

The Halogenation of Oils with
Special Attention to the Method
of Wijs

by Edmund O. Rhodes

May 15, 1913

Submitted to the Graduate School of the
University of Kansas in partial fulfillment of the
requirements for the Degree of Master of Science

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WITH SPECIAL ATTENTION
TO THE METHOD OF WIJS

EDMUND O. RHODES

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PREFACE.

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The work carried on by the author for the past year on the " Hydrogenation of Cotton Seed Oil " required frequent determinations of the iodine value. Owing to the unsatisfactory condition of the literature on this subject, it was impossible to determine the most satisfactory method for use when rapid determinations were to be made.

A research was undertaken, therefore, for the purpose of finding the minimum time that could be used for any one determination, and the conditions necessary for the maximum degree of accuracy.

It is the purpose of this paper to present the results obtained from this research and the conclusions that may be drawn from them. In

addition there is given, as completely as possible,
a review of the literature that has appeared on
this subject to date.

Edmund C. Rhodes

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HISTORICAL.

Dr. Lewkowitsch once remarked before the Society of Chemical Industry,¹ that " The literature on the subject of iodine values was so startling in its proportions that he had himself stated in that room that he congratulated any chemist who did not add to it. " It might at first seem almost unnecessary, therefore, to spend more effort or time in the investigation of this interesting subject. However, in spite of the voluminous literature there have as yet been but few chemists who would agree upon all or even a part of the details concerned in this subject. " The iodine value, " as Lewkowitsch remarks, " has become one of the safest guides in the technical analysis of fats and waxes, " but granting this, it must be acknowledged that several important considerations

1. J.Soc.Chem.Ind.,1900,215.

must become fixed before a method can be chosen that will serve as a standard for all iodine value determinations.

Previous to the year 1884, the only tests performed in the analysis of oils, fats and waxes could be grouped into two general classes; (1) those purely physical in nature, among which were the determinations of the specific gravity, fusion and solidification points and solubility in various reagents; (2) those purely chemical in nature. Among the chemical processes the only ones of much importance were Hehner's determinations of the insoluble fatty acids, Köttstorfer's saponification test and the bromine number. Of all these tests, the most important one was probably the determination of the bromine value, which was a measure of the proportion of unsaturated fatty acids, that both in their free state and in combination with glycerol have the property of assimilating halo-

gens with the formation of additive compounds.

The bromine value served for a considerable time, having been first proposed by Cailletet in 1857, but, owing to the fact that both addition and substitution products were formed in the reaction, many difficulties were encountered. For that reason, when Hübl proposed a method in 1884, which would eliminate most of these difficulties, it was received with great appreciation, and immediately superceded the bromine value determination and all other halogenation processes previously devised.

Hübl, as his predecessors had done, based his method upon the fact that almost all fats contain members of three different groups of fatty acids, viz., acids of the acetic series, of the acrylic series and of the tetrolic series. Further, in their behavior toward the halogens, these three groups are clearly distinguishable from each other. This had previously been proven by determinations

of the bromine value but Hübl, who saw serious obstacles in the use of either chlorine or bromine, decided to employ iodine as his active agent.

After some experimentation, he found that iodine alone reacts too slowly to be of use in methods of analysis, but by employing an alcoholic solution of iodine in conjunction with mercuric chloride, in the proportion of one molecule of iodine to, at least, one of mercuric chloride, even at ordinary temperatures, halogen addition products can be easily formed from either free or combined unsaturated fatty acids.

Hübl prepared his solution as follows:-
by dissolving on the one hand 25 grams of iodine in 500 c.c. of pure 95 per cent alcohol, and on the other hand 30 grams of mercuric bichloride in the same amount of alcohol (filtering this solution if necessary) and mixing the two solutions.

Hubl was unable to explain definitely the reactions occurring in his method but ascribed the results obtained to the formation of a chloro-iodo-addition compound, from the fact that he succeeded in obtaining from oleic acid, treated by his method, a fatty substance of the formula $C_{18}H_{34}ClIO_2$.

Immediately following the proposal of this method by Hübl, various experimenters began to report results showing wide degrees of variation. After investigation, a few of the experimenters discovered the presence of a free acid other than acetic in the reaction product and immediately attributed the discrepancies obtained to this substance. This led to a series of investigations by a number of scientists for the next decade.

Among the first of these investigators were Schweitzer and Lungwitz,¹ who explained

1. J.Soc.Chem.Ind., 1902, 587.

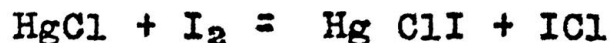
the presence of this free acid by the substitution of some of the hydrogen in the oil by iodine, with the subsequent formation of free hydrochloric acid. Basing their arguments upon these assumptions, they decided that the "correct iodine number" (i.e., if pure^{ly} additive) would be the difference between twice the amount of iodine thus converted into acid and the total quantity absorbed.

Waller¹ also proved the presence of free hydrochloric acid in the reaction product obtained by Hübl's method but, unlike his predecessors, ascribed its formation to the action of free chlorine on the water present in the 95 per cent alcohol. Waller concluded that the addition of hydrochloric acid to Hübl's solution should make the latter more stable, and established a method based upon this assumption. In the case of oils and fats, the numbers obtained by him do not vary greatly from those obtained by Hübl, but the results ob-

1. Zeits. angew. Chem., 1895, 1786, 1831.

tained for mineral oils, cholesterol, and naphthenic acids do not agree with the values obtained by any other method.

In the same year that Waller proposed his method, and an explanation for the presence of free acid in Hübl's reaction, Ephraim¹ obtained fairly accurate results by the use of an alcoholic solution of iodine monochloride. He had observed that the Hübl solution required a much greater amount of sodium thiosulphate, after addition of potassium iodide, than without it, and concluded therefrom that on mixing the components of the Hübl solution there is formed at once a substance capable of liberating iodine from potassium iodide. He expressed the chemical change by the following equation:



Ephraim regarded the fact that he could obtain results identical to those of Hübl, by using

¹. Zeits.analyt.Chem.1895, 254.

a solution of iodine monochloride in alcohol as conclusive proof of the correctness of his assumptions that iodine monochloride is added on to the unsaturated acid radicles directly.

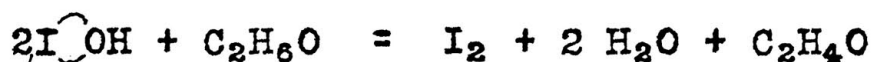
The presence of free acid, as claimed by both Waller and Ephraim, was confirmed by Wijs, who in 1898 and 1899 published a series of classical papers in explanation of the reactions occurring in Hübl's process.¹ His theories were the first that led to any satisfactory explanation of these reactions.

With regard to the presence of free acid, Wijs' earlier views presupposed an interaction between iodine and alcohol with the formation of hydriodic acid. Later, however, from the fact that Hübl's solution loses free iodine rapidly at first, and afterwards more slowly, the solution turns acid, and that the amount of acid

1. Chem.Rev., 1898,137.

xx J.Soc.Chem.Ind., 1898, 610,698,699; 1899,405.

