BAND SPECTRA AND DISSOCIATION OF IODINE MONOCHLORIDE

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Abstract

Thirty-three band heads of ICl were measured in absorption and found to consist of two series, one of them converging at $\nu = 17410 \pm 30$ cm^{-1} ($\lambda = 5744$A). Two heads of a third series were faintly in evidence just beyond the convergence, fading out in the region of continuous absorption. The maximum of continuous absorption is about 4800A. Intensity variations with temperature indicate that all three series come from excited states of normal ICl, the observed convergence coming from the first vibrational level. The vibration frequency of normal ICl is 382 cm^{-1}. Interpreted according to the theory of Franck our results indicate that ICl dissociates in light (1) into unexcited atoms, (2) into an unexcited iodine atom and a chlorine atom in the 2^2P_1 state. The convergence corresponding to dissociation into chlorine and excited iodine was not found. Combined with the optical data of Kuhn on Cl_2 and I_2 our results require an evolution of 3.8 Cal. for the reaction $ICl = \frac{1}{2}I_2 + \frac{1}{2}Cl_2$, assuming the observed convergence to correspond to process (1). Thermodynamic data give 3.6 Cal. for the same reaction. The two faint heads of the third series probably correspond to (2). The thermodynamic measurements are susceptible of determination with accuracy sufficient to exclude definitely other possible interpretations.

Introduction

The absorption spectra of the halogens Cl_2, Br_2, I_2 have been investigated by Mecke[1] and by Kuhn.[2] They all show band series in the visible, the spacing of the bands becoming progressively smaller toward the violet and converging to definite limits in the green. By analysis of the bands of Cl_2 and Br_2 Kuhn has shown that in each case the convergence corresponds to the dissociation of the molecule into an unexcited atom and an excited atom in the $2\,^2P_1$ state, in accordance with the theory of Franck[3] which had already been so well borne out in the case of iodine. In the case of I_2 and Br_2 Pringsheim[4] and Kuhn[2] showed that the series ending in the convergence diminished in intensity with rise in temperature and must therefore come from the vibrationless state of the normal molecule. In the case of Cl_2, however, the series ending in the observed convergence increases in intensity as the temperature is raised, from which Kuhn concludes that it must come from a vibrating state of the molecule. By quantitative measurements of the variation in intensity with temperature Kuhn was able to show that this state was the first vibrational level of the normal molecule. The convergence in all three halogens is followed by a region of continuous absorption which in the case of iodine comes to a maximum just beyond the convergence, while in

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[1] Mecke, Ann. d. Physik **71,** 104 (1923).

[2] Kuhn, Zeits. f. Physik **39,** 77 (1926).

[3] Franck, Trans. Faraday Soc. **21,** Part 3 (1925); Zeits. f. phys. Chem. **120,** 144 (1926).

[4] Pringsheim, Zeits. f. Physik **5,** 130 (1921).

bromine this maximum is 900A, in chlorine 1400A, beyond the convergence toward the violet. This, as Kuhn points out, is an excellent confirmation of the prediction of Franck that the more the electron excitation weakens the bond between the atoms in the molecule the greater the amount of vibrational (or atomic translational) energy resulting from the electron jump. The weakening of the bond is shown by the diminution in the spacing of the vibration levels ω'' and ω' in going from the normal to the excited state of the molecule. Thus we have approximately, for iodine $\omega^{0''}=213$ cm^{-1}, $\omega^{0'}=122$ cm^{-1}; for bromine, $\omega^{0''}=325$ cm^{-1}, $\omega^{0'}=160$ cm^{-1}; and for chlorine $\omega^{0''}=565$ cm^{-1}, $\omega^{0'}=180$ cm^{-1}. The calculated heats of dissociation of the molecule into atoms agree with the thermochemical data within the rather large limit of error of the latter. With a view to obtaining a further check on the theory of Franck the absorption spectra of IBr and ICl were photographed with the 15 ft. concave grating of the Physics Department of the University of California. In the case of IBr we found that the dissociation was already so marked at room temperature that the spectrum of IBr was completely obscured by the strong absorption of I_2. There seems little hope of obtaining the spectrum of IBr in this manner.[5] This is in agreement with the experiments of Bodenstein and Schmidt[6] who found that IBr was largely dissociated at room temperature.

