- I. POTENTIOMETRIC DETERMINATION OF IRIDIUM.
- II. REDUCTION POTENTIAL OF QUADRIVALENT TO TRIVALENT IRIDIUM IN HYDROCHLORIC ACID SOLUTION.
- III. THE ABSORPTION SPECTRA, STRUCTURE, and DISSOCIATION ENERGIES OF THE GASEOUS HALOGEN CYANIDES.

Thesis

by

Sho-Chow Woo

In partial fulfillment of the requirements

for the degree of Doctor of Philosophy

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THE POTENTIOMETRIC DETERMINATION OF IRIDIUM

BY SHO-CHOW WOO AND DON M. YOST

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Introduction

In connection with a study of the reduction potential of the chloroiridous-iridic acids¹ it was necessary to develop good volumetric methods for the determination of the concentrations of the metal in its higher state of oxidation. In addition to this it was necessary to prepare solutions of chloroiridous and chloroiridic acids free from other elements of the platinum group and from the baser metals. Owing to the incomplete knowledge of the chemistry of the platinum group elements and the high cost of the iridium itself, both problems presented especial difficulties. In this paper are described a new method and a modified method for the volumetric determination of iridium, and incidentally the procedures used for the preparation of pure solutions of chloroiridous and chloroiridic acids.

The authors are indebted to Professor A. A. Noyes for valuable suggestions given during the course of the work.

Preparation of the Materials

Ammonium Hexachloroiridate.—Fairly pure metallic iridium in a finely divided state was first digested for three hours with a hot mixture of hydrochloric and nitric acids. This treatment removes any organic matter and the base metals as well as some of the platinum, the iridium not being much attacked. The residual metal was next intimately mixed with three times its weight of pure sodium chloride, and the mixture was heated to 650° for one hour in a quartz tube through which was passed a stream of chlorine. All of the platinum metals were converted by this procedure into the double chlorides. The mixture of the chlorides was dissolved in a small volume of dilute hydrochloric acid and the resulting solution was saturated with chlorine and then heated on a water-bath. This treatment resulted in the oxidation of the iridious to the iridic chloride and in the decomposition by heat of any quadrivalent palladium compounds.

To remove the palladium and rhodium, the solution of the chlorides was saturated with ammonium chloride and then cooled in an ice-bath. The precipitate (which contains the iridium) was filtered off and redissolved, and the solution was again precipitated as before. This procedure was repeated several times and yielded a product free from palladium and rhodium.

The resulting ammonium hexachloroiridate was next heated with concentrated nitric acid, fresh acid being added from time to time. To the residue in the flask was added concentrated perchloric acid, and the mixture was boiled until the greater part of the acid had been driven off; then more acid was added and the treatment repeated. Continued application of this procedure caused the complete volatilization of osmium and ruthenium as the tetroxides, leaving the iridium free from all platinum metals except platinum.

The residue was heated nearly to dryness and dissolved in a small amount of water.

¹ Sho-Chow Woo, This Journal, 53, 469 (1931).

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To the solution was added an excess of sodium bicarbonate solution and bromine water, and the resulting mixture was boiled. This caused the precipitation of iridic hydroxide, but not that of platinum. The precipitate was redissolved in hydrochloric acid and subjected again to the bicarbonate precipitation. This treatment was repeated several times. The final product, iridium hydroxide, was dissolved in hydrobromic acid and, after treatment with nitric and hydrochloric acids to convert the bromides to chlorides, the solution was saturated with ammonium chloride and cooled, and the resulting precipitate of ammonium hexachloroiridate was filtered off. In order to make sure that no sodium salts were present, the ammonium chloride precipitation was repeated several times. The resulting ammonium chloroiridate was washed with ice-cold water and then dried over concentrated sulfuric acid in a vacuum desiccator.

After each separation procedure a portion of the iridium-containing mixture was tested for the element being removed, using the dimethylglyoxime² test for palladium and the methods of Noyes and Bray³ for the other elements. These tests show the presence of 0.3 mg. or less of the elements tested for. The procedures for the removal of osmium and ruthenium give a very complete separation, and the test for palladium is quite sensitive. Therefore the only contaminating elements present to the extent of 0.3% or less are rhodium and platinum, since the purification was always carried out until the tests for the contaminating elements were negative.

