

Quenching of Iodine Fluorescence by Iodine and Argon

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In iodine below pressures of 0.8 mm fluorescence was excited monochromatically by the mercury green and yellow lines and measured by photographic photometry with a spectrograph. Absorption measurements were made under similar conditions with two compensating photoelectric cells: Beer's law holds here; and argon does not alter the absorption of iodine. The ratio of probability of

an excited molecule losing all energy in an iodine collision to probability of radiation is evaluated per unit time. The ratio exceeds unity for pressures above 0.05 mm. The yellow excited series is quenched more than the green by both iodine and argon. The complex nature of argon quenching is discussed.

IN analogy to the theory of Loomis and Fuller¹ on oxygen quenching, Turner has suggested that argon may also enhance a predissociation of the excited iodine molecule,² both of these phenomena being similar to the magnetic predissociation shown by Turner³ and supported theoretically by Van Vleck.⁴ The present investigation was undertaken to learn more of the action of argon upon iodine fluorescence. The resonance series excited in iodine vapor by monochromatic mercury light was discovered by Wood.⁵ The accepted interpretation is that of Lenz,⁶ *viz.*, that molecules are excited to one particular vibration and rotation state, and that transitions down to states of lower vibrational quantum numbers (with rotational quantum numbers differing by ± 1) give rise to the observed series.⁷ With the hot arc used here the green line may be absorbed by as many as 12 lines in the iodine absorption spectrum, but exposures as short as 20 minutes are permitted. The use of either the green or yellow lines of a

hot arc produced two distinctly separate groups of excited states, enabling one to find the effect of the quenching collisions on each group of vibration levels.

In general when a foreign gas quenches fluorescence radiation, it thereby shortens the mean lifetimes of the radiating molecules; and with this is associated a broadening of the absorption lines to those states. It was therefore necessary to know what effect the argon had on the amount of mercury light absorbed, and absorption experiments were made. This absorption work also showed how the exciting light was weakened by the iodine vapor before reaching the sheath from which the fluorescence was photographed. The absorption measurements will be discussed first.

An interpretation of the quenching of argon, as shown later, demands a knowledge of the quenching of iodine by itself. So the absorption of pure iodine and the autoquenching of pure iodine have been experimentally obtained. In fact this forms the major portion of this paper. No use could be made of the work of Wood and Speas⁸ on iodine autoquenching, since they excited with the full mercury spectrum.

ABSORPTION MEASUREMENTS

Pure iodine

The absorption of the iodine was measured by dividing the light from the end of a mercury arc

* The experimental work was done in the Palmer Physical Laboratory of Princeton University.

¹ F. W. Loomis and H. Q. Fuller, *Phys. Rev.* **39**, 180 (1932).

² L. A. Turner, *Phys. Rev.* **41**, 627 (1932).

³ L. A. Turner, *Zeits. f. Physik* **65**, 464 (1930).

⁴ J. H. Van Vleck, *Phys. Rev.* **40**, 544 (1932).

⁵ R. W. Wood, *Phil. Mag.* [6] **21**, 261 (1911); **35**, 236 (1918).

⁶ W. Lenz, *Phys. Zeits.* **21**, 691 (1920).

⁷ For a fuller account and bibliography through 1927, see P. Pringsheim, *Fluorescenz und Phosphorescenz*, p. 40 ff., Springer, Berlin, 1928.

⁸ R. W. Wood and W. P. Speas, *Phil. Mag.* [6] **27**, 531 (1914).

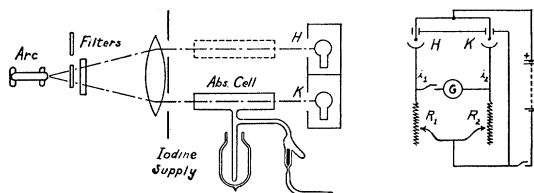


FIG. 1. Absorption apparatus and circuit.

into two parallel beams (see Fig. 1), each of which fell on a photoelectric cell (new G.E. type PJ14) with the absorption chamber in the path of one beam. The arc operated at 2.8 amperes under a drop of 90 volts. In both the absorption and fluorescence experiments the mercury green line (5462.23Å) and the un-separated yellow lines (5771.2Å and 5792.3Å) were isolated by Zeiss monochromatic filters. These were mounted edge to edge on the end of a moveable arm, and afforded data for both the green and yellow absorption at each pressure of iodine. For the absorption work an additional filter of nickel nitrate solution was used to remove all but one percent of the wave-lengths longer than 6000Å,⁹ which are not absorbed by iodine.

