THE EFFECT OF FLUORESCENCE AND DISSOCIATION ON THE IONIZING POTENTIAL OF IODINE VAPOR.

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SYNOPSIS.

Fluorescence and ionization.—When fluorescing under the influence of the mercury green line, *iodine vapor* shows weak ionization at a potential about 2.6 volts less than the normal ionizing potential. This is attributed to ionization by impact against molecules whose electrons have been displaced by absorption of the exciting radiant energy.

Dissociation and ionization.—Another weak ionization always observed at about 1.5 volts less than the normal ionizing potential was attributed to ionization of atomic iodine, present as result of the dissociating action of the hot filament. This was verified by experiments in a pyrex glass apparatus at such high temperatures as to cause a high percentage of dissociation, when it was found that this new type of ionization was very intense.

The observed ionizing potentials were: 6.8 volts, due to fluorescing molecules; 8 volts, due to iodine atoms; 9.4 volts due to iodine molecules. The difference between the first and last values corresponds roughly to the *quantum* of absorbed radiant energy, while the difference between the two latter values agrees accurately with the *heat of dissociation* of iodine molecules.

PART I. FLUORESCENCE.

Introduction.

ACCORDING to present theories of atomic structure an electron in an atom is in stable equilibrium only in certain definite positions or orbits and the transfer of an electron from one position to another is accompanied by the absorption or emission of energy. In an atom of gas in the normal state the electrons are grouped as closely as possible about the center leaving the outer, less stable, orbits unoccupied. On the other hand, during the emission of light, as has been very clearly set forth in a recent paper by Drs. Foote and Mohler,[1] an electron is supposed to be falling back toward the normal oribit after having been knocked wholly (ionization) or partly out of the atom. Careful researches by Whiddington[2] and by Henry[3] have failed to detect any ionization in fluorescing iodine vapor. Apparently, therefore, since fluorescence is not accompanied by ionization, it must result from the temporary dis-

[1] Phil. Mag., 40, p. 80, 1920.

[2] Whiddington, Proc. Camb. Phil. Soc., 15, p. 189, 1909.

[3] Henry, Proc. Camb. Phil. Soc., 9, p. 319, 1898.

placement of an electron to one of the outer orbits. On this hypothesis it is obvious that the work required to ionize a fluorescing atom or molecule should be less than that necessary to ionize an atom or molecule in the normal state. As suggested by Hughes,[1] this is probably the explanation of the results of Franck and Westphal,[2] who found the current in a glow discharge through iodine increased by fluorescence. The present research was undertaken in the hope of observing this predicted reduction in the ionizing potential of iodine vapor, the fluorescence of which has been so thoroughly investigated by Wood.

Apparatus and Procedure.

The ionization tube used was of the ordinary three-electrode type with plate, *P*, gauze, *G*, and filament, *F*, of platinum and a ground-glass joint to allow replacement of the filament. As will be seen from the diagram in Fig. 1, its only unusual features are its dimensions. The

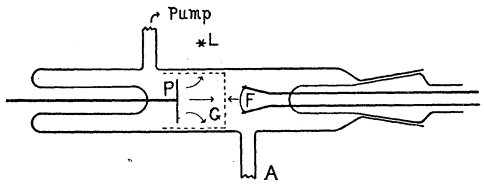

Fig. 1.

diameter of the tube was made small, about 1.5 cm., in order that the exciting light might not be too greatly cut down by the absorption of the vapor before getting into the region where impacting electrons were most numerous. The direction of the retarding field resulting from the shape of the gauze tended to spread the electrons toward the walls of the tube and was thus a second factor favoring impact of electrons with fluorescing molecules. An accelerating field was applied between *F* and *G* and a retarding field larger by a constant amount, between *P* and *G*. The gauze *G* was connected to a Leeds & Northrup high sensitivity galvanometer which measured the electronic current between *F* and *G*. The disc *P* was connected to Dolazelek electrometer of sensitivity about 3,000 millimeters per volt, making the capacity of the electrometer system of the order of magnitude of 50 cm. The potentials were read on a Robt. W. Paul voltmeter.