Chloroiridic and Chloroiridous Acids.—The ammonium chloroiridate was digested for ten hours with aqua regia upon a water-bath until all of the ammonia had been destroyed, and the nitric acid was then destroyed by repeated digestion with hot concentrated hydrochloric acid. The resulting solution consists principally of a mixture of chloroiridic acid and hydrochloric acid. For use in the electromotive force measurements a portion of this solution was reduced to chloroiridous acid with pure redistilled alcohol, using the procedure described by Delépine.⁴ The small quantity of metallic iridium which separated was removed by filtering the solution through a hardened filter after the alcohol had been driven off by heating, and the solution was finally evaporated to dryness in a vacuum desiccator. The residue was dissolved in dilute hydrochloric acid of known strength.

Hydrochloric Acid and Other Analytical Reagents.—The best obtainable hydrochloric acid was redistilled and diluted with redistilled conductivity water. The other analytical reagents used were of c. P. grade.

The Methods of Analysis Studied

The iodometric method of analysis that has been described by Delépine⁴ was first tested. In this method a hydrochloric acid solution of the chloroiridate is reduced to the chloroiridite by potassium iodide, and the liberated iodine is titrated with thiosulfate with starch as an indicator. In this form the method was not accurate since the color of the solution obscured the end-point; but it was found to give very satisfactory results when benzene was used to determine the point at which all of the iodine had been reduced. The titrations were carried out in 0.1 to 0.2 N hydrochloric acid solutions in a volumetric flask whose volume was such that the benzene layer rose

² Wunder and Thuringer, Z. anal. Chem., 52, 101-104, 660-664 (1913); H. B. Wellman, THIS JOURNAL, 52, 985 (1930).

³ Noyes and Bray, "Qualitative Analysis for the Rare Elements," The Macmillan Co., New York, 1929, pp. 39, 117, 118.

⁴ Delépine, Ann. chim., 7, 277 (1917).

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into the neck when the last portions of thiosulfate were added. This procedure facilitated the determination of the end-point, especially when the narrow column of benzene was observed against a white background.

In the second method studied, titanous chloride was used for the estimation of quadrivalent iridium. This standardized reagent was added to a hydrochloric acid solution, and the end-point was determined electrometrically. During the initial stages of the titration the potential reaches a steady value after a short time, and at the end-point it changes abruptly from 0.65 to 0.4 volt. Some time, however, is required for the electromotive force to become constant near the end-point, and the stage at which the sharp change occurs may be considered to be the end-point only in case the titanous chloride is added very slowly. The addition of sodium chloride to solutions of chloroiridic acid free from other salts was found to increase the sharpness of the end-point. The initial concentration of the hydrochloric acid in the solutions titrated was from 0.1 to 0.2 N, and the total initial volume was 50 cc. The amounts of sodium chloride added to the titration mixtures varied from 2 to 3 g. The other half-cell consisted of a saturated calomel electrode.

For comparison the iridium in the ammonium salt and in the solutions was determined by the well-known gravimetric method of igniting the salt in a current of hydrogen. With the small amounts of material used extreme care was necessary to avoid the small accidental losses that usually accompany this method of analysis. The determinations differed by less than 1% in all cases, usually by not more than 0.5%.

An attempt was also made to determine iridium by precipitating it with strychnine sulfate, but the precipitation was found to be incomplete.

Results of the Test Analyses

In Tables I, II and III are presented, the results of analytical experiments in which the above-described methods were used. The iridium solutions were measured by weighing them in a pipet designed for the

L	A	B	LE	1	

Consistency of the Results by the Iodometric Method and Comparison with Those by the Titanous Chloride Titration

No.	H2IrCle soln., g.	Solution u Na ₂ S ₂ O ₃	sed, cc. TiCl3	Iridium per gram of solution, mg.
1	2.0483	7.57	1. 181	4.44
2	3.2762	12.10		4.44
3	2.5943	9.56	No Delitik	4.43
4	10.3615	14.05	A about a	1.630
5	10.4763	14.23	minger, Z.	1.634
6	8.1114	11.00	. 52. 985 (1.630
limost/7 1	9.4657	ve Analysis for 1	8.03	1.629
8	10.4119	811	8.87	1.635
9	11.2136	(1917)	9.55	1.634