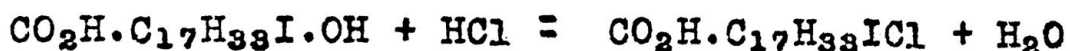
formed corresponds exactly with the amount of iodine that has disappeared, Wijs drew the following conclusions: that a portion of the hypoiodous acid first oxidises the alcohol to aldehyde as follows:



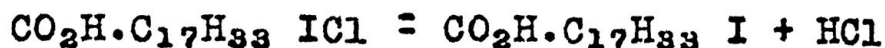
This then causes the formation of fresh hypoiodous acid, but owing to the increased amount of hydrochloric acid now present not quite the full quantity of hypoiodous acid can be formed, notwithstanding the fact that the free iodine liberated, according to the above equation, interacts with HgCl_2 (present in excess) to form fresh ICl and consequently fresh hypoiodous and hydrochloric acids.

The hydrochloric acid which is formed by the reaction in establishing the equilibrium is considered by Wijs as the explanation for the increased acidity of the solution.

In one of his articles,¹ Wijs explains this acidity as follows: In determinations of the iodine number, there is invariably an increase in the excess acid, and besides the addition of halogen there is a further reaction with hydrochloric acid which in the case of oleic acid may be expressed thus:-



In strongly acid solution, however, (like Waller's) there is formed excess acid in accordance with the equation -



The following are Wijs' conclusions on this subject of excess acid:

1. The excess acid is, *ceteris paribus*, proportional to the amount of absorption.
2. Under the same conditions the same fats all yield about the same quantities of acids,

¹. J. Soc. Chem. Ind., 1898, 698 from
Zeits. angew. Chem. 1898, 291.

proportioned to the amount of fat taken. But with substances of different constitution, such as cholesterol, allyl alcohol, etc., different figures are obtained.

3. The greater the acidity of the solution the smaller the amount of acid separated.

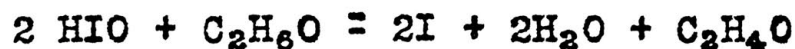
4. The splitting off of the hydrochloric acid is most thorough in liquids which most readily dissolve that acid. Thus, it is greater in alcohol containing water than in chloroform and in methylic alcohol than in ethylic alcohol.

In connection with his investigations on the acidity of Hübl's solution, Wijs presented several equations which in his opinion represented the reactions encountered. They have been summarized by him in the following manner:

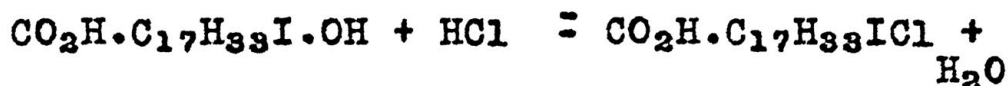
1. In the preparation of the solutions.



2. On keeping the solution.



3. In the absorption (oleic acid).



In spite of the fact that Wijs was strong in support of his belief that hypoiodous acid and not iodine monochloride was the active agent in Hübl's solution, he practically admitted the latter to be the correct view when he produced a process in which he used a solution of iodine monochloride in glacial acetic acid.

The solution he made up in either of two ways; by dissolving 7.9 grams of iodine trichloride and 8.7 grams of iodine in a litre of glacial acetic acid, or by dissolving 13 grams of iodine in a litre of the glacial acetic and

then passing in washed and dried chlorine until the original titer was exactly doubled. The method for the preparation of the solution is the most applicable for technical use because of its low cost, and according to Wijs the results obtained are equally as accurate as those obtained with the first solution mentioned.

Wijs' method has almost superceded that of Hübl's, and although it has objectionable features, yet its stability, increased speed of reaction and degree of accuracy make it much more desirable in fat analysis than any other halogenation process yet devised.

Lewkowitsch¹ states that " for oils and fats having an iodine value below 100, half an hour is quite sufficient for the completion of the reaction, that semi-drying oils require about one hour and drying oils two to six hours, according to the unsaturation of the glycerides. "

1. Oils, Fats and Waxes, Vol. I, P. 322.

Wijs, however, in his original paper¹ stated that " for oils with low iodine values, three to four minutes were sufficient for the completion of the reaction, while for oils with higher iodine values not more than ten minutes should be required providing too large a quantity of oil is not used. "

Wijs tested both his own and Hübl's method by using purified allyl alcohol and obtained results that proved his process to be the more accurate of the two.

Wijs' assumption that HCl and not ICl is the active agent in Hübl's solution and his own which he prepared at that time, does not agree with the subsequent literature.

Henrigues and Künne² were among the first to dispute Wijs' statements. They found that

1. Ber., 1898, 750-752; J.Soc.Chem.Ind., 1898, 699.

2. J. Soc.Chem.Ind., 1899, 377.

the mixed glyceride, oleo-distearin, which, isolated from Mkanyi fat, gives an iodo-chloride and this, by the action of caustic potash first loses its iodine. From this they conclude that any free acid form^{ed}, in Hubl's solution is more probably hydriodic acid¹ than hydrochloric acid split off from the iodo chlorides as stated by Wijs!

Marshall² also disputed Wijs' statements that HIO is the active agent and attempted to prove it in the following manner. He prepared a solution of iodine monochloride in dry carbon tetrachloride and kept the solution over fused calcium chloride to prevent the presence of any trace of moisture. The results obtained with this solution were exactly analogous to those obtained by Wijs, proving that iodine chloride would act exactly in the same way in the ab-

 1. Chem. Rev., 1899, 45.

2. J.Soc.Chem.Ind., 1900, 213.

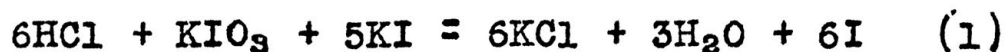
sence of water as in the presence of it. In fact, he found his solution to be even more energetic than the one employed by Wijs, for Wijs had found the action of his solution, containing 5 per cent of water, on linseed oil to require about seven minutes, whereas in Marshall's experiments the addition was evidently complete at the end of one minute.

Marshall in addition to the above mentioned experiments performed others to determine the amount of substitution. According to his results any considerable amount of substitution should be apparent to the eye by the liberation in the carbon tetrachloride of free iodine, giving the carbon tetrachloride a brilliant purple color. Iodine chloride, on the other hand, would only color the carbon tetrachloride a bright yellow.

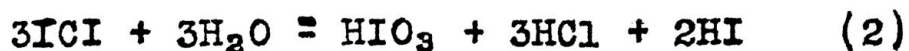
To detect any very slight substitution,

however, Marshall used the following method:

After the titration of the iodine in the regular manner with sodium thiosulphate, he added to the solution, potassium iodate. When this is done, every equivalent of acid present liberates an equivalent of iodine.



The liberated iodine is then titrated with sodium thiosulphate solution. In all of the experiments performed, using Marshall's carbon tetrachloride solution and taking proper precautions to exclude all moisture, the addition of potassium iodate failed to cause any coloration of carbon tetrachloride, proving the absence of free acid. However, only a mere trace of water rapidly produced the change,



the hydriodic acid then reacting with more

iodine chloride with the liberation of free iodine.