The dissociation, however, is very much less in the case of ICl, as might be expected from the more polar nature of the molecule, and the I_2 bands do not make their appearance at temperatures below 200°C. We have found the absorption spectrum of ICl to consist of two series of bands coming respectively from the first and second vibrating states of the normal molecule. The first of these series comes to a convergence at 5744A, which, as we shall show later, is in excellent agreement with thermodynamic data if we assume that the convergence corresponds to dissociation into normal unexcited chlorine and iodine atoms. At and just beyond the convergence two heads of a third series were observed which appear to correspond to dissociation into a normal iodine atom and an excited chlorine atom in the 2 $^2P_1$ state. The weakening of the molecular bond due to electron excitation is intermediate between that of Cl_2 and I_2, namely, $\omega^{0''}=382$ cm^{-1} and $\omega^{0'}=170$ cm^{-1} approximately. In agreement with the theory of Franck, measurements of the continuous absorption which we have also carried out, show that the absorption maximum occurs about 950A beyond the convergence, which, as the theory predicts, is intermediate between the corresponding values for Cl_2 and I_2.

In reply to a preliminary report of these results sent to Professor Franck he was kind enough to call our attention to the improbability that a comparatively non-polar molecule like ICl should dissociate into unexcited atoms.

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[5] The intensity distribution in the iodine bands from IBr is, however, very different at low temperatures from that in pure iodine, so that with low dispersion the bands appear to be just twice as close together as the iodine bands. At higher temperatures the intensity distribution is the same as in pure iodine.

[6] Bodenstein and Schmidt, Zeits. f. phys. Chem. **123,** 28 (1926).

Experiments performed by Kuhn and by Rollefson in his laboratory showed that very polar molecules, such as those of salt vapors, which can be dissociated adiabatically into ions can be dissociated by light into unexcited atoms, or with nearly equal probability into one unexcited and one excited atom. It would certainly seem surprising if ICl, which is intermediate in polarity between the salt vapors and the halogens, should decompose most readily by light into unexcited atoms. The thermodynamic data, however, point very strongly to this conclusion, and would have to be in error by an improbably large amount if the convergence in ICl is to be interpreted as corresponding to dissociation into excited chlorine atoms and normal iodine atoms. There is yet another difficulty in this latter interpretation. The third faint series which we observed just beyond the convergence corresponds very well to dissociation into a chlorine atom in the 2 $^2P_1$ state and a normal iodine atom if we accept the interpretation given in the text, but would be hard to explain otherwise. At first we had erroneously supposed these bands to correspond to the dissociation into excited iodine and normal chlorine atoms, but this interpretation we have now found to be inadmissible.

II. OPTICAL MEASUREMENTS

The absorption spectra were photographed with a 15 foot Rowland concave grating giving a dispersion in the first order, which was used throughout, of 37A per cm. The source of light was a Pointolite lamp whose anode, consisting of a small sphere of tungsten, is brought to bright incandescence by a low pressure arc. The absorption cell was of Pyrex glass, 10 cm long, 3 cm diameter, with plane windows fused on at either end. A side tube, which could be heated independently of the absorption cell, permitted regulation of the vapor pressure of the ICl. A quantity of Kahlbaum's purest ICl was introduced into the cell, which was then rapidly evacuated and sealed. Subsequent experiments showed that there was no excess of iodine in the cell such as might have been produced by preferential evaporation of chlorine during this operation. The fine structure of the bands was plainly visible on the plates, but only band heads were measured. The iron arc was used as reference spectrum. Photographs were made on Wratten panchromatic

TABLE I

Absorption spectrum of ICl.