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Con	APARISON OF THE I	ODOMETRIC AN	D GRAVIMETRIC N	AETHODS
Expt.	Milligram (NH4)2IrCl6	s taken Iridium	Milligrams of Iodometric	iridium found Gravimetric
610 V	37.4	16.3	16.3	monium. herael
2	47.5	20.8	20.7	trically is the sa
3	68.3	29.8	29.7	m the forming (
4	68.3	29.8	29.8	
5	81.3	35.5	· · ·	35.6

#### TABLE III

IODOMETRIC, TITANOMETRIC AND GRAVIMETRIC RESULTS COMPARED WITH THE CALCULATED IRIDIUM CONTENT OF AMMONIUM CHLOROIRIDATE

	(NH4)2ITC18	Milligrams per gram of	of iridium solution
Method	soln., g.	Found	Presenta
Iodometric	7.3742	2.758	
Iodometric	6.8145	2.763	
	I	Mean 2.761	2.766
Titanous chloride	9.6965	2.755	
Titanous chloride	8.7137	2.755	
Titanous chloride	9.0680	2.755	
	1	Mean 2.755	2.766
Gravimetric	15.9696	2.786	
	15.3795	2.766	
	1	Mean 2,776	2.766

 $^{\alpha}$  As calculated from the amount of  $(\rm NH_4)_2 Ir Cl_6$  known to be present per gram of solution.

purpose. The thiosulfate used was 0.00623 N. The titanous chloride used was 0.00994 N for the experiments of Table I and 0.009285 N for those of Table III.

It is seen from the tables that the two volumetric methods yield concordant results, the maximum deviation from the mean being about 0.3%. Moreover, the amount of iridium in the salt  $(NH_4)_2IrCl_6$  as determined volumetrically and gravimetrically is, within a few tenths of one per cent., the same as that calculated from the formula.⁵

#### Summary

The results (given in Tables I–III) show that the new titanometric method of determining iridium gives results in agreement with those given by the earlier iodometric method, which was refined by using benzene to

⁵ This tendency to form non-hydrated chloro salts is not found with some other platinum metals. The results of Howe [THIS JOURNAL, **49**, 2381 (1927)] and of Crowell and Yost [*ibid.*, **50**, 374 (1928)] emphasized this for the case of ruthenium, and at the same time clarified an important question in the chemistry of coördination compounds. Werner, "Neuere Anschaungen auf dem Gebiete der anorganischen Chemie," Vieweg und Sohn, Braunschweig, **1909**, 2d. ed., p. 292.

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detect the liberated iodine. Both these methods gave results in agreement with the gravimetrically determined amounts of iridium present in the solutions. They show, moreover, that the iridium content of crystalline ammonium hexachloroiridate as determined volumetrically and gravimetrically is the same, within a fraction of one per cent., as that calculated from the formula  $(NH_4)_2IrCl_6$ .

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" As calculated from the amount of (NH₂),IrCl₂ known to be present per gram of plation.

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I he value of this potential was derived from measurements of the electromotive force of the cell.

[Reprint from the Journal of the American Chemical Society, 53, 469 (1931).]

In order to reduce the liquid potential to a very low value, the concentration of the hydrochloric acid in the inidium solutions was made the same as that used in the hydrogen half-cell, and the total concentration of indium neutral value well.

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 273]

## REDUCTION POTENTIAL OF QUADRIVALENT TO TRIVALENT IRIDIUM IN HYDROCHLORIC ACID SOLUTION

By Sho-Chow Woo

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# any double because Introduction

It is well known that the most stable compounds of iridium in hydrochloric acid solution are the ions of hexachloriridic and hexachloriridous acids,  $H_2IrCl_6$  and  $H_3IrCl_6$ , in which the iridium is present in the quadrivalent and the trivalent states, respectively. Earlier investigations of these compounds were restricted to the determination of their formulas, and until very recently no studies had been made to determine their physico-chemical properties. Since this research was undertaken, however, Ogawa¹ has published measurements of the electromotive force of cells in which the sodium salts of the chloriridic and chloriridous acids were used. He observed steady changes in the electromotive force, and

¹ E. Ogawa, J. Chem. Soc. Japan, 50, 123 (1929).

