

The addition of a small quantity of hydrochloric acid to a solution containing the hydroxide diminishes the quantity of the latter, and therewith the intensity of the brown colour of the solution, to a marked extent. I found, for example, by filtration through the Chamberland Pasteur candle, that the addition of one-sixth of an equivalent of HCl to a dilute solution of ferric chloride reduced the quantity of  $\text{Fe}(\text{OH})_3$  present by nearly a half. The following are the numbers :—

Concentration in gram mols. per litre before filtering.		After filtering.		Loss per cent.	
$\text{FeCl}_3$ .	HCl.	Fe.	Cl.	Fe.	Cl.
0·001263	—	0·000445	0·00376	64·77	—1·48
0·001263	0·000635	0·00084	0·00432	33·49	+0·46

\* 'Chem. Soc. Journ.,' 1892, p. 142.



Larger quantities of acid seem to prevent the formation of ferric hydroxide altogether, as the acid solutions could all be filtered through the porous cell without leaving any deposit. The analyses also showed that their concentration was not diminished by the filtration.

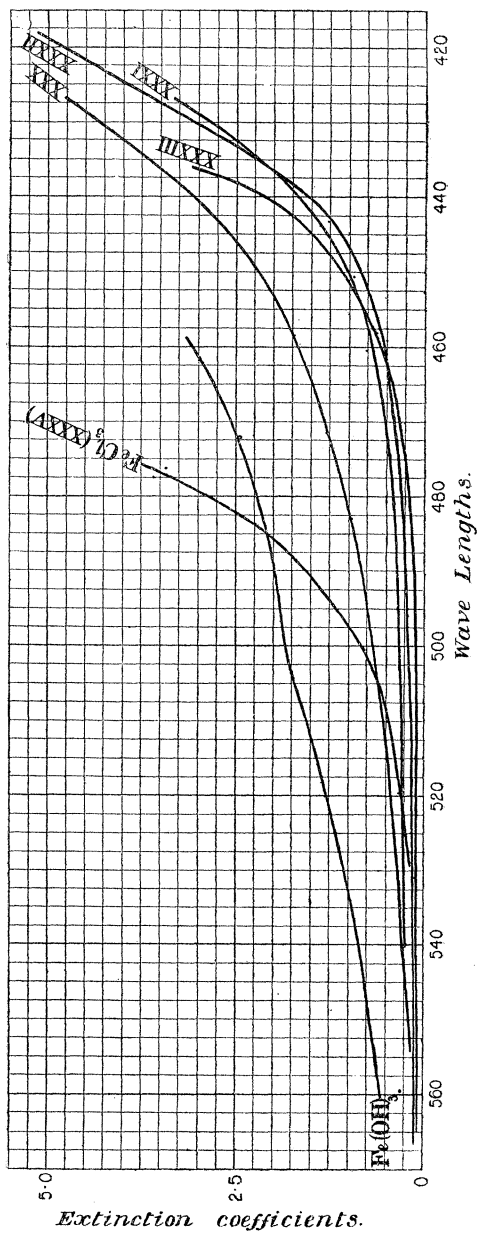
Table XIV contains the numbers which were obtained with a series of acid solutions. The arrangement of the table is the same as before, only the number of equivalents of free hydrochloric acid added to one equivalent of iron are also given.

Table XIV.

Conc. { Fe HCl Eq. acid.. Eq. Fe... }	0·001925	0·001284	0·001279	0·00425	0·0013	0·3095
	0·00466	0·0094	0·0178	0·06	0·035	0·814
	0·7786	2·44	4·64	4·706	8·97	0·8767
λ.	XXX.	XXXI.	XXXII.	XXXIII.	XXXIV.	XXXV.
580	0·098	—	—	—	—	—
560	0·139	—	0·122	0·083	0·061	0·117
540	0·265	0·233	0·115	0·084	0·080	0·135
520	0·419	0·242	0·130	0·082	0·112	0·290
500	0·661	0·289	0·182	0·099	0·157	0·775
480	1·043	0·424	0·298	0·178	0·219	2·950
460	1·682	0·601	0·777	0·575	0·493	11·01
440	3·175	1·643	1·495	2·100	1·555	—
430	4·340	2·83	—	—	3·375	—