In order to get increased emission the filament was coated with barium oxide. It was found, however, that a very large emission in vacuum was tremendously reduced by the presence of iodine and after a few hours use became so small as to make the detection of minor effects difficult.

[1] A. L. Hughes, Photo-Electricity, p. 21, 1914.

[2] Franck & Westphal, Verh. d. D. Phys. Ges., 14, p. 159, 1912.

To introduce the iodine, the distillation apparatus shown in Fig. 2 was sealed on to the side tube, A, of the ionization tube. The whole system was first heated and pumped out with a Gaede mercury pump for several hours, and a liquid air trap between the pump and the apparatus was given time to take out all mercury vapor. Then the distillation tube at C was opened, Kahlbaum resublimed iodine introduced into M, and the glass again sealed off. Keeping liquid air on M, the pump was started again and after further heating of N and evacuation the iodine was sublimed over into N. Now, by raising N above liquid-air temperature iodine vapor was made to flow through the apparatus to the trap on the other side, thus giving a pressure in the apparatus somewhere between the vapor pressures at the temperature of N and at the temperature of liquid air. By the above procedure and by keeping the pump running continuously, disturbances due to gases evolved by the glass or by the filament were reduced to a minimum.

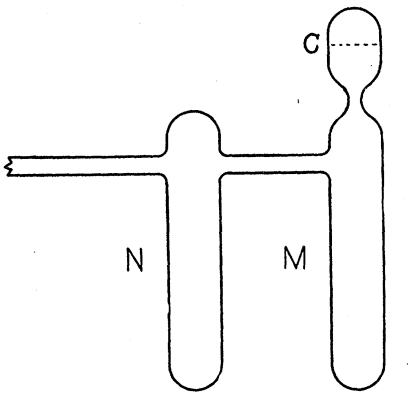

Fig. 2.

To excite fluorescence, a Cooper Hewitt quartz mercury arc was used. It was mounted about 2 in. above the ionization chamber and across it, so that the maximum amount of light fell on the part of the tube between P and G. A sheet copper shutter was arranged so as to completely cut off the light, making possible alternate readings with and without fluorescence.

Since the electrometer system had a considerable zero leak, readings were started with the accelerating field V_A sufficiently low to establish a good zero line. Then V_A was increased in small steps and two readings taken at each value, one with the shutter open and one with it closed. In several runs this was further checked by reading with the shutter closed, then open, then closed again at each voltage. Ionization was, as usual, detected by a sharp change in the rate of deflection of the electrometer. Velocity distribution measurements were made frequently though, as will appear later, no great importance was attached to them.

Experimental Results.

The results of two typical runs are plotted in Figs. 3 and 4 below. In each case there are two curves for each run, one drawn through points

taken with the shutter open (circles) and one through the points with the shutter closed (dots).

On the first of these runs, No. 4, Fig. 3, in the fluorescence curve there are three distinct break points at about 5.5, 6.6 and 8.4 volts respectively,

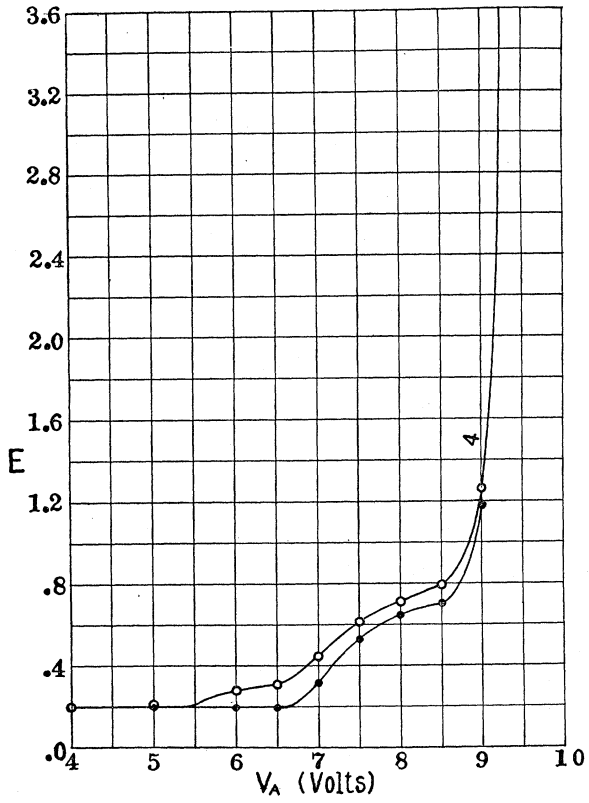

Fig. 3.