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attributed this to the hydrolysis of the salts in the absence of any added acid. In view of the inconstancy of his results it seems desirable to present the determinations that have been made in this Laboratory of the reduction potential for the combination quadrivalent-trivalent iridium in hydrochloric acid solution

The value of this potential was derived from measurements of the electromotive force of the cell

Ir, 
$$\left\{ \frac{\operatorname{IrCl}_{6^{-}}(c_{1}f.)}{\operatorname{IrCl}_{6^{-}}(c_{2}f.)} + \operatorname{HCl}(1f.) \right\}$$
, HCl (1f.), H₂ (p atm.), Pt

The methods of preparation of the iridium solutions and the analytical procedures employed will be described in a later article.

This research was suggested by Professor A. A. Noyes, and to him and to Professor Don M. Yost the author is indebted for many helpful suggestions.

**Procedure for the Electromotive Force Measurements.**—The type of electrode vessel used was that commonly employed in this Laboratory.² The hydrogen was prepared by electrolyzing a solution of sodium hydroxide between nickel electrodes, and it was freed from oxygen by passing it over a glowing tungsten spiral. Before entering the cell, the gas passed through a hydrochloric acid solution of the same concentration as that in the cell.

In order to reduce the liquid potential to a very low value, the concentration of the hydrochloric acid in the iridium solutions was made the same as that used in the hydrogen half-cell, and the total concentration of iridium was made small.

The concentration of the hydrochloric acid in the iridium stock solutions was determined by titrating them with sodium hydroxide, using phenolphthalein as an indicator, after the quadrivalent compound had been reduced to the trivalent state with pure silver. The desired acid concentration for the cell solutions was attained by diluting the stock solutions with the proper amount of hydrochloric acid of known strength. The two half-cells were separated by an ungreased stopcock which was moistened with the acid but was kept closed.

It was found that gold and platinum (to a much less extent) were attacked by the chloriridic acid, but that iridium was not so attacked as was shown by the constancy of the potentials and concentrations. This fact resulted in the use of an iridium-plated glass tube as the electrode in the iridium half-cell. When nitrogen was bubbled through the iridium solution for the purpose of stirring it, the potential did not attain a constant value but usually decreased steadily. With a mechanical stirrer, however, the final electromotive force was reached in a few hours and then remained constant over long periods. The nitrogen may have

² Schuhmann, THIS JOURNAL, 46, 52 (1924).

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contained some oxidizable impurity, for the concentration of the quadrivalent iridium was found to be always less (even 30-40% less) at the end of an experiment than at the beginning. No concentration changes were observed when the mechanical stirrer was used.

**Results of the Electromotive Force Measurements.**—In Table I is given a summary of the observed values of the electromotive force. The total acid concentration was always 0.998 f. (hereafter regarded as 1.0 f.). The "corrected" electromotive forces given in the last column are the values of the electromotive force calculated by the usual logarithmic formula for the case that the pressure of hydrogen is one atmosphere and the concentrations of the two forms of iridium are equal. The given electromotive forces, expressed in volts, are those of the cell in the direction in which it was written above.

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$\mathbf{n}$	D		<u> </u>	

	<b>Results of the Electromotive Force Measurements</b>							
Ce	ll Temp °C.	., Formal c IrCl6	oncentration IrCle	Pressure of hydrogen	Electromoti Observed	ve force Corrected		
1	25	0.004864	0.005163	719.5	-1.02403	-1.0263		
.2	25	.004838	.005189	720.2	-1.02365	-1.0261		
3	25	.002477	.007631	719.7	-0.99689	-1.0265		
. 4	25	.001976	.008148	720.1	98910	-1.0262		
5	25	.001976	.008148	719.7	98953	-1.0267		
					Mean	-1.0264		
6	25			721.6	-1.02355	-1.0264		
	20			719.8	-1.02840	-1.0313		
7	25			721.7	-1.02243	-1.0264		
	20			720.7	-1.02735	-1.0313		

#### Discussion of the Results

The constancy of the corrected electromotive forces in Cells 1–5 shows that the ratio of the activity coefficients of the chloriridate ion and chloriridite ion does not change appreciably with change in their relative concentrations within the limits here involved. This behavior was to be expected since the difference in the ionic strengths of the solutions is small. Mention should be made, however, of the fact that less satisfactory corrected values were obtained with cells in which a large excess of the chloriridate was present. No explanation of this fact could be found. The difference, however, did not exceed 10 millivolts.