These numbers appear to be somewhat irregular, but a glance at fig. 5 will show that this is due to the way the curves cross each other. The curve XXX of the solution containing the smallest excess of hydrochloric acid has a strong resemblance to the curve for  $\text{Fe}(\text{OH})_3$ , which is included in the figure for comparison (with ordinates divided by 100). If the whole absorption of solution XXX were due to hydroxide, the amount of hydrolysis would only be  $\frac{1}{2}$  to  $\frac{1}{3}$  per cent. of the salt present. In the curve for the next solution, XXXI, the similarity to that of the hydroxide has disappeared, and as the quantity of acid is increased the curves evidently approach more and more towards that of the concentrated acid solution XXXV, which may be taken as representing approximately the absorption spectrum of the undecomposed molecule of ferric chloride. Whether these changes are due to the change of the dissociated ferric chloride into undissociated, or to the conversion of a soluble oxychloride into ferric chloride cannot be decided. It is certain that these solutions contain none of the colloid hydroxide, but they possibly contain a soluble oxychloride. Wiedemann found that solutions of ferric nitrate and sulphate, containing excess of acid, still contain a con-

FIG. 5.



siderable quantity of hydroxide. He has given no measurements on acid solutions of the chloride, but as I found that the acid solutions of ferric nitrate and sulphate behave very much in the same way as the chloride with respect to colour, we may perhaps conclude that all these solutions contain some really soluble substance standing between the undissociated normal molecules and colloid ferric hydroxide.

Some measurements which were made with ferric nitrate and sulphate gave results similar to those obtained with the chloride, but they are very much less complete.

The following table contains the measurements made on concentrated acid solutions of ferric sulphate and nitrate, and with a solution of ferric sulphocyanide in ether; owing to the ease with which the latter decomposes the numbers are only approximate, they will serve, however, to give some notion of the relative magnitude of its absorption.

For comparison the numbers obtained for the concentrated, acid, ferric chloride solution, and for ferric hydroxide are given.

Table XV.—Acid Solutions of Ferric Salts.

Conc. {		$\text{Fe}(\text{NO}_3)_2$	$\frac{1}{2}\text{Fe}_2(\text{SO}_4)_3$	$\text{FeCl}_3$	$\text{Fe}(\text{OH})_3$	$\text{Fe}(\text{SCN})_3$
{		Fe.... 0·4221	0·7498	0·3095		0·00148
{		Acid.. 0·633HNO <sub>3</sub>	1·524( $\frac{1}{2}\text{H}_2\text{SO}_4$ )	0·814HCl		in ether.
$\lambda$						
660	0·0492	0·0835	—	—	211	
640	0·0534	0·0995	—	—	310	
620	0·0600	0·1143	—	—	428	
600	0·0675	0·1300	—	—	574	
580	0·0771	0·1428	—	39·3	821	
560	0·0863	0·1560	0·117	56·6	1152	
540	0·0923	0·1644	0·135	85·0	1527	
520	0·0920	0·1583	0·290	127·7	1926	
500	0·0877	0·1367	0·775	181·7	2503	
480	0·0888	0·1255	2·950	221·7		
460	0·1072	0·1390	11·61	308·1		
440		0·7300				

It will be noticed that the different salts of iron all have different absorption spectra, the nitrate is very slightly coloured indeed; the sulphate brown, and the chloride bright yellow. Ferric hydroxide absorbs several hundred times more light than the salts, and ferric sulphocyanide absorbs nearly twenty times as much light as the hydroxide.

## APPENDIX.—Table I.

T is the light transmitted by a tube full of water 100·1 cm. long, as directly determined.

Wave-length.	Mean.	T.	Wave-length.	Mean.	T.
752 —708	730	0·2447	589·2—571·5	580	0·8332
752 —708	730	0·2471	582 —576·8	579·4	0·8228
740 —697	718·5	0·3060	572 —562·5	567·2	0·8471
708 —692	700	0·4497	572 —562·5	567·2	0·8424
693 —676	684·5	0·5460	568·5—562·5	565·5	0·8499
693 —673	683	0·5445	570 —561	565·5	0·8363
693 —668	680·5	0·5396	551·5—540	545·7	0·8650
679 —666·5	672·7	0·5983	551·5—540	545·7	0·8625
681·5—658·5	670	0·5904	523 —517·2	520·1	0·8675
678 —661·5	669·7	0·5984	519·7—510·2	514·9	0·8696
663 —651·5	657·2	0·6215	513·3—506·7	510	0·8749
646·5—626	636·2	0·6586	513·3—506·7	510	0·8700
641·5—627	634·2	0·6661	507·5—501	504·2	0·8763
636·5—622	629·2	0·6777	496·2—487·5	491·8	0·8705
636·5—622	629·2	0·6596	488·3—481·5	484·9	0·8752
629 —620·7	624·8	0·6830	468·3—461·5	464·9	0·8694
623 —603	613	0·6915	468·3—461·5	464·9	0·8742
612 —594·2	603·1	0·7057	460·3—455·3	457·8	0·8632
607·5—592·3	599·9	0·7185	454·2—446·8	450·5	0·8689
603·5—589	595·7	0·7260	446·7—441·2	443·9	0·8702
597·5—590	593·7	0·7365	432 —428	430	0·8456
598·5—584	591·2	0·7868	432 —427·8	429·9	0·8296
593·5—578·7	586·1	0·7925	433·5—426·4	429·9	0·8277
593·5—578·7	586·1	0·7855	427·3—420	423·6	0·8178
590 —576·7	583·3	0·8117	418 —411	414·5	0·8147