λ(A)	ν(cm^{-1})	λ(A)	ν(cm^{-1})	λ(A)	ν(cm^{-1})	λ(A)	ν(cm^{-1})
5732.0*	17446	5915.5	16905	6215.8	16088	6481.1	15430
5793.4	17261	5941.6	16831	6221.8	16073	6515.8	15347
5801.7	17237	5971.4	16747	6268.6	15953	6544.7	15280
5812.3	17205	6003.5	16657	6315.5	15834	6611.6	15125
5824.2	17170	6039.6	16557	6325.0	15810	6682.4	14965
5837.9	17129	6078.7	16451	6366.9	15706	6757.8	14798
5853.3	17084	6120.9	16338	6385.3	15661	6836.6	14627
5871.2	17032	6167.0	16215	6422.5	15570		
5892.2	16972	6180.8	16179	6447.8	15509		

* This band head belongs to a different band series from those immediately following. Another head of the same series was found by visual observation at approximately 40A to the violet, and evidence of a third band was faintly visible although the head could not be measured.

plates and the exposures varied from 10 to 30 minutes. The measured wavelengths and frequencies of the band heads are given in Table I.

In Table II the frequencies of the band heads are shown arranged in two series. The notation is that used by Birge in Bull. Nat. Research Council, **11**, No. 57, Chap. 4 (1927). Thus n'' is the vibrational quantum number of the level of lower, n' that of higher, energy. The values of n'' are absolute values as determined by variation in intensity with temperature, to be described later. The values of n' are on an arbitrary scale. The spacing of the n' levels correspond to the vertical differences $\Delta\nu'$, those of the n'' levels to the horizontal differences $\Delta\nu''$.

TABLE II

Band series of ICl.

n'	$n''=2$	$\Delta\nu'$	$n''=1$	$\Delta\nu'$	$\Delta\nu''$
0	14627	171			
1	14798	167			
2	14965	160	15347	162	382
3	15125	155	15509	152	384
4	15280	150	15661	149	381
5	15430	140	15810	143*	380
6	15570	136	15953*	135*	383*
7	15706	128	16088	127	382
8	15834	119*	16215	123	381
9	15953*	120*	16338	113	385*
10	16073	106	16451	106	378
11	16179		16557	100	378
12			16657	90	—
13			16747	84	382 (average)
14			16831	74	
15			16905	67	
16			16972	60	
17			17032	52	
18			17084	45	
19			17129	41	
20			17170	35	
21			17205	32	
22			17237	24	
23			17261		
			17410 ± 30 (convergence)		

* The band head at 15953 is really double, the two series nearly coinciding at this point. From the $\Delta\nu$ values the two heads should be about 2.5A apart here, but the fine structures overlap in such a manner that it is impossible to distinguish them. The $\Delta\nu$ values affected by this uncertainty are likewise indicated by an asterisk.

The convergence limit was obtained by extrapolation in two ways. The first, which was that adopted by Kuhn, is to extrapolate the plot of $\Delta\nu'$ against ν. The second way, which is quite independent theoretically, is that adopted by Birge and Sponer,[7] and consists of a graphical evaluation of the dissociation frequency using the equation $\nu_D = \int_0^{n_0'} \omega^{n'} dn'$, where $\omega^{n'}$ is the average value of $\Delta\nu'$ and n_0' is the value of n' for which $\omega^{n'}$ vanishes. The plot of $\omega^{n'}$ against n' is shown in Fig. 1. The dotted line indicates the extrapolated portion which was continued beyond the limits of the figure in a more or less arbitrary manner to the axis of abscissas. In this way we obtained from the area under the curve the value 17,380 cm^{-1} for the con-

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[7] Birge and Sponer, Phys. Rev. **28**, 259 (1926).

vergence limit. Extrapolation of the plot of ν against $\Delta\nu$ gave 17,435 cm^{-1}. As final value we chose the average 17,410 cm^{-1} in round figures, and the difference of this from the value obtained by either method, approximately 30 cm^{-1}, may be taken as representing the uncertainty in the extrapolation.