The mean value of the electromotive force at  $25^{\circ}$  is -1.0264 volts for the cell

M,  $IrCl_6=(cf.) + IrCl_6=(cf.) + HCl (1.0f.)$ , HCl (1.0f.), H₂ (1 atm.) By taking the mean activity coefficient of the ions in 1.0 f. HCl to be 0.823 as given by Lewis and Randall³ and assuming that the H⁺ and Cl⁻

³ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 336.

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ions have in this acid equal activities, this electromotive force may be referred to the molal hydrogen electrode, in which case it becomes -1.021 volts. This is the value for the hypothetical cell

M,  $IrCl_6^{=}(cf.) + IrCl_6^{-}(cf.) + HCl(1.0f.) H^{+}(1m.), H_2(1atm.)$ 

Under the usual conventions⁴ this value is also the molal electrode potential for the electronic reaction

#### $IrCl_6 = (c f.) = IrCl_6 - (c f.) + E^- (1 f.) in 1.0 f. HCl at 25^\circ$

In all these cases c is understood to have a value between 0.002 and 0.008 molal.

This potential corresponds to a greater reducing power than the value (-1.369 volts) for the chlorine electrode. It shows that chloriridous acid is oxidized to chloridic acid by chlorine at atmospheric pressure so completely that the unoxidized portion is entirely inappreciable.

The corresponding value of the free energy decrease attending the reaction

 $IrCl_6= (c f. in 1.0 f. HCl) + H^+ (1 m.) = IrCl_6- (c f. in 1.0 f. HCl) + 1/2 H_2 (1 atm.)$ or attending the above formulated electronic reaction (under the convention that the free energy change H⁺ at 1 m. + E⁻ = 1/2H₂ at 1 atm. is zero), is -23,540 cal. at 25°.

From the measurements of the electromotive force of cells 6 and 7 at 25 and at 20° the value  $\pm 0.00098$  volt/degree is obtained for the temperature coefficient dE/dT; and from this the corresponding value of the heat content increase  $\Delta H$  attending this last reaction is found to be  $\pm 30,400$  cal.

### Summary

There have been here presented measurements which show that halfcells consisting of metallic iridium in contact with a 1.0 formal hydrochloric acid solution of equimolal quantities of chloriridic and chloriridous acids (H₂IrCl₆ and H₃IrCl₆) at a concentration (c) between 0.002 and 0.008 formal, when measured against a half-cell consisting of a platinum electrode in contact with hydrogen gas at one atmosphere and with 1.0 formal hydrochloric acid solution, have an electromotive force of -1.0264 volts at 25°, and of -1.0313 volts at 20°. Referred to the molal hydrogen electrode (H⁺ with activity 1.0 molal), the value of the reduction potential at 25° is computed to be -1.021 volts for the reaction

 $\operatorname{IrCl}_{6}^{=}(c f. \text{ in } 1.0 f. \text{ HCl}) = \operatorname{IrCl}_{6}^{=}(c f. \text{ in } 1.0 f. \text{ HCl}) + \text{E}^{-}(1 f.)$ 

The corresponding value of the free energy decrease is -23,540 calories. From the temperature coefficient of the electromotive force, the heat content decrease for this electronic reaction is found to be -30,400 cal.

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⁴ See Noyes and Sherrill, "Chemical Principles," The Macmillan Co., New York, 1922, pp. 255–258.

# THE ABSORPTION SPECTRA, STRUCTURE, AND DISSOCIATION ENERGIES OF THE GASEOUS HALOGEN CYANIDES

# A. Introduction

Spectroscopic investigations have yielded a great deal of interesting and useful information regarding the nature and strength of binding of diatomic molecules, and it is now desirable to extend studies of this sort to cases of molecules built up of several atoms. Several attempts have been made to do this but in many instances the results obtained are difficult to interpret in an exact way since the nature and energy states of the products into which more complicated molecules may dissociate are not known. In order to obtain quantitative information regarding the strength of individual molecular bonds it seems advantageous to proceed gradually from very simple to more complicated cases, and in particular to choose for study those molecules about whose possible dissociation products we know as much as possible.