Table II.

The letters have the following significations:—

$c$  = concentration of the solution in gram-molecules per litre. The molecular weight used is given after the formula of the substance.

$l$  = length of the layer of solution.

$T$  = light transmitted by the tube of solution.

$\epsilon$  = extinction coefficient for 1 cm. of solution containing 1 gram-molecule per litre.

I.—CuSO <sub>4</sub> = 159·6. $c$ = 0·003768. $l$ = 100·1 cm.				II.—CuSO <sub>4</sub> . $c$ = 0·00366. $l$ = 100·1 cm.			
Wave-length.	Mean $\lambda$ .	T.	$\epsilon$ .	Wave-length.	Mean $\lambda$ .	T.	$\epsilon$ .
657·3—647·5	652·4	0·0576	2·764	512·7—508	510·8	0·8357	0·0477
637 —625·8	631·4	0·1400	1·806	535 —528	531·5	0·7961	0·1018
618 —608	613	0·2524	1·165	558·5—551	554·2	0·7108	0·2230
603 —592·7	597·8	0·3852	0·7166	570 —564	567	0·6131	0·3791
587·2—578·5	582·8	0·5292	0·5004	584 —578	581	0·5369	0·5041
570 —564	567	0·6317	0·3339	601·5—592·5	597	0·3649	0·8066
558·3—553·7	556	0·7119	0·2129	618 —608	613	0·2331	1·293
547·2—542	544·6	0·7568	0·1514	638 —625·5	631·7	0·1314	1·934
519 —510·2	514·6	0·8404	0·0407	657·5—645	651·2	0·0495	3·033
486 —478	482	0·8733	0·00127				

III.—CuSO <sub>4</sub> . $c$ = 0·003754. $l$ = 100·25 cm.				IV.—CuCl <sub>2</sub> = 134·6. $c$ = 0·003969. $l$ = 100·1 cm.			
Wave length.	Mean $\lambda$ .	T.	$\epsilon$ .	Wave-length.	Mean $\lambda$ .	T.	$\epsilon$ .
643·5—632	637·7	0·0931	2·264	486 —478·5	482·2	0·8728	0·00176
621 —613·5	617·2	0·2004	1·426	519 —510·5	514·7	0·8423	0·0360
606·5—597	601·7	0·3106	0·9070	537 —529·5	533·2	0·7879	0·1052
589·5—582	585·7	0·4801	0·5958	547 —542	544·7	0·7402	0·1715
575 —565·5	570·2	0·5930	0·4020	559·5—554·5	557	0·6870	0·2394
561 —555·5	558·5	0·6802	0·2631	570 —564	567·2	0·6085	0·3577
538·5—531	534·7	0·7752	0·1286	586 —578·5	582·2	0·4931	0·5535
516 —510·5	513·2	0·8437	0·0372	602·5—592·5	597·5	0·3446	0·8029
484 —476·5	480·2	0·8693	0·0061	615·5—608	611·7	0·2131	1·292
				637 —627·5	632·2	0·1127	1·950
				657 —647·5	652·2	0·0441	2·916