At the same time the solution becomes cloudy, due to the separation of iodic acid, but upon drying over calcium chloride again becomes clear.

Marshall concludes from his experiments that

" the so-called iodine absorption " consists simply in the addition of iodine chloride to the double linking of the unsaturated acid and that no other reaction takes place to any appreciable extent.

Marshall's experiments were followed in 1902 by those of Ingle.¹ Ingle in his address before the Society of Chemical Industry made the following statement: " However, I think I shall be able to prove this evening that none of the above theories, substitution, splitting off of HCl from the iodine chloride addition product

1. J.Soc.Chem.Ind., 1902, 587; 1905, 242; 1908, 314.

or incomplete conversion of the oxyiodides into iodochlorides, are the real source of the free acid. " He then explained that the double linkages in the unsaturated compounds absorb iodine chloride and then the water which is always present, both in Wijs' and in Hübl's solution, acts upon the iodo chloride and eliminates iodine or chlorine or both and forms hydroxy compounds of the nature of alcohols or glycols, thus:



No new double linkages are formed and consequently the iodine absorption is independent of the amount of acid formed.

Ingle also performed tests to determine the amount of substitution using Wijs' solution. He used potassium iodate for this purpose in the same manner that it had been previously used by Schweitzer and Lungwitz and by Marshall.

He noticed the separation of iodine when various substances were treated with Wijs' solution and offered the following suggestions as to the causes:

1. The addition of chlorine by the substance, and liberation of free iodine, but this does not explain the formation of free acid.

2. The substitution of chlorine for hydrogen in the compound and consequent formation of hydriodic acid -



The hydrochloric acid thus liberated acts upon the excess of iodine chloride and forms hydrochloric acid and free iodine thus:



which would explain both the liberation of iodine and the formation of some free acid.

Ingle further states that the liberation of iodine in Marshall's solution was not due to the action of water upon the iodine chloride itself

and bases his arguments upon the fact that when water was added to a portion of Marshall's solution to which stilbene had been added, immediate liberation of iodine resulted, while with Marshall's solution alone the addition of water caused the liberation of iodine only after the solution had stood some little time in contact with the water.

In addition to the methods of Hübl and Wijs a third method of halogenation has recently been produced by Hanus after whom it is named. Hanus followed up a suggestion made by Bellier¹ and substituted for the iodine chloride of Wijs' solution, iodine bromide. The results obtained, however, are claimed by Marshall,² Harvey,³ Archbutt⁴ and also Wessen and Lane, to be incorrect. Lewkowitsch deprecates the use of

1. Annal.Chim.analyt.appl., 1900, 128.
2. J. Soc. Chem.Ind., 1900, 213.
3. J. Soc. Chem.Ind., 1902, 1437; 1904, 414.
4. J. Sod. Chem.Ind., 1905, 306.

Hanus' method because, according to him, " the publication of numbers obtained by this process only serves to encumber the already too bulky literature on this subject. "

A comparison of the relative merits of Hübl's, Wijs' and Hanus' methods has been the object of several researches carried on within the last few years. In every case this study was made in an attempt to fix a method for the determination of iodine numbers which should be accepted as a standard for analytical use.

Such a research was reported by F. W. Hunt¹ in a paper designated as " A Comparison of Methods Used to Determine the Iodine Value of Oils. " He secured a considerable amount of data of a comparative nature but was unable to come to any definite conclusion as to the relative merits of the methods of Hübl, Wijs and

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1. J. Soc.Chem.Ind., 1902, 454.

Hanus.

Under the direction of the Food Laboratory of the Bureau of Chemistry, United States Department of Agriculture, L. M. Tolman¹ compared the halogen absorption of oils by the Hübl, Hanus and McIlhiney methods. He arrives at the following conclusions:

1. That much better results are obtained by the Wijs and Hanus solutions than by the Hübl.

2. That the Hanus solutions give results much more closely agreeing with the existing data and is easier to prepare but an excess of 60 to 70 per cent is necessary to obtain quick action.

3. That the Wijs solution is more rapid in its action and an excess of 35 per cent is sufficient, effecting a large saving in

1. J. Am.Chem.Soc., 1904, 826.

reagents and time of titrating but it gives higher results.

4. That thirty minutes is sufficient time for the action of either the Hanus or Wijs solutions.

5. That acetic acid is a better solvent for the work than carbon tetrachloride.

6. That the bromine solution or iodine chloride or iodine bromide in carbon tetrachloride are not satisfactory for ordinary work.

7. That iodine chloride in carbon tetrachloride is the most satisfactory solution if determination of substitution is to be made.

8. That both the iodine chloride and iodine bromide, being much less volatile than the bromine, there is much less danger of loss in that way with the former reagents. Tolman found a substitution of 2.20 in sixty minutes using Wijs' method on an oil having an iodine

value of 198.6.

M. Augnet¹ in an investigation similar to the one last mentioned, concludes that the low results, obtained by using a new Hübl solution, are due to the fact that hydriodic acid is the necessary component and that it is formed in insufficient quantities in the solution to give the latter its maximum efficiency in less than a month. He, therefore, returns to Waller's method and adds 3.5 grams of hydriodic acid or hydrochloric acid to the new Hübl solutions. According to him, the iodine number, as determined by either Wijs' or Hübl's process is not materially affected by changes of temperature between 10° and 25° C. He found the absorption to be complete in twenty minutes with the Wijs' solution and one hour with that of Hübl.

D. A. Bartlett and H. C. Sherman of the

1. Ann. fals. 5,459.

Havenmeyer Laboratory, Columbia University, School of Mines Quarterly 31, 55-63, 1910, have investigated the effect of excess of reagent and time of reaction for the various methods. The following are their conclusions:

1. In both the Hübl and Wijs method the use of liberal excess of reagent greatly shortens the time required for a complete reaction.

2. In the Hübl method it is preferable to use a large excess of reagent for three to four hours rather than a small excess for eighteen hours, because on long standing the results tend to become irregular, probably through deterioration of the iodine solution remaining in excess.

3. In the case of linseed oil a freshly mixed Hübl solution (less than twenty-four hours old) should be used as with solutions even three days old the reaction is much retarded and requires long standing for completion.

4. In the examination of fatty oils of unknown capacity for halogen absorption, it is recommended that 2 c.c. of fresh Hübl's solution of equivalent strength be used for each centigram of sample and that three hours be allowed for the reaction in case of the Hübl or thirty minutes in the case of the Wijs reagent.

References to other investigations, relating to the subject of iodine values are here given:-

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J. Am. Chem. Soc., 1900, 12.

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Apoth.Ztg., 27, 297-8.

PROBLEM.

The investigations, reported in the remaining portion of this paper, were not undertaken with the view of making a comparison of the existing methods for the determination of iodine values for, as already shown sufficient literature of a comparative nature has been produced to warrant the acceptance of the method devised by Wijs, as the most suitable for technical application. The real purpose of the investigation, however, was to study Wijs' ¹ method and try to arrive at some conclusions as to the most favorable conditions for its manipulation.