For this reason the cyanides seem to be very well suited for study, since the lower energy states of the cyanide radical are well known. Of these two have already been investigated, potassium cyanide by Villars,¹ and hydrogen cyanide by Badger and Binder.² As the subject of the investigation here described we have chosen the halogen cyanides, not only for the reason given, but because there has been considerable discussion as to the structure of these compounds without any very definite conclusion being arrived at, and because certain inconsistencies in the literature make an independent determination of their heats of formation of interest.

# B. Experimental Details

The substances used in the investigation were prepared as described below. In all cases chemically pure reagents were used.

<u>cyanogen chloride</u>. In the preparation of this substance concentrated hydrochloric acid was dropped from a separatory funnel into an all-glass generator containing a solution of potassium chloride, potassium chlorate, and potassium cyanide. The gas evolved was condensed in a receiver cooled with ice-water. The liquid collected had a slight yellowish-green tint which might have been due to the presence of some free chlorine. The liquid was then allowed to evaporate into the absorption cell which consisted of a pyrex tube 6 feet in length, closed at the ends with quartz plates attached by sealing wax. When the absorption spectrum of the gas was photographed immediately after preparation, the chlorine bands as well as bands in the rather far ultra-violet due to cyanogen, came out rather strongly. After the gas had stood for some time these disappeared completely. No polymerization occurred even when the gas was kept in the tube for several days.

Cyanogen bromide. The preparation of this substance was similar to that of the chloride. Potassium bromide and bromate were used instead of the corresponding chlorine compounds. The gas was driven from the solution of these substances and potassium cyanide by heating to 70-80°, and was condensed as a solid in the form of white crystals in a receiver cooled with ice-water. These crystals were then sublimed into the absorption cell and the pure solid condensed there could be preserved for over a month without any polymerization being evident. The gas used in the

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absorption experiments was that in equilibrium with the solid at room temperature, and was confined in an absorption cell three feet in length.

Cvanogen Iodide. In thepreparation of this substance pure iodine was resublimed and dissolved in ether to which an excess of mercuric cyanide was then added. After vigorous shaking the solution became colorless, indicating the completion of the reaction. The mercuric iodide which precipitated, and the excess mercuric cyanide were removed by filtration. On evaporation of the filtrate cyanogen iodide was obtained, mixed with considerable mercuric iodide. A purification by recrystallization from ether solution, and by sublimation, yielded a product with only a very faint orange tint. The three-foot absorption cell was used in this case, but as the absorption of the gas in equilibrium with solid ICN at room temperature was rather small it was found necessary to heat the absorption cell, which contained some crystals of the solid. to about 60°. In order to eliminate any absorption of free iodine which might be liberated by the dissociation of the compound, some cyanogen was introduced into the absorption cell. This gas gives rise to a set of discrete bands beyond  $\lambda$  2100, which are easily identified and were in no way troublesome.

As source of a continuous spectrum in the ultraviolet a conventional hydrogen discharge tube was used. The spectra were photographed with a small Hilger quartz spectrograph. Eastman D-C ortho plates were used, and in order to obtain a greater sensitivity in the ultra-violet they were oiled with a light transformer oil which was found to be especially suitable for the purpose.

# C. Experimental Results and Discussion

In the case of each gas only continuous absorption was found, and a careful search failed to detect any discrete bands. The spectra of the three compounds are entirely similar except that in the order ICN, BrCN, ClCN the absorption regions are displaced toward the short wave side, and the absorption becomes weaker in the same order. In the iodine compound two absorption regions were found, in the other cases only one, undoubtedly for the reason that the analogous second regions were further in the ultra-violet than could be reached by the quartz spectrograph. Since the absoprtion regions shade off rather gradually on the long wave side (and on the other side as well, where it can be observed), and since the apparent long wave limit shifts toward the red when the depth of absorbing gas is increased, it is not possible to give any definite long wave absorption limit. However, it is certain that absorption extends on the long wave side at least as far as the wave lengths given in Table I.