Two evacuated sealed-off absorption cells were used, each constructed of 4 cm Pyrex tubing with internal lengths of 9.34 cm and 3.93 cm, and with optical Pyrex windows fused on. Iodine crystals were in a side tube immersed in a constant temperature bath, and the absorption cell was in an oven maintained at 50°C. Vapor concentration was calculated from pressure-temperature tables,¹⁰ by using the formula

$$n_i = (P \cdot N) / (R \cdot T) = (P/T) 9.72 \times 10^{18}$$

(P in mm of mercury).

The electrical circuit embodied a null compensation principle. (Fig. 1.) If i_1 is the current from the photoelectric cell receiving light directly from the arc; and if i_2 is the current from the cell in whose path is placed an *empty* absorption tube; and if R_1 and R_2 are the respective resistances in series with these cells: then at zero galvanometer deflection

$$i_1/i_2 = R_2/R_1 \quad \text{and again} \quad i_1'/i_2' = R_2'/R_1,$$

where the primed quantities indicate the presence of iodine in the tube. The transmission of the iodine is

$$(i_2' \cdot i_1/i_1')/i_2,$$

the factor i_1/i_1' representing the correction that must be applied to i_2' if the intensity of the mercury arc has changed. Therefore the transmission is $R_2R_1'/R_1R_2' = R_1'/R_1$ because the resistance R_2' is kept equal to R_2 . With the circuit balanced variations in the intensity of the mercury arc affect both photoelectric cells alike and the balance is undisturbed. However, the shifting column of the arc did alter the light distribution, causing small galvanometer fluctuations which were overcome by averaging readings.

To overcome local e.m.f. disturbances within the circuit, the absorption cell and its bath were attached to a very accurate sliding platform, enabling the cell to be precisely fixed in either of the two optical paths (H or K). The procedure of the above paragraph was followed, first with the cell in H and again in K . This amounted to reversing the circuit; and an average of the two transmission values for each iodine concentration eliminated the effect of any local e.m.f. The apparatus measured transmissions with an extreme uncertainty <1.6 percent under green excitations, this being slightly larger for the yellow.

Data from runs made on two different days with the two tube lengths of 3.93 cm and 9.84 cm are plotted on Fig. 2 as a function of nL (L =tube length in cm). The agreement of data from tubes of two different lengths shows that the absorption is a function of the number of molecules in the line of sight (Beer's law), and that at least up to 0.7 mm the interaction between molecules does not affect the absorption. Any line broadening due to the numerous collisions (see later) must be negligible in comparison with the Doppler width. The validity of Beer's law for pure iodine has also been established by Miss Dlugosch¹¹ working with the

⁹ L. A. Jones, *J. Opt. Soc. Am.* **16**, 259 (1928).

¹⁰ C. P. Baxter, C. H. Hickey, W. C. Holmes, *J. Am. Chem. Soc.* **29**, 127 (1907).

¹¹ G. Dlugosch, unpublished Breslau dissertation (1922) which was made available through the kindness of Professor R. Ladenburg.

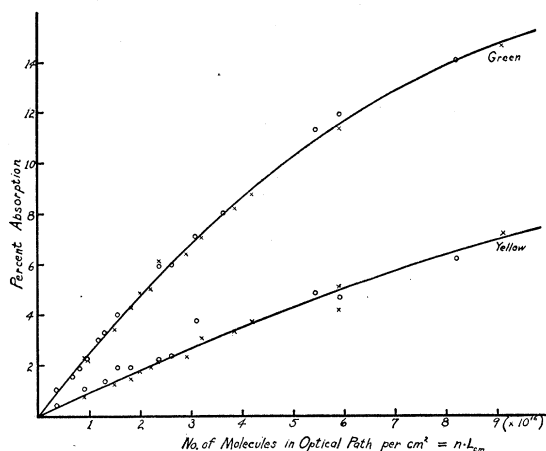


FIG. 2. Absorption in iodine: circles from 3.93 cm cell; crosses from 9.84 cm cell.

green and yellow lines of the mercury arc, but using an eleven-fold variation of tube length and a bath temperature variation from -20°C to $+40^{\circ}\text{C}$. She reports collision broadening appearing at pressures above 1 mm.

