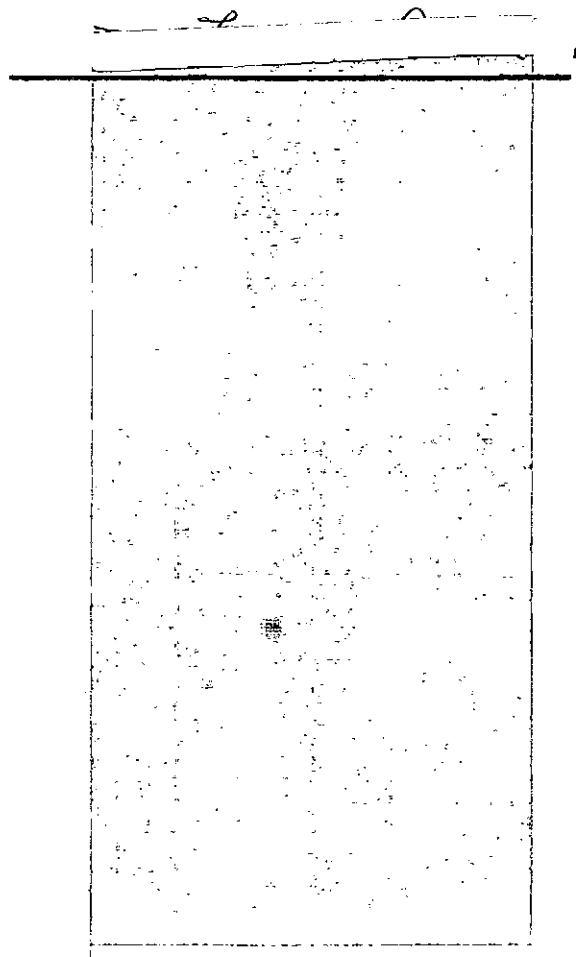


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STUDIES OF EQUILIBRIA INVOLVING  
CHLORO-COMPLEXES OF IODINE

A THESIS

Presented to  
the Faculty of the Graduate Division

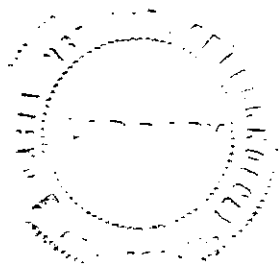
by

Dennis Lamar Cason

In Partial Fulfillment  
of the Requirements for the Degree  
Master of Science in Chemistry

Georgia Institute of Technology

June 1959



STUDIES OF EQUILIBRIA INVOLVING  
CHLORO-COMPLEXES OF IODINE

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Date Approved by Chairman:

4 June 1959

## ACKNOWLEDGEMENTS

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## SUMMARY

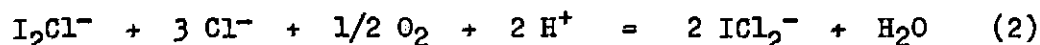
The purpose of this study is to determine by spectrophotometric techniques the kind of equilibria involving chloro-complexes of iodine existing in aqueous solution.

The first system studied involved the dichloroiodate (I) ion,  $\text{ICl}_2^-$ . This ion has characteristic absorption maxima at 224 and 343  $\text{m}\mu$ , and spectral measurements were made in the regions of these maxima. In the presence of perchloric acid, which suppresses the hydrolysis of  $\text{ICl}$ , the only important equilibrium is  $\text{ICl}_2^- = \text{ICl} + \text{Cl}^-$ . Calculation of the dissociation constant of  $\text{ICl}_2^-$  ( $K = [\text{ICl}][\text{Cl}^-]/[\text{ICl}_2^-]$ ) from the data in the 224  $\text{m}\mu$  region gave a value of  $(30-40) \times 10^{-3}$ , while the data in the 343  $\text{m}\mu$  region gave a value of  $(6-8) \times 10^{-3}$ . This discrepancy suggests that further work must be done before any value is definitely accepted as the true value for the dissociation constant.

The second system studied involved the chloroiodoiodate (I) ion,  $\text{I}_2\text{Cl}^-$ . It is not possible to isolate the spectrum of  $\text{I}_2\text{Cl}^-$ , but it can be reconstructed from mathematical treatment of the spectra of solutions of iodine in aqueous  $\text{HCl}$ . This reconstructed spectrum has maxima at 246 and 437  $\text{m}\mu$ , and spectral measurements were made in the regions of these maxima. In the course of this study, two different side reactions were indicated, a practically instantaneous disproportionation reaction



which was observed only at extremely low concentrations of iodine, and a slower, oxidation reaction

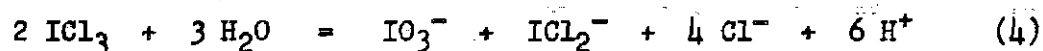


which becomes important with increasing HCl concentrations. These two reactions interfere with the determination of the predominant equilibrium

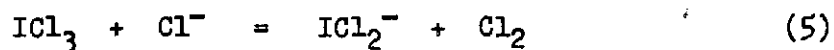


In the experiments involving the 437 mμ peak, the concentration of iodine is high enough to make the contribution from reaction (1) small and the concentration of HCl is low enough (3 M or less) to make reaction (2) very slow. The dissociation constant for reaction (3) calculated from these data was  $0.62 \pm 0.05$ , in excellent agreement with the value found from solubility and distribution measurements. Quantitative results from the 246 mμ peak were not possible because of interference from reaction (1).

The third system involved studies on solutions which might contain the tetrachloroiodate (III) ion,  $\text{ICl}_4^-$ . The possible formation of this ion from  $\text{ICl}_3 + \text{Cl}^-$  was investigated. Spectral measurements of solutions of  $\text{ICl}_3$  in 0.5-12 M HCl indicated that the reaction in 0.5-1 M HCl is

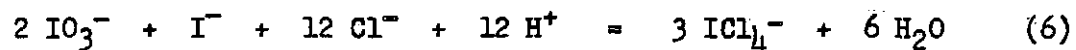


and that in 3-12 M HCl is





A second possible way of forming  $\text{ICl}_4^-$  is the reaction



which was reported in the literature recently. Spectral measurements of mixtures of solutions of  $\text{KIO}_3$  and  $\text{KI}$  indicate that the actual reaction is



and that reaction (6) is incorrect.

No evidence was found for the existence of  $\text{ICl}_3$  or  $\text{ICl}_4^-$  under the above conditions.

## CHAPTER I

## INTRODUCTION

## Discussion

The purpose of this study is to determine by spectrophotometric techniques the kind of equilibria involving chloro-complexes of iodine existing in aqueous solution. The most common chloro-complexes of iodine are the dichloriodate (I) ion,  $\text{ICl}_2^-$ , the chloriodoiodate (I) ion,  $\text{I}_2\text{Cl}^-$ , and the tetrachloriodate (III) ion,  $\text{ICl}_4^-$ .

The first complex ion,  $\text{ICl}_2^-$ , can dissociate into either  $\text{ICl} + \text{Cl}^-$  or  $\text{I}^- + \text{Cl}_2$ . The iodine atom has the larger atomic number and in all known triatomic interhalogen compounds the atom with highest atomic number is in the center. Hence, the last reaction is unlikely, and so, in addition to hydrolysis of  $\text{ICl}$ , there is only one important equilibrium, that of dissociation of  $\text{ICl}_2^-$  into  $\text{ICl}$  and  $\text{Cl}^-$ .

The second complex ion,  $\text{I}_2\text{Cl}^-$ , can dissociate into either  $\text{ICl} + \text{I}^-$  or  $\text{I}_2 + \text{Cl}^-$ . Either is possible from a geometrical standpoint. The standard free energy of the formation (25° C) of  $\text{I}_2\text{Cl}^-(\text{aq})$  from  $\text{ICl}(\text{aq})$  and  $\text{I}^-(\text{aq})$  is listed by Sneed (1) as -11.6 kcal/mole and that from  $\text{I}_2(\text{aq})$  and  $\text{Cl}^-(\text{aq})$  as -0.44 kcal/mole. This gives stability constants of  $3.2 \times 10^8$  and 2.10, respectively, which means that the amounts of  $\text{ICl}$  and  $\text{I}^-$  are practically zero in comparison with those of  $\text{I}_2$  and  $\text{Cl}^-$ . Therefore, the only important equilibrium is that of dissociation of  $\text{I}_2\text{Cl}^-$  into  $\text{I}_2$  and  $\text{Cl}^-$ .

The third complex ion,  $\text{ICl}_4^-$ , could dissociate into  $\text{ICl}_3 + \text{Cl}^-$  or  $\text{ICl}_2^- + \text{Cl}_2$ . Since little has been done on elucidating these two reactions in aqueous solution, this study will be restricted to this task. We will also try to see whether  $\text{ICl}_4^-$  and/or  $\text{ICl}_3$ , both of which are iodine (III) species, can exist in aqueous solution.

In the case of the first two complex ions, we will try to determine their dissociation constants. They have been determined long ago, it is true, but by other methods, primarily by classical distribution and solubility methods. The spectrophotometric data should provide a useful check on these older values.

The quantity measured on a spectrophotometer usually is the absorbancy or optical density,  $D$ , an excellent dimension for quantitative work since it is proportional to the concentrations of the absorbing species. It is defined to be  $\log I_0/I$ , where  $I_0$  is the intensity of the light passing through a reference solution and  $I$  is that of the light passing through the solution being read. The equation expressing  $D$  in terms of the concentration of the absorbing species,  $c$  (moles per liter), and of the light path,  $L$  (cm) is

$$D = a_M c L \quad (1)$$

where  $a_M$  is the molar absorbancy index of the absorbing species. The linearity of this equation means that where there are two or more absorbing species, the individual absorbancies are additive.

We are interested in the wavelength where the  $a_M$  is at a maximum; this wavelength will be designated as  $\lambda_{\text{max}}$  and the value of  $a_M$  at this wavelength will be designated as  $a_{\text{max}}$ .

One characteristic of the absorption spectra of the species studied here is that they have two peaks in the ultraviolet and visible region. The one lying at shorter wavelengths is very high, having an  $a_{\max}$  of the order of 10,000-100,000. The other one, which may or may not lie in the visible region, is much smaller and has an  $a_{\max}$  of the order of 100-1,000. The first one will be called the far UV peak and the second the near UV peak, the latter irrespective of whether it actually lies in the near UV or in the visible region.

#### Mathematical Treatment

For an equilibrium of the type  $AB = A + B$ , the dissociation constant is given by (ignoring activity coefficients)

$$K = \frac{[A][B]}{[AB]} \quad (2)$$

where  $[A]$ ,  $[B]$ , and  $[AB]$  are the molar concentrations of A, B, and AB, respectively. For absorption at one wavelength,

$$D = (a_{AB}[AB] + a_A[A] + a_B[B])L \quad (3)$$

For the systems we are concerned with, only two of the above species absorb in the selected wavelength regions. Let those be AB and A, and L be 1 cm. Then

$$D = a_{AB}[AB] + a_A[A] \quad (3')$$

Suppose that  $[A] + [AB] = C_0$ , or

$$[A] = C_0 - [AB] \quad (4)$$

But, from (2),

$$[A] = \frac{K[AB]}{[B]} \quad (2')$$

Combining (2') and (4):

$$C_0 - [AB] = \frac{K[AB]}{[B]} \quad (5)$$

Solving for  $[AB]$  gives

$$[AB] = \frac{[B] C_0}{K + [B]} \quad (5')$$

Substituting this value for  $[AB]$  into (4) gives

$$[A] = \frac{K C_0}{K + [B]} \quad (6)$$

These two equations, (5') and (6), are thus expressions of  $[AB]$  and  $[A]$  in terms of  $K$ ,  $C_0$ , and  $[B]$ . Let us suppose that  $C_0$  and  $[B]$  are fixed in any given experiment; then it remains to find  $K$ .

Substituting these values for  $[AB]$  and  $[A]$  into (3'):

$$D = \frac{a_{AB}[B]C_0}{K + [B]} + \frac{a_A K C_0}{K + [B]} \quad (7)$$

Let us define  $a_{ABC_0} = D_{AB}$ , i. e., the  $D$  of a solution whose  $C_0$  is 100 per cent complexed as  $AB$ , and  $a_A C_0 = D_A$ , i. e., the  $D$  of a solution whose  $C_0$  is not complexed at all. Then,

$$D = \frac{D_{AB}[B]}{K + [B]} + \frac{D_A K}{K + [B]} \quad (7')$$

There are now three unknowns,  $K$ ,  $D_{AB}$ , and  $D_A$ . Usually, by proper adjustment of the experimental conditions, it is possible to observe directly either  $D_{AB}$  or  $D_A$ , so that there are now only two unknowns. If  $D_A$  is known, manipulation of (7') gives

$$D = D_{AB} + \frac{K(D_A - D)}{[B]} \quad (8)$$

If  $D$  is plotted versus  $(D_A - D)/[B]$  from data collected for a series of solutions having  $C_0$  fixed but varying  $[B]$ , the slope will be  $K$  and the intercept on the  $D$ -axis will be  $D_{AB}$ . If this plotting is done for several wavelengths, the  $K$  can be checked and the spectrum of  $AB$  reconstructed as well.

If, on the other hand,  $D_{AB}$  is known, (7') is best expressed as

$$D = D_A + \frac{[B](D_{AB} - D)}{K} \quad (9)$$

so that a plot of  $(D_{AB} - D)[B]$  versus  $D$  gives the slope as  $K$  and the intercept on the  $D$ -axis as  $D_A$ .

On the spectrophotometer, it is hard to read the absorbancy with a precision better than  $\pm 0.002$ , so that the  $D$  co-ordinate on a graph of the above type becomes subject to an error of about  $\pm 0.002$  and the other co-ordinate to one of about  $\pm 0.004$ . In order to minimize these errors, we can choose those wavelengths where  $D$  and the separation between the spectra are large. But in these solutions whose  $D$  is not greatly different from  $D_A$  (or  $D_{AB}$ ), the relative error is so large that it cannot be ignored. In that case, it would be wise to plot both extremes of that

range of error, i. e., on the D-axis plot both  $D + 0.002$  and  $D - 0.002$ , etc., and then draw a box all around the extremes. The object in drawing the straight line for the determination of K will then be to intersect all the boxes as close as possible to the center of them. This line will be called the line of best fit.

## CHAPTER II

## EXPERIMENTAL

## Absorption Spectra Measurements

The absorption spectra were determined almost entirely with a Beckman Model DU spectrophotometer equipped with a photomultiplier. A water jacket was used in most of the runs to keep the cells at a constant temperature of  $25.0 \pm 0.5^\circ \text{C}$ . The cells used were matched, fused silica cells having a light path of  $1.000 \pm 0.003 \text{ cm}$ .