#### TABLE I

Long wave	Length	Limits	s of th	e continuous	Absorption	
	of	the l	Halogen	Cyanides		

Gas	Regi	Region a.		Region b.		t for dissociation olt electrons)
	λ	V	λ	ν	8.	b
ICN	>2900	ζ 34470	> 2100	<i><b>₹</b>47600</i>	4.26	5,88
BrCN	>2450	<b>&lt; 40800</b>			5.05	
CICN	72270	<b>&lt;</b> 44040			5.43	

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It is reasonable to assume that as a result of light absorption in the continuum of any of the halogen cyanides, a dissociation of the molecule takes place. This being the case we may calculate from the long wave limit of the absorption region an upper limit for a dissociation energy of the molecule. Values so obtained are given in the right of Table I. Before discussing the nature of the dissociation products we must consider the probable structure of the halogen cyanide molecules. As mentioned above there has been considerable discussion in this regard, though particularly relating to the molecules in solution. As regards the gaseous molecules, the similarity of the spectra, and the fact that they fall into a reasonable series, strongly indicates a similarity of structure for the three. In a previous paper² it has been shown that the hydrogen cyanide molecule has a linear structure represented by the formula HCN, and that the HNC molecule, if it exists, must be energetically very unstable. Similar but much stronger arguments may be advanced in this case. From a study of the heats of formation of CCl4 and COCL2 we may estimate the energy of the carbon-chlorine bond to be of the order 3.5 - 4.5 volts, while the energy of the nitrogen-chlorine bond is much smaller, say about 2 volts, as may be seen from data on NOCl and NCl. Consequently a CINC molecule which would be formed from an excited CN radical, probably that in the  $^{2}\pi$  state with 1.78 volts excitation energy,³ should lie at least 3.3 volts (75,000 calories) higher in the energy scale than CLCN formed from the normal CN radical. Though CLNC should consequently be very unstable the argument of course does not exclude the possibility that iso-cyanide molecules may be produced under certain conditions, and may have a relatively long lifetime. However, in the case of gaseous iodine cyanide it is known that an equilibrium is

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readily reached between this gas and iodine and cyanogen. It seems likely then that this gas can exist for an appreciable length of time in the unstable form. We shall assume for the time being that all three gases exist in the stable cyanide form, and, as will be seen later, this assumption is justified by the energy relations.

Since the optical dissociation energies are far too small to account for the splitting of the carbon-nitrogen bond, we may conclude that the dissociation products are a CN radical and a halogen atom, one or both of which may be in excited states. We may compare the spectroscopic values with the dissociation energies of the molecules calculated from the chemical heats of formation, the known energies of activation of the products, etc. The necessary data are expressed in the following equations:

 $E_{0} \quad C \text{ (graphite)} + \frac{1}{2}N_{2} = CN(normal) - 3.4 \text{ volts } (78,200 \text{ cals})^{2}$   $H_{298} \quad C \text{ (graphite)} + \frac{1}{2}N_{2} + \frac{1}{2}Cl_{2} = ClCN(g) - 1.58 \text{ volts } (36,400 \text{ cals})^{3}$   $H_{298} \quad C \text{ (graphite)} + \frac{1}{2}N_{2} + \frac{1}{2}I_{2}(c) = ICN(c) - 1.83 \text{ volts } (42,000 \text{ cals})^{3}$   $E_{0} \quad \frac{1}{2}Cl_{2} = Cl - 1.23 \text{ volts } (28,400 \text{ cals})^{4}$   $E_{0} \quad \frac{1}{2}I_{2}(c) = I(g) - 1.10 \text{ volts } (25,000 \text{ cals})^{3},4$ 

Unfortunately heat data on BrCN are lacking. Specific heats are also lacking for correcting the chemical heats of formation at room temperature to the absolute zero, but in any case the correction will be small in comparison with the dissociation energies. The heat of sublimation of ICN is not known but we shall probably not be greatly in error of we estimate it at -0.4 volts.

The dissociation energies of ClCN and BrCN into normal halogen atom, and normal cyanide radical, and into normal halogen atom and excited CN radical ( $^{2}\pi$  with 1.78 volts excitation energy) calculated from the above data are tabulated in columns 2 and 3, respectively, of Table II. In columns 4 and 5 are given the spectroscopic values for all three substances.

#### TABLE II

Dissociation Energies of the Gaseous Halogen Cyanides

Gas	Dissociation Energy							
	Chemical		Spectros	copic				
	products:	products:	(a)	(b)				
	halogen(normal) + CN(normal)	halogen (normal + $CN^*(^2 1)$						
ClCN	3.04 volts (74,700 cal)	4.82 volts (112,000 cal)	ζ5.43 τ.					
BrCN			ζ5.05					
ICN	2.27 volts (52,000 cal)	4.05 volts (93,000 cal)	<b>&lt;</b> 4.26	<5.88 v.				