The absorption should be given by

$$A = 1 - \int e^{-k_p n L} dv.$$

Here it is convenient to consider the absorption as approximately a linear function of nL for the small values of this product that appear in the following fluorescence work ($nL < 1 \times 10^{16}$). Dlugosch¹¹ has also shown that at the wave-lengths used here (longer than the dissociation continuum) a small part of the iodine absorption is continuous—a very small part below $p = 1$ mm. No explanation has been given. Because of this a part of the measured absorption does not excite fluorescence; but assuming this continuous absorption coefficient to be constant over a small wave-length region, the above approximation still holds: the absorption that does lead to fluorescence is $A = KnL$.

The absolute absorption values given by Dlugosch are considerably larger than those obtained here (at 25°C they are about $3/2$ as large). No reason for this is at hand. But the calculations in this paper depend upon the proportionality of absorption to concentration, rather than on absolute values.

Iodine with argon

The previous absorption technique was followed. The iodine crystals were at 25.6°C and the oven at 50°C the same conditions under which the fluorescence with argon was photographed. The tube length was 3.93 cm. To vary the argon pressure, the moving absorption cell was connected to the vacuum system through the flexibility of 8 mm Pyrex tubing bent into a U-shape with $1\frac{1}{2}$ turns at the bend. The iodine, purified by distillation, was kept in sealed-off tubes which could be broken by a magnetically operated plunger after a satisfactory vacuum had been obtained. A magnetically controlled plunger valve slowed the diffusion of the iodine into the liquid air trap. Argon was purified in a misch metal arc.

Results of several measurements indicated that the argon up to pressures of 82 mm did not change the absorption of the iodine by more than 3 percent of that absorption.

From the fluorescence work an effect of some six times this magnitude would have been expected. In the fluorescence work the light came broadside from the arc; here it came from the end of the same arc similarly operated. But the possibility of the components of the mercury line being changed in intensity distribution depending on the part of the arc from which the light comes had been removed by Dlugosch.¹¹ She examined the mercury green and yellow lines under high dispersion and showed that the energy distribution changed very little with the voltage across the arc, i.e., with the total energy of the arc, and presumably therefore with regions of different energy density within the arc.

It was further found that the addition of oxygen at a pressure of 192 mm had no effect on the absorption of iodine (at a pressure of 0.3 mm), which seems to complicate the explanation of Loomis and Fuller.¹ Dlugosch,¹¹ using monochromatic mercury light, reports that nitrogen up to 10 mm does not change the iodine absorption.

FLUORESCENCE MEASUREMENTS

The fluorescence was produced in a Pyrex tube of diameter 3.9 cm with a window sealed to one end and the other drawn out to a horn (Fig. 3).

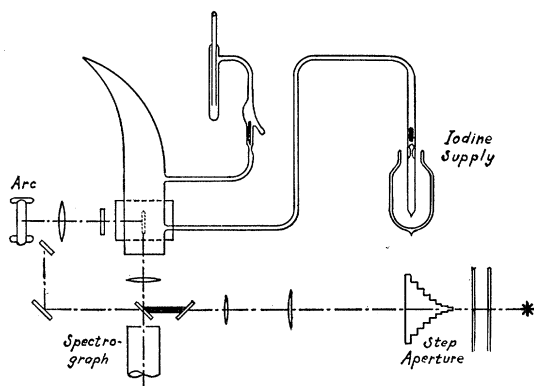


FIG. 3. Fluorescence apparatus.

The tube was horizontal, and blacked with Duco except for two opposite spaces near the window end, where the exciting light passed through it vertically. This gave a thin sheath of fluorescence parallel and end-on to the slit of a Steinheil spectrograph (high light power, dispersion about 80A per mm). A wide slit width was necessary for the argon work (see later) and was also used for pure iodine. The use of only a 2 mm height of this slit meant that the light came from a small trapezoidal region in the fluorescence sheath of average height 3.9 mm. Before reaching this effective part of the sheath, the mercury light was absorbed in a layer of molecules 5.65 mm high. On the lower half of the spectrograph slit fell a comparison beam directly from the arc.

Intensity marks were photographed on each plate, with the use of the step-diaphragm method developed by Hansen¹² and critically described by von Hippel.¹³ The step aperture was made by milling the desired profile from two thin steel plates fastened face to face and framing them. The longest opening was 2 cm, and the eight steps were each 2 mm high.