Sometimes it is necessary to allow for one cell having more absorbancy than the other. This is easily done by measuring the absorbancy of the sample cell relative to the reference cell, with reference solution in both. Calling this correction term,  $x$ , the correct absorbancy is given by

$$D_{\text{corr}} = D_{\text{obs}} - x \quad (10)$$

where  $D_{\text{obs}}$  is the experimentally measured absorbancy. This term,  $x$ , was observed to fluctuate in the shorter wavelength range of 200-250  $\text{m}\mu$  after use, whereas outside this range it is little affected. Since the fluctuations appeared to be due to impurities in the cells, the following procedure was adopted for measurements made in the far UV region: the cells were soaked in soap solution (and in a mixture of ethanol and 3 M HCl if necessary) repeatedly until, with distilled water, they gave a correction term of no more than  $\pm 0.010$  in the 200-210  $\text{m}\mu$  region and  $\pm 0.005$  in the 210-250  $\text{m}\mu$  region. The cells were then filled with reference solution (blank) and the correction term was determined exactly. The sample cell was then filled with the solution whose absorbance is to

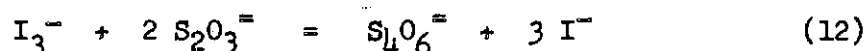
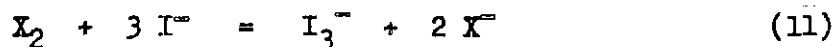


be measured, taking care not to wet the outside polished sides, and the spectral run began. It must be noted that the cells used were selected out of a group of several cells as having low correction term, especially in the far UV region.

In the case of the series used to calculate the dissociation constants of  $\text{ICl}_2^-$  and  $\text{I}_2\text{Cl}^-$ , the slit width was kept constant at any one wavelength used for measurements so that the readings would be comparable. The hydrogen lamp was used for all the measurements.

#### Analytical Methods

The solutions of  $\text{ICl}$ ,  $\text{I}_2$ , etc., were analyzed iodometrically in the following way: A definite volume of the halogen solution was withdrawn and added to a flask containing enough water to dilute the acid of the sample to 0.5 M or less and enough potassium iodide to convert all the halogen into triiodide ions. This solution was then titrated with (usually) 0.01 N thiosulfate to the starch end point. The titration was made within a few minutes after the addition of the sample in order to minimize the oxidation of iodide to iodine by oxygen in the acid solution. The calculation of the halogen concentration follows:



Suppose that the titer of  $n$  N thiosulfate is equivalent to the halogen contained in the volume of the solution taken,  $V$ . Then,

$$[\text{X}_2] = \frac{1}{2} \left( \frac{\text{titer} \times n}{V} \right) \quad (13)$$

### Preparation of Compounds

The preparation of the iodine monochloride to be used in the study of the  $\text{ICl}_2^-$  system was done in the following way:

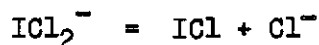
Iodine was first purified by following the procedure outlined in Walton's "Inorganic Preparations" (2). A sample of commercial iodine was ground to powder and treated with successive portions of water to dissolve salts. It was transferred to a sintered glass filter and sucked as dry as possible. Then it was covered with sulfuric acid in a casserole and melted under gentle heat. After it was cooled, it was in the form of a solid cake and was dried with filter paper. The final step was sublimation.

This iodine was combined with condensed chlorine according to the method of Cornog and Karges (3). First, chlorine was condensed into a flask immersed in a dry ice-ether bath; then roughly half its equivalent of iodine was added slowly. The reaction mixture was weighed after it warmed up to room temperature and the exact amount of chlorine present calculated from the weights of the flask and of the added iodine. Then the amount of iodine necessary to make the composition correspond to  $\text{ICl}$  was added and the mixture kept in a liquid condition for 24 hours. It was purified by two or three recrystallizations, viz.: the mixture, in a liquid condition, was placed in an ice-water bath and allowed to freeze until about 80 per cent was solid. The liquid portion was then decanted. No attempt was made to check its purity other than to observe whether any color was left in a solution of  $\text{ICl}$  in carbon tetrachloride after shaking with 0.5 M  $\text{HCl}$  to extract the  $\text{ICl}$ . (A pink color would indicate excess iodine present in the  $\text{ICl}$ .)

The iodine purified in the way previously mentioned was used in the study of the  $\text{I}_2\text{Cl}^-$  system.

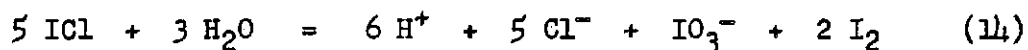
There are several ways of preparing iodine trichloride,  $\text{ICl}_3$ , which was used in the study of the third system. One, an outmoded method, involves the sublimation of iodine into a current of chlorine gas and yields poor results. Another one involves the addition of finely powdered iodine to an excess of liquid chlorine, which is then boiled away (3a). Because a plentiful supply of  $\text{ICl}$  was on hand, a modification of the last method was used: An excess of chlorine was condensed into a flask immersed in a dry ice-ether bath. A small amount of  $\text{ICl}$  was added from a medicine dropper, a drop or two at a time, swirling the flask to suspend the solid  $\text{ICl}_3$  that separated. After all the  $\text{ICl}$  was added, the flask was allowed to warm up to room temperature. (As it warmed up, the solid remained pale lemon yellow until it came close to room temperature; then it turned to orange and finally to dark red-orange. It was observed that in the refrigerator the color was bright orange, much brighter than the dark red-orange that exists at room temperature.) As soon as most of the chlorine was evaporated, the glass stopper was put on. From time to time, especially when part of the contents was sampled (stopper removed), chlorine gas was passed into this storage flask. This was to prevent  $\text{ICl}_3$  from decomposing into  $\text{ICl}$  and  $\text{Cl}_2$ —it was stated (4) that  $\text{ICl}_3$  crystals may be preserved in an atmosphere of chlorine. When solutions of  $\text{ICl}_3$  were desired, some  $\text{ICl}_3$  crystals would be shaken out on a piece of paper, allowed to stand for a few seconds to let the excess chlorine escape, and then dumped into the solvent without further delay.

## CHAPTER III



## Historical Discussion

The dissociation constant of the dichloroiodate (I) ion,  $\text{ICl}_2^-$ , was determined by Faull (5) by means of a distribution method. Aqueous solutions were made by dissolving  $\text{ICl}$  to give concentrations in the range 0.15-0.4 M in mixtures of  $\text{HCl}$  and  $\text{HClO}_4$ , and these were extracted with carbon tetrachloride. The concentrations of  $\text{HCl}$  in the aqueous phase were less than 0.4 M and those of  $\text{HClO}_4$  were in the range 1-5.5 M. The purpose of the  $\text{CCl}_4$  was to dissolve some of the  $\text{ICl}$  so that its concentration in the aqueous phase could be calculated, and to do the same for  $\text{I}_2$  so that the extent of hydrolysis of  $\text{ICl}$  in the aqueous phase could be found. Because of the rather large concentrations of  $\text{ICl}$  the hydrolysis reaction



was quite extensive. At equilibrium the aqueous phase contained the following iodine species:  $\text{ICl}$ ,  $\text{ICl}_2^-$ ,  $\text{I}_2$ ,  $\text{I}_2\text{Cl}^-$ ,  $\text{HOI}$ , and  $\text{IO}_3^-$ . The organic phase contained  $\text{ICl}$  and  $\text{I}_2$ .

By titration methods Faull determined the total iodine in both phases, the  $\text{I}_2$  in the organic phase, and the excess  $\text{IO}_3^-$  in the aqueous phase. By use of appropriate stoichiometric relations and literature values for the distribution ratio of  $\text{I}_2$  and the dissociation constant of  $\text{I}_2\text{Cl}^-$ , he was able to calculate simultaneously the distribution ratio

of  $\text{ICl}$  and the dissociation constant for  $\text{ICl}_2^-$ . He obtained a value of 0.34 for the distribution ratio in 2.2 M  $\text{HClO}_4$  and a value of 1.3 in 5.5 M  $\text{HClO}_4$ . For the dissociation constant he obtained an average of  $6.0 \times 10^{-3}$  from 8 runs in solutions 1-2 M in  $\text{HClO}_4$ .

Although Faull's work was done carefully and he took into account all the equilibria that are known to complicate the system, it seems that a spectrophotometric method would be more direct and would introduce less complications.

A search of the literature provided the following information about the absorption spectrum of  $\text{ICl}_2^-$ :

Gilbert, Goldstein, and Lowry (6) found the near UV peak of  $\text{CsICl}_2$  to be at 346  $\text{m}\mu$  in alcohol, but reported only a general absorption in the far UV region. They did determine its spectrum in water, but no substance was present to suppress hydrolysis, and so the near UV peak was found to be at 460  $\text{m}\mu$ , which is where iodine absorbs in water.

Gillam and Morton (7) determined the  $\lambda_{\text{max}}$  and  $a_{\text{max}}$  of the near UV peak of  $\text{ICl}$  in aqueous  $\text{HCl}$  (0.2-10 M) to be 343  $\text{m}\mu$  and 275, respectively, and stated that this  $a_{\text{max}}$  was independent of the acidity over this range. On the other hand, if Faull's value ( $6 \times 10^{-3}$ ) for the dissociation constant of  $\text{ICl}_2^-$  holds true for the low  $\text{ICl}$  concentrations used, this ought to be true only for  $\text{HCl}$  concentrations 0.5 M and greater.

Popov and Jessup (8), in their investigation of the  $\text{ICl}_4^-$  complex in acetonitrile, report the absorption maxima of the  $\text{ICl}_2^-$  complex in acetonitrile to be at 338  $\text{m}\mu$  ( $a_{\text{max}} = 410$ ) and at 227  $\text{m}\mu$  (55,000).

Buckles and Mills (9) found the following for  $R_4N\text{ICl}_2$  (R = butyl or methyl):

<u>Solvent</u>	<u><math>\lambda_{\text{max}}</math></u>	<u><math>a_{\text{max}}</math></u>	<u><math>a_{\text{max}}^*</math></u>
Acetonitrile	337 m $\mu$	319	320
	227	53,000	56,000
Ethanol	343	262	303
	227	14,000	—

\* with sufficient chloride ion  
to repress dissociation

From the above, the maxima of  $\text{ICl}_2^-$  would be expected to fall at 343 and near to 227 m $\mu$  in water.

#### Treatment of Data and Experimental Conditions

It was shown that, if  $[A] + [AB] = C_0$  and  $D_{AB}$  can be measured, a plot of  $(D_{AB} - D)[B]$  versus D from data for a series of solutions having  $C_0$  fixed but varying  $[B]$  will have its slope equal to K and the intercept on the D-axis equal to  $D_A$ , according to equation (9). This equation expressed in terms of the present system is

$$D = D_{\text{ICl}} + \frac{[\text{Cl}^-](D_{\text{ICl}_2} - D)}{K} \quad (9')$$

How shall  $D_{\text{ICl}_2}$  be found? If Faull's value ( $6 \times 10^{-3}$ ) for K is the correct one, then, for 0.5 M HCl,  $[\text{ICl}]/[\text{ICl}_2^-]$  will be 0.006/0.5 or 0.012, if  $C_0$  is so small that it does not affect  $[\text{Cl}^-]$ . This means that the fraction of ICl not complexed is about 0.01, or 1 per cent. Since this is about the error of measurement normally encountered in the use of

the spectrophotometer,  $D$  of a 0.5 M HCl solution of ICl will be equal to, or very close to,  $D_{\text{ICl}_2^-}$ .

Stock solutions of ICl in a solution of enough HCl concentration to stabilize ICl (i. e., convert it into non-volatile  $\text{ICl}_2^-$ ) were made. Series of dilutions were made by placing a fixed amount of the stock solution (usually by a micropipette) into volumetric flasks and filling to the mark with solutions of varying HCl concentration. (A good choice for the range of HCl concentrations is 0.01-0.5 M.) This fulfills the conditions of fixed  $C_0$  ( $= [\text{ICl}]_0$ ) and varying  $[B]$  ( $= [\text{Cl}^-]$ ). The extent of the dilution is that required for obtaining the optimum values of  $D_{\text{max}}$ , 0.3-0.8. Since  $a_{\text{max}}$  for the near UV peak is around 275 for  $\text{ICl}_2^-$ , this means a  $C_0$  of the order of  $10^{-3}$  M, which is very small compared with all but the lowest HCl concentrations, and so  $[\text{Cl}^-] = [\text{Cl}^-]_0$ . For the far UV peak  $C_0$  is still lower, on the order of  $10^{-5}$  M. We will study the far UV peak first.

### Experimental

At first, ICl was added directly to 0.5 M HCl to prepare the stock solution for dilution. But black particles were observed to fall out of solution when this was done, and they dissolved very slowly. In one such solution, these black particles were removed from the body of the solution and dissolved in 0.5 M HCl. The resulting color was yellow-brown and not lemon yellow like solutions of ICl. Its spectrum had a peak near 445 m $\mu$ , which is where iodine absorbs when dissolved in HCl. It was at first thought that this meant there was excess iodine present in the ICl, and repeated purifications of this ICl were attempted. The curious behavior in 0.5 M HCl was still observed. Another batch of ICl prepared by the

Cornog and Karnes method also gave this behavior. It seemed possible that iodine particles may form when the very concentrated ICl first came into contact with 0.5 M HCl. This reaction would be consistent with equation (14) on page 11. A picture of the behavior began to form: ICl in very <sup>high</sup> concentrations may form iodine particles rapidly, even in 0.5 M HCl, and then, when the body of the ICl dissolved in the large volume of solution, the iodine particles would commence to re-dissolve and form  $\text{ICl}_2^-$ . This re-dissolving would be very slow.

This picture was confirmed by the following experiments: When ICl is dissolved in 0.5 M HCl, the black particles being allowed to re-dissolve, and then shaken with  $\text{CCl}_4$ , a pink color appears in the  $\text{CCl}_4$  layer. But if this procedure is reversed, i. e., ICl is dissolved first in  $\text{CCl}_4$  and then shaken with 0.5 M HCl, no color remains in the  $\text{CCl}_4$ . Then 3 M and 6 M HCl were tried. No black particles separated at all in either when ICl was added directly to them, and those solutions of ICl failed to color  $\text{CCl}_4$  when shaken with it.

It was decided to prepare the stock solution of ICl in 0.5 M HCl by shaking 0.5 M HCl with successive portions of a solution of ICl in  $\text{CCl}_4$  until the ICl concentration in the aqueous layer is satisfactory. This method will preclude the possibility of hydrolysis and iodine formation.

Series 1.—Such a solution of ICl in 0.5 M HCl was made, and a series of dilutions were made with HCl solutions ranging from 0.5 to 0.01 M. Spectral runs were made in the far UV region of 200–250  $\text{m}\mu$ . At that time, the eccentric behavior of the correction term had not been observed, and since this series was used only to indicate what may be expected, we shall



not discuss it at length. We can say, however, that the slope of a  $(D_{\text{ICl}_2} - D)[\text{Cl}^-]$  versus  $D$  graph (assuming the  $D$  of the 0.5 M HCl solution to be  $D_{\text{ICl}_2}$ ) was about  $12 \times 10^{-3}$  and that the intercepts on the  $D$ -axis were negative, and not positive as was expected. The slope should be the value of the dissociation constant of  $\text{ICl}_2^-$ , but it is very different from Faull's value of  $6 \times 10^{-3}$ . The negative intercepts may mean that species other than  $\text{ICl}_2^-$  and  $\text{ICl}$  are present.