The determination of the absolute value of n' was carried out in the following manner, which in principle is equivalent to that adopted by Kuhn.

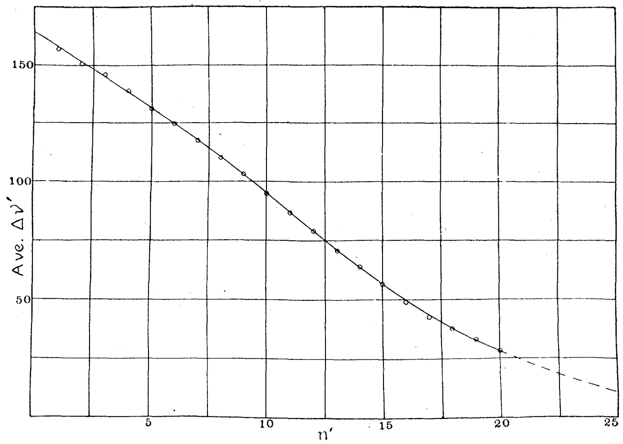

Fig. 1. Plot of the average values of the spacings of the n' levels as a function of n'.

The ratio of the number of oscillators which at 350°K have vibrational energy corresponding to $n''=1$ to those in the same vibrational state at 473°K is given by the equation

$$N_{350}/N_{473}=e^{-E/kT_1}/e^{-E/kT_2}.$$

Substituting for E the energy of the first vibrational state, namely, $\nu''=$ 382 cm^{-1}, we obtain $N_{350}/N_{473}=2/3$. The corresponding ratio for the oscillators in state $n''=2$ is the square of this ratio, namely 4/9. If therefore we keep the concentration of ICl constant in the absorption cell and photograph at these two temperatures, but with exposures in the ratio 3 to 2, the blackening on the plate will be the same for the series whose lower level is $n''=1$. It is of course necessary to use a plate for which the blackening is independent of the intensity or the time, provided that the product of intensity and time is kept constant. This was found to be the case for the Wratten panchromatic plates used in these experiments for a range of exposures about twice as great as that actually used. The calibration was carried out with the wire absorption screens described by Ramsperger and Porter[8] and it was found to be easily possible to detect by eye a ten percent deviation in the product of intensity and time.

The cell was charged with an amount of ICl which could be completely vaporized at 350°K. Two photographs were taken, one at 350°K with 10 minutes exposure, the other at 473°K with 15 minutes exposure. The blackening was found to be identical in both photographs for the series

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[8] Ramsperger and Porter, J. Am. Chem. Soc. **48**, 1267 (1926).

extending to the convergence, which from now on we will call Series A. The other series, which we will call Series B shows much less absorption at the lower temperature. On another plate with the same exposure at both temperatures Series A showed much less absorption at the lower temperature. Since a ten percent deviation from the 2/3 ratio could easily have been detected, this experiment proves definitely that the two series correspond to $n''=1$ and $n''=2$ respectively. The two faint heads of the third series, which we will call Series C, were found similarly to correspond to $n''=1$. Since these heads are approximately 40A apart we may form an estimate of the frequency at which Series C would converge if we assume the rate of convergence to be approximately the same as for Series A whose convergence we have already measured. This would probably be nearly true if the two series differ only in that their convergences correspond to dissociation into excited and unexcited chlorine atoms, respectively, since the separation of the 2 ^2P levels is small, namely 0.109 volts. We need therefore only