Pure iodine

Each plate contained an intensity mark spectrum and six fluorescence spectra, the first and last of these taken with the iodine bath at 0°C, and the other four at any temperature up to 45°C. All exposures were 20 minutes. Prior to all 0°C pictures the iodine was entirely condensed into the bath tube. The fluorescence tube

oven was at 50°C. The densitometer slit was moved across each spectrum on the plate at usually six wave-length regions. The intensities read from the plate characteristic curves were corrected from the comparison spectra for variations in the arc, and then divided by the average intensity of the first and last 0°C pictures. A further correction to account for the weakening of the mercury light in passing through the preliminary sheath of vapor was made by multiplying each relative intensity by $(100 - A_0) / (100 - A_t)$ where A_0 and A_t are the percent absorptions at the indicated temperature for a path length $L = 0.565$ cm. Absolute absorption values are required for this, but the magnitude of the correction is under one percent. Measurements made on the green fluorescence between the third and fourteenth orders, and on the yellow between the third and eleventh orders, showed that within these limits for a given series and a given temperature the intensities were constant, i.e., no reabsorption. So it was possible to average the intensity values obtained from a given spectrum and thereby reduce the errors inherent in the densitometry. These relative intensities (I_t/I_0) were comparable even when derived from different plates.

Iodine with argon

Argon is one of the gases which Franck and Wood¹⁴ found to produce a band spectrum background in iodine fluorescence by transferring some energy from the excited molecule to nearby vibrational or rotational states, from which radiation then occurs. These new band lines overlapped the original fluorescence lines, unless one employed large dispersion and prohibitively long exposure times. Since it was found difficult to correct for the intensity of this background because of the irregularity in its structure, no measurement could be made of the way in which the *original resonance series* lines were diminished. The method actually adopted was to open the slit of the spectrograph to a width of 2 mm, which blurred and overlapped the lines. A measurement at any fixed position in such a spectrum gave an intensity proportional

¹² G. Hansen, Zeits. f. Physik **29**, 356 (1924).

¹³ A. von Hippel, Ann. d. Physik [4] **80**, 672 (1926).

¹⁴ J. Franck and R. W. Wood, Phil. Mag. [6] **21**, 314 (1911).

not only to the adjacent lines of the original resonance series, but also to the energy that had been transferred and radiated. Any diminution of this intensity, as argon was added, was then due entirely to *total-energy-removing collisions* of the argon on the iodine.

The iodine was held constant at 25.6°C, the oven at 50°C, and the argon pressure varied up to 16 mm. The procedure was as given above, except that no absorption correction was applied to the exciting light—the iodine density was constant, and no change in absorption was found to be caused by the argon. This yielded the ratios I_p/I_0 , the reciprocals of which are plotted against argon pressure on Fig. 4

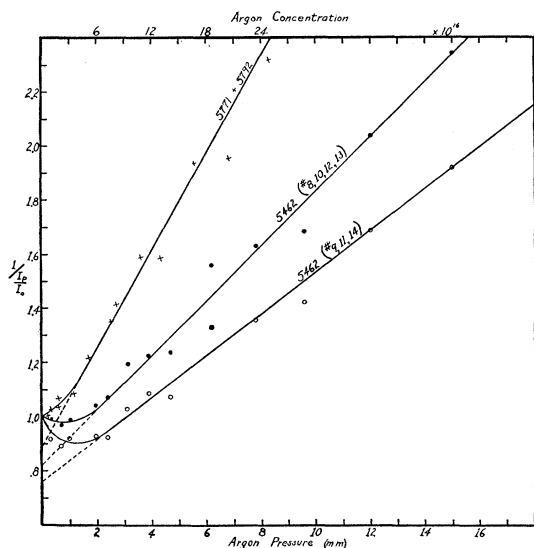


FIG. 4. Argon quenching of iodine fluorescence.

Reabsorption was noticeable at wave-lengths shorter than 6000Å and measurements were made at longer wave-lengths. In the case of the green series it was noticed that for a given argon pressure, the I_p/I_0 ratios for wave-lengths above 6000Å did not fluctuate about one constant value (as in pure iodine), but about *two* mean values, whose spacing increased with argon pressure. No meaning has been given to this phenomenon, but both green values are shown in Fig. 4.