Series 2.—The relatively high tentative value of the dissociation constant,  $12 \times 10^{-3}$ , makes 1 M HCl a better solvent than 0.5 M HCl for the determination of  $D_{\text{ICl}_2}$ . Accordingly, a second stock solution of  $\text{ICl}$  was made in 1 M HCl in the way previously mentioned, and  $[\text{ICl}]$  was found iodometrically to be  $1.38 \times 10^{-2}$  M. A series of 1/1000 dilutions was made by placing 100 microliters of this solution into 100-ml volumetric flasks and filling to the mark with solutions of 1, 0.5, 0.1, 0.05, 0.02, and 0.01 M HCl. The blanks were made in exactly the same way, except that 100 microliters of 1 M HCl was substituted for the 100 microliters of the  $\text{ICl}$  solution. The spectral runs were made as soon as possible after the dilutions in the 200–250  $\text{m}\mu$  range, the cells being thermostatted at 25° C and their correction term being determined before each run. The results are plotted in Figure 1 and the mathematical treatment tabulated in Table 1 (Appendix). Notice that an isosbestic point is formed at about 206  $\text{m}\mu$ . The mean slope, which gives the dissociation constant, is  $13 \times 10^{-3}$ , but this value is doubtful since the intercepts on the  $D$ -axis are negative, as has already been observed in Series 1.

Series 3.—It was decided to make another series, this time using perchloric acid to repress hydrolysis. The acidity,  $[\text{H}^+]$ , was kept constant at 2 M

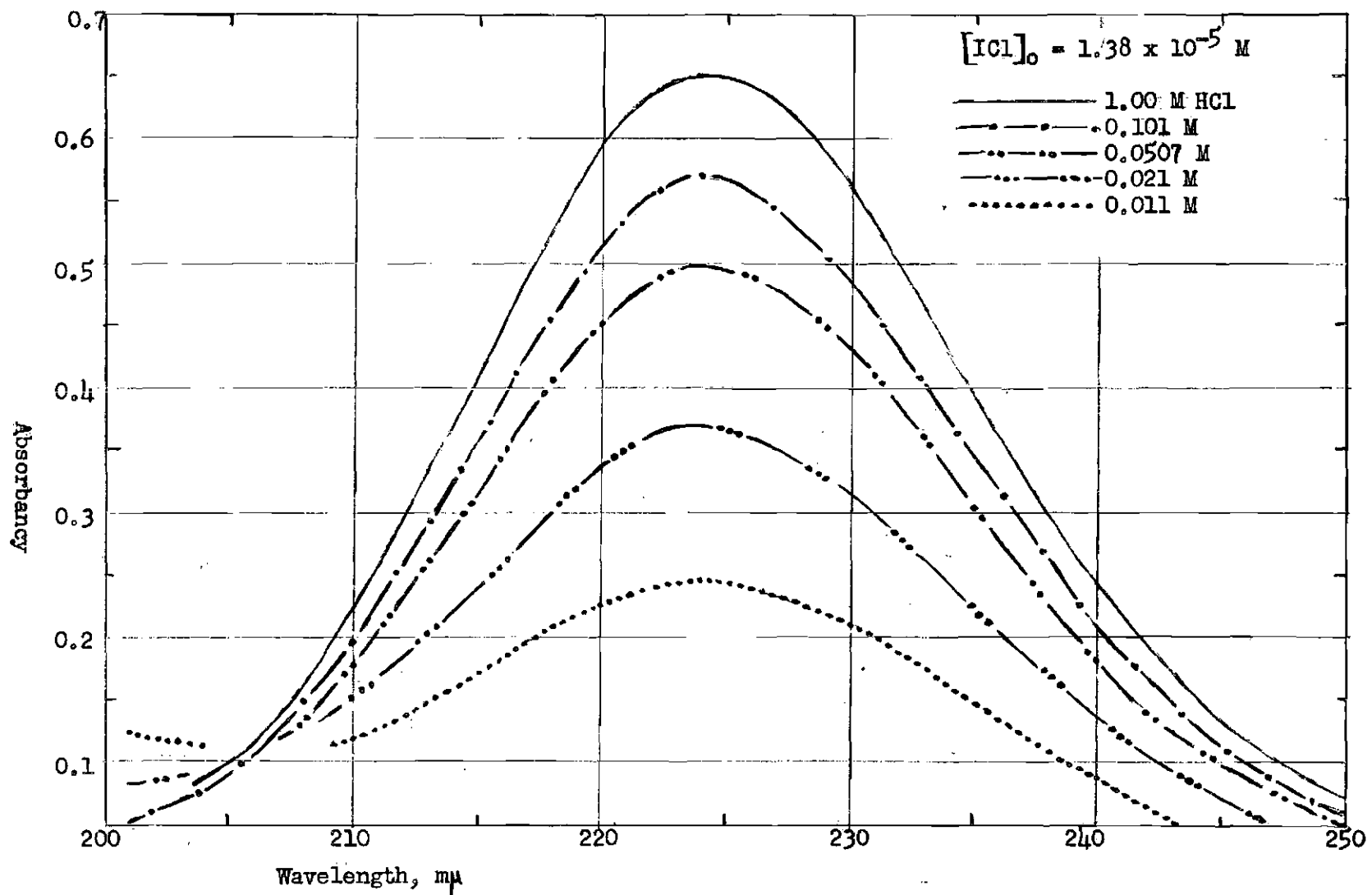


Figure 1. Far UV Spectrum of ICl in HCl Solutions. Series 2.

by this means and the procedure of Series 2 repeated in every detail, using the stock solution whose  $[ICl]_0 = 1.38 \times 10^{-2}$  M. The spectral data are plotted in Figure 2 together with the 0.02 M HCl curve from Series 2 for comparison with the corresponding one of Series 3. Notice that an isosbestic point is formed at 206  $m\mu$ , as in Series 2, and that the spectrum of ICl in 0.02 M HCl is raised when perchloric acid is added. The data for 1 M and 0.1 M HCl were virtually identical for both series.

The mathematical treatment of Series 3 data is in Table 2. First, the D of the 1 M HCl solution was taken to be  $D_{ICl_2^-}$  —see second item in each row in Table 2. It led to good results, all the slopes being nearly the same (see Figure 3-a for a few examples) and the intercepts being positive as required by equation (9') on page 13. The K is  $(27 \pm 5) \times 10^{-3}$ . This rather high value means that it is not correct, for if it were so, the ratio of  $[ICl]$  to  $[ICl_2^-]$  in 1 M  $[Cl^-]$  now becomes 0.027, invalidating the assumption that ICl is 100 per cent complexed in 1 M HCl.

Accordingly, another run was made using 3 M HCl as diluent. The spectrum showed fluctuations; D at 224  $m\mu$  rose from 0.666 (five minutes after dilution) to 0.673 (25 minutes after dilution). After about two hours,  $D_{224}$  commenced to drop. This behavior so soon after dilution was not observed with any of the more dilute HCl solutions and likely is due to some unknown reaction. The readings used were those made at around the time  $D_{224}$  was at a maximum, about  $\frac{1}{2}$  hour after dilution. The cells were thermostatted at 25° C here also.

The treatment of the Series 3 data was repeated, assuming that the D of the 3 M HCl solution was  $D_{ICl_2^-}$  —see third item in each row in Table 2. A few plots are in Figure 3-b. The results are disappointing;

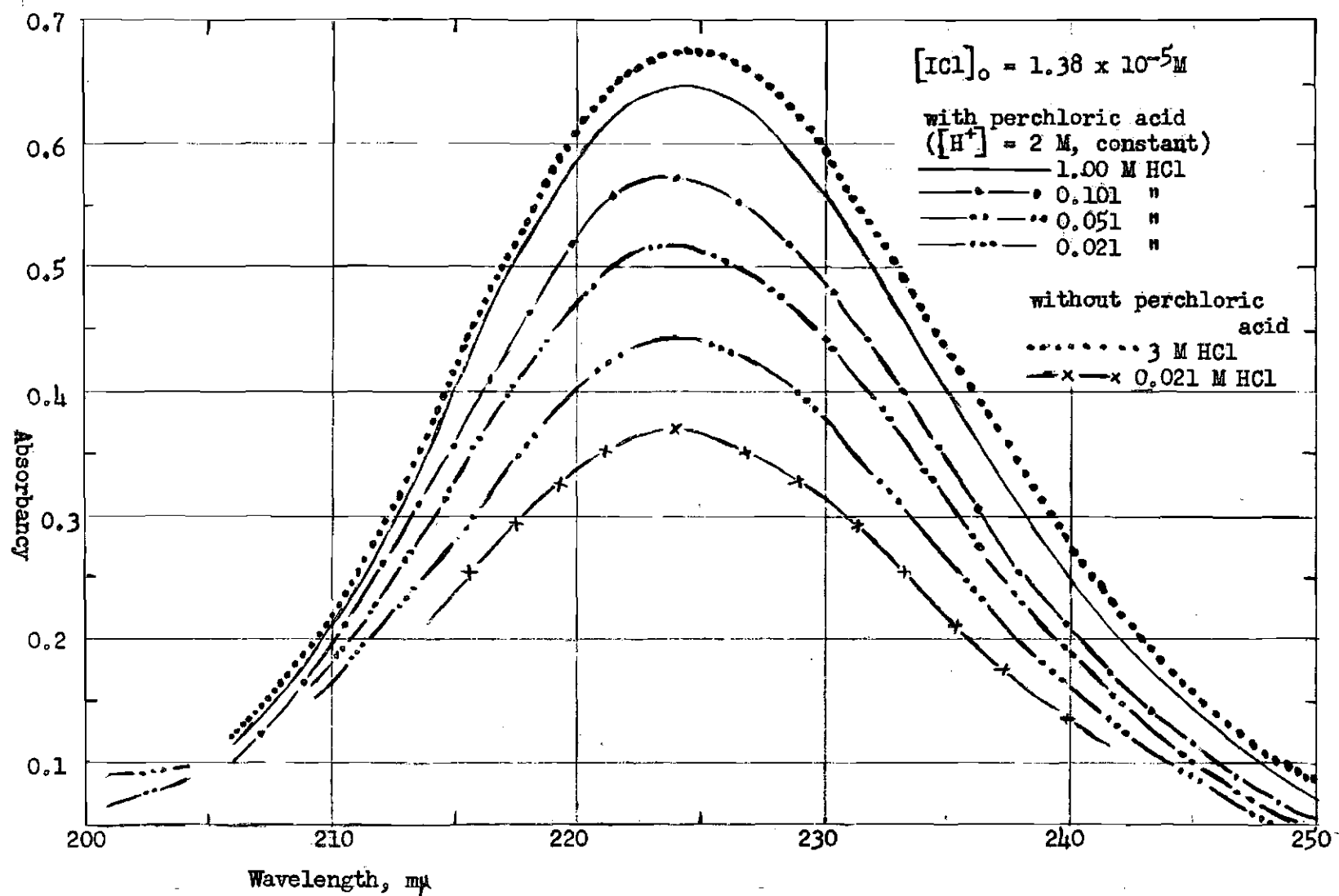


Figure 2. Far UV Spectrum of ICl in HCl, with Added Perchloric Acid. Series 3.

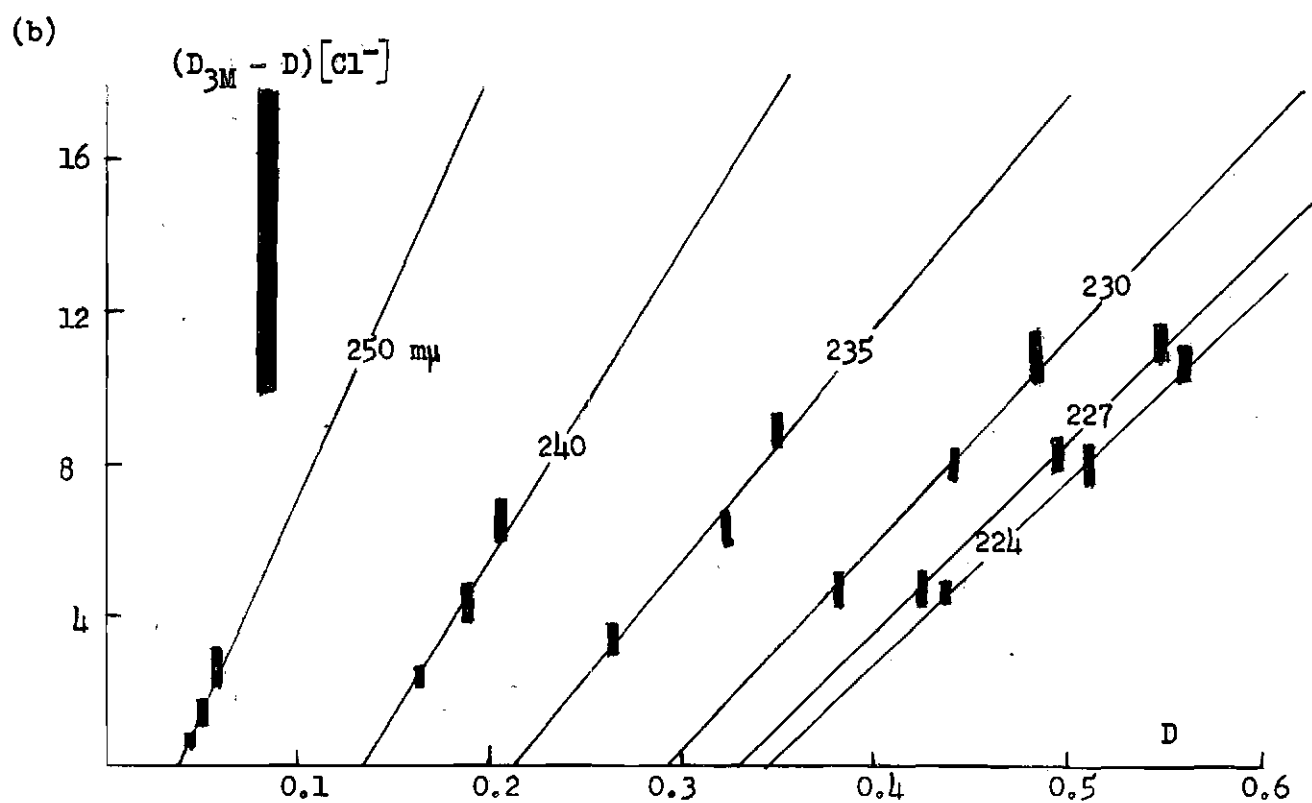
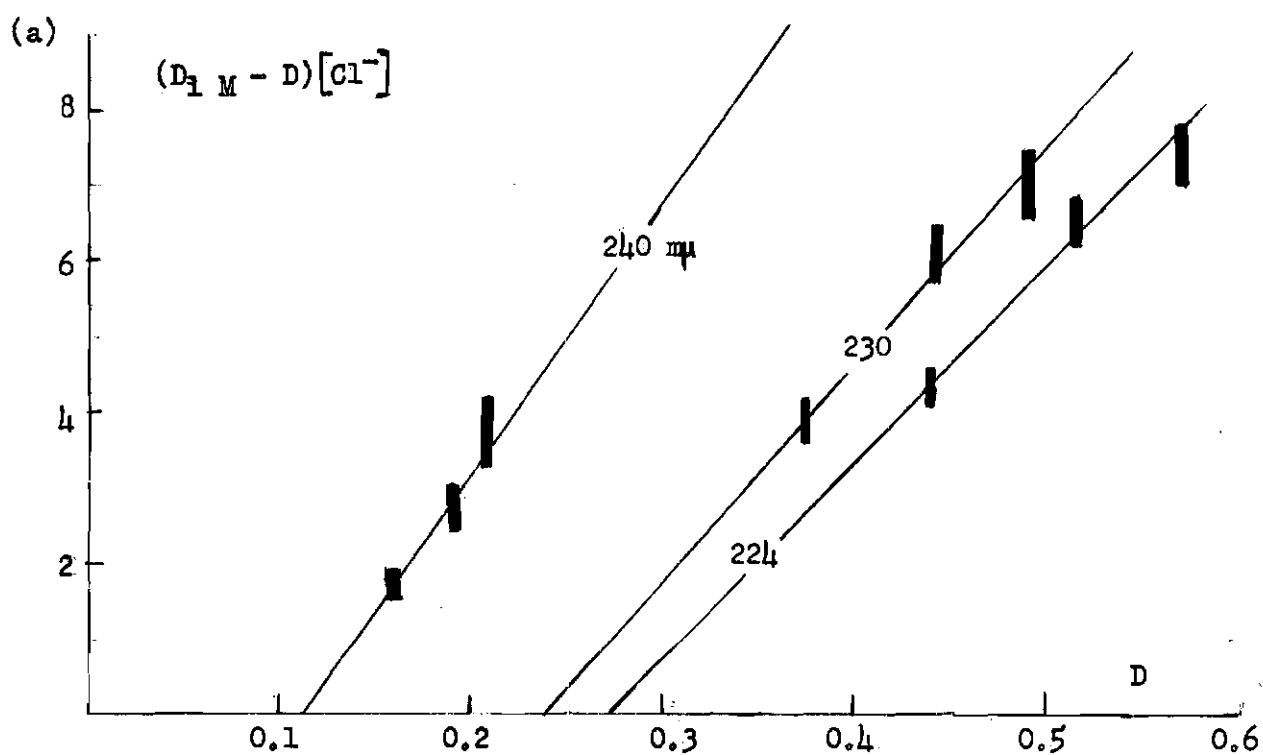