but only the two higher of these appear on the normal curve. Run No. 5, Fig. 4, shows exactly the same effects coming at 6, 7.3, 8.5 and 7.4 and 8.5 volts, but the curves rise much less steeply, as would be expected from the fact of smaller emission. Apparently the two lower breaks are due to very improbable types of impact since they both seem to approach saturation rapidly as the voltage is raised. The lowest break appearing only on the fluorescence curves, is naturally attributed to ionization of fluorescing molecules. To explain the middle break which was totally unexpected, the authors were forced to the conclusion that it is due to the ionization of atomic iodine produced by the dissociation of molecules by the hot filament. The correctness of this view was

demonstrated by further experiments which are described in the second part of the present paper. Since atomic iodine has no absorption bands in the visible spectrum[1] it would not be affected by the presence of the mercury arc. All discussion of this second effect will therefore be post-

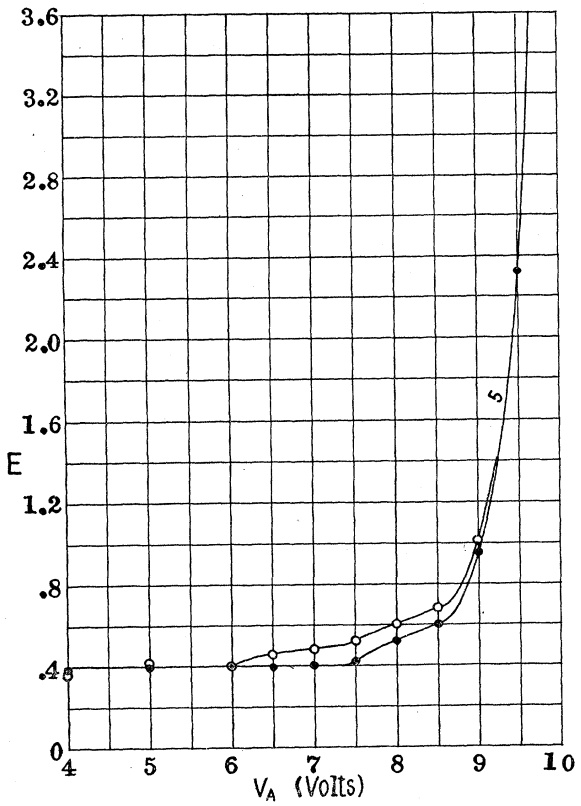

Fig. 4.

poned to the second part of the paper. The third break point which appeared very strongly even with very small emission is presumably due to ionization of normal, unexcited, diatomic iodine vapor.[2] Before further discussion it will be well to present a complete summary of our experimental results.

where

p = pressure in mm. Hg. (approximate),

G = current to gauze in amperes $\times 10^{-9}$.

[1] E. J. Evans, Astro. Phys. J., 32, p. 1, 1910.

[2] F. L. Mohler & P. D. Foote, PHYS. REV., 15, p. 321, 1920.

Discussion of Results.

The values given in this table have been corrected for velocity distribution as nearly as possible according to the formula derived in a previous paper[1] but on account of the shape of the gauze used and the difficulty of estimating the probability of ionization by a collision in iodine, no great degree of accuracy can be claimed, probably considerably less than indicated by the calculated probable error.

However, it is not so much the absolute values of the points a and c which concern us here as it is the difference between them, as given by the last column of Table I., and this is independent of the velocity

TABLE I.