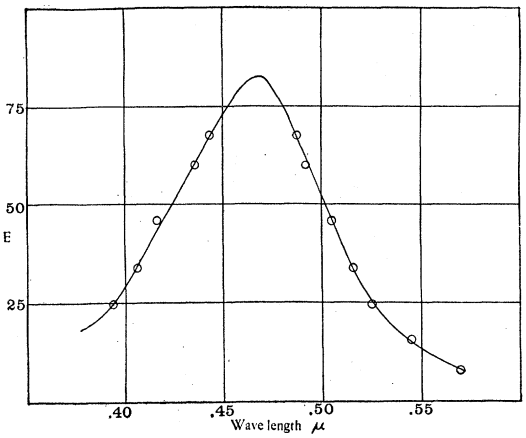

Fig. 2. Absorption of ICl in the visible region.

find the pair of band heads which differ by 40A in Series A and subtract the frequency of either head of this pair from the frequency of the corresponding head in Series C to obtain the difference in frequency of the two convergence limits. In this way the head at 17,446 cm^{-1} of Series C is found to correspond to the head 16,451 cm^{-1} of Series A. The difference is 995 cm^{-1}, or 0.12 volts, which is as close as could reasonably be expected to the excitation of chlorine (0.11 volts). We therefore conclude that this series corresponds, at the convergence, to dissociation of normal ICl, $n''=1$, into normal iodine atoms and chlorine atoms in the 2 $^2P_1$ state.

The variation of intensity with wave-length is just what we would expect from the theory of Franck. The maximum of absorption in Series B corresponds to smaller values of n' than Series A, while the absorption of the vibrationless state $n''=0$ appears only as continuous absorption, just as Kuhn found in the case of Cl_2. We have made quantitative measurements of the absorption in the continuous region by the method of Ramsperger and Porter and the results are shown graphically in Fig. 2. There is a decided maximum at about 4700A which shows that the most probable process of absorption for molecules in state $n''=0$ is one which results in dissociation into atoms having about 0.5 volts energy of translation. Without making quantitative measurements it is difficult to say whether the most probable value of n' for Series C is greater or less than the corresponding value for Series A. For both series the most probable value of n' is less than n_0', the value at the convergence. An energy level diagram for Series A and B is shown in Fig. 3.

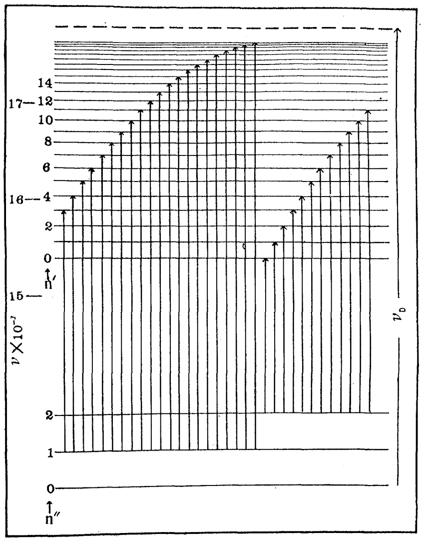

Fig. 3. Energy level diagram for series A and B.

III. Thermodynamic Calculations

To avoid circumlocution we shall use the following notation throughout. We shall adhere as closely as possible to the thermodynamic notation of Lewis and Randall.[9] Thus the equation $ICl(l)=\frac{1}{2}I_2(s)+\frac{1}{2}Cl_2(g)$; $\Delta H_{298}=5800$ cal. reads: liquid iodine monochloride dissociates into solid iodine and gaseous chlorine with an absorption of 5800 calories. The symbol $Cl_2(g)$ represents one mol of an equilibrium mixture of chlorine molecules in their various vibrational states. In discussing optical data it becomes necessary to distinguish between these. We shall indicate the vibrational levels by writing in parentheses after the symbol of the molecule the value of n' or n'' as the case may be. Thus $Cl_2(n''=1)$ reads: a molecule of chlorine in the first vibration state of the lower electronic level. Since the energy difference between $ICl(g)$ and $ICl(n''=0)$, although not entirely negligible, is too small to affect our conclusions in any way it is not necessary as a rule to discriminate between these two symbols. This applies also to the corresponding symbols of I_2 and Cl_2. The error resulting from this approximation affects

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[9] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.

our final results by less than 100 calories. The only atomic levels we need consider are the 2 $^2P_{1,2}$ levels of Cl and I. The level of higher energy will always be indicated by an asterisk; thus Cl* reads: an atom of chlorine gas in the 2 $^2P_1$ state.