After a study of the literature, the following questions arise:-

1. What is the effect of time on the reaction and what is the most favorable time for ordinary purposes.

Lewkowitsch¹ makes the statement that for drying oils, one-half hour is sufficient for the completion of the reaction, while semi-drying and non-drying oils should have, at least, one hour and two hours respectively. Wijs, however, in his original paper² states that the reaction should not require more than three to ten minutes for its completion. This consideration of time is extremely important from a technical standpoint and deserves close attention.

2. What is the proper amount of iodine monochloride required in excess of the quantity which reacts with the oil? According to Wijs' directions there is always wasted approximately two hundred per cent of this solution.

1. " Oils, Fats and Waxes, Vol. I, P. 322.
2. Ber., 1898, 31 (6), 750-752.
J. Soc.Chem.Ind., 1898, 699.

3. If the velocity of the reaction is in any way dependent upon the rates of diffusion of the solutions, why should not the velocity be increased by vigorous stirring of the reagents during the reaction period?
4. What is the proper strength for the iodine monochloride, and what is the effect of varying the strength of the solution used.
5. What effect upon the reaction has an excess or insufficient quantity of chlorine in the iodine monochloride solution above or below the amount necessary to make the solution exactly double its original titer (before the addition of any chlorine).

Each of these problems was investigated and the experimental results will be presented in the above order.

APPARATUS.

The apparatus used in the investigation of this problem consisted, for the most part, of simple articles such as may be found in any well equipped laboratory, and in addition, a few special instruments which were designed and constructed for the particular work in hand.

The first of these was a small pipette, suitable for holding a quantity of oil sufficient for nine or ten determinations. It consisted of a bent glass tube about three eighths of an inch in diameter and three inches long bent in the manner shown in the accompanying illustration (Figure I). The delivery end of the tube consisted of a capillary of such a size that when the tube was held in a vertical position, the oil flowed from it one drop at a time, thus preventing the danger of running out a large excess of oil for any one determination.

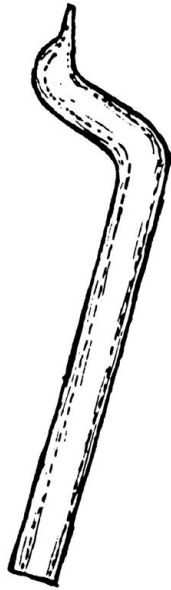


Fig. 1

The pipette was supported in a horizontal position on the balance pan by means of the balance specimen tube rack.

One of the most important pieces of special apparatus used is illustrated in Figure 2. It consisted of an ordinary pipette (of any volume desired) connected through a three way stopcock, with a filter pump. By means of this instrument, it was very easy to measure the desired quantity of an iodine monochloride solution without the possible danger of drawing the fumes or some of the solution into the mouth.

As shown by the illustration, the pipette was connected by a short piece of rubber tubing with one of the tubes projecting from a three-way stopcock. A second tube extending from the side of the cock was bent upward and its edges rounded by fusing in a flame. The third tube connected directly with a one hundred c.c.

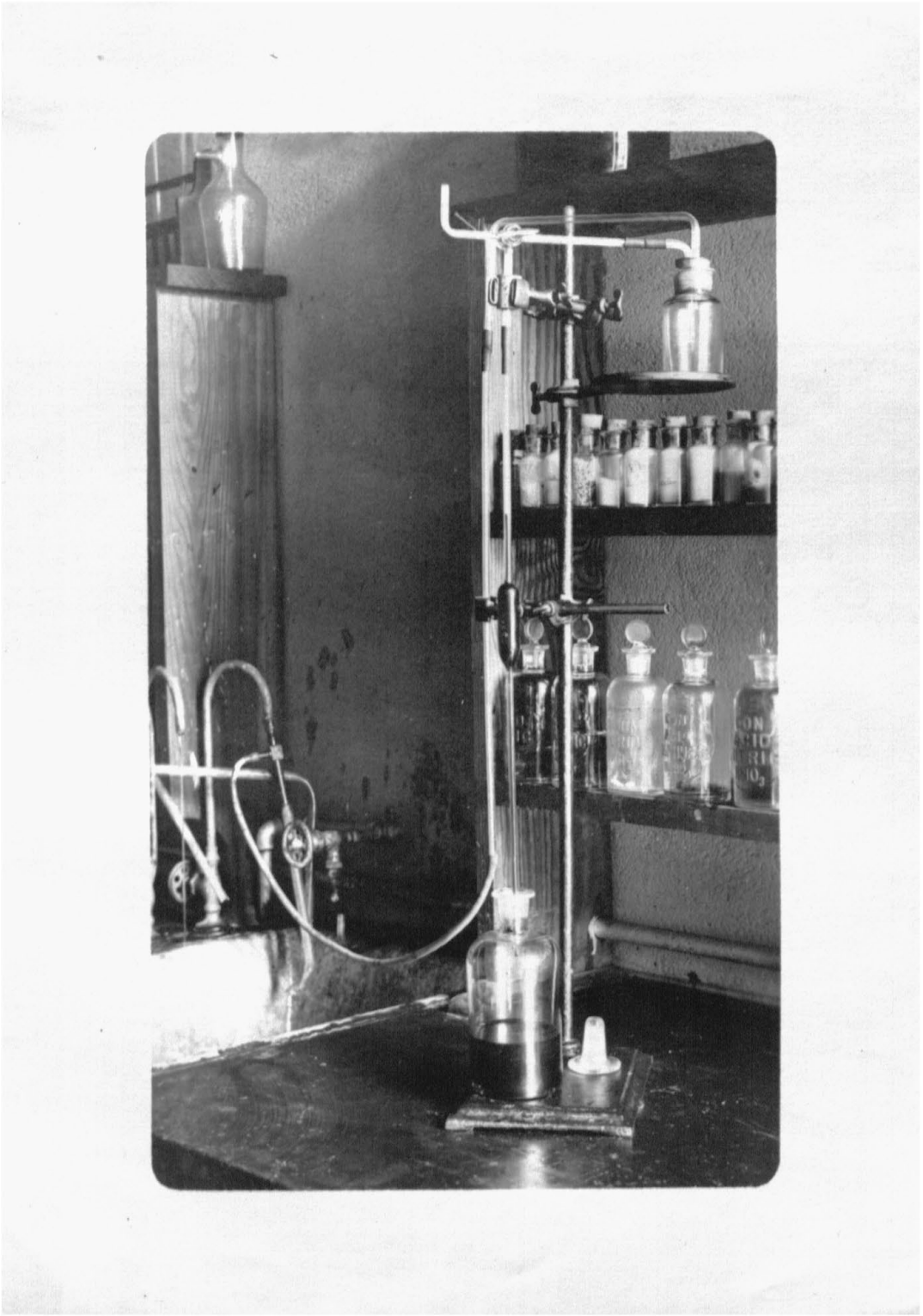


Fig. 2

bottle, which served as a trap for any solution drawn beyond the cock. This bottle in turn was provided with a glass tube which could be quickly connected with a filter pump whenever desired.