Figure 3. Illustrations of the Slope Method.

at each wavelength, the block calculated for the 1 M HCl solution was far out of range of the line of best fit. (As an example, this block is shown in Fig. 3-b for the 250 mμ data only.) As can be seen from Table 2, the slopes gradually decrease from 0.090 for 250 mμ to 0.033 for 222 mμ, and thereafter remain about the same, 0.03-0.04. The most likely cause is a solvent effect—it will be noticed (Fig. 2) that the 3 M HCl solution's curve is not exactly like the others in shape. It appears to have shifted its maximum slightly toward the longer wavelengths. This is not unprecedented; Bower and Scott (10) observed such a shift for iodine in concentrated sulfuric acid solutions, said to be noncomplexing with iodine. And we shall see (page 38) that iodine exhibits a similar shift in concentrated HCl solutions.

It does appear that the K cannot be determined from the available data. However, there are two facts that enable us to estimate the K: (1) the slopes gradually decrease down to 0.03-0.04 and thereafter remain about the same. This behavior could be ascribed to the shift toward the longer wavelengths, presumably due to a solvent effect. (2) This range, 0.03-0.04, is closer to the value obtained for K from 1 M HCl as a basis than the higher slopes.

Therefore, K is estimated to fall in the range of  $(30-40) \times 10^{-3}$ .

Since this seemed to provide as much information as we can get from the far UV peak, we turned to the near UV peak.

Series 4.—A rather concentrated solution of ICl in 1 M HCl was made in the same way as before. Iodometric titrations gave  $[ICl]_0$  as 0.284 M. The diluent solutions of HCl and  $HClO_4$  ( $[H^+] = 2$  M, constant) from Series 3 were used here also. A series of 1/100 dilutions was made by placing

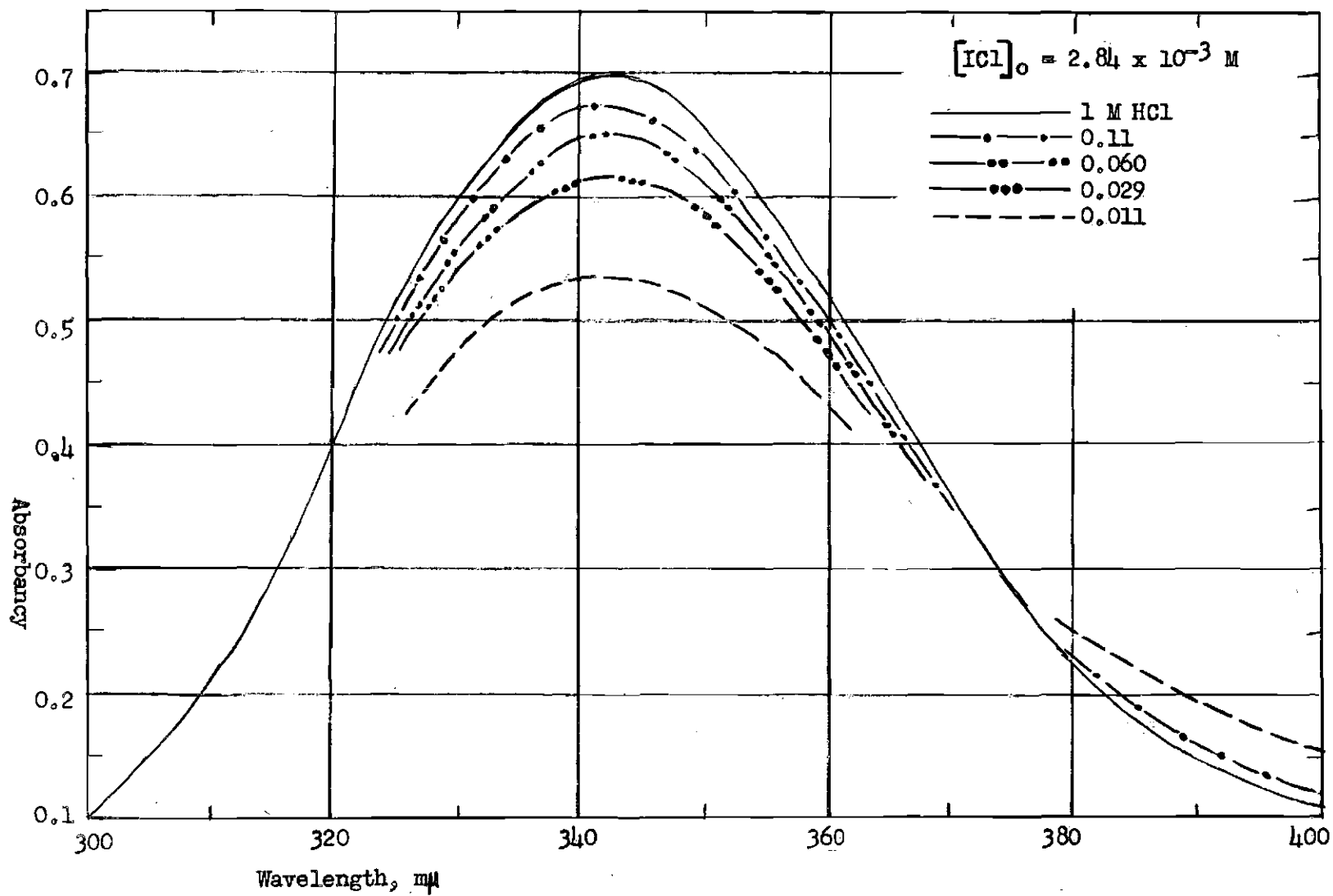


Figure 4. Near UV Spectrum of ICl in HCl, with Added Perchloric Acid. Series 4.

500 microliters of the ICl solution into 50-ml volumetric flasks and filling to the mark with the above diluents. The blanks were made in exactly the same way, except that 500 microliters of 1 M HCl was substituted for that of the ICl solution. The spectral runs were made in the 280-420  $m\mu$  range, as soon as possible after dilution. In the case of the most dilute HCl solution, 0.011 M, the spectral run was completed within ten minutes after dilution because the spectrum was changing, presumably due to hydrolysis. The other runs had the cells thermostatted at 25° C.

The spectral data are plotted in Figure 4. There are isosbestic points at about 310 and 375  $m\mu$ ; they were also observed in an earlier experiment done with HCl alone. The curves are rather close together (compare Fig. 4 with Fig. 2). This fact explains why Gillam and Morton (7) made the statement that the absorbance of ICl does not change in HCl solutions in the range 0.2-10 M. Here, at 345  $m\mu$ ,  $D = 0.688$  for 1 M HCl and 0.670 for 0.11 M HCl, so that the  $D$  of 0.2 and 10 M HCl solutions of ICl would be close together.

The treatment of the data is tabulated in Table 3. (A correction for the amount of  $Cl^-$  tied up in  $ICl_2^-$  was applied to the  $[Cl^-]$  of the most dilute HCl solution, 0.012 M.) The  $D$  of the 1 M HCl solution was assumed to be  $D_{ICl_2^-}$ , and the mean slope is of the order of  $(6-8) \times 10^{-3}$ , very divergent from that of  $(30-40) \times 10^{-3}$  yielded by the far UV peak determinations, but in agreement with Faull's work. No reason could be adduced for this discrepancy, except possibly the weak one of the high concentrations of ICl used in this series.



Absorbancy Indexes.—The far UV peak of ICl in 1 M HCl was observed to fall at 224 m $\mu$  and to have an  $a_{\max}$  of 47,000. The  $a_{\max}$  of ICl in 3 M HCl, to be sure, was appreciably higher, but its spectrum is rather unstable. (So far as an extensive search of the literature could show, the far UV peak in water has not been investigated before.)

The near UV peak of ICl in 1 M HCl was observed to have its  $\lambda_{\max}$  at 343 m $\mu$ , in excellent agreement with Gillam and Morton (7), and an  $a_{\max}$  of 243, considerably below the value of 275 reported by the above reference. This difference could not be due to an impurity present in the ICl used in the present study, since another batch of ICl gave the same  $a_{\max}$  and a solution of ICl made up by the classical analytical method of mixing solutions of KIO<sub>3</sub> and KI with HCl gave the value of 258.

Test of Beer's Law.—A pair of 10-cm cells was used in conjunction with 1-cm cells and the DK spectrophotometer since they would fit only the DK. The stock solutions of ICl in 1 M HCl from the previous series were used, with 1 M HCl as both diluent and blank.

The far UV (224 m $\mu$ ) of a solution of  $1.38 \times 10^{-5}$  M ICl in 1-cm cells had a  $D_{\max}$  of 0.66. The  $D_{\max}$  of a solution of 1/10 of this concentration in 10-cm cells was observed to drop with time. Five minutes after dilution,  $D_{\max}$  was 0.61; 10 min., 0.59; and 35 min., 0.52. Another solution identical with the last solution was found to have a slower drop; its  $D_{\max}$  was 0.65 soon after dilution, 0.60 the next day, and 0.08 after 5 days. The possibility of adsorption was ruled out because the solution showed the same amount of drop whether kept in the cells or in the storage flask, and destruction of ICl<sub>2</sub><sup>-</sup> (possibly by reduction) by organic impurities is indicated. However, this doesn't invalidate all

the data collected on the far UV peak because the spectral runs were made immediately after dilution and no change of any spectrum (with the exception of that in 3 M HCl) was observed until after several days.

For the near UV peak (343 mμ), no such drop was observed. Solutions of  $2.84 \times 10^{-3}$  M ICl and of 1/2 of that concentration in 1-cm cells were found to have a  $D_{\max}$  of 0.71 and 0.355, respectively. Solutions of 1/10 and 1/20 of that concentration in 10-cm cells were found to have a  $D_{\max}$  of 0.71 and 0.37, respectively. This is a rather good adherence to Beer's Law.

#### Summary and Recommendations

Two series of dilutions of stock solutions of ICl, with perchloric acid added to keep the acidity constant at 2 M, were made, one for the far UV and the other for the near UV peak. Treatment of their spectral data gives the values for K of  $(30-40) \times 10^{-3}$  and  $(6-8) \times 10^{-3}$ , respectively. The latter value is in agreement with Faull's value of  $6 \times 10^{-3}$  found from distribution measurements (5), but the low ICl concentrations and the greater separation between the curves of the far UV peak make the former value sound more reliable. This discrepancy suggests that further work must be done on this system before either of these values is accepted as the true value of the dissociation constant of  $\text{ICl}_2^-$ . For example, the near UV peak might be studied with lower concentrations of ICl, using 10-cm cells.

The drop of the 224 mμ peak at low concentrations of ICl, observed in the test of Beer's Law, might also be investigated. Reduction by dust is a possible cause, as in the case of iodine. Wolfenden (11) states

that  $I_3^-$  formation in aqueous solutions of iodine is influenced by dust, as well as the extent of hydrolysis, and that in a row of cuvettes filled up with iodine solution, one in perhaps a dozen show an abnormal absorbance in the  $I_3^-$  peak region, and this absorbance builds up still further with the passage of time.

## CHAPTER IV



## Historical Discussion

Because the solubility of iodine in aqueous solutions of many chlorides has been determined many times it is possible to calculate the dissociation constant,  $K$ , for the chloroiodoiodate (I) ion,  $\text{I}_2\text{Cl}^-$ . In addition to the effect of complex formation on the solubility, there is a salting-out effect. For systems where complex formation does not occur, most investigators use the exponential type of equation

$$s = s_0 e^{-k'C} \quad \text{or} \quad s = s_0 10^{-kC} \quad (15)$$

where  $s_0$  is the solubility of iodine in pure water,  $C$  is the concentration of the salt used, and  $k$  is the salting coefficient.

(All the quoted measurements were made at 25° C, unless stated otherwise.)

The first notable investigation of this equilibrium was that of Ray and Sarkar (12), who studied the distribution of iodine between non-aqueous solvents  $\text{CS}_2$ ,  $\text{CCl}_4$ , and  $\text{CHCl}_3$  and HCl solutions, as well as the solubility of iodine in HCl solutions. They neglected the salting-out effect, which was tantamount to saying that  $[\text{I}_2] = s_0$  in all solutions. An extensive number of experiments was done on  $\text{CS}_2$ ; the HCl concentrations ranged from 0.0625 to 2 M. They gave  $K = 0.62 \pm 0.02$ . A more limited number of experiments each was done on  $\text{CCl}_4$  and  $\text{CHCl}_3$ , using 1, 0.5, and

0.25 M HCl solutions; the mean K is 0.610 and 0.603, respectively. Their determinations of the solubility of  $I_2$  in dilute HCl solutions are given here, together with the calculated K's:

<u>N HCl</u>	<u>Total solubility (g/l.)</u>	<u>K</u>
0	0.3454	
1	0.9526	0.57
0.5	0.6299	0.607
0.25	0.4852	0.618
0.125	0.4191	0.600
0.0625	0.3810	0.607
Mean		0.600

The fact that they got relatively constant values of K indicates that the salting-out effect may be small for HCl. We shall see later that this possibility is correct.

Carter and Hoskins (13) determined the solubility of iodine in solutions of HCl, KCl,  $MgCl_2$ ,  $BaCl_2$ , NaBr, KBr, and HI. The first four are of interest to us. They allowed for the salting-out effect in the following way: they calculated the K neglecting this effect and then plotted it versus C. The  $K_0$  found from extrapolation back to  $C = 0$  was taken to be the true K and then used to find k by means of the equation

$$k = 1/C \log \left\{ \frac{s_0(1 + C/K_0)}{s} \right\} \quad (16)$$

Ordinarily, their data would be of much interest, especially the calculated K's, but unfortunately they used an awkward unit of concentration, moles per 1000 moles of water. In order to convert their results into the usual units of moles per liter of solution, it is necessary to have density data. Some such data of solutions of these chlorides are available in the International Critical Tables and can be used in an interpolation or estimation manner, if it is assumed that the iodine dissolving

does not change the volume. This is a valid assumption since the maximum amount of iodine that can dissolve is on the order of 2 grams per liter.