Table II—*continued.*

V.—Cu(NO <sub>3</sub> ) <sub>2</sub> = 187·6. <i>c</i> = 0·003964. <i>l</i> = 100·1 cm.				VI.—Cu(NO <sub>3</sub> ) <sub>2</sub> . <i>c</i> = 0·003819. <i>l</i> = 100·25 cm.			
Wave-length.	Mean λ.	T.	ε.	Wave-length.	Mean λ.	T.	ε.
656 —645	650·5	0·0519	2·749	662 —651	656·5	0·0292	3·4785
636 —623·5	629·7	0·1245	1·849	639·5—629	634·2	0·0926	2·2416
617 —608	612·5	0·2289	1·214	620 —612	616	0·1963	1·4264
602·5—591	596·7	0·3551	0·7600	604 —594·5	599·2	0·3123	0·9364
586 —578·5	582·2	0·5055	0·5265	587 —579·5	583·2	0·4665	0·6332
570 —564·5	567·2	0·6247	0·3284	572 —565	568·5	0·5924	0·3965
548 —542	545	0·7718	0·1220	560 —554·5	557·5	0·6735	0·2703
519 —511	515	0·8478	0·0290	536 —529·5	532·7	0·7767	0·1254
				514 —509	511·5	0·8197	0·0695
				482 —476·5	479·2	0·8618	0·0133
VII.—Cu(NO <sub>3</sub> ) <sub>2</sub> = 187·6. <i>c</i> = 0·00564. <i>l</i> = 100·25 cm.				VIII.—CuBr <sub>2</sub> = 223·6. <i>c</i> = 0·005304. <i>l</i> = 100·1 cm.			
Wave-length.	Mean λ	T.	ε	Wave-length.	Mean λ.	T.	ε
639 —623·5	631·2	0·0579	1·8827	637 —625	631	0·0533	2·0738
618·5—608·7	613·6	0·1439	1·2078	617 —607	612	0·1373	1·3264
603·3—591	597·1	0·2655	0·7671	601·5—592	596·7	0·2558	0·8498
570 —563	566·5	0·5496	0·3299	586·5—578	582·2	0·4132	0·5583
545·7—540	542·8	0·7236	0·1360	568·5—562·5	565·5	0·5288	0·3837
512 —508	510	0·8419	0·0269	557 —549	558	0·6346	0·2430
				533 —527	530	0·7750	0·0921
				511·5—506·5	509	0·8342	0·0362
				481 —474·5	477·7	0·8689	0·0041
IX.—CuBr <sub>2</sub> . <i>c</i> = 0·003303. <i>l</i> = 100·25 cm.				X.—Cu(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> = 181·6. <i>c</i> = 0·003748. <i>l</i> = 100·1 cm.			
Wave-length.	Mean λ.	T.	ε	Wave-length.	Mean λ.	T.	ε
668 —653	665·5	0·0436	3·4522	636·5—624·5	630·5	0·0147	4·4274
643 —633·5	638·2	0·1234	2·2028	616 —609	612·5	0·0494	3·0594
622 —612·5	616·2	0·2279	1·4536	602·5—592	597·2	0·1261	2·0170
605·5—595	600·2	0·3526	0·9175	586 —578	582	0·2569	1·3402
589·5—581	585·2	0·5064	0·6116	571·5—565	568·2	0·4068	0·8417
573·5—567·5	570·5	0·6272	0·3814	559 —554	556·5	0·5226	0·5704
560·5—555	557·7	0·7051	0·2519	547 —541	544	0·6436	0·3396
538 —531	534·5	0·7976	0·1087	537·5—531	534·2	0·7173	0·2188
483·5—477	480·2	0·8690	0·0073	516 —510	513	0·8217	0·0672

Table II—continued.

XI.—Cu(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> . <i>c</i> = 0·004203. <i>l</i> = 100·1 cm.				XII.—Cu(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> . <i>c</i> = 0·0007144. <i>l</i> = 100·25 cm.							
Wave-length.	Mean λ.	T.	ε	Wave-length.	Mean λ.	T.	ε				
480 —474·5	477·2	0·8642	0·0114	658·5—646·5	652·5	0·2981	4·595				
510·7—506·4	508·5	0·8243	0·0582	639 —625	632	0·4069	3·038				
533·5—525·8	529·7	0·7206	0·1921	603 —591·5	597·2	0·6183	0·9285				
555·5—547·6	551·6	0·5549	0·4516	572 —563	567·5	0·7764	0·5055				
568 —560·5	564·2	0·4110	0·7452	XIII.—Cu(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> . <i>c</i> = 0·00289 + 0·00885 g. mol. acetic acid. <i>l</i> = 100·25 cm.							
582·7—574·5	578·6	0·2633	1·1811								
596·5—590	593·2	0·1305	1·797								
613·5—605	609·2	0·0466	2·794								
634·5—622	628·2	0·0157	3·885								
XIV.—Cu(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> . <i>c</i> = 0·00479 + 0·136 g. mol. acetic acid. <i>l</i> = 100·25 cm.				Wave-length.				Mean λ.	T.	ε	
				620·5—611				615·7	0·1003	2·893	
				588 —580				584	0·3658	1·196	
				561 —555				558	0·6074	0·5108	
				XV.—Cu(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> . <i>c</i> = 0·0007395 + 0·00155 g. mol. acetic acid. <i>l</i> = 100·25 cm.							
				Wave-length.				Mean λ.	T.	ε	
				658·5—646·5				652·5	0·2874	4·651	
				639 —625				632	0·3947	3·113	
				603 —591·5				597·2	0·5968	1·103	
				572 —563				567·5	0·7801	0·460	