To operate this instrument, the bottle containing the solution to be measured was placed on the supporting platform of the apparatus. The cock was then opened and the solution drawn up into the pipette by the suction from the filter pump. As soon as the solution had passed slightly above the volume mark, the cock was closed and the solution remained at the position originally reached. The operator then placed a finger over the end of the bent tube from the stopcock, opened the latter by turning a quarter of a turn, and allowed the solution to flow down to the mark after the fashion of an ordinary pipette. Upon reaching the mark the cock was again turned back, and the liquid held in pos-

ition until the proper receptacle could be placed under the pipette, when the top was opened and the contents allowed to flow out.

Another instrument for measuring the volume of solutions was constructed and used when volumes were required, which were different from those represented by the pipettes. This piece of apparatus consisted of the bottle containing the solution to be measured, provided with a syphon which delivered directly into a D. R. burette. By opening a glass cock at the end of the syphon, the burette was quickly filled and then from it the desired volume of solution could be delivered.

The only other piece of special apparatus was a rotating machine shown in an accompanying illustration (Figure 3). This machine was originally constructed for an investigation of phenol determinations, carried on by the author

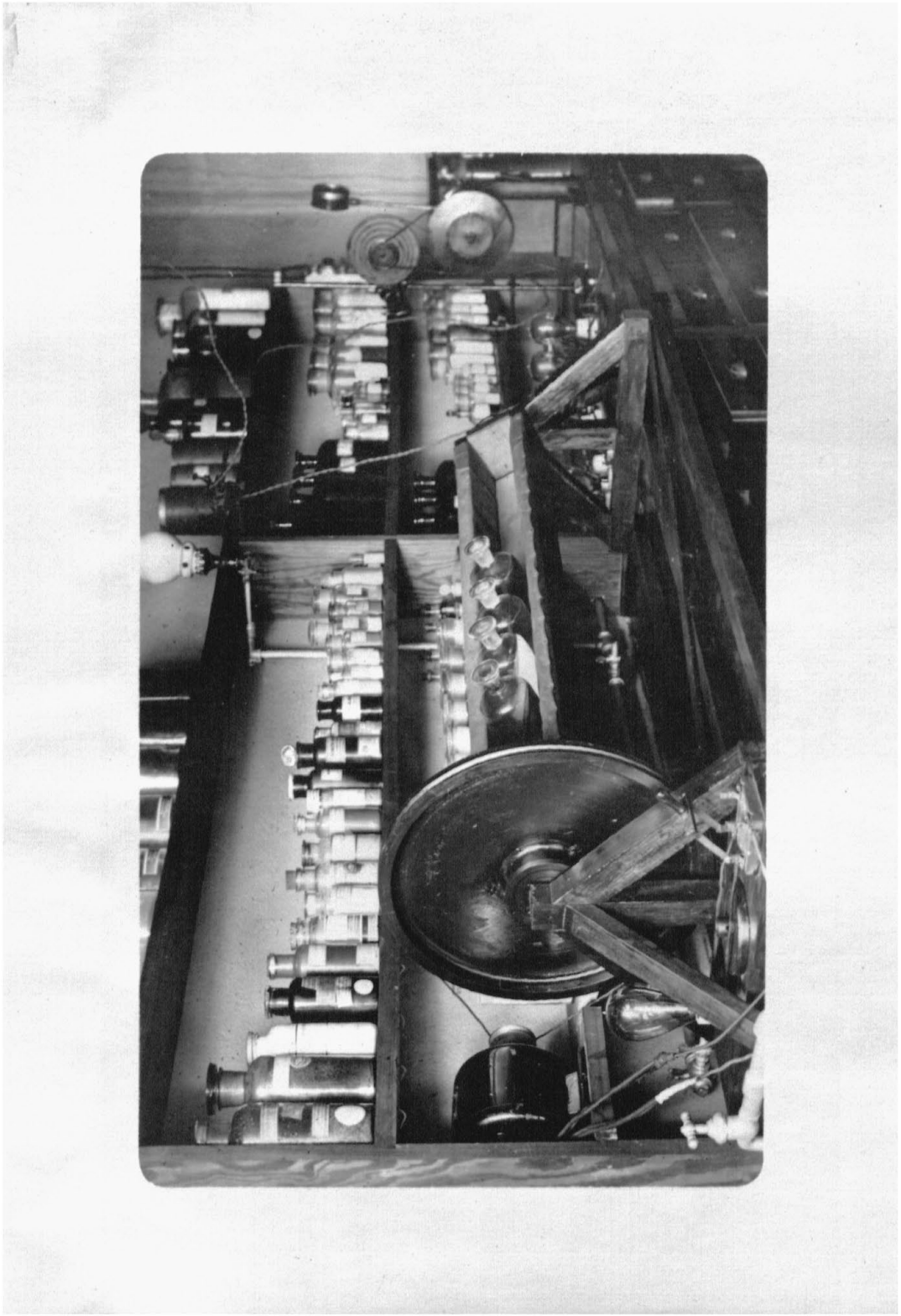


Fig. 3.

and Dr. L. V. Redman, and has been described in the report of that investigation.¹ However, for the sake of completeness, an explanation of the machine will be included in this paper.

As shown by the illustration, the machine consisted of a long, narrow and shallow box provided with a grooved pulley at one end, and supported upon a frame work at each end, by means of iron shafts, seated in wooden bearings. For the work now under discussion, this rotating or shaking machine was connected directly with and driven by a small electric motor; and^a switch provided for quick starting and stopping of the machine.

The box was of sufficient size to hold eight 500 c.c. bottles, and owing to the fact that its sides were padded with felt, no fastenings were needed to hold the bottles in the machine.

1. J. Ind. & Eng. Chem., 1912, 655.

The bottles used were selected from the ordinary stock but had to be of nearly uniform size and shape. They had ground glass stoppers provided with horizontal flat heads rather than the vertical type. The reason for this being that in case there is any spattering during the opening of the bottles, most of the drops are caught by the flat top of the stopper and can be washed back into the bottle.

When it was desired to make a determination, the solutions were first placed in the bottle, the stopper was then inserted, given a short, sharp twist and the bottle was pressed down between the padded sides of the box. The current was then thrown on and the bottle rotated for the desired length of time.

The burettes used in all of the determinations were standard D. R. burettes of sufficient accuracy that they needed no callibration.

SOLUTIONS.

Two sodium thiosulphate solutions were used for the work. Each was approximately N/10 and made up by dissolving 125 grams c. p. $\text{NaS}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 5 litres of water. They are referred to in this paper as Nos. 1 and 2, respectively.

Eight iodine monochloride solutions were used. They were prepared as follows:

No. 1.

14 grams of iodine in 1 litre of glacial acetic acid and chlorine added to change of color. Normality against standard sodium thiosulphate solution 0.2240. The original titer of the iodine solution before the addition of chlorine is not known.

No. 2.

30.5 grams of iodine in 5 litres of glacial acetic acid. Chlorine was added to change of

color. In this case, the original normality of the iodine solution was approximately 0.05, and after addition of chlorine 0.09789.

No. 3.

65 grams iodine (resublimed) dissolved in 5 litres of glacial acetic acid. No chlorine added. Normality 0.1008.

No. 4.

Chlorine added to two litres of iodine solution No. 3 to distinctive change of color. Normality 0.2219.