When transfer occurs, the measurements made on the blurred spectrum tacitly assume that the transferred energy reappears in the close neighborhood of the fluorescence line to which it

would otherwise have gone. While the appearance of early plates taken with a fine slit indicates that this is approximately true of the stronger transferred lines, still the presence of the reabsorption just mentioned seems only to be explained as a shifting of some energy to longer wave-lengths, as Franck¹⁵ has suggested; for argon does not broaden the absorption lines. Therefore the I_p/I_0 values for the argon-iodine mixture are subject to a small but unknown error.

THEORY OF THE EXPERIMENT

The intensity of the fluorescence (after making all corrections) is proportional to the number of excited molecules and to their rate of radiation. The number of excited molecules present depends on the balance between the absorption and the rate of removal. In this latter connection the effect of collisions with other iodine molecules must be considered. Using the type of theory developed by Stern and Volmer¹⁶ for the quenching of iodine fluorescence by itself, define:

- n = number of normal iodine molecules per cc.
- n' = number of excited iodine molecules per cc.
- N = number of argon atoms per cc.
- r = probability of one excited iodine molecule radiating in unit time.
- b = probability of one normal iodine molecule making a total-energy-removing collision in unit time with one excited iodine molecule per cc.
- a = probability of one argon atom making a total-energy-removing collision in unit time with one excited iodine molecule per cc.
- A = the number of excited iodine molecules formed per cc in unit time (proportional to the absorption).

Then the equation for the equilibrium state of the fluorescence is:

$$A = rn' + bnn' + aNn' \tag{1}$$

or

$$n' = A / (r + bn + aN). \tag{2}$$

¹⁵ J. Franck, *Ergebnisse der Exakten Naturwissenschaften* 2, 118 (1923).

¹⁶ O. Stern and M. Volmer, *Phys. Zeits.* 20, 183 (1919).

Collisions with the walls are negligible, as Stern and Volmer¹⁶ have shown. Under the condition of a wide slit the quantities n' , r , b and a do not refer to only the original excited states to which the iodine is raised directly by the exciting line, but they may also include the nearby states from which energy is radiated after transfer. Since r , b and a are a kind of average for all the excited states producing fluorescence, and since the number of such states will vary with the amount of transfer occurring, and because the amount of transfer depends on the concentration, r , b and a , in the event of transfer, are not constants, but functions of concentration.

To examine this in more detail,* irrespective of the slit used let the following terms be defined more closely than was done above:

- n = conc. of iodine molecules (normal).
 N = conc. of argon atoms.
 A_r = number of molecules excited into one of the original states r per sec. (some 12 such green states with a hot arc).
 $r_r n_r'$ = number of radiation acts from the state r per sec.
 $b_r n_r'$ = number of molecules in state r quenched by iodine per sec.
 $a_r N n_r'$ = number of molecules in state r quenched by argon per sec.
 $c_{rs} n n_r'$ = number of transfer acts from state r to the state s due to iodine per sec. (s also includes any of the other r states.)
 $d_{rs} N n_r'$ = number of transfer acts, etc., due to argon per sec.

Then for the equilibrium of the state r

$$A_r + \sum_s c_{sr} n_s' n + \sum_s d_{sr} n_s' N = r_r n_r' + b_r n_r' n + a_r n_r' N + \sum_s c_{rs} n_r' n + \sum_s d_{rs} n_r' N.$$

This supposes that transfer can also act to bring excited molecules into any one of the r states, either from one of the original r states, or from an s state which has been occupied as the result of a previous transfer. For any other state

* I am indebted to Professor E. U. Condon for the more formal treatment of this matter.

t (not one of those originally excited) the equilibrium is expressed by

$$\sum_s c_{st} n_s' n + \sum_s d_{st} n_s' N = r_t n_t' + b_t n_t' n + a_t n_t' N + \sum_s c_{ts} n_t' n + \sum_s d_{ts} n_t' N,$$

where s is any state except t . These two equations are typical of the two varieties of excited states (r and t) present in the assembly. If q be used to indicate any excited state, without restriction, then on adding all equations similar to the above two:

$$\begin{aligned} \sum_r A_r + \sum_q \sum_s c_{sq} n_s' n + \sum_q \sum_s d_{sq} n_s' N \\ = \sum_q r_q n_q' + \sum_q b_q n_q' n + \sum_q a_q n_q' N \\ + \sum_q \sum_s c_{qs} n_q' n + \sum_q \sum_s d_{qs} n_q' N. \end{aligned}$$