Table III.

XVI.— $C_6H_3(NO_2)_2OK = 222$ . $c = 0.001646$ . $l = 100.25$ cm.				XVII.— $C_6H_3(NO_2)_2OK$ . $c = 0.0004107$ . $l = 100.25$ cm.			
Wave-length.	Mean $\lambda$ .	T.	$\epsilon$ .	Wave-length.	Mean $\lambda$ .	T.	$\epsilon$ .
680.5—659	669.8	0.5675	0.1248	532.5—521	526.8	0.6921	2.392
640.5—620	630.2	0.6083	0.2703	522 —512	517	0.5328	5.159
604 —588	596	0.6788	0.1806	512 —502.5	507.2	0.3105	10.88
572 —560	566	0.7716	0.2400	502 —494.5	498.2	0.0961	23.26
548 —536	542	0.6397	0.7903				
537 —526	531.5	0.4421	1.7726	XIX.— $C_6H_3(NO_2)_2OK$ . $c = 0.0001027$ . $l = 100.25$ cm.			
527 —517	522	0.1798	4.144				
XVIII.— $C_6H_3(NO_2)_2OK$ . $c = 0.0001027$ . $l = 25.11$ cm.							
Wave-length.	Mean $\lambda$ .	T.	$\epsilon$ .	Wave-length.	Mean $\lambda$ .	T.	$\epsilon$ .
494 —486.5	490.2	0.5635	77.4	510 —502	506	0.5996	15.78
486.5—478.5	482.5	0.3626	151.8	502.3—493.5	497.9	0.4114	31.7
480 —473	476.5	0.1844	265.4	493 —486	489.5	0.1848	65.5
474 —466	470	0.0834	398.6	486.5—478	482.2	0.0413	128.7
XXI.— $C_6H_3(NO_2)_2ONH_4$ . $c = 0.004739$ . $l = 25.11$ cm.				XX.— $C_6H_3(NO_2)_2OK$ . $c = 0.0000986$ . $l = 100.25$ cm.			
Wave-length.	Mean $\lambda$ .	T.	$\epsilon$ .	Wave-length.	Mean $\lambda$ .	T.	$\epsilon$ .
528 —520.3	524.2	0.4335	2.652	511.3—505	508.2	0.6449	13.22
538 —531.5	534.8	0.6663	1.084	503.5—498.8	501.2	0.4937	24.99
549.5—541	545.2	0.7820	0.499	487 —482.5	484.8	0.0646	114.3
562.7—554.5	558.6	0.8188	0.322	484.5—479.5	482	0.0345	141.9
XXII.— $C_6H_3(NO_2)_2ONH_4$ . $c = 0.001185$ . $l = 100.25$ cm.							
Wave-length.	Mean $\lambda$ .	T.	$\epsilon$ .	Wave-length.	Mean $\lambda$ .	T.	$\epsilon$ .
518.5—511.5	515	0.1243	7.108	518.5—511.5	515	0.1243	7.108
528 —520.5	524.2	0.3640	3.177	528 —520.5	524.2	0.3640	3.177
539 —530	534.5	0.5615	1.583	539 —530	534.5	0.5615	1.583
552 —541	546.5	0.6477	1.045	552 —541	546.5	0.6477	1.045



Table III—continued.