No. 5.

One liter of iodine monochloride No. 4 diluted with iodine solution No. 3 to 1201.3 c.c. The object of this was ^{to} exactly double the original titer of the iodine solution, (0.1008 N.) Normality 0.2012.

Method of Calculation.

$$0.2219 \text{ N.} - 0.1008 \text{ N.} = 0.1211 \text{ N.} =$$

Normality of No. 4 due to chlorine. In order to make ICl solution No. 5 0.2016 N., the normality of No. 4 due to chlorine must be 0.1008.

$$\frac{0.1211}{0.1008} \times 1000 = 1201.3 = \text{No. of c.c. to}$$

which one litre of iodine monochloride solution No. 5 must be diluted to become 0.2016 N.

No. 6.

Chlorine added to one litre of iodine solution No. 3 until solution showed first indication of changing color. Normality 0.1866.

No. 7.

Chlorine added to one litre of iodine solution No. 3 considerably in excess of the amount required to change the color. Normality 0.5849.

No. 8.

250 c.c. of iodine solution No. 3 added to an equal volume of iodine monochloride solution No. 4. Normality 0.3201.

In addition to the solutions above mentioned, a potassium iodide solution was used which contained 10 per cent KI by weight.

Also a starch solution, made up in the ordinary manner from potato starch, was used as indicator. No other solutions were needed.

EXPERIMENTAL.

" White " cotton seed oil was used for all of the following experiments so that it is referred to whenever the word " oil " occurs.

Each series of experiments is represented by one or more tables in each of which the substances are arranged in their order of addition.

The results presented are not a few chosen from many because of a great^{er} degree of accuracy, but represent all of those obtained, in order that a more definite idea may be formed of the accuracy of the method under conditions such as would be met with in commercial practice. In all of the following tables, unless statement is made to the contrary, the columns marked " time " refer to time of shaking.

The iodine value for each experiment is calculated as follows:

The volume of sodium thiosulphate solution required for an experiment subtracted from the volume required for a blank test, represents the amount of that solution necessary to react with a quantity of iodine monochloride equal to the quantity used up by the oil during the reaction. Multiply this difference by the number of grams of iodine to which one c.c. of the sodium thiosulphate solution is equivalent, and then divide by the weight of oil used as a sample.

Each experiment was performed in the following manner:-

Approximately 0.2 gram $\frac{1}{2}$ of the "white" cotton seed oil was weighed, by means of the small pipette already described, into one of the 500 c.c. glass stoppered bottles. 10 c.c. of carbon tetrachloride and a known quantity of iodine monochloride solution were added to the oil in the order named, and the mixture was then shaken

in the rotating machine for the length of time desired. It was then removed from the machine, a quantity of 10 per cent potassium iodide solution added and again shaken; this time, however for only one minute. 250 c.c. of water were then added and the entire mixture again shaken for one minute.

In Table I are given a number of results obtained from experiments performed to determine the effect of time of shaking upon the reaction. In all of the experiments represented by this table, the quantity of iodine monochloride used was approximately two hundred per cent in excess of the actual volume required.

The results seem to indicate that for periods ranging from one minute to thirty, there is a slight increase in the iodine number. This has indeed been found to be the case in every series of experiments in which varying time was used,

TABLE I.
Effect of Time of Shaking.
200% Excess Iodine Monochloride Solution.

No.	Weight of Oil grams	CCl ₄ c.c.	Iodine Sol. c.c.	Time min.	KI	Time min.	H ₂ O c.c.	Time min.	Thio c.c.	Iodine No.
1.	0.2025	10	25	1	10	1	250	1	46.98	108.21
2.	0.1929	10	25	1	10	1	250	1	47.95	108.32
3.	0.1839	10	25	10	10	1	250	1	48.77	108.95
4.	0.1948	10	25	10	10	1	250	1	47.45	109.96 ⊕
5.	Blank	10	25	10	10	1	250	1	67.88	
6.	Blank	10	25	10	10	1	250	1	67.87	
7.	0.2049	10	25	30	10	1	250	1	46.45	109.66
8.	0.1991	10	25	30	10	1	250	1	46.80	111.01 ⊕

Iodine Monochloride No. I 0.2240 N.

Thiosulphate No. I 0.08268 N.

⊕ Seem unaccountably high.

as will be noted from time to time in this paper while explaining the various tables.

Following the completion of Table No. I, a series of experiments represented by Tables II, III, IV and V were performed to determine the effect of excess iodine monochloride solution.

An interesting point brought out by Tables II, III and IV is, that in every case the iodine number obtained lies between 101 and 104, while all of the results obtained in Table I lie between 108 and 110. In every case the conditions were exactly the same and the only change made was in the iodine monochloride solutions. For Table I a solution was used which had a normality of 0.2240, while the one used for Tables II, III, IV and V was 0.9789 normal, or a little less than half as strong as the solution used for Table I. Unfortunately the original titer for each of these solutions is not known, but

TABLE II
Effect of Excess Iodine Monochloride Solution.

200% Excess.

No.	Weight of Oil grams	CCl ₄ c.c.	ICL c.c.	Time min.	KI c.c.	Time min.	H ₂ O c.c.	Time min.	Thio c.c.	Iodine No.
1.	0.1922	10	50	1	10	1	250	1	40.63	101.35
2.	0.2078	10	50	1	10	1	250	1	38.77	103.13
3.	0.1907	10	50	5	10	1	250	1	40.67	101.92
4.	0.1867	10	50	5	10	1	250	1	40.97	102.42
5.	0.1926	10	50	10	10	1	250	1	40.33	102.77
6.	0.2000	10	50	25	10	1	250	1	39.40	103.85
7.	Blank	10	50	30	10	1	250	1	59.20	
8.	0.1822	10	50	40	10	1	250	1	41.27	103.23
9.	0.1918	10	50	60	10	1	250	1	40.20	103.91
10.	0.2104	10	50	60	10	1	250	1	38.34	104.00

(?)

Iodine Monochloride No. 2 0.08268 N

Thiosulphate No. 2 0.09789 N.

TABLE III.
Effect of Excess Iodine Monochloride Solution.

100% Excess.

No.	Weight of Oil grams	CCl ₄ c.c.	ICl Sol. Req'd c.c.	ICl Sol. Added c.c.	Time min.	KI c.c.	Time min.	H ₂ O c.c.	Time min.	Thio c.c.	Iodine No.
1.	0.2016	10	16.90	33.79	1	10	1	250	1	20.20	102.35
2.	0.1945	10	16.35	32.70	1	10	1	250	1	19.53	102.74
3.	0.1973	10	16.61	33.20	10	10	1	250	1	19.74	103.30
4.	0.1982	10	16.66	33.31	15	10	1	250	1	19.80	103.15
5.	0.1941	10	16.35	32.70	25	10	1	250	1	19.40	103.65
6.	0.1970	10	16.58	33.16	30	10	1	250	1	19.63	103.78
7.	Blank	10	-- --	25.00	30	10	1	250	1	29.60	

Solutions

Iodine Monochloride No. 2 0.09789 N

Sodium Thiosulphate No. 1 0.08268 N

TABLE IV.
Effect of Excess Iodine Monochloride Solution.