We may now summarize the results of the optical measurements as follows. The process corresponding to the convergence of Series A may be

$$\mathrm{ICl}(n''=1)=\mathrm{I}+\mathrm{Cl},$$

or

$$\mathrm{ICl}(n''=1)=\mathrm{I}^*+\mathrm{Cl},$$

or

$$\mathrm{ICl}(n''=1)=\mathrm{I}+\mathrm{Cl}^*.$$

The results of Kuhn for I_2 and Cl_2 show that the processes at the convergence limits are $I_2(n''=0)=I+I^*$ and $Cl_2(n''=1)=Cl+Cl^*$. Thermodynamically we shall obtain the following: $ICl(g)=\frac{1}{2}I_2(g)+\frac{1}{2}Cl_2(g)$; $\Delta H_{298}=3500$ cal. Before discussing the method by which this value is obtained we shall calculate the heat of the same reaction as it follows from our optical data combined with those of Kuhn by the alternative schemes:

Process 1

$$\begin{array}{lll}
\mathrm{ICl}(n''=0)=\mathrm{ICl}(n''=1) & \Delta H= +1090 \text{ cal.} & (\nu=382)\\
\mathrm{ICl}(n''=1)=\mathrm{I}+\mathrm{Cl} & \Delta H=+49590 \text{ cal.} & (\nu=17410)\\
\mathrm{I} \qquad =\frac{1}{2}\mathrm{I}_2(n''=0) & \Delta H=-17600 \text{ cal.} & \text{(Kuhn)}\\
\mathrm{Cl} \qquad =\frac{1}{2}\mathrm{Cl}_2(n''=0) & \Delta H=-29250 \text{ cal.} & \text{(Kuhn)}\\
\hline
\mathrm{ICl}(n''=0)=\frac{1}{2}\mathrm{I}_2(n''=0)+\frac{1}{2}\mathrm{Cl}_2(n''=0); & \Delta H=3830 \text{ cal.} &
\end{array}$$

Process 2.

$$\begin{array}{ll}
\mathrm{ICl}(n''=0)=\mathrm{ICl}(n''=1) & \Delta H= +1090 \text{ cal.}\\
\mathrm{ICl}(n''=1)=\mathrm{I}+\mathrm{Cl}^* & \Delta H=+49590 \text{ cal.}\\
\mathrm{I} \qquad =\frac{1}{2}\mathrm{I}_2(n''=0) & \Delta H=-17600 \text{ cal.}\\
\mathrm{Cl}^* \qquad =\frac{1}{2}\mathrm{Cl}_2(n''=0) & \Delta H=-31760 \text{ cal.}\\
\hline
\mathrm{ICl}(n''=0)=\frac{1}{2}\mathrm{I}_2(n''=0)+\frac{1}{2}\mathrm{Cl}_2(n''=0); & \Delta H= \quad 1320 \text{ cal.}
\end{array}$$

The alternatives involving dissociation into I* evidently need not be considered since they introduce 0.9 volt or 20,700 cal. additional. Evidently alternative 1 is in very close agreement with the thermochemical value, which we shall now discuss in detail.