XXIII.— $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{ONH}_4$ . $c = 0\cdot001185$ . $l = 25\cdot11$ cm.				XXIV.— $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{ONH}_4$ . $c = 0\cdot0004027$ . $l = 6\cdot08$ cm.			
Wave-length.	Mean $\lambda$ .	T.	$\epsilon$ .	Wave-length.	Mean $\lambda$ .	T.	$\epsilon$ .
539 —530	534·5	0·7918	1·758	469·5—466	467·8	0·0744	441·1
526·7—521	523·8	0·7441	2·736	476·5—472·7	474·6	0·2022	264·0
518 —511	514·5	0·5580	6·920	484·5—478·5	481·5	0·3844	150·5
508 —502	505	0·2919	16·37	491 —486·5	488·8	0·5631	83·2
499 —493	496	0·0798	35·26				

Table IV.—Dinitrophenol (Acid Solution.)

$c = 0\cdot001202$  gram molecule dinitrophenol. } per litre.  
 $+ 0\cdot2132$  " " HCl.  
 $l = 100\cdot25$  cm.

Wave length.	Mean $\lambda$ .	T.	$\epsilon$ .
517·5—510	513·8	0·7884	0·3577
498·5—492	495·2	0·7783	0·4149
481 —478	479·5	0·7444	0·5776
467·3—464	465·6	0·6956	0·8100
467·5—464	465·8	0·7110	0·7328
457 —451·5	454·2	0·5396	1·713
446 —440	443	0·3680	3·0606
507 —500	503·5	0·7963	0·3303

Table V.—Dinitrophenol.

Wave length.	Mean $\lambda$ .	Concentration.	$l$ .	T.	$\epsilon$ .
482·4—478	480·2	0·001581	6·08	0·3194	46·69
499 —493	496	—	—	0·7316	9·44
500 —495	497·5	—	25·11	0·4380	7·829
500·4—495	497·7	—	—	0·4977	6·421
489 —485·3	487·2	—	—	0·1335	20·8
481·5—477	479·2	0·0007905	6·08	0·4539	61·58
496 —490·7	493·3	—	25·11	0·5285	11·52
483 —478·5	480·8	—	—	0·1650	36·93
496 —491·2	493·6	0·000395	25·11	0·6055	17·11
478·5—475	476·8	—	—	0·1337	83·07
474·2—470	472·1	0·0001581	25·11	0·1992	163·9
496 —490·5	493·2	—	—	0·7200	23·83
499·3—493	496·2	0·00001581	100·25	0·7761	32·3
475·6—472	473·8	—	—	0·3153	278·5
482·5—477·7	480·1	0·002886	6·08	0·2378	32·86
481·5—476·5	479	0·002886	6·08	0·2329	33·37

Table VI.

XXV.—FeCl <sub>3</sub> = 162·5. <i>c</i> = 0·00002525 <i>l</i> = 25·11 cm.				XXVI.—FeCl <sub>3</sub> . <i>c</i> = 0·000332 + 0·000407 gr. mol. NH <sub>3</sub> . <i>l</i> = 25·11 cm.			
Wave-length.	Mean λ.	T.	ε.	Wave-length.	Mean λ.	T.	ε.
450 —443	446·5	0·5364	342·3	502·3—496·3	499·3	0·0192	200·5
474 —466	470	0·5981	272·4	507 —502	504·5	0·0314	174·6
486·5—478·5	482·5	0·6627	204·9	517·3—511	514·2	0·0508	149·5
<i>c</i> = 0·00002525				527·5—521	524·2	0·0898	119·9
<i>l</i> = 100·25 cm.				539·5—530·5	535	0·1443	95·1
503 —496	499·5	0·3265	168·5	550·5—544	547·2	0·2165	73·9
522 —515	518·5	0·4133	127·2	576·5—568·5	572·5	0·4064	40·7
569·5—558	563·8	0·6196	53·6	XXVII.—FeCl <sub>3</sub> . <i>c</i> = 0·000101. <i>l</i> = 25·11.			
598 —585	591·5	0·6298	32·1				
XXVIII.—FeCl <sub>3</sub> . <i>c</i> = 0·000101. <i>l</i> = 6·08 cm.				Wave-length.	Mean λ.	T.	ε.
Wave-length.	Mean λ.	T.	ε.	472·5—465	469·2	0·2342	228·5
460·5—454·5	457·5	0·5866	296·4	486 —478	482	0·2803	198·3
480 —473	476·5	0·6857	190·2	502 —493	497·5	0·3574	157·2
503·5—495·5	499·5	0·7356	144·6	522 —511·5	516·8	0·4444	120·1
<i>c</i> = 0·000101.				544 —534	539	0·5713	77·1
<i>l</i> = 25·11 cm.				584·5—570	577·2	0·7316	33·2
514·2—503·5	508·9	0·4067	135·2	XXIX.—FeCl <sub>3</sub> . <i>c</i> = 0·00036. <i>l</i> = 25·11.			
534 —524	529	0·5122	95·9				
XXXa.— <i>c</i> = 0·000505. <i>l</i> = 6·08 cm.				Wave-length.	Mean λ.	T.	ε.
Wave-length.	Mean λ.	T.	ε.	502·3—496·3	499·3	0·0328	158·9
473·5—466·3	469·9	0·1473	255·2	507 —502	504·5	0·0381	151·7
487·5—478·5	483	0·1714	234·2	517·3—511	514·2	0·0664	125·0
503·5—495·5	499·5	0·2735	168·7	527·5—521	524·2	0·1063	102·4
523 —514·3	518·7	0·3987	115·7	539·5—530·5	535	0·1789	77·4
570·5—558	564·2	0·7288	30·6	550·5—544	547·2	0·2473	61·8
				576·5—568·5	572·5	0·4173	36·3