It is seen that the energy of dissociation into normal products, calculated from the chemical heat of formation, is about what one would expect for the breaking of a carbon-halogen bond, and is much larger than would correspond to breaking a nitrogen-halogen bond. We may conclude that the molecules in their normal state are built from the normal CN radical and normal halogen atom. Since the spectroscopic dissociation energies are much larger than the energy of dissociation into normal products, dissociation by light absorption must result in at least one excited product. Since the lowest excitation energy of the iodine atom is 0.94 volts it is evident that only one of the dissociation products of ICN can be excited when dissociation takes place as a result of absorption in region (a). The rough agreement between the spectroscopic value and the second chemical value in the table indicates that it is the CN which is excited. This is confirmed by the data on ClCN, since the excitation energy of chlorine is only 0.11 volts. The relatively large discrepancy in this case between the spectroscopic value and the second chemical value is to be explained by the weak absorption of this gas which leads one to estimate the long wave absorption limit relatively further in the ultra-violet than in the other cases. To make the results strictly comparable it would have been necessary to use a much longer tube of gas than circumstances permitted.

It is not possible to decide definitely whether absorption in the region (b) of ICN results in dissociation into an excited iodine atom with 0.94 volts energy and a CN radical ( ${}^{2}\mathbf{T}$ ) with 1.78 volts energy, or into a normal iodine atom and a CN radical ( ${}^{2}\mathbf{\Sigma}$ ) with 3.19 volts energy.

Several attempts were made to demonstrate directly the nature of the dissociation products by fluorescence experiments, but unfortunately they were unsuccessful. One might expect that when the gases are illuminated with light of a wave length lying in the region of continuous absorption one should obtain the red cyanogen bands in fluorescence. The conditions are, however, very unfavorable for obtaining such a fluorescence. The absorption, even at the maximum of the continuum, is not very strong and if one uses sufficient gas pressure to obtain appreciable absorption one should expect the fluorescence to be almost completely quenched. Some experiments were made in which ICN gas was illuminated with a mercury arc, and some in which BrCN was illuminated with a cadmium arc, and some in which BrCN was illuminated with an iron arc. No

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fluorescence was visible to the eye even under very staisfactory conditions as to a black background, etc. In an investigation using a very fast glass spectrograph and dicyanin plates it was found that any fluorescence present was weaker than stray light which was excluded as far as possible.

As noted above the chemical dissociation energies show that the halogen cyanide molecules in the lowest energy state are formed from normal halogen atom and normal cyanide radical. The nature of the absorption spectra is strong indication that in the two next higher excited electronic states we have a case of repulsion at all distances, or possibly a very small minimum in the potential energy curve at a relatively large distance of separation of halogen atom and cyanide radical. The probable state of affairs is represented in Figure 1.

This is indeed what one should expect. The normal cyanide radical, since it is formed from a normal nitrogen atom and a carbon atom in the ⁵S state (tetravalent)⁵, is capable of forming one shared electron pair bond between the carbon atom and some other atom and radical. The ² $\Pi$ cyanide radical, on the other hand, is formed from the ³P carbon atom (divalent) and one should expect no tendency for molecule formation when an atom is brought up on the carbon side of this radical.

# FIGURE I

# GENERAL SHAPE OF POTENTIAL ENERGY CURVES FOR HALOGEN CYANIDES

(ICN AS AN EXAMPLE)



# Summary

1. The absorption spectra of the gaseous halogen cyanides has been investigated in the ultra-violet. Regions of continuous absorption only were found, with the following long wave length limits: ClCN,  $\lambda > 2270$ ; BrCN,  $\lambda > 2450$ ; ICN,  $\lambda > 2900$  and  $\lambda > 2100$ .

2. The similarity of the spectra and their relation to each other suggests a similar structure for all three molecules.

3. Consideration of thermochemical and spectroscopic data together shows that in the normal state the halogen cyanide molecules are built from normal halogen atoms and normal cyanide radical, and in the first excited electronic state from normal halogen atom and excited CN radical in the  $^{2}T$  state. The structures are probably those represented by the formulas: ClCN, BrCN, ICN.

4. The thermochemical heats of formation of the ClCN and ICN seem to be in substantial agreement with the spectroscopic values.

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