Run.	p.	G.	Corrected Breaks.					$c-a$.
			Fluorescence.			Normal.		
			a.	b.	c.	b'.	c'.	Volts.
1	.005	2.6	6.4		9.		9	2.6
2	.15	14.2	6.9	8.2?	9.5	8.2	9.7	2.6
3	.15	4.9	6.7	8.2	9.7	8.2	9.7	3.
4	1.	155.	6.2	7.3	9.0	7.3	9.2	2.8
5	.25	9.5	6.	7.3	8.5	7.4	8.5	2.5
6	.15	2.5	5.5?	6.7?	8.5		8.5	3. ?
7	1.	700.		8.7?	10.2?	8.7	10.2	
8	1.	150.	6.9	7.8	9.7	7.8	9.7	2.8
9	.13	11.4	7.	8.6	9.5	7.7	9. ?	2.5
10	.13	21.	6.	7.7	9.5?	7.2	9.5?	3.5?
11	1.	11.5	5.7	6.8	8.2	6.8	8.4	2.5
Average omitting doubtful (?) values			6.42 ±0.11	7.67	9.07 ±.42	7.7	9.21	2.66 ±.04

distribution corrections. The mean value of $c - a$, 2.66 ± .04 volts, should be the difference in the work necessary to remove an electron from a fluorescent molecule and from a normal molecule. Now the shortest lines observed by Wood[2] in the fluorescent spectrum of iodine excited by a quartz mercury arc are of the group of − 1 order having a wave-length about 5370 Å.U. while the wave-length of the exciting light is 5460.7. If we apply the quantum relation to these wave-lengths we get 2.3 volts and 2.26 volts respectively. We would expect, then, 2.3 volts to be the maximum gain in potential energy of a molecule due to fluorescence and the greatest possible shift in its ionizing potential. The value of the resonance potential for iodine found by Mohler and Foote[3] is 2.34 ± .2 volts

[1] Smyth, PHYS. REV., 14, p. 409, 1919.

[2] R. W. Wood, Researches in Physical Optics, Part II., p. 29.

[3] Loc. cit.

which would indicate that this is a natural quantum for an iodine molecule to absorb and thus agrees approximately with our last statement.

The discrepancy between this theoretical value of about 2.3 volts and the observed values of 2.66 ± .04 may very likely be due to some constant experimental error but this seems sufficiently improbable to make a brief consideration of other more deep-seated possibilities worth while. The first of these is the fact that there is a strong absorption band[1] for iodine in the blue green region corresponding to 2.66 volts and there are lines in the mercury arc at $\lambda = 4358$ and 4916.4 corresponding to 2.83 and 2.51 volts. The iodine molecule might absorb energy in this region but radiate it in two or more steps so that it would not give lines of such short wave-length in the fluorescent spectrum. In this case, however, we would still expect a stronger effect from the much more intense green line.

A second possibility is that, due to the increased radius and instability of a fluorescent molecule, the probability both of collision and of ionization at collision is greatly increased. This ionization effect is therefore much more probable per molecule than an ordinary ionization and therefore tends to be detected at a relatively earlier point on the curve. The much greater number of the normal molecules would counteract this tendency to a greater or less degree.

A third possible contributing factor is the absorption of heat waves from the filament after the molecule has already absorbed the quantum corresponding to 2.26 from the mercury arc. The difference between 2.26 and 2.66, or 0.4 volt, gives a wave-length of 2.09 $\mu\mu$ which would certainly be present in the radiation from the filament.

Finally, the discrepancy between the observed and expected values may be due to the effect of a negative surface layer on the platinum gauze G, tending to repel electrons and consequently tending to make the observed values of V_A greater than the actual values. Such layers are known to occur in the electronegative gases. If present, such a layer would reduce the effective accelerating field to the greatest extent where the electron current is most intense, *i.e.*, near the center of the gauze. The electrons whose impacts contribute most to the ionizaton of fluorescent molecules pass through the gauze near the outside of the tube, while the intensity of the ordinary ionization is due principally to electrons which pass near the center of the gauze. Consequently the observed value of the normal ionizing potential would be shifted more than the fluorescent ionizing potential, and in a direction to account for the discrepancy.