Table VII.—Colloid Ferric Hydroxide.

The concentration is given in gram molecules per litre, a gram molecule being taken as that quantity which contains 1 atom of iron.

$\text{Fe(OH)}_3$ $c = 0.09855$ . $l = 0.338$ cm.				$\text{Fe(OH)}_3$ $c = 0.02531$ . $l = 0.932$ cm.			
Wave-length.	Mean $\lambda$ .	T.	$\epsilon$	Wave-length.	Mean $\lambda$ .	T.	$\epsilon$
545 —536	540.5	0.0293	44.5	533 —523	528	0.0324	61.05
557 —547	552	0.0702	33.1	544.5—534	539.2	0.0782	47.76
570 —558.5	564.2	0.1402	23.9	555.5—545	550.2	0.1471	33.04
584 —570	577	0.2227	17.87	567 —557	562	0.2357	24.29
600 —584	592	0.2980	14.32	594 —582	588	0.4009	14.35
616 —600	608	0.3767	10.91	628.5—613.5	621	0.5279	9.16
634.5—616	625.2	0.4142	9.63	674.5—653	663.8	0.6218	5.61
674.5—656	665.2	0.5409	6.12				
$c = 0.000568$ . $l = 25.11$ cm.				$c = 0.000568$ . $l = 6.08$ .			
521—511	516	0.0469	89.98	436 —432.3	434.1	0.0691	320.7
532—521.5	526.8	0.0966	67.81	446 —442.5	444.2	0.1089	263.8
555—542	548.5	0.2736	36.07	464 —458.5	461.2	0.1598	216.3
577—564	570.5	0.4590	20.94	486 —478.5	482.2	0.1920	193.9
606—592	599	0.5666	12.52	500.5—494	497.2	0.2804	146.8
				519 —511	515	0.4260	94.4
				542 —530	536	0.5926	53.1
Ferric Hydroxide. $c = 0.0001254$ . $l = 25.11$ cm.							
577.5—562.5	570	0.7583	22.23				
518.5—508	513.2	0.4118	107.2				
485 —475.5	480.2	0.2056	202.4				
$c = 0.0001254$ . $l = 6.08$ cm.							
426 —421.5	423.8	0.5590	263.5				
446 —439.5	442.8	0.4132	431.6				

Table VIII.—Acid Solutions of Ferric Chloride.