But

$$\sum_q \sum_s c_{sq} n_s' n = \sum_q \sum_s c_{qs} n_q' n$$

and similarly for the other double sum. So that

$$\sum_r A_r = \sum_q r_q n_q' + n \sum_q b_q n_q' + N \sum_q a_q n_q'. \quad (3)$$

If no transfer of energy occurs, $q=r$, and comparing Eqs. (1) and (3)

$$A = \sum_r A_r, \quad an' = \sum_r a_r n_r',$$

$$rn' = \sum_r r_r n_r', \quad \text{where } n' = \sum_r n_r'.$$

$$bn' = \sum_r b_r n_r',$$

The coefficients r , b and a are seen to be average values over the r states. They do not, however, remain constants after the gas concentration is changed; for due to inherent inequalities between the actual values r_r (which are in themselves constants), the new n' may consist of a different distribution of the n_r' values and this may shift the center of gravity of the average. This may perhaps become more apparent upon comparing equations like Eq. (2) written for states r_1 , r_2 , etc. Since it is impossible in this experiment to say anything of the coefficients of a single state, it can only be assumed that for the several states excited by one line the individual r_r values (and b_r and a_r) are nearly alike, so that a constant r , b and a can be used as in Eq. (1). Within the

limits of its accuracy, the present experiment justifies this assumption.

In the autoquenching of iodine very little transfer occurs. It is not even apparent at 0.2 mm on plates which had strong resonance series lines, and Wood's¹⁷ pictures of it were twenty hour exposures. For pure iodine, then, r and b will be considered practically constant, although subscripts will be appended to indicate molecular concentration.

For argon quenching the transfer effect is marked. With a wide slit this transferred radiation is also measured, and the unknown dependence of the effective r , b and a values on argon pressure prevents the deduction of exact quantitative results.

Returning to Eqs. (2) and (3), since the fluorescence intensity (resonance series and background) is proportional to rn' :

$$I = crn' = crA / (r + bn + aN). \quad (4)$$

If the previously defined A be now taken to represent the percent absorption of the iodine, then

$$A/I = (1/C)(1 + (b/r)n + (a/r)N). \quad (5)$$

From this it appears that the ratio of the absorption to the fluorescence intensity of the iodine ($n = \text{constant}$) should increase linearly with the argon concentration (N): and the ratio of slope to intercept yields a/r in terms of $(1 + (b/r)n)$.

Suppose that the concentration of the iodine is varied in the *absence of argon*. Eq. (5) freed of its last term shows that A/I varies linearly with n ; and in this case the ratio of slope to intercept gives b/r , so that a determination of a/r should be possible. The quenching of iodine by iodine and the absorption values were therefore measured. Only later was it realized that rigorous evaluation of the argon quenching was still impossible because of the transfer effect.

$$\frac{b_i}{r_i} = \frac{\text{Probability of energy loss per single excited molecule due to collisions with } n_i \text{ normal molecules}}{\text{Probability of energy loss per single excited molecule due to radiation}}$$

A few values of this quantity within the experimental range are given in Table I (the concen-

¹⁷ R. W. Wood, Phil. Mag. [6] 35, 236 (1918).

Pure iodine

Actual measurements of the fluorescence gave values which were relative to the intensity for a fixed condition of the vapor (i.e., crystals in a 0°C bath). Indicating temperature by subscripts, any two states of the vapor are related by

$$\frac{I_0 \cdot A_t}{I_t \cdot A_0} = \frac{r_0}{r_0 + b_0 n_0} \left(1 + \frac{b_t}{r_t} n_t \right). \quad (6)$$

By using the approximation that $A = KnL$, then for a constant path length L , this becomes

$$\frac{I_0 \cdot n_t}{I_t \cdot n_0} = \frac{r_0}{r_0 + b_0 n_0} \left(1 + \frac{b_t}{r_t} n_t \right). \quad (7)$$

In Fig. 5 the left member of Eq. (7) is plotted against n_t . For densities greater than 6×10^{15} molecules per cc the approximation $A = KnL$ does not hold. But within this range the curve is linear, providing that r_t and b_t are constant which is practically the case in pure iodine. The slope to intercept ratio of this line, by Eq. (7) gives

$$b_i/r_i = \frac{5462A}{4.50 \times 10^{-16}} = \frac{5771 + 5792A}{6.28 \times 10^{-16}}$$

TABLE I.