Kiss and Urmanczy (14) measured the solubility of iodine in solutions of KCl, NaCl, LiCl,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{NaNO}_3$ , and  $\text{KNO}_3$ .

There is enough overlapping of data from these three sources above to suggest that the data are reliable.

Hertz and Hiebenthal (15) measured the solubility of iodine in LiCl, NaCl, KCl,  $\text{MgCl}_2$ ,  $\text{SrCl}_2$ , and  $\text{BaCl}_2$ , but their data disagree with those of (13) and (14).

Oliveri-Mandala and Angenica (16) measured the solubility of iodine in HCl at  $25.4^\circ\text{C}$ , but their data disagree with those of (12) and (13).

Winther (17) measured the solubility of iodine in HCl at 20 and  $30^\circ\text{C}$ , and the distribution of iodine between  $\text{CCl}_4$  and HCl at those temperatures. He obtained  $K = 0.47$  at  $20^\circ$  and  $0.527$  at  $30^\circ$ , but he made the assumption that disproportionation to  $\text{I}^-$  and  $\text{I}^+$  is appreciable.

Lee and Chen (18) measured the solubility of iodine in HCl at 25, 35, and  $45^\circ\text{C}$  and report values of  $K$  of 0.81, 0.77, and 0.72. The journal was not available, so the original data could not be evaluated.

It would be expected that the sets of data most useful for determining the equilibrium constant would be those from chlorides whose salting-out power is small. These salts can readily be found from a graph of the solubility of iodine in chlorides. Such a graph is Figure 5, which uses data from (12), (13), and (14). The bivalent metal salts have been excluded since they are known to possess considerable salting-out power. The two best salts appear to be KCl and HCl.

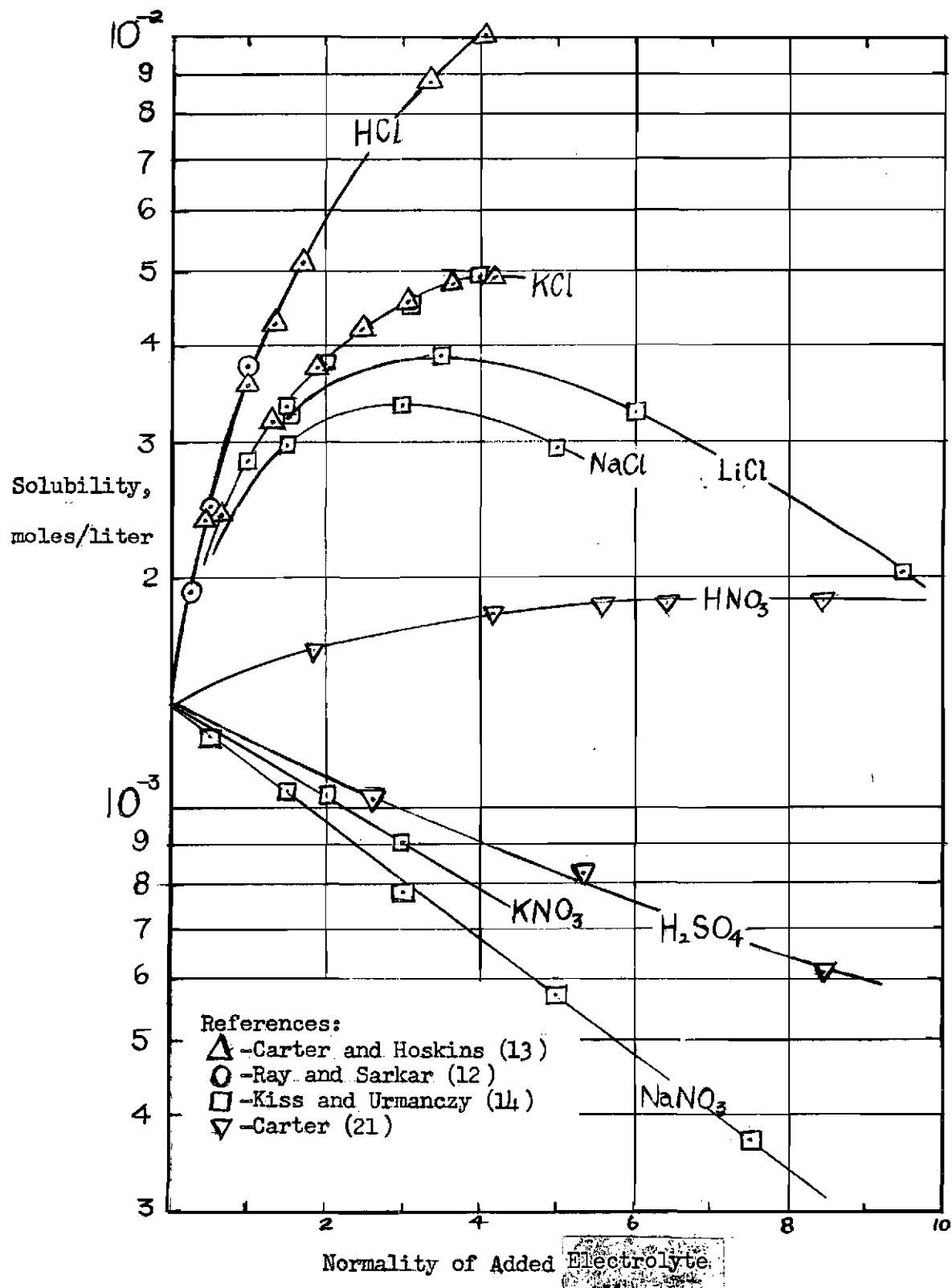


Figure 5. Solubility of Iodine in Various Aqueous Solutions. (25° C)

Consider KCl. How can the salting-out effect, which is still appreciable, be allowed for? Aside from Carter and Hoskins' mathematical treatment which involved no experimental work on solutions of other salts, one can estimate the  $k$  from the  $k$  of iodine in some noncomplexing salt solution. Such a noncomplexing salt is a nitrate, and Kiss and Urmanczy (14) have determined the solubility of iodine in  $\text{NaNO}_3$  and  $\text{KNO}_3$  solutions. The data plotted on Fig. 5 show the  $k$  to be 0.075 and 0.058, respectively. If  $S$  = total solubility of  $\text{I}_2$  and  $s$  = solubility of  $\text{I}_2$  as such, calculated from equation (15), it is seen that a plot of  $C_s$  vs.  $(S - s)$  would be a good way of finding both the  $K$  and the best value of  $k$ . From such a graph, plotting for several choices of  $k$  in the range 0.05-0.10, it appears that the best choice of  $k$  is about 0.070. Using this value, the following table is computed:

<u>C</u>	<u>S(smoothed)<math>\times 10^3</math></u>	<u>s <math>\times 10^3</math></u>	<u><math>C_s \times 10^3</math></u>	<u><math>(S-s)\times 10^3</math></u>	<u>K</u>
0.5 M	2.20	1.25	0.625	0.95	0.658
1	2.82	1.15	1.15	1.67	0.688
1.5	3.31	1.06	1.59	2.25	0.707
2	3.76	0.98	1.96	2.78	0.705
2.5	4.20	0.905	2.26	3.29	0.687
3	4.50	0.835	2.505	3.66	0.685
3.5	4.70	0.77	2.70	3.93	0.686
4	4.88	0.71	2.84	4.17	0.681
				Mean	0.687

Let us next consider HCl. It will be recalled that Ray and Sarkar obtained surprisingly good values of  $K$  from the solubility of iodine in HCl, neglecting the salting-out effect, and that this constancy of  $K$  suggests that the  $k$  for HCl is small. If we look at a table of salting coefficients for several gases in salt solutions in Harned and Owens(19), we find that this is the case. And an empirical observation that can be

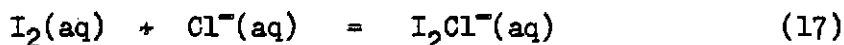


made from the data of Geffcken (20) on the solubility of  $H_2$ ,  $O_2$ ,  $CO_2$ , and  $N_2O$  in  $HNO_3$ ,  $HCl$ , and  $H_2SO_4$  solutions is that the solubility in a given  $HCl$  solution is always about halfway between that in  $HNO_3$  and  $H_2SO_4$  solutions of the same normality. (Following the common practice, the normality of  $H_2SO_4$  is taken to be twice the molarity, even though ionization gives only small amounts of  $SO_4^{=}$  under these conditions.) Since Carter (21) measured the solubility of iodine in these two acids, his data are plotted in Fig. 5. It will be seen that a 'mean' curve for those two curves is nearly a horizontal and straight line, which means that the  $k$  for iodine in  $HCl$  will be very nearly zero. Letting  $k = 0$ , the following table is computed:

<u>C</u>	<u>S(smoothed)<math>\times 10^3</math></u>	<u>s <math>\times 10^3</math></u>	<u>Cs <math>\times 10^3</math></u>	<u>(S-s)<math>\times 10^3</math></u>	<u>K</u>
0.5 M	2.43	1.33	0.665	1.10	0.605
1	3.70	"	1.33	2.37	0.561
1.5	4.70	"	1.995	3.37	0.592
2	5.72	"	2.66	4.39	0.606
2.5	6.80	"	3.32	5.47	0.607
3	7.90	"	3.99	6.57	0.607
3.5	9.0	"	4.65	7.67	0.606
4	10.0	"	5.32	8.67	0.613
				Mean	0.600

In conclusion of the history of the determination of the dissociation constant of  $I_2Cl^-$  by solubility and distribution measurements, it can be said that the evidence is overwhelmingly in favor of  $K$  being 0.6-0.7, with the more probable value being about 0.61. Note that  $K$  has been expressed in terms of concentrations rather than activities and that its constancy in  $KCl$  and  $HCl$  solutions must mean that  $\gamma_{I_2} \gamma_{Cl^-} / \gamma_{I_2Cl^-}$  is constant for these solutions. This constancy is an unexpected result, but one that seems definite enough.

By treating these data in other ways, incorrect values have appeared in the literature, and some books of a review nature have quoted them. For example, Sneed (1) lists  $-0.44$  kcal/mole ( $25^{\circ}$  C) as the standard free energy change,  $\Delta F^{\circ}$ , for the reaction



The reciprocal of the equilibrium constant of this reaction, which is equal to the dissociation constant, was computed from the equation  $\Delta F^{\circ} = RT \ln 1/K$  and found to be  $0.476$ , very different from  $0.6$ . Upon tracing the source of this value, we find that it is tabulated in Sidgwick (22), with Kiss and Urmanczy (14) given as the source. It is hard to see how this reference's data (which have been mentioned and some of them plotted on Fig. 5) could be used to derive the value  $0.476$ , although there is one remote possibility of explanation. Since solid iodine is in equilibrium with a saturated solution it would be convenient to take solid iodine as the standard state for  $\text{I}_2$ , and hence the activity of iodine in saturated solutions would be unity. If the equilibrium constant is expressed in these terms, and if its numerical value was  $0.476$ , it could be converted into the usual units by multiplying it by the solubility of iodine in water ( $1.33 \times 10^{-3}$  M from Kiss and Urmanczy), which gives  $0.633 \times 10^{-3}$ . Perhaps the factor of  $10^3$  was supposed to be included along with  $0.476$ , but ignored.

Another improbable value is that of  $0.28$ – $0.30$ , found by Korenman (23). He treated the available solubility data for NaCl and KCl solutions by a method using several concepts now obsolete. First, he assumed that salts like KCl were only partially dissociated and that conductance data could

be used to estimate the extent of dissociation. (Nowadays, the drop in the equivalent conductance with increase of salt concentration is attributed to interionic attraction, rather than to association.) Second, he ignored the salting-out effect and assumed that the solubility of iodine in water gave  $[I_2]$  in salt solutions saturated with iodine. This work would ordinarily be ignored, but it has been quoted in Sneed (1a) and in the supplementary volume on the halogens of Mallor's treatise (24).

As to the kind of spectrum to be expected for the  $I_2Cl^-$  ion, Katzin (25) found that iodine dissolved in chloride solution gave a peak at about 247  $m\mu$  and stated that this peak is probably due to formation of  $I_2Cl^-$ .

But Popov and Skelly (26) report otherwise for the spectrum of  $R_4NI_2Cl$  ( $R$  = methyl) in acetonitrile. They state that considerable disproportionation of  $I_2Cl^-$  takes place, as is shown by the four peaks, two of which coincide with those of  $I_3^-$  and one with that of  $ICl_2^-$ . The remaining peak, at 261  $m\mu$ , was believed to be due to the  $I_2Cl^-$  ion.

#### Treatment of Data

In the historical discussion, it was seen that the dissociation constant of  $I_2Cl^-$  is about 0.6. For a 12 M HCl solution, this value gives  $[I_2]/[I_2Cl^-] = 0.6/12 = 0.05$ , much too high for the experimental observation of  $D_{I_2Cl^-}$ . Also, the higher HCl concentrations may well change the spectrum of  $I_2Cl^-$  in water. But the  $D_{I_2}$  can easily be determined, since it does not hydrolyse to the extent ICl does. So the equation that is called for is

$$D = D_{AB} + \frac{K(D_A - D)}{[B]} \quad (8)$$

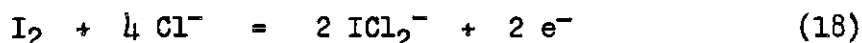
Converting the AB, A, and B terms into relevant terms, we have

$$D = D_{I_2Cl^-} + \frac{K(D_{I_2} - D)}{[Cl^-]} \quad (8')$$

If D is plotted versus  $(D_{I_2} - D)/[Cl^-]$  for a series of solutions having  $C_0$  fixed but varying  $[Cl^-]$ , the slope will be K and the intercept on the D-axis will be  $D_{I_2Cl^-}$ . Thus, if this plotting is done for several wavelengths, the spectrum of  $I_2Cl^-$  can be reconstructed.

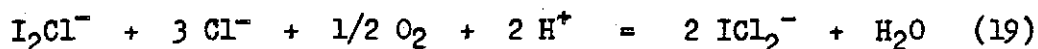
### Experimental

A trial run of iodine in 12 M HCl showed that after a few days the absorption maximum initially present at about 440 mμ dropped and a new one rose near 340 mμ. The amount of free halogen calculated as  $X_2$  also changed; when the 440 mμ peak disappeared entirely,  $[X_2]$  was double its original amount. This suggests that the reaction is



Series 5.—Since we desired to study this reaction with a view to minimizing it, we decided to run on the recording DK spectrophotometer a series of dilutions of a stock solution of iodine in 12 M HCl over an extended period of time. The final HCl concentrations of the dilutions were 12, 9, 6, 3, and 1.2 M. The blanks were made in the same way but not carefully, since the range of the spectral runs was in the near UV where HCl does not absorb, and this series was only a rough, semi-quantitative study. The spectra after a few days (a spectral run was made on every solution every 1 or 2 days) showed conclusively that the rate of conversion of  $I_2$  into  $ICl_2^-$  was strongly dependent on the acidity, and incidentally also on the volume of air in the closed storage flask.