IV. Thermochemical Data

$\frac{1}{2}I_2(s)+\frac{1}{2}Cl_2(g)=ICl(l)$. The heat of formation of ICl has been determined by Berthelot[10] and by Thomsen.[11] Berthelot used three different methods, the first two depending on the reaction $ICl+SO_2(aq)+2H_2O=HCl(aq)+HI(aq)+H_2SO_4(aq)$. From the large heat of this reaction, approximately 40,000 cal., he obtains the heat of formation of ICl(s) by subtracting his previously determined values for the heats of formation of the dilute acids, obtaining for the reaction $\frac{1}{2}I_2(s)+\frac{1}{2}Cl_2(g)=ICl(s)$; $\Delta H=6600$ cal. as a mean of the two values 7400 and 5800 cal. This method is obviously so inaccurate that we can give it no weight whatever. His third method was to introduce a weighed amount of solid iodine into a glass-stoppered vessel containing chlorine of a volume calculated to be equivalent to the iodine

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[10] Berthelot, Ann. chim. phys., [5] **21,** 370 (1880).

[11] Thomsen, Ber. **15,** 3021 (1882).

added. It is practically certain that this method will give low results since the chlorine could not have been free from air. The value which he obtains in this way is 6800 cal. Subtracting the heat of fusion, 2500 cal., we obtain 4300 cal. for the heat of formation of liquid ICl.

Realizing the imperfections in Berthelot's method, Thomsen repeated the direct determination using an improved method. He introduced a measured volume of chlorine into a weighed glass vessel containing a known weight of solid iodine, and checked the amount of chlorine added by determining the increase in weight of the vessel. He finds by this method for the reaction $\frac{1}{2}\mathrm{I}_2(\mathrm{s})+\frac{1}{2}\mathrm{Cl}_2(\mathrm{g})=\mathrm{ICl}(\mathrm{l})$; $\Delta H=5800$ cal. This determination certainly should not be in error by more than 500 cal. and we shall adopt it in the following. Berthelot's mean value is evidently in error by about 1500 cal.

ICl(l) = ICl(g). Stortenbeker[12] has made determinations from which we may readily obtain the vapor pressure of liquid ICl. Interpolating from his tables on page 24, and correcting for the excess chlorine in the vapor, we obtain the figures in Table III.

TABLE III

Vapor pressure of ICl.

Temperature (°C)	7.9	27.2	30.0	80.3
Pressure (mm Hg)	13.8*	38.2	42.8	422.6

*This value was obtained from Stortenbecker's Table 11, page 23, assuming that Raoult's law is obeyed for liquid solutions of I_2 in ICl and that the liquid contains only these components.

Plotting log p against $1/T$ we obtain a straight line, the slope of which gives the heat of vaporization. $\mathrm{ICl}(\mathrm{l})=\mathrm{ICl}(\mathrm{g})$; $\Delta H=9500$ cal.

$\frac{1}{2}I_2(s)=\frac{1}{2}I_2(g)$. For the heat of sublimation of I_2 Baxter, Hickey and Holmes[13] obtain from their own measurements 7270 cal.

$ICl(g)=\frac{1}{2}I_2(g)+\frac{1}{2}Cl_2(g)$. We may now calculate the heat of this reaction by combining the data just obtained as follows:

$$
\begin{array}{ll}
\mathrm{ICl}(\mathrm{l})=\frac{1}{2}\mathrm{I}_2(\mathrm{s})+\frac{1}{2}\mathrm{Cl}_2(\mathrm{g}); & \Delta H=5830\ \mathrm{cal.} \\
\mathrm{ICl}(\mathrm{g})=\mathrm{ICl}(\mathrm{l}); & \Delta H=-9500\ \mathrm{cal.} \\
\frac{1}{2}\mathrm{I}_2(\mathrm{s})=\frac{1}{2}\mathrm{I}_2(\mathrm{g}); & \Delta H=7270\ \mathrm{cal.} \\
\hline
\mathrm{ICl}(\mathrm{g})=\frac{1}{2}\mathrm{I}_2(\mathrm{g})+\frac{1}{2}\mathrm{Cl}_2(\mathrm{g}); & \Delta H=3600\ \mathrm{cal.}
\end{array}
$$

It is evident that this value is in excellent agreement with the optical value 3830 cal. obtained according to Process 1. However, in view of the uncertainty in such thermochemical data it seemed desirable to check this conclusion in other ways, although it is unlikely that the values we have obtained should be in error by 2500 cal., the amount necessary to bring it into agreement with Process 2. Carefully performed, the experimental redetermination of the thermochemical data alone would suffice to decide between the two alternatives.