[1] Wood, op. cit., p. 23.

In view of these considerations, the agreement of observed and expected values is probably as good as could be expected. In any case, it is important to have definitely established the effect of fluorescence in decreasing the ionizing potential.

PART II. DISSOCIATION.

Introduction.

According to the results of Starck and Bodenstein,[1] iodine vapor at a pressure of .01 mm. and temperature of 450° C. would be nearly 50 per cent. dissociated or at a pressure of .05 mm. it would be 25 per cent. dissociated. At 500° C. and .03 mm. the degree of dissociation would be about 40 per cent. From this it is evident that any effect due to atomic iodine should be greatly accentuated by running at a temperature between 450° C. and 500° C. if the pressure is kept low. This suggested the following method for investigating the ionization of atomic as distinguished from molecular iodine.

Apparatus and Procedure.

As has already been stated the effect *b* in the experiments on fluorescence was attributed to the ionization of atomic iodine. In order to test this theory a new apparatus, made of pyrex glass, was mounted in an electric heater so that its temperature could be raised to more than 500° C. The electrodes were the same as before but the tube was about twice as long so that each end projected outside the heater. This made it possible to keep the ends of the tube cool and so helped to prevent electrical leaks. Platinum guard rings wrapped around the outside of the tube served the same purpose. The temperature was measured by a platinum resistance thermometer.

The iodine distilling apparatus in this case was connected with a T-joint between the ionization tube and the pump. As before, mercury vapor was kept out by a liquid air trap but now the pressure was regulated by the temperature of a U-tube between the T-joint and the main apparatus, a large amount of iodine being first condensed in it by using liquid air. In this way, using the equation given by Baxter and Grose[2] for the vapor pressure of iodine, and knowing the exact temperature of the U-tube a much more accurate value for the pressure could be obtained than in the previous case, where there was a flow through the tube.

In spite of all precautions the electrical leak at high temperature was serious. It was found, however, that it increased uniformly with voltage

[1] G. Starck & M. Bodenstein, Zs. Elch., 16, p. 966, 1910.

[2] G. P. Baxter and M. R. Grose, J. Am. Ch. S., 37, p. 1061, 1915.

so that a good zero line could be determined for each run by a series of measurements with the filament turned off. Otherwise the procedure was similar to that of the previous experiment.

Experimental Results.

In Figs. 5 and 6 below are given the graphs of three runs which illustrate the confirmation of our theory by this high temperature apparatus. Thus, in run 15, Fig. 5, taken at 515° C., we have both break points appearing at 8.3 and 9.7 volts, respectively, but by comparing with Figs. 3 and 4 we see that the first effect is very much greater than in any

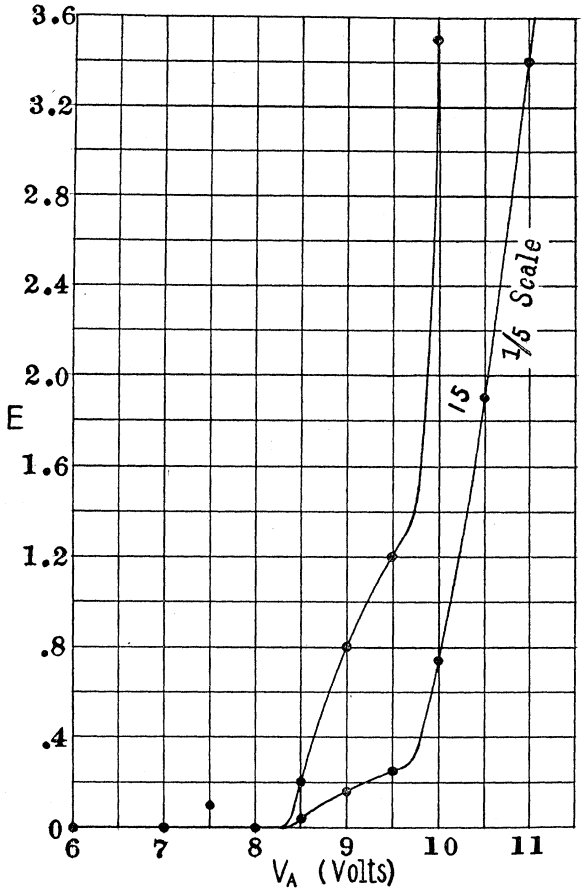

Fig. 5.