36% Excess.

No.	Wt. Oil grams	CCl ₄ c.c.	ICl Sol. c.c.	Time min.	KI c.c.	Time min.	HgO c.c.	Time min	Thio c.c.	Iodine No.
1.	0.1939	10	25	1	10	1	250	1	10.32	104.30
2.	0.2169	10	25	1	10	1	250	1	8.03	104.31
3.	0.2216	10	25	10	10	1	250	1	7.44	104.90
4.	0.1985	10	25	10	10	1	250	1	9.70	105.16
5.	0.1954	10	25	30	10	1	250	1	10.10	104.68
6.	0.2171	10	25	30	10	1	250	1	7.95	104.61
7.	Blank	10	25	30	10	1	250	1	29.58	
8.	Blank	10	25	30	10	1	250	1	29.62	

Solutions

Iodine Monochloride No. 2 0.09789 N.

Sodium Thiosulphate No. I 0.08268 N.

TABLE V.
Effect of Excess Iodine Monochloride Solution.

1% Excess.

No.	Weight of Oil grams	CCl ₄ c.c.	ICl Sol. Req'd c.c.	ICl Sol. Added c.c.	Time min.	KI min.c.c.	Time min.	H ₂ O c.c.	Time min.	Thio c.c.	Iodine No.
1.	0.2213	10	18.55	18.73	1	10	1	250	1	2.05	94.99
2.	0.1927	10	16.15	16.31	10	10	1	250	1	1.10	98.73
3.	0.1963	10	16.45	16.61	30	10	1	250	1	0.76	100.09

Solutions.

Iodine Monochloride No. 2 0.09789 N.

Sodium Thiosulphate No. I 0.08268 N.

from the quantity of iodine weighed out, the normality of the original iodine solution in each case should have been approximately half of the final normality, as given above. As yet the author has not been able to account for this large discrepancy and further investigations will be made to discover its cause.

In all of the experiments in the series represented by Table II, the volume of iodine monochloride solution used was approximately 200 per cent in excess of the actual volume required to complete the reaction with the oil. This is the same excess as was used in Table I and was obtained by using a volume of iodine monochloride solution double that used in the preceding table.

For the series shown in Table III, only 100 per cent excess iodine monochloride solution was used. In order to secure the same excess in every case, the volume of solution was

measured with the burette, described under "Apparatus", instead of the automatic pipette.

Measuring out a volume of 25 c.c. of the same solution as used in Tables I and II gave an excess of approximately thirty-six per cent, which was used in all of the experiments represented by Table IV.

For Table V, however, the actual quantity of iodine monochloride solution was calculated which would be required to react with the weight of oil taken as a sample in each experiment. By means of the burette previously mentioned, a volume was then measured out which represented 1 per cent excess solution. The calculations in each case were based upon an average of the results obtained in Table No. IV.

It will be noticed that in Tables II, III and IV, the results obtained for equal periods

of time agree fairly well, and that even with only 1 per cent in excess for a period of thirty minutes, as shown in Table No. V, the number obtained was only about 4 per cent lower than the one obtained when 200 per cent excess was used.

These tables seem to indicate that as long as an excess of iodine monochloride solution is present, the actual quantity has very little effect upon the reaction.

The fact that there is a slight increase in the magnitude of the iodine number with increased time of shaking is clearly shown in each of the above mentioned tables and gives rise to a question as to its cause.

If this increase were due to a secondary reaction whose^{se} velocity is dependent upon the rate of diffusion of the solutions, then it would be logical to assume that an increase in the rate of diffusion would bring about a cor-

responding increase in the rate of reaction. Supposing, for instance, that in addition to the main reaction between the oil and iodine monochloride solution for the formation of additive compounds, there were a secondary reaction of substitution in which chlorine replaced some of the hydrogen with the subsequent formation of hydrochloric acid. Such a reaction should be hastened by increased velocity of diffusion.

In order to test this assumption, two series of experiments were performed and the results obtained are given in Table VI and Table VII, respectively. In both series of experiments all conditions were kept exactly parallel, except that in the first (represented by Table VI) the solutions were shaken continuously during the period of reaction, while in the second (represented by Table VII) the solutions were only shaken sufficiently to insure thorough

TABLE VI.

Wij's Standard Method and Iodine Monochloride Solution.

With Shaking.

No.	Wt. Oil grams	CCl ₄ c.c.	ICl Sol. c.c.	Time min.	KI c.c.	Time min.	H ₂ O c.c.	Time min.	Thio c.c.	Iodine No.
1.	0.1929	10	20	1	10	1	250	1	24.04	106.32
2.	0.2175	10	20	1	10	1	250	1	21.94	106.56
3.	0.2076	10	20	5	10	1	250	1	22.68	107.11
4.	0.1955	10	20	5	10	1	250	1	23.66	107.33
5.	0.1989	10	20	10	10	1	250	1	23.28	107.97
6.	0.2150	10	20	10	10	1	250	1	21.90	108.04
7.	Blank	10	20	30	10	1	250	1	40.21	
8.	Blank	10	20	30	10	1	250	1	40.17	
9.	0.2005	10	20	30	10	1	250	1	22.90	108.03
10.	0.2059	10	20	30	10	1	250	1	22.60	108.49
11.	0.2070	10	20	60	10	1	250	1	22.41	109.09
12.	0.2073	10	20	60	10	1	250	1	22.30	109.60

Solutions
 Iodine Monochloride No. 5 0.2012 N.
 Sodium Thiosulphate No. 2 0.1001 N.

TABLE VII.

Wijs' Standard Method and Iodine Monochloride Solution.

Without Shaking.

No.	Wt. Oil grams	CCl ₄ c.c.	ICl Sol. c.c.	Time min	KI c.c.	Time min.	H ₂ O c.c.	Time min.	Thio c.c.	Iodine No.
1.	0.2049	10	20	1	10	1	250	1	23.05	106.23
2.	0.2132	10	20	10	10	1	250	1	22.20	107.11
3.	0.2059	10	20	10	10	1	250	1	22.78	107.39
4.	0.2018	10	20	30	10	1	250	1	23.11	107.48
5.	0.1995	10	20	30	10	1	250	1	23.24	107.90
6.	0.2039	10	20	60	10	1	250	1	22.80	108.31
7.	0.2018	10	20	60	10	1	250	1	22.99	108.93

Solutions

Sodium Thiosulphate No. 2 0.1001 N.

Iodine Monochloride No. 5 0.2012 N

mixing, and were then allowed to stand motionless for the remainder of the reaction period.

The iodine monochloride solution (No. V) used for both series of experiments was prepared, as described on page 40 of this paper, and conforms exactly with the directions given by Lewkowitsch¹ for the preparation of Wijs' standard solution.

Table VI shows the same uniform increase in the iodine number with increased time of reaction that was noticed in preceding experiments but the results in Table VII, although they show this same increase, are in every case slightly lower than the results for corresponding reaction periods in Table VI. This seems to confirm the assumption that there is a primary reaction of addition which becomes complete immediately upon the addition of iodine monochloride solution to the solution of oil in carbon tetrachloride, but

that there is a secondary reaction of substitution which continues as long as the iodine monochloride solution is allowed to remain in contact with the oil and may be considerably hastened by vigorous shaking.