Temp. (°C)	Press. (mm)	n_t ($\times 10^{15}$)	$(b_i/r_i)n_t$ (green)	$(b_i/r_i)n_t$ (yellow)
-6	0.015	0.55	0.25	0.35
0	0.03	1.06	0.48	0.67
6	0.055	1.92	0.87	1.21
7.5	0.064	2.22	1.00	1.40
12	0.098	3.34	1.50	2.10
20	0.20	6.63	3.00	4.16

When it is recalled that b_t is only the probability of energy loss when but one normal molecule per cc is colliding, then for an actual condition of the iodine, such as n_t molecules at $t^\circ C$:

trations given are for both vapor and crystals at the one indicated temperature). In the usual iodine experiments around room temperature,

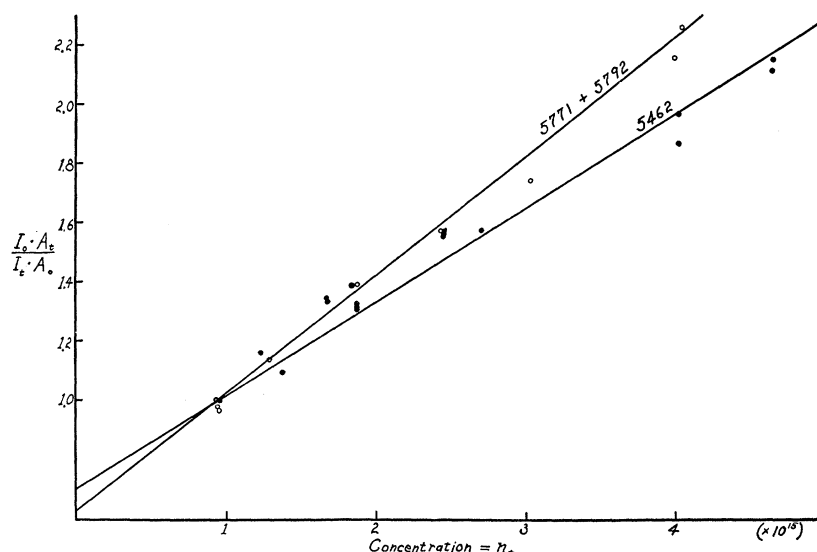


FIG. 5. Combined absorption and fluorescence in iodine: *points green*; *circles yellow*.

therefore, collision and radiation play rôles of the same order of magnitude in ridding excited molecules of their energy. Stern and Volmer were led to the same conclusion, but expressed it in a qualitative manner.

The fact that the pure iodine fluorescence is quenched in the yellow series more than it is in the green, is not in accord with any theory of collision enhancement of predissociation. For the work of Turner³ on magnetic quenching shows that predissociation is most effective in the green series. The observed quenching is probably due to collisions of the second kind.

Iodine with argon

When argon was used the iodine concentration was held constant at $t^\circ\text{C}$ ($t=25.6^\circ\text{C}$; $n_t=9.76 \times 10^{15}$ molecules per cc). If the subscript p indicates the argon pressure, the equation analogous to (7) is

$$\frac{I_0 \cdot A_p}{I_p \cdot A_0} = \frac{r_0}{r_0 + b_t n_t} \left\{ \left(1 + \frac{b_p}{r_p} n_t \right) + \frac{a_p}{r_p} N_p \right\}. \quad (8)$$

This equation is appropriate to the data plotted on Fig. 4. But the initial increase of green fluorescence shown by the experimental points is remarkable, in view of the result that argon did not increase the absorption ($A_p/A_0=1$). The failure of Eq. (8) to explain Fig. 4 may be due to the unknown dependence of the r , b and a values on argon pressure (because of transfer), or to other imaginable processes: such as a hindering of the autoquenching, or a change in the ratio of continuous to line absorption. Certainly no evaluation of the quenching efficiency of argon (a_p/r_p) is at present possible. While the yellow series is quenched more than the green, this cannot be taken as positive evidence against the enhancement of predissociation by argon; for with the possibility of variation in the b_p/r_p term, the actual values of a_p/r_p in both series would have to be known.

The opportunity is taken here to express my very warm gratitude to Professor Louis A. Turner, from whom came the idea of undertaking this investigation, and under whose counsel it has developed.