of the runs on fluorescence. Again, in Fig. 6, are plotted two runs taken one immediately after the other under conditions identical except for the temperature of the furnace. In the case of run 17 at 475°, the first

type of ionization is so intense as to completely mask the second whereas in run 18 at 25° it is barely detectable.

The other curves obtained were similar to those shown. A summary

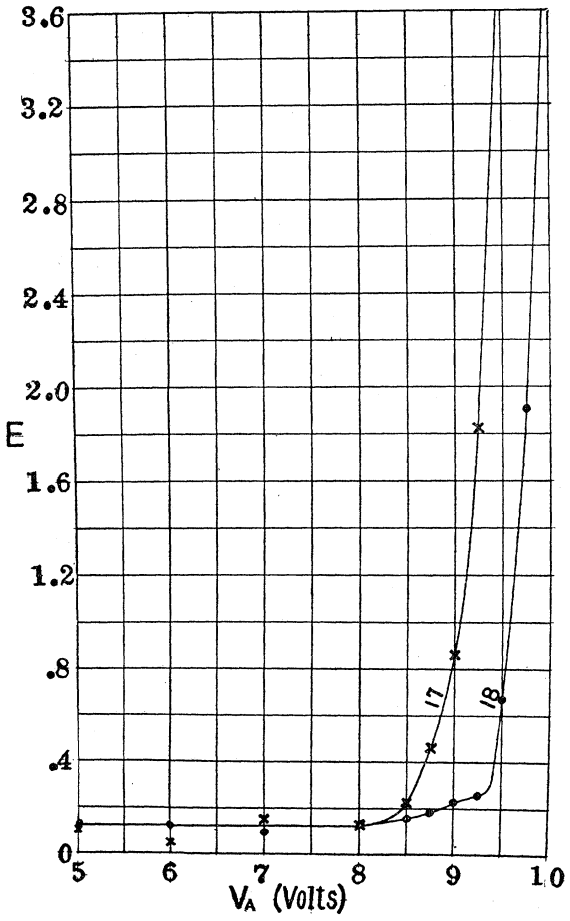

Fig. 6.

of results is given in Table II. The same uncertainty applies to the velocity distribution correction as in the former runs.

where

p = pressure in mm. Hg.;
T = centigrade temperature of apparatus;
G = current to gauze in amperes $\times 10^{-9}$.

TABLE II.

Run.	p.	T.	G.	Corrected Breaks.		
				b.	c.	$c-b$.
12	.01	430°	38–15	8.6	10.2	1.6
13	.01	475°	9–2	8.5	10.2	1.7
14	.032	476°	1.8–2.6	8.7?	——	
15	.032	515°	3.7±	8.9	10.3	1.4
16	.032	475°	5.5	9.3	10.5	1.2
17	.032	475°	3.5	8.5	——	
18	.032	25°	4.5–4	8.4	9.6	1.2
Average omitting doubtful values.....				8.7	10.16	1.42
Average including b, c, and b', c' from runs 1–11				8.0±0.1	9.4±0.1	1.47±.045

Discussion of Results.

The final values at which we arrive, therefore, are 8.0 ± 0.1 volts for ionization of an iodine atom and 9.4 ± 0.1 for ionization of the molecule where uncertainties not taken care of by the calculated probable error may probably reduce the accuracy of these values considerably. The fact that the values in runs 12 to 18 are consistently larger than in runs 1 to 11 emphasizes the possibility of some constant error. Due consideration of the various doubtful factors leads to the conclusion that 8.0 ± 0.5 and 9.4 ± 0.5 would roughly represent the accuracy of our results. The value 9.4 ± 0.5 for molecular iodine agrees within the limits of experimental error with 10.1 ± 0.5 found by Mohler and Foote.[1] The ionizing potential of atomic iodine has not been measured before.