XXX.—FeCl <sub>3</sub> = 0·001995 gram. mol. HCl = 0·00466. l = 100·25 cm.				XXXI.—FeCl <sub>3</sub> = 0·001284. HCl = 0·0094. l = 100·25.			
Wave-length.	Mean λ	T.	ε.	Wave-length.	Mean λ	T.	ε.
597·5—585	591·2	0·7322	0·0890	429·6—424·5	427·1	0·3150	3·254
558 —547	552·5	0·7955	0·1700	439 —434·3	436·7	0·4713	1·999
523·5—516	519·8	0·7172	0·4185	453·5—448·5	451·0	0·6548	0·949
490 —482	486	0·5770	0·9000	488·5—480	484·2	0·7802	0·332
475·5—468	471·8	0·4815	1·289	544·3—536	540·2	0·8077	0·232
462 —455	458·5	0·3900	1·744	XXXII.—FeCl <sub>3</sub> = 0·001279. HCl = 0·0178 cm. l = 100·25.			
450 —445	447·5	0·2907	2·368	Wave-length.	Mean λ.	T.	ε.
452 —445·5	449	0·2929	2·353				
430·5—428·8	428·8	0·1056	4·500	422·5—415·5	419	0·1903	4·950
XXXIII.—FeCl <sub>3</sub> = 0·00425. HCl = 0·06. l = 100·25 cm.				435 —424·5	429·8	0·3391	3·078
Wave-length.	Mean λ	T.	ε.	446 —438·5	442·2	0·5861	1·299
				464 —457	460·5	0·6939	0·767
439 —434	436·5	0·0456	2·984	482·5—477·5	480	0·8101	0·299
444 —438	441	0·1231	1·979	507·5—501·5	504·5	0·8304	0·169
462 —454·2	458·1	0·4558	0·658	534 —528	531	0·8389	0·116
487·5—480·5	484	0·7550	0·149	568·5—562·5	565·5	0·8144	0·129
520·5—516	518·2	0·7995	0·086	XXXV.—FeCl <sub>3</sub> = 0·3095. HCl = 0·814. l = 6·08 cm.			
566·5—560·5	563·5	0·7769	0·090	Wave length.	Mean λ.	T.	ε.
XXXIV.—FeCl <sub>3</sub> = 0·0013. HCl = 0·035. l = 100·25 cm.							
Wave length.	Mean λ.	T.	ε.	511·5—506	508·8	0·1200	0·4658
				520·3—517	518·6	0·2718	0·2772
431 —426·3	428·6	0·2640	3·851	530·5—525·5	528	0·4030	0·1864
446·8—439·8	443·3	0·5879	1·272	567·5—561	564·2	0·5380	0·1197
462·7—456·2	459·5	0·7472	0·507	l = 0·932 cm.			
482·6—478·5	480·5	0·8197	0·214	479·5—475·5	477·5	0·0808	3·6025
517 —511	514	0·8388	0·124	486·5—482	484·2	0·2040	2·2074
561·6—554	557·8	0·8392	0·062	494 —490	492	0·3524	1·3846
				502·5—498·5	500·5	0·5379	0·7480
				512 —508	510	0·6445	0·4758
				522 —517·5	519·8	0·7108	0·3284
				l = 0·338 cm.			
				480 —473	476·5	0·3878	3·4210
				470 —463·5	466·8	0·1643	6·9865
				460·5—454·5	457·5	0·0316	13·825

Table IX.

Ferric Sulphate (Acid Solution). $c = 0.7498$ gram molecule ferric sulphate ( $\frac{1}{2}\text{Fe}_2(\text{SO}_4)_3$ ) + $1.528$ gram eq. $\frac{1}{2}\text{H}_2\text{SO}_4$ . $l = 5.74$ cm.				Ferric Nitrate (Acid Solution). $0.422$ gram molecule $\text{Fe}(\text{NO}_3)_3$ . $0.633$ " " $\text{HNO}_3$ . $l = 24.77$ cm.			
Wave length.	Mean $\lambda$ .	T.	$\epsilon$ .	Wave length.	Mean $\lambda$ .	T.	$\epsilon$ .
682 —661	571.5	0.4623	0.0756	680 —660	670	0.2876	0.0474
626.5—610.5	618.5	0.4060	0.0895	587 —570	578.5	0.1503	0.0780
586.5—572	579.2	0.2494	0.1433	524 —515	519.5	0.1083	0.0919
535 —524	529.5	0.1953	0.1650	$l = 5.74$ cm.			
503.5—495.5	499.8	0.2579	0.1369	486.5—480	483.2	0.6131	0.0874
$l = 0.257$ cm.				459.5—454	456.8	0.5297	0.1136
474 —467	470.5	0.9449	0.1281	Ferric Sulphocyanide (Ether Solution). $c = 0.00148$ gram molecule $\text{Fe}(\text{SCN})_3$ . $l = 0.34$ cm.			
460.5—455	457.8	0.9383	0.1436	Wave length.	Mean $\lambda$ .	T.	$\epsilon$ .
443 —438	440.5	0.7277	0.7180	603.2—588	595.6	0.0352	2769.3
				618.5—603.2	610.8	0.0973	1871.7
				638.5—622	630.2	0.2305	1147.3
				650 —630	640	0.3348	825.1
				669 —651	660	0.5308	427.5
				695 —669	682	0.6983	190.8