Another interesting fact brought out by Tables VI and VII is that in these tables the results are almost identical to those in Table I for which an iodine monochloride solution was used that had a normality of 0.2240, while they are about 4 per cent higher than the numbers in Tables II, III and IV for which the solution was only 0.09789 N.

According to all of the directions given in the literature for the preparation of Wijs' solution, the titer after the addition of chlorine should be double the titer of the original iodine solution (before the addition of chlorine). The statement is also made that

this point of double titer can be accurately determined by observing the change of color that takes place upon the conversion of all of the iodine to iodine monochloride. No information is given, however, as to the effect which would be produced upon the iodine value if the final titer were not exactly double that of the original solution, i.e., what the effect would be if there were either an excess or an insufficient quantity of chlorine in the iodine monochloride solution.

Three iodine monochloride solutions containing different proportions of iodine and chlorine were prepared from the same iodine solution. In the first (No.6) only enough chlorine was used to cause a slight change of color and its normality upon standardization was found to be 0.1866 or 0.015 less than it should have been to have contained the same quantities of iodine and of chlorine. The second and third, how-

ever (Solutions 1 and 8 respectively) contained a large excess of chlorine.

As shown by Table VIII the results obtained at the end of thirty minutes, (using iodine monochloride solution No. 6) are almost identical to those for the same period of time in Tables VI and VII, showing that an insufficient quantity of chlorine in Wijs' solution has little or no effect on the reaction.

A decided effect was obtained, however, when the solutions (Nos. 7 and 8) were used which contained an excess of chlorine.

Table IX shows that an excess of 260 per cent chlorine above the theoretical amount, gave values approximately 25 per cent higher than those obtained with a solution which contained no excess chlorine (Tables VI and VII). An excess of 85 per cent, however, gave results 18 per cent higher than those in Tables VI and VII.

TABLE VIII.

Effect of varying the concentration of Chlorine in the
Iodine Monochloride Solution.

Normality of ICl solution due to Iodine - 0.1008
Normality of ICl solution due to Chlorine $\frac{0.0858}{0.1866}$
Total normality of ICl solution - 0.1866

No.	Wt. Oil grams	CCl ₄ c.c.	ICl Sol. c.c.	Time min.	KI c.c.	Time min.	H ₂ O c.c.	Time min.	Thio c.c.	Iodine No.
1.	0.1914	10	25	30	10	1	250	1	30.25	108.4
2.	0.2108	10	25	30	10	1	250	1	28.60	108.3
3.	Blank	10	25	30	10	1	250	1	46.55	
4.	Blank	10	25	30	10	1	250	1	46.63	

Solutions.

Iodine Monochloride No. 6 0.1866 N.

Sodium Thiosulphate No. 2 0.1001 N.

TABLE IX.

Effect of varying the concentration of Chlorine in the Iodine Monochloride Solution.

Normality of ICl solution due to Iodine 0.1008
 Normality of ICl solution due to Chlorine 0.1193
 Total normality of ICl solution 0.3201

No.	Wt. Oil grams	CCl ₄ c.c.	ICl Sol. c.c.	Time min.	KI c.c.	Time min.	H ₂ O c.c.	Time min.	Thio c.c.	Iodine No.
1.	0.2029	10	20	30	40	1	250	1	44.20	132.93
2.	0.2014	10	20	30	40	1	250	1	44.94	128.76
3.	Blank	10	20	30	40	1	250	1	65.20	Average
4.	Blank	10	20	30	40	1	250	1	63.97	65.36
5.	Blank	10	20	30	40	1	250	1	65.52	

Solutions.

Iodine Monochloride No. 8 0.3201 N.

Sodium Thiosulphate No. 2 0.1001 N.

TABLE X.

Effect of varying the concentration of Chlorine in the
Iodine Monochloride Solution.

Normality of ICl solution due to Iodine - 0.1008
Normality of ICl solution due to Chlorine $\frac{0.4841}{0.5849}$
Total Normality of ICl solution

No.	Wt. Oil grams	CCl ₄ c.c.	ICl Sol. c.c.	Time min.	KI c.c.	Time min.	H ₂ O c.c.	Time min.	Thio c.c.	Iodine No.
1.	Blank	10	20	30	40	1	250	1	116.87	
2.	Blank	10	20	30	40	1	250	1	116.90	
3.	0.2024	10	20	30	40	1	250	1	95.75	132.58
4.	0.1985	10	20	30	40	1	250	1	95.43	137.26

Solutions

Iodine Monochloride No. 7 0.5849 N.

Sodium Thiosulphate No. 2 0.1001 N.

While performing the experiments, the results of which are given in Table IX, an interesting development occurred that seems more than anything else to indicate that the secondary reaction is one of substitution.

It was found that when the usual order for the addition of carbon tetrachloride and of iodine monochloride solution was reversed, i.e., the iodine monochloride solution added before the carbon tetrachloride that the iodine number was considerably increased.

Table XI gives the results for two such experiments. With the exception of the reverse order of addition, all of the conditions were exactly identical to those for the experiments represented by Table IX, but the iodine values in Table XI are approximately 22 higher than those obtained when the correct order was maintained. This can best be explained by the

TABLE XI.

Effect of addition of ICl solution before CCl_4 .

No.	Wt. Oil grams	ICl Sol. c.c.	CCl_4 c.c.	Time min.	KI c.c.	Time min.	H_2O c.c.	Time min.	Thio c.c.	Iodine No.
1.	0.1909	20	10	30	40	1	250	1	93.73	154.00
2.	0.2025	20	10	30	40	1	250	1	92.38	153.42
3.	Blank	20	10	30	40	1	250	1	116.87	
4.	Blank	20	10	30	40	1	250	1	116.90	

Solutions

Iodine Monochloride No. 7 0.5849 N.

Sodium Thiosulphate No. 2 0.1001 N.

assumption that the iodine monochloride being concentrated upon the few drops of oil, caused the substitution of hydrogen by chlorine to proceed much more rapidly than it had in the cases where the oil was first dissolved in carbon tetrachloride.

SUMMARY.

From the results of the preceding experiments the following conclusions may be drawn -

In determinations of the iodine value by Wijs' method:

1. The magnitude of the iodine value increases continuously from one minute to 60 minutes but in the shortest possible time in which a determination may be made, the number in every case reaches a value which is only slightly below the one obtained at the end of an hour.
2. The rate of reaction is seemingly almost entirely independent of the amount of excess iodine chloride solution.
3. The only effect of shaking seems to be the increase in velocity of minor reactions by increasing the rate of diffusion of the

solutions.

4. An insufficient quantity of chlorine to double the original titer of the iodine solution has apparently no effect while an excess of chlorine in the solution causes the iodine number to be raised by an amount proportional to the amount of excess chlorine.
5. The increased action of iodine chloride solution upon the oil directly (i.e. without the addition of carbon tetrachloride) indicates a substitution.