The latter factor is shown by the fact that a 12 M HCl solution stored in a bottle about 3/4 full had only half of its 440 mμ peak gone after 11 days, whereas another solution, identical in every way to the first, stored in a bottle less than 1/2 full had its 440 mμ peak entirely gone after 11 days. These facts suggest that the complete reaction is



The spectral runs for 12 M and 3 M HCl are illustrated in Figure 6. Notice that  $D_{\text{max}}$  in 12 M HCl is 0.66 at 440 mμ when fresh and 0.33 at 340 mμ when conversion seems complete. The  $\epsilon_{\text{max}}$  for iodine in 12 M HCl is about 1,000 and that for ICl in HCl is about 250. If equation (19) is correct, i. e., 1 mole  $\text{I}_2$  forms 2 moles  $\text{ICl}_2^-$ , the ratio of the  $D_{\text{max}}$  before the reaction to that after the reaction should be  $1,000/2 \times 250$  or 2, which is exactly what is observed (0.66/0.33).

It seems fairly well established that the reaction is that expressed in equation (19), and we can attack the problem of minimizing this. As can be seen from Fig. 6, the 3 M HCl solution's spectrum does not change much after 11 days, which suggests 3 M HCl as a solvent for the stock solution of iodine. Experiments on the solubility of  $\text{I}_2$  in 3 M HCl over a period of 1-2 hours showed this to be feasible, since a 1/10 dilution of such a solution would have its  $D_{\text{max}}$  on the order of 0.6 at 440 mμ. Water was not considered as a solvent because of the low solubility of iodine in it alone.

Series 6.—A solution of iodine in 3 M HCl was made by shaking powdered iodine in it for about half an hour, then decanting. Iodometric titrations gave its concentration as  $[\text{I}_2]_0 = 5.33 \times 10^{-3} \text{ M}$ . A series of 1/10 dilutions

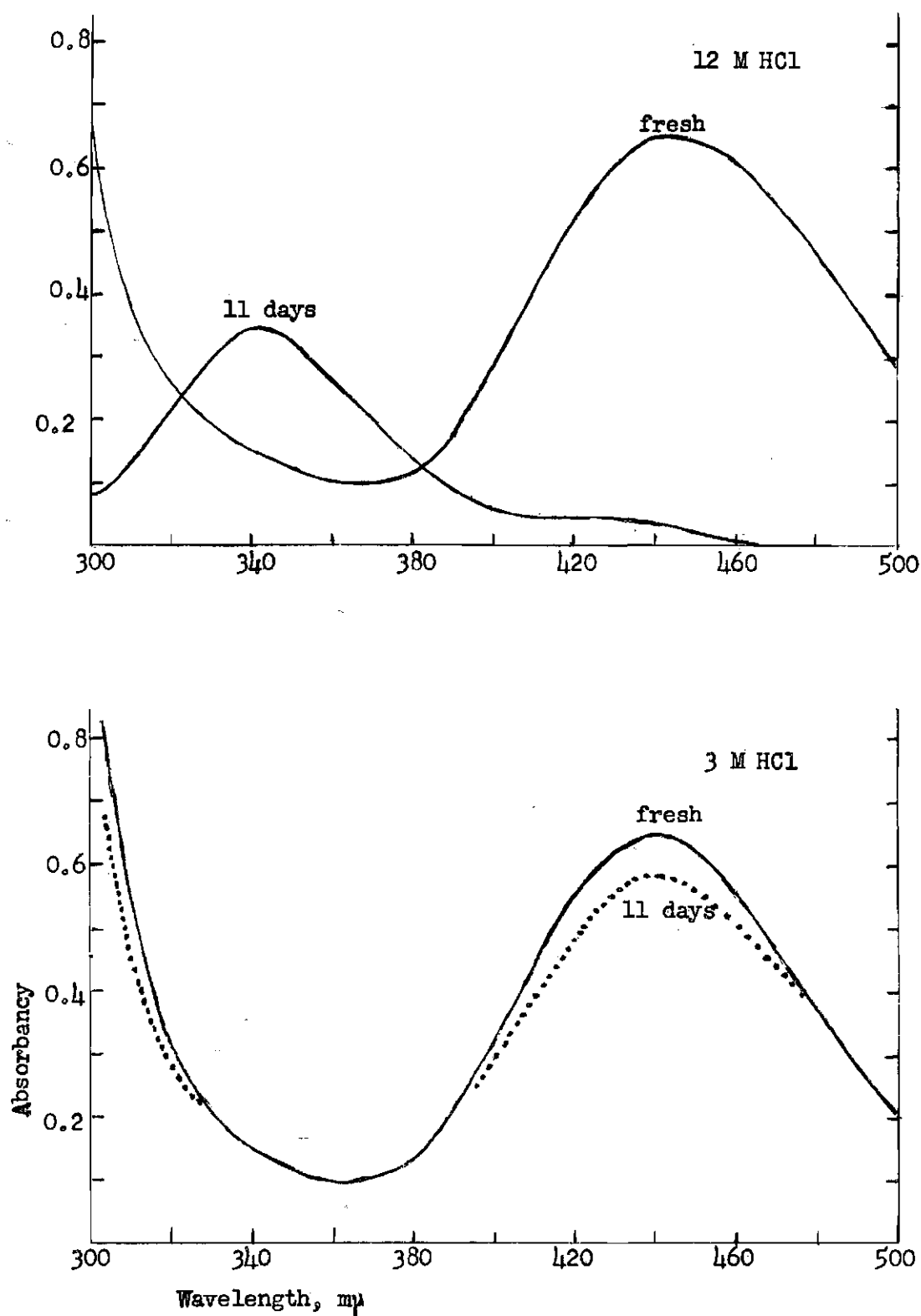


Figure 6. Changes with time of Near UV Spectrum of  $I_2$  in HCl Solutions.  
 $[I_2]_0 = 6.35 \times 10^{-4} \text{ M}$

was made by pipetting 10 mls of this stock solution into 100-ml volumetric flasks and filling to the mark with 12, 6, 3, 0.5 M HCl and water. The same 10-ml pipette was used throughout. The blanks were made in exactly the same way, except that 10 mls of 3 M HCl was substituted for the 10 mls of the  $I_2$  solution. The spectral runs were made in the 280-600  $m\mu$  range, and most of them were thermostatted at 25° C. The data of the unthermostatted runs did not at any point in the mathematical treatment deviate from the expected behavior, so that it was judged unnecessary to repeat.

Additional runs were made on iodine in more dilute HCl solutions by dilutions of a stock  $I_2$  solution in 0.2 M HCl, and then the readings were adjusted to a concentration of  $[I_2] = 5.33 \times 10^{-4}$  M.

In order to obtain  $D_{I_2}$  for the mathematical treatment, iodine in approximately 0.12 M  $HClO_4$  was read, and the readings adjusted also.

All these data are plotted in Figure 7. The presence of an isosbestic point at 470  $m\mu$  for all these solutions except the 11.8 M HCl one is strong evidence for the existence of only two absorbing species, probably  $I_2$  and  $I_2Cl^-$ . The one exception, 11.8 M HCl, shows a slight shift toward the longer wavelengths, which might be ascribed to a solvent effect, as mentioned on page 21.

The treatment of the data is tabulated in Table 4, where the D of a 0.12 M  $HClO_4$  solution is assumed to be  $D_{I_2}$ . All the slopes are nearly the same, and K is estimated to be  $0.62 \pm 0.05$ , in good agreement with that found by solubility and distribution measurements. The intercepts, or  $D_{I_2Cl^-}$ , are plotted in Fig. 7 and called the reconstructed spectrum of  $I_2Cl^-$ .

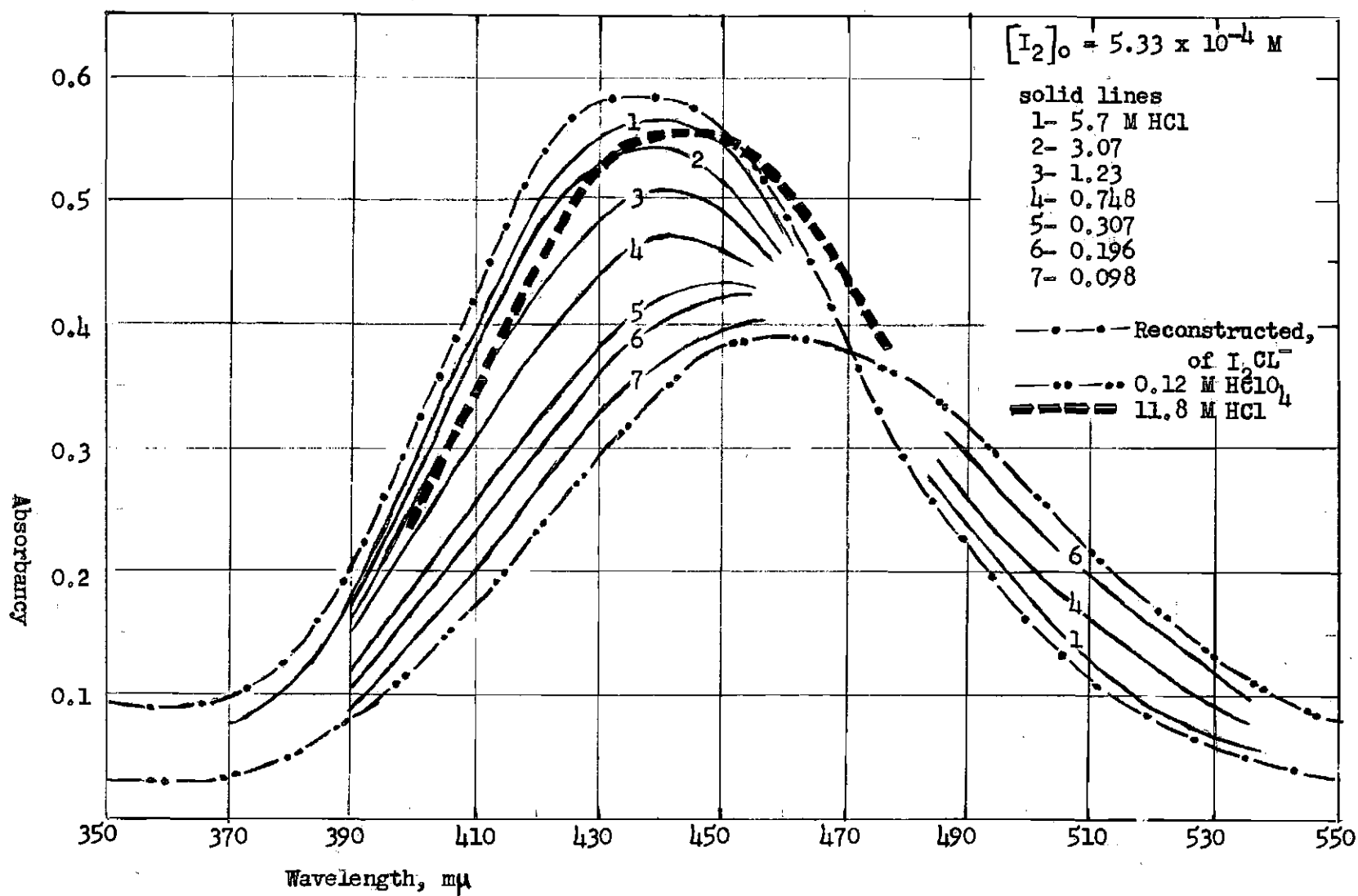


Figure 7. Near UV Spectrum of  $I_2$  in HCl Solutions. Series 6.



Series 7.—We shall now turn to the far UV peak. A solution of iodine was made in the same way as before. Iodometric titrations gave its concentration as  $[I_2]_0 = 3.95 \times 10^{-3}$  M. A series of 1/200 dilutions was made by placing 500 microliters of this solution into 100-ml volumetric flasks and filling to the mark with 3, 1.5, 0.75, 0.3, and 0.05 M HCl. The blanks were made in exactly the same way, except that 500 microliters of 3 M HCl was substituted for that of the  $I_2$  solution. The spectral runs were made very soon after dilution in the 200–300  $m\mu$  range, the last reading being made within 75 minutes after the time of dilution. The cells were thermostatted at 25° C.

The treatment of the data, tabulated in Table 5, gives a value of  $0.47 \pm 0.03$  for  $K$ . The spectral data are plotted in Figure 8, together with the reconstructed spectrum of  $I_2Cl^-$  and the adjusted data for  $I_2$  in 0.12 M  $HClO_4$ . Notice that all the curves, with the exception of the 0.064 M HCl and 0.12 M  $HClO_4$  curves, intersect at the same point, 215.5  $m\mu$ . A curious flattening-out of the left side of the curve is observed for the two most concentrated HCl solutions in the neighborhood of the far UV peak of  $ICl_2^-$  (224  $m\mu$ ). This 'hump' was thought to be due to oxidation of  $I_2Cl^-$  to  $ICl_2^-$ , so another spectral run on a solution of  $I_2$  in 3 M HCl was made, this time on the DK recording spectrophotometer within 2–4 minutes after the dilution. The same hump was observed. Then 3 M KCl was used as a solvent, but the hump was observed in it also. So it appears that the hump is not due to oxidation as expressed in equation (19). Since a test of Beer's Law would be appropriate here, the conclusions will be postponed.

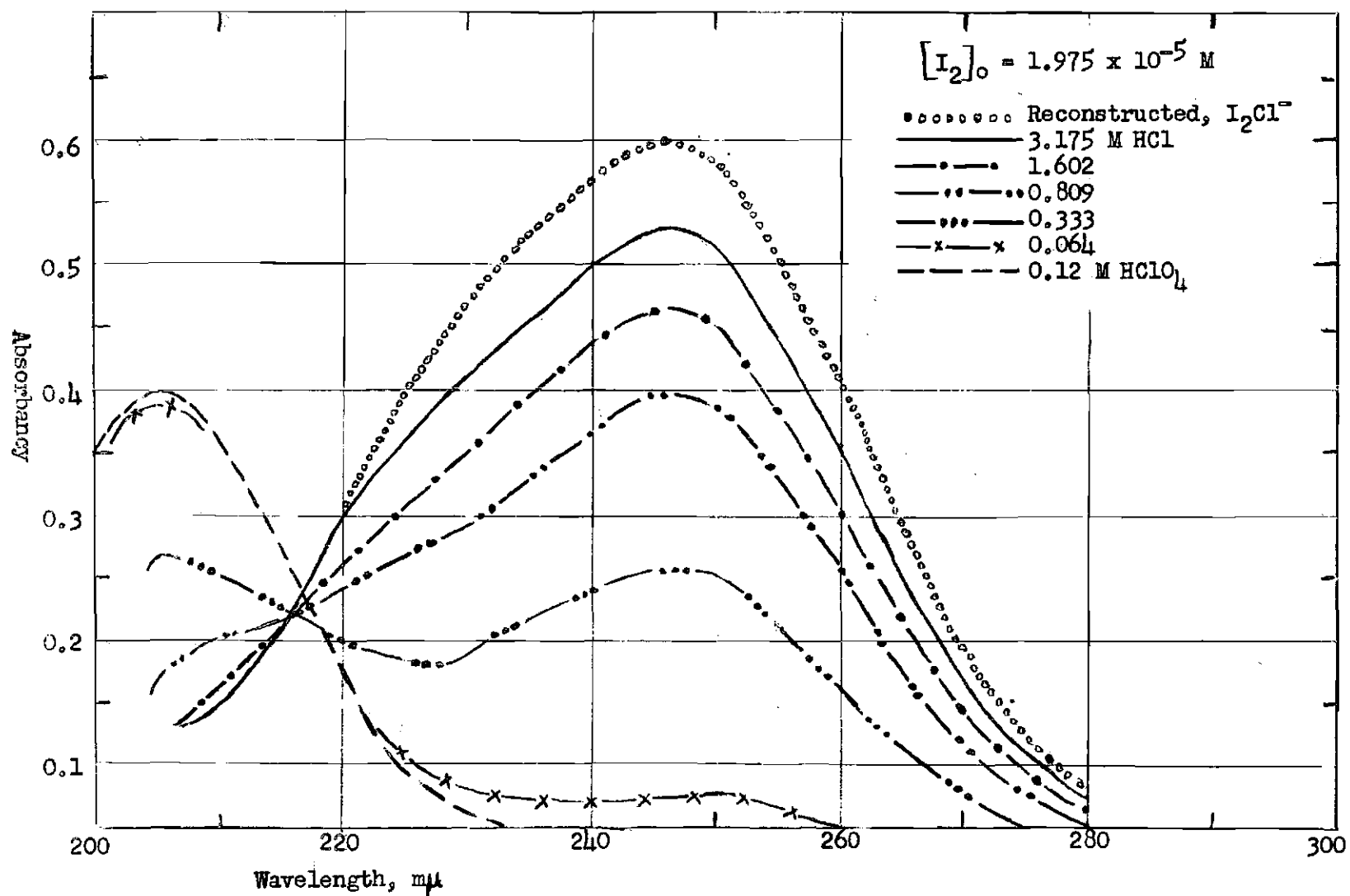


Figure 8. Far UV Spectrum of  $I_2$  in HCl Solutions. Series 7.