However uncertain may be the determination of absolute values of the above potentials, the difference between them is definitely given. By averaging the values of $c - b$ and $c' - b'$ for runs 1 to 11 and $c - b$ for runs 12 to 18 we get the value 1.47 ± .045. Now the heat of dissociation of iodine vapor is about 35,000 calories per gram molecule[2] which corresponds to 1.52 volts per molecule. The natural inference drawn from this close agreement is that ionization of molecular iodine is accompanied by dissociation. This is predicted by Bohr's theory for hydrogen and has apparently been found experimentally by Mohler and Foote[3] and by Franck, Knipping and Krüger.[4] The latter authors, however, also attribute one of their effects to ionization without dissociation, the occurrence of which in iodine was not observed. Due to the difficulty

[1] Loc. cit.

[2] Starck & Bodenstein, loc. cit.
Bjerrum, Zs. Physikal. Ch., 81, p. 281, 1912.

[3] F. L. Mohler and P. D. Foote, J. Optical Soc. Am., IV, p. 49, 1920.

[4] Franck, Knipping and Krüger, Ber. d. D. Phys. Ges., 21, p. 728, 1919.

in getting thermal dissociation of hydrogen, the methods of distinguishing effects of atomic and molecular ionization are necessarily indirect and there has as yet been no work done on this question for other diatomic gases.

PART III. GENERAL DISCUSSION.

The results of the foregoing investigations are of interest in that they afford evidence regarding possible modes of ionization and of photochemical action.

It has been suspected that ionization may, under suitable conditions, be accomplished in two stages, the first being the removal of an electron to a less stable position by the absorption of the appropriate amount of radiant energy of proper frequency, and the second being the further complete removal of this electron by a collision. This method of ionization would account for the ionization which has been observed at the resonance potential in low voltage arcs, and has been indirectly shown to be effective in the ionization of helium.[1] It appears to be proven directly in the present experiments.

It is generally assumed that the primary effect of light in photochemical reactions is to displace or "loosen" an electron of the activated molecule so as to render it physically less stable, or chemically more active. There is some doubt regarding the nature of this "loosening." Experimental evidence, and also the known conditions of ionization, render it unlikely that this loosening consists in complete ionization in the great majority of cases. On the other hand, partial ionization or displacement seems capable of accounting for the so-called "primary" photochemical actions; and such displacement with reëmission of radiant energy following the chemical reaction seems to account for the "secondary" actions.[2] The present investigation of fluorescing iodine may be thought of as a measurement of the degree of loosening of the electrons by light, and such loosening has been found to be given, at least approximately, by the quantum relation. Apparently the effect of the light is not, in this case at least, the dissociation of some of the molecules—an explanation of photochemical action recently suggested by Nernst.

The results of the present investigation are evidently in accord with the viewpoint recently suggested by Perrin,[3] whereby quanta of radiant energy are emitted or absorbed in all chemical reactions.

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[1] K. T. Compton, Phil. Mag. in print.
K. T. Compton, E. G. Lilly, and P. S. Olmstead, PHYS. REV. in print.

[2] Bodenstein, Zeitsch. Phys. Chem., 85, p. 329, 1913.

[3] Ann. de Phys., 11, p. 5, 1919.

Note added with the proof.—Clifton G. Found has published data on the ionizing potential of iodine, among other gasses, in a recent number of the PHYSICAL REVIEW (Vol. 16, p. 41, 1920). He interpreted his results as due to a *single* type of ionization, drawing an average smooth curve through his plotted points, and concluding that the ionizing potential is $(25)^{2/3}$ or 8.5 volts. A closer examination of his results shows, however, that there are *two* break points, a pronounced one at $(31)^{2/3}$ or 9.8 volts and another, less sharply defined, at about $(24)^{2/3}$ or 8.3 volts. It is significant that these agree, within the limits of probable error, with the ionization potentials of molecular and atomic iodine found by us.