V. THE DEGREE OF DISSOCIATION OF ICl

At 7.9°C, ICl is certainly stable since Stortenbeker finds the vapor pressure of the equilibrium liquid solution of ICl and I_2 to be 11 mm with

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[12] Stortenbeker, Zeits. phys. Chem. **3,** 11 (1889).

[13] Baxter, Hickey and Holmes, J. Am. Chem. Soc. **29,** 127 (1907).

practically no dissociation in the gas phase. Actually his analysis of the vapor leads to an amount of iodine slightly in excess of the vapor pressure of solid iodine (0.055 mm) at this temperature, but this is certainly the result of experimental error. For the sake of argument let us assume that the equilibrium pressure of iodine actually is just equal to the vapor pressure, 0.055 mm of the solid. This is clearly the upper limit. We have then $K = 0.055/11 = 0.005$, whence $\Delta F = -RT \ln K = 3010$ cal., and by Process 1 $\Delta S = (\Delta H - \Delta F)/T = (3830 - 3010)/284 = 2.9$ cal/deg. Since we have taken the upper limit for the iodine pressure this is an upper limit for ΔS, and therefore is quite compatible with the low value of ΔS which we would expect for reactions like this. By Process 2 we have $\Delta S = (1320 - 3010)/284 = -6.4$ cal/deg. This value is inadmissibly high, and would be still higher if the iodine pressure actually were lower than 0.055 mm.

In order to obtain a rough estimate of the amount of the dissociation at higher temperatures, the absorption tube containing ICl used in the experiments on the variation of intensity of absorption with temperature and containing ICl at about 500 mm was again placed in the furnace and by visual inspection the iodine bands were found to be absent at low temperatures, but strongly in evidence above 200°C. Another absorption cell, 5.3 cm long, containing iodine at known vapor pressure was then placed in series with the ICl tube, and the intensity of the iodine bands was compared visually (a) when the ICl was below 200° (showing no iodine bands) and the I_2 vapor pressure was 1.6 mm (corresponding to about 46°C), and (b) when the I_2 vapor pressure was zero (liquid air) and the ICl was slightly above 200°C. The intensity of the bands was nearly the same in (a) and (b). Unfortunately the experiment as carried out is faulty since a small excess of chlorine in the ICl will displace the equilibrium considerably and make the iodine bands appear too faint. With proper precautions, however, this experiment should give conclusive results, but unfortunately time was not available for a repetition.

Assuming that there was no excess chlorine in our rough experiment, we find $K = 0.53 \times 1.6/500 = 0.0017$, whence $\Delta F = R \times 473 \ln 0.0017 = 60{,}000$ cal.

Hence by Process 1, $\Delta S = (3830 - 6000)/473 = -4.6$ cal/deg, and by Process 2, $\Delta S = (1320 - 6000)/473 = -10$ cal/deg.

Even Process 1 gives too high a result, so that chlorine was probably present. A very large pressure of chlorine would have to be assumed, however, in order to reduce the 10 cal/deg of Process 2 to a reasonable figure. In all three thermodynamic calculations Process 1 is to be preferred, and taking this fact in conjunction with the interpretation of Series C given on page 604, it seems difficult to avoid the conclusion that dissociation by light into normal unexcited atoms actually takes place with somewhat greater intensity than the dissociation into excited chlorine and normal iodine.

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UNIVERSITY OF CALIFORNIA,
July 16, 1927.