Test of Beer's Law.—Both pairs of 1-cm and 10-cm cells were used in this test on the DK recording spectrophotometer. A stock solution of  $I_2$  in 3 M HCl was used with 3 M HCl as both diluent and blank.

For the near UV peak (440 m $\mu$ ), a solution of  $6.6 \times 10^{-4}$  M  $I_2$  and another one of 1/2 of this concentration were made and read immediately in the 1-cm cells. Then a solution of 1/10 of this concentration was made and read in the 10-cm cells. The data follows:

<u>Concentration</u>	<u>Dilution factor, f</u>	<u>L (cm)</u>	<u><math>D_{max}</math></u>	<u><math>D_{max}f/L</math></u>
$6.6 \times 10^{-4}$ M	1	1	0.65	0.65
$3.3 \times 10^{-4}$	2	1	0.32	0.64
$6.6 \times 10^{-5}$	10	10	0.60	0.60

The drop in  $D_{max}f/L$  with lower concentrations of  $I_2$  apparently cannot be explained by equation (19), for the readings were made within 5-10 minutes after dilution and no change was observed half an hour later (a drop would be expected if oxidation is the cause). Nevertheless, this divergence from Beer's Law is not great at the magnitude of  $I_2$  concentrations used in Series 6, so that we may expect the value for K calculated from Series 6 to be close to the true value.

For the far UV peak (246 m $\mu$ ), a solution of  $3.3 \times 10^{-5}$  M and solutions of 1/2 and 1/10 of that concentration were made and read within 5-10 minutes after dilution. The first two solutions, read in 1-cm cells, gave  $D_{max}$  of 0.85 and 0.40 at 246 m $\mu$ , respectively. But the last one, read in 10-cm cells, showed no peak at 246 m $\mu$ ; instead, there was a high peak ( $D_{max} = 1.18$ ) at 224 m $\mu$ . As with the near UV peak, no change occurred after half an hour.

Some reaction other than that in equation (19) is responsible for this odd behavior noted in the last two paragraphs, a reaction that increases as the  $I_2$  concentration is decreased. It might be a disproportionation of the following type



Such a disproportionation would be favored with increasing dilution. The hump in Fig. 8 might be due to absorption by  $ICl_2^-$  ( $\lambda_{max} = 224 \text{ m}\mu$ ) and  $I^-$  ( $226 \text{ m}\mu$ ). The fact that the hump is more pronounced in solutions of high  $Cl^-$  concentration is consistent with equation (20), although the same thing might be said for equation (19).

It is then judged that the far UV peak data (Series 7) cannot be interpreted in terms of the presence of  $I_2$  and  $I_2Cl^-$  only, and that the value of  $0.62 \pm 0.05$  found from the near UV peak (Series 6) is the most reliable value that can be derived from the spectral data.

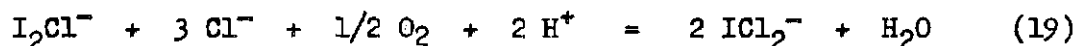
Absorbancy Indexes.—The reconstructed near UV peak of  $I_2Cl^-$  has its maximum at  $437 \text{ m}\mu$  and an  $a_{max}$  of 1,100. Solutions of iodine in chloride solutions show a maximum between  $437 \text{ m}\mu$  and the  $460 \text{ m}\mu$  maximum of iodine in water. The  $\lambda_{max}$  and  $a_{max}$  of iodine in  $0.12 \text{ M HClO}_4$  are virtually identical with those of iodine in water, namely,  $460 \text{ m}\mu$  and 728.

The reconstructed far UV peak of  $I_2Cl^-$  has its maximum at the same position as the maxima of solutions of iodine in chloride solutions,  $246 \text{ m}\mu$ , since the absorption by iodine in water in that region is so slight. Its  $a_{max}$  is 30,400. Incidentally, the  $\lambda_{max}$  is in good agreement with that of Katzin (25),  $247 \text{ m}\mu$ .

### Summary and Recommendations

Two series of dilutions, one for the near UV and the other for the far UV peak, yield the values for K of  $0.62 \pm 0.05$  and  $0.47 \pm 0.03$ , respectively. The first one is in good agreement with that found from solubility and distribution measurements, which indicate that K is in the range 0.6-0.7, with the more probable figure being about 0.61. The divergence of the second value can be ascribed to the nonadherence to Beer's Law at the low iodine concentrations necessary for observations of the far UV peak. This nonadherence is possibly due to disproportionation of  $I_2$  into (-I) and (I) oxidation states ( $I^-$  and  $ICl_2^-$ ), which would be favored with increasing dilution of iodine.

A new reaction was uncovered at the beginning of these experiments; it is the oxidation of  $I_2$  species into  $ICl$  species. The data so far indicate that the reaction is

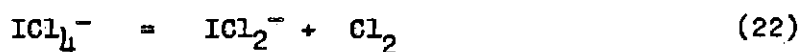


It is believed that experiments to ascertain whether or not the reaction really is as represented in equation (19) would be profitable. Perhaps this reaction would be an easier way of preparation of solutions of  $ICl_2^-$  than the commonly used one of mixing solutions of  $IO_3^-$  and  $I^-$ .

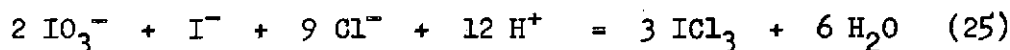
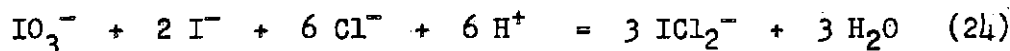
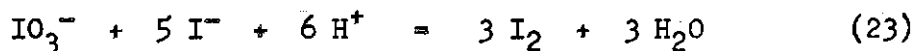
## CHAPTER V

## IODINE (III) SPECIES

It will be convenient to separate all the possible equilibria involving iodine (III) species into two types. The first one is the simple, dissociation type



and the second is the oxidation type. There are three distinct possibilities for the reaction of  $\text{IO}_3^-$  and  $\text{I}^-$  in presence of  $\text{HCl}$ :



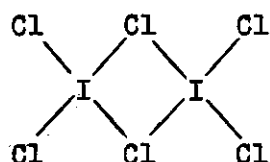
That is,  $\text{IO}_3^-$  and  $\text{I}^-$  may form the (0), (I), and (III) oxidation states of iodine. The first two reactions, (23) and (24), are known; we shall mention (25) later.

## Historical Discussion

There are two possible iodine (III) species, iodine trichloride,  $\text{ICl}_3$ , and its complexed form, the tetrachloroiodate (III) ion,  $\text{ICl}_4^-$ . We have the problem of deciding whether or not it is possible for  $\text{ICl}_4^-$  and  $\text{ICl}_3$  to exist in aqueous solution. Observations on the behavior of

these species in other solvents may suggest some of the reactions to be expected.

$\text{ICl}_3$  is one of the two compounds possible in the  $\text{I}_2\text{-Cl}_2$  system, the other being  $\text{ICl}$ . It is a solid and will decompose into  $\text{ICl}$  and  $\text{Cl}_2$  if left open to air; however, it may be preserved in an atmosphere of chlorine (4). Recent x-ray analysis (27) showed the structure of  $\text{ICl}_3$  in the solid state to be planar molecules of  $\text{I}_2\text{Cl}_6$ :



The I-Cl distances all are considerably greater than those in  $\text{ICl}$ . The Cl-Cl distances within the molecule are similar to the distance of closest approach of two chlorine atoms in different molecules.

Gillam and Morton (28) compared the spectrum of  $\text{ICl}_3$  in  $\text{CCl}_4$  with those of  $\text{ICl}$  and  $\text{Cl}_2$  in the same solvent and found the former to be very nearly identical with the sum of the latter two. This indicates that  $\text{ICl}_3$  dissociates completely or almost so in  $\text{CCl}_4$ . The  $\text{ICl}$  band (464  $\mu$ ) of  $\text{ICl}_3$ , however, differed slightly from that of  $\text{ICl}$  alone in that it was less intense on the long  $\lambda$  side of the peak. This difference was attributed to the inhibition of the decomposition of  $\text{ICl}$  into  $\text{I}_2$  and  $\text{Cl}_2$  by the  $\text{Cl}_2$  produced by the dissociation of  $\text{ICl}_3$ . Any iodine present would broaden the  $\text{ICl}$  band on its long  $\lambda$  side, by reason of its large peak at 520  $\mu$ .

As for other solvents,  $\text{ICl}_3$  gave 233 as its molecular weight in phosgene (29), which indicates no dissociation. But the molecular weight of  $\text{ICl}_3$  in glacial acetic acid, as given by freezing point depressions, approached 120 with increasing dilution (30). This value indicates dissociation, although ionization is possible.

The existence of the  $\text{ICl}_4^-$  ion in solids is well established, and its structure has been determined by x-ray methods (31). Both wet and dry methods are available for the preparation of salts containing this ion, and these methods have been summarized recently (32).

The dissociation of  $\text{ICl}_4^-$  has been studied in nonaqueous solvents, especially acetonitrile. Popov and Jessup (8) dissolved trimethylsulfonium tetrachloroiodate in acetonitrile and saw that the spectrum changed its peaks from 214 and 340  $\mu$  to 227 and 338  $\mu$  over a 24-hour period and after that no further change occurred. The new peaks coincide with those of the  $\text{ICl}_2^-$  salt. The authors believe that the equilibrium expressed in equation (22) on page 45 is established rapidly, and that the fresh spectrum illustrates the equilibrium conditions. The slow spectral change is probably due to a shift in equilibrium because of removal of  $\text{Cl}_2$  by chlorination of the solvent. They mentioned Gillam and Morton's finding (28) that  $\text{ICl}_3$  is dissociated immediately and completely in  $\text{CCl}_4$ , and stated that complex formation apparently stabilizes the (III) oxidation state. They tried to obtain the spectra of  $\text{ICl}_3$  and  $\text{Cl}_2$  in acetonitrile, but failed because of rapid chlorination of the solvent.

Buckles and Mills (33) determined the dissociation constants of  $\text{R}_4\text{NICl}_4$  (R = butyl) in acetonitrile and ethylene dichloride from spectral data. The K, expressed as  $[\text{ICl}_2^-][\text{Cl}_2]/[\text{ICl}_4^-]$ , were found to be  $(1.43 \pm 0.19) \times 10^{-4}$  and  $(1.85 \pm 0.11) \times 10^{-4}$ , respectively. They state that equilibrium was reached in 1-2 hours.

Many salts containing the  $\text{ICl}_4^-$  ion have been crystallized from aqueous media, and it is apparent that this ion does exist in aqueous solutions under some conditions. However, there has been no quantitative



investigation of the equilibria involving  $\text{ICl}_4^-$  in such media, and it is not clear from the preparative procedures what solution conditions are most favorable for forming  $\text{ICl}_4^-$ .

Cremer and Duncan (34), as part of their extensive studies of the polyhalides, did considerable work with salts containing  $\text{ICl}_4^-$ . They identified  $\text{IO}_3^-$  as one of the major products resulting from the hydrolysis of  $\text{KICl}_4$ . Extraction of the hydrolysis mixture with  $\text{CCl}_4$  showed that a small amount of  $\text{I}_2$  was formed, but the amount was never great enough to lead to separation of solid  $\text{I}_2$ . The authors concluded that the hydrolysis reaction was



Fialkov and Kagan (35) report the use of solutions of  $\text{ICl}_3$  for volumetric analysis, but the composition of their solutions is unknown. Their solutions were prepared either by dissolving solid  $\text{ICl}_3$  in 0.2-0.4 M HCl, or by adding KI and  $\text{KIO}_3$  in a mole ratio of 1:2 to the acid solution. These solutions were stable over a period of six months and had an oxidizing power equivalent to that of an iodine (III) species, but it is uncertain whether either  $\text{ICl}_3$  or  $\text{ICl}_4^-$  was actually present in solution. A mixture of  $\text{KIO}_3$  and KI in this ratio would have this oxidizing power irrespective of whether they actually formed  $\text{ICl}_3$  or not.

#### Experimental

An approach to the problem stated at the beginning of this chapter, i. e., whether  $\text{ICl}_3$  and/or  $\text{ICl}_4^-$  exist in aqueous solution, is to investigate the spectra of (1) solutions of  $\text{ICl}_3$  in HCl solutions of various concentrations, and (2) solutions of the type prepared by Fialkov and Kagan by reacting  $\text{IO}_3^-$  and  $\text{I}^-$  in HCl solution.

ICl<sub>3</sub> in HCl solutions.—Solutions of ICl<sub>3</sub> in 0.5, 1, 3, and 12 M HCl were prepared, analyzed iodometrically, and run on the DU and DK spectrophotometers. The concentrations of the analyzed halogen was expressed in terms of ICl<sub>3</sub> and the  $a_{\max}$  calculated therefrom. (Of course, ICl<sub>3</sub> might decompose into ICl and Cl<sub>2</sub>, some of the latter escaping and all of the former forming ICl<sub>2</sub><sup>-</sup>.) The results are tabulated in Table 6. In the case of the rows marked 'aged', the solution was kept open to air for some time.

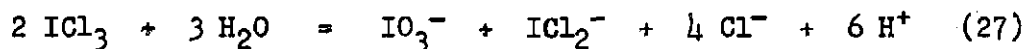
The solutions in 0.5 M HCl were quite stable, and the  $\lambda_{\max}$  values coincide with those of ICl<sub>2</sub><sup>-</sup>. To see whether Cl<sub>2</sub> could be lost, a solution of this type was aged together with its blank (0.5 M HCl). Once it was heated in a water bath in an attempt to make it lose Cl<sub>2</sub>. It did not do so. After a period of 27 days, both the spectrum and titer were found to be the same as when fresh. After 2½ months, the spectrum showed no change. The same appears to be true for solutions of ICl<sub>3</sub> in 1 M HCl.

On the other hand, when ICl<sub>3</sub> is dissolved in 3 M HCl, a definite halogen odor can be detected; it is very similar to chlorine. Notice that, from Table 6, the  $\lambda_{\max}$  is shifted from 335 to 340 mμ (approximately) and that the ratio of the  $a_{\max}$  of the far UV peak to that of the near UV peak comes closer to the ratio for ICl<sub>2</sub><sup>-</sup> as the solution is aged. If the tabulated  $a_{\max}$  values of the aged solution are expressed in terms of ICl rather than ICl<sub>3</sub>, they would be halved, which makes them of the right order of magnitude, 265 and 49,800 for the near and far UV peaks respectively. This definitely indicates that ICl<sub>3</sub> dissociates to a large extent in 3 M HCl. The same is true for aged solutions in 12 M HCl.

Potentiometric titrations of reduced solutions of ICl<sub>3</sub> with AgNO<sub>3</sub> solution was used as a means of determining the iodine content alone,

as distinguished from the total reducible halogen that is found from iodometric titrations. This method found the above conclusions to be correct, that is, in 0.5 M HCl the iodine is present in a form or forms equivalent in oxidizing power to  $\text{ICl}_3$ , whereas in 3 M HCl loss of chlorine had reduced the oxidizing power almost to that equivalent to  $\text{ICl}$ .

All these facts are consistent with the following reaction being favorable in 0.5 M HCl:



Here, 2 moles  $\text{ICl}_3$  form 1 mole  $\text{ICl}_2^-$  so that the  $a_{\text{max}}$  should be multiplied by two in order to compare with that for  $\text{ICl}_2^-$ . From Table 6, it is seen that doubling the  $a_{\text{max}}$  for 0.5 M HCl solutions does, indeed, bring them close to those listed for  $\text{ICl}_2^-$ .

In 3 M and higher HCl solutions, on the other hand, most of  $\text{ICl}_3$  appear to dissociate into  $\text{ICl}_2^-$  and  $\text{Cl}_2$ , as expressed in equation (22).

Mixtures of  $\text{KIO}_3$  and KI solutions.—One way to test the reaction reported by Fialkov and Kagan and expressed in equation (25) on page 45 would be to mix solutions of  $\text{KIO}_3$  and KI (together with HCl) in 4:2 and 1:2 mole ratios, both having the same KI concentration. If equation (25) is not favored, as we suspect it is not, and the only reaction that happens is that expressed in equation (24), the excess  $\text{IO}_3^-$  ions in the 4:2 solution undergoing no reaction, then these two solutions ought to have identical spectra in a part of the spectrum where  $\text{IO}_3^-$  does not absorb. Such a region is 300-400 m $\mu$ , where  $\text{ICl}_2^-$  has its near UV peak (343 m $\mu$ ), and it will be used in this investigation.

Stock solutions of 0.0776 M  $\text{KIO}_3$  and of 0.310 M KI were made.

Solutions of 1:2 and 4:2 mole ratio of  $\text{IO}_3^-$  to  $\text{I}^-$  were made by mixing 500 and 2,000 microliters of the  $\text{KIO}_3$  solution with 250 microliters of the  $\text{KI}$  solution (each) in 50-ml volumetric flasks. (0.5 M  $\text{HCl}$  served as both diluent and blank.) A rather intense yellow-brown color developed immediately upon mixing, probably due to formation of  $\text{I}_3^-$  by equation (23). However, within a few minutes it was replaced with the expected light lemon-yellow color. The spectral runs were made on these solutions long after this shift of colors took place, in the 270-400  $\text{m}\mu$  range. The cells were not thermostatted. The  $D_{\text{max}}$  of both solutions were identical, 0.600 at 343  $\text{m}\mu$ ; this would mean an  $a_{\text{max}}$  of 258 if equation (24) is correct. The rest of the spectra were found to be identical except for the small range 270-290  $\text{m}\mu$ , which is on the rise to far UV absorption, where the 4:2 solution had a slightly higher absorbance. This could be ascribed to absorbance by the excess  $\text{IO}_3^-$  ions. There was no appreciable change after a week.

These facts mean that the best representation of the reaction under these conditions is expressed in equation (24), rather than that given by Fialkov and Kagan (equation (25)).

#### Summary and Recommendations

Under the conditions employed in these experiments, no evidence was found for the existence of  $\text{ICl}_3$  or  $\text{ICl}_4^-$  in aqueous solutions. Of course, other conditions, such as the presence of excess chlorine, may prove favorable to their existence. It may well prove profitable to investigate these conditions.

## APPENDIX

Table 1. Mathematical Treatment of Series 2 data

$$[\text{ICl}]_0 = 1.38 \times 10^{-5} \text{ M}$$

$$f = (D_{\text{ICl}_2} - D) [\text{Cl}^-]$$

Assuming  $D_{\text{ICl}_2} = D$  of 1 M HCl solution

M, HCl	1.00 M	0.101	0.0507	0.021	0.011	Slope Intercept	
250mμ $\frac{D}{f \times 10^3}$	0.070	0.058 1.2	0.051 0.96	0.036 0.72	0.025 0.050	0.018	0
230 $\frac{D}{f \times 10^3}$	0.562	0.483 8.0	0.430 6.6	0.313 5.23	0.208 3.9	0.0132	-0.09
224 $\frac{D}{f \times 10^3}$	0.649	0.568 8.2	0.498 7.65	0.367 5.93	0.246 4.44	0.0127	-0.11
222 $\frac{D}{f \times 10^3}$	0.632	0.552 8.1	0.482 7.6	0.357 5.77	0.235 4.37	0.013	-0.09
220 $\frac{D}{f \times 10^3}$	0.594	0.513 8.3	0.451 7.25	0.335 5.45	0.225 4.06	0.0135	-0.07
215 $\frac{D}{f \times 10^3}$	0.409	0.355 5.45	0.313 3.84	0.240 3.55	0.168 2.66	0.0125	-0.04

Table 2. Mathematical Treatment of Series 3 data

$$f = (D_{\text{ICl}_2} - D)[\text{Cl}^-] ; [\text{ICl}]_0 = 1.38 \times 10^{-5} \text{ M}$$

M, HCl	3 M	1.00 M	0.101	0.051	0.021	Slope	Intercept
250 mp. D	0.085	0.071	0.057	0.053	0.044		
f x 10 <sup>3</sup> (1 M)			1.41	0.92	0.57	0.039	0.03
f x 10 <sup>3</sup> (3 M)		14	2.82	1.63	0.86	0.18	0.04
240 D	0.273	0.243	0.206	0.189	0.160		
f x 10 <sup>3</sup> (1 M)			3.74	2.76	1.74	0.040	0.12
f x 10 <sup>3</sup> (3 M)		30	6.75	4.3	2.4	0.090	0.14
235 D	0.433	0.397	0.344	0.312	0.264		
f x 10 <sup>3</sup> (1 M)			5.35	4.3	2.8	0.031	0.18
f x 10 <sup>3</sup> (3 M)		36	9.0	6.2	3.55	0.066	0.21
230 D	0.597	0.560	0.489	0.440	0.375		
f x 10 <sup>3</sup> (1 M)			7.2	6.1	3.9	0.029	0.24
f x 10 <sup>3</sup> (3 M)		37	10.9	8.0	4.65	0.054	0.29
227 D	0.660	0.625	0.552	0.497	0.424		
f x 10 <sup>3</sup> (1 M)			7.4	6.5	4.2	0.027	0.27
f x 10 <sup>3</sup> (3 M)		35	10.9	8.3	4.95	0.046	0.31
224 D	0.673	0.646	0.572	0.516	0.440		
f x 10 <sup>3</sup> (1 M)			7.5	6.63	4.33	0.026	0.28
f x 10 <sup>3</sup> (3 M)		37	10.2	8.0	4.9	0.041	0.32
222 D	0.656	0.630	0.569	0.505	0.430		
f x 10 <sup>3</sup> (1 M)			6.15	6.4	4.2		
f x 10 <sup>3</sup> (3 M)		26	8.8	7.7	4.75	0.033	0.29
220 D	0.611	0.590	0.523	0.471	0.402		
f x 10 <sup>3</sup> (1 M)			6.76	6.06	3.95	0.026	0.26
f x 10 <sup>3</sup> (3 M)		21	8.9	7.14	4.4	0.039	0.29
217 D	0.503	0.488	0.436	0.392	0.335		
f x 10 <sup>3</sup> (1 M)			5.25	4.9	3.22	0.025	0.21
f x 10 <sup>3</sup> (3 M)		15	6.76	5.65	3.5	0.032	0.23
215 D	0.420	0.409	0.366	0.330	0.283		
f x 10 <sup>3</sup> (1 M)			4.35	4.0	2.65	0.024	0.17
f x 10 <sup>3</sup> (3 M)		11	5.45	4.6	2.88	0.032	0.195
210 D	0.222	0.214	0.197	0.181	0.163		
f x 10 <sup>3</sup> (1 M)			1.7	1.7	1.07	0.024	0.12
		8	2.5	2.1	1.24	0.037	0.13

Table 3. Mathematical Treatment of Series 4 data

$$[\text{ICl}]_0 = 2.84 \times 10^{-3} \text{ M}$$

$$f = (D_{\text{ICl}_2^-} - D)[\text{Cl}^-]$$

Assuming  $D_{\text{ICl}_2^-} = D$  of 1 M HCl solution

M, HCl	1.00 M	0.11	0.060	0.029	0.011 *	Slope
330 mμ $\frac{D}{f \times 10^3}$	0.595	0.580 1.65	0.555 2.40	0.539 1.63	0.472 1.3	0.0082
340 $\frac{D}{f \times 10^3}$	0.693	0.670 2.5	0.647 2.76	0.612 2.35	0.533 1.75	0.0082
345 $\frac{D}{f \times 10^3}$	0.688	0.670 1.98	0.641 2.82	0.610 2.26	0.528 1.75	0.0073
350 $\frac{D}{f \times 10^3}$	0.653	0.632 2.3	0.611 2.52	0.588 1.89	0.508 1.6	0.0073
360 $\frac{D}{f \times 10^3}$	0.518	0.500 1.98	0.487 1.86	0.471 1.36	0.439 0.87	0.017

\* Calculation of  $[\text{Cl}^-]$  from  $[\text{Cl}^-]_0 = 0.012 \text{ M}$ :

Let  $K = 12 \times 10^{-3}$ ; then  $[\text{ICl}]/[\text{ICl}_2^-] = K/[\text{Cl}^-]_0 = 1$ .

$$\begin{aligned} \text{So, } [\text{Cl}^-] &= 0.012 - \frac{1}{2}(2.84 \times 10^{-3}) = 0.012 - 0.0014 \\ &= 0.0106, \text{ or } 0.011. \end{aligned}$$



Table 4. Mathematical Treatment of Series 6 data

$$[I_2]_0 = 5.33 \times 10^{-4} \text{ M}$$

$$f = (D - D_{I_2}) / [Cl^-]$$

Assuming  $D_{I_2} = D$  of 0.12 M  $HClO_4$  solution

M, HCl		5.7 M	3.07	1.23	0.748	0.307	0.196	0.098	0.12 M HClO <sub>4</sub>
400 mμ	D fx10 <sup>3</sup>	0.285 30.0	0.284 55.4	0.248 109	0.225 148	0.184 228	0.165 260	0.138 245	0.114
410	D fx10 <sup>3</sup>	0.394 39.3	0.381 69	0.345 142	0.312 190	0.258 286	0.233 321	0.202 327	0.170
420	D fx10 <sup>3</sup>	0.489 44.5	0.473 77.2	0.430 157	0.385 199	0.328 300	0.306 356	0.270 347	0.236
430	D fx10 <sup>3</sup>	0.551 45.0	0.530 77	0.483 154	0.443 199	0.386 300	0.362 347	0.328 347	0.294
440	D fx10 <sup>3</sup>	0.564 38.8	0.541 64.5	0.501 128	0.467 166	0.421 254	0.408 331	0.373 306	0.343
450	D fx10 <sup>3</sup>	0.539 28.2	0.515 44.6	0.491 92	0.460 110	0.432 176	0.420 214	0.397 194	0.378
490	D -fx10 <sup>3</sup>	—	0.239 25.1	0.259 46.3	0.259 76	0.288 91	0.294 112	0.301 153	0.316
520	D -fx10 <sup>3</sup>	0.097 13.7	0.098 25	0.110 52.8	0.122 70.8	0.142 107.5	0.155 102	0.161 143	0.175

$\lambda$	Slope	Intercept (on D-axis)
400 mμ	0.577	0.307
410	0.535	0.413
420	0.650	0.522
430	0.650	0.578
440	0.593	0.584
450	0.685	0.552
490	0.673	0.226
520	0.512	0.085

Mean 0.61

Table 5. Mathematical Treatment of Series 7 data

$$[I_2]_0 = 1.975 \times 10^{-5} \text{ M}$$

$$f = (D - D_{I_2})/[Cl^-]$$

Assuming  $D_{I_2} = D$  of 0.12 M  $HClO_4$  solution

M, HCl	3.175	1.602	0.809	0.333	0.064	0.12 M $HClO_4$	Slope	Inter- cept
270 mm D f x 10 <sup>3</sup>	0.170 52.5	0.143 87.5	0.120 145	0.079 228	0.024 329	0.003	0.497	0.194
260 D f x 10 <sup>3</sup>	0.357 112	0.301 186	0.253 310	0.165 489	0.049 735	0.002	0.51	0.41
250 D f x 10 <sup>3</sup>	0.511 160	0.450 279	0.384 471	0.251 744	0.074 1110	0.003	0.445	0.58
245 D f x 10 <sup>3</sup>	0.527 165	0.467 289	0.396 484	0.256 756	0.077 1140	0.004	0.44	0.60
240 D f x 10 <sup>3</sup>	0.499 155	0.437 268	0.365 441	0.238 690	0.072 1000	0.008	0.495	0.57
230 D f x 10 <sup>3</sup>	0.410 112	0.349 183	0.292 294	0.189 402	0.083 437	0.055	0.775	0.50

Note: Since  $D_{I_2}$  is unusually small here,  $(D - D_{I_2})$  is assumed to be accurate to  $\pm 0.002$  (same precision as that of  $D$ ) til  $D_{I_2}$  exceeds 0.010. Thereafter,  $(D - D_{I_2})$  is taken to be within  $\pm 0.004$ , as in earlier treatments.

Table 6

Aqueous HCl Solutions of  $\text{ICl}_3$ 

<u>HCl</u>	<u><math>\lambda_{\text{max}}</math></u>	<u><math>a_{\text{max}}</math></u>	<u>Ratio of Far UV <math>a_{\text{max}}</math> to Near UV <math>a_{\text{max}}</math></u>
0.5 M	342 mμ 225	135 26,000	$1.93 \times 10^2$
1 M	342 225	160 29,500	1.85
3 M fresh	ca. 335 225	ca. 590 ca. 79,000	1.34
aged	342 225	530 99,700	1.88
12 M fresh	342	515	
aged	342	535	
ICl in 1 M HCl	342 225	243 47,000	1.93

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