reports a lower value than found by our method. Because of the indirectness of his experimental approach and the difficulties he reports in making observations at different gas pressures, we believe our cross section for nitrogen is the better one.

ACKNOWLEDGMENTS

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Effects of Added Gases on the Sensitized Fluorescence Spectrum of a Hg-Tl Mixture*†

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An investigation of the sensitized fluorescence of a mercury thallium mixture without and with the addition of argon and helium gases is discussed. Data taken without the addition of foreign gases are used to extend the theory of Frish and Karaulinya to a mercury thallium mixture. Relative collision cross sections for the excitation of the thallium energy states, $9\,^2S_{\frac{1}{2}}$, $7\,^2D_{\frac{5}{2},\frac{3}{2}}$, $8\,^2S_{\frac{1}{2}}$, $6\,^2D_{\frac{5}{2}}$, and $6\,^2D_{\frac{3}{2}}$ were calculated for mercury thallium collisions. Data taken with the addition of argon and helium gases are given to indicate the variation of the intensity of the thallium lines as a function of argon and helium gas pressures at one constant thallium and three mercury temperatures. The explanation of the results depends on the role of mercury $6\,^3P_1$ excited atoms, metastable atoms, and mercury molecules in collision with thallium atoms for energy exchange, and also requires the use of Winans' partial selection rule and other generally accepted ideas concerning energy transfer, emission, and absorption.

INTRODUCTION

FRANCK[1] first extended the ideas of Klein and Rosseland[2] to the collisions of excited atoms of one kind with unexcited atoms of another kind. If this second atom had energy levels below the excited energy state of the first atom, energy exchange could occur followed by the emission of characteristic spectral lines of this element. Franck called this phenomenon sensitized fluorescence.

Shortly after Franck and Cario[3] completed this work, both Donat[4] and Loria[5] performed experiments in sensitized fluorescence using a mercury thallium mixture with added foreign gases. The results of these investigators did not completely agree, but both authors attributed the behavior of the thallium lines to the increased formation of metastable $6\,^3P_0$ mercury atoms caused by the addition of argon and nitrogen. In this paper the work of Donat and Loria will be repeated for argon and extended to helium. Their experiments will be repeated with improved vacuum and measurement techniques. The data obtained in this investigation will be discussed in light of recent data obtained on the role of metastable atoms,[6–9] mercury molecules,[10–13] and the HgTl quasi-molecules,[8,14,15] in sensitized fluorescence; and in light of recent studies on mercury resonance radiation.[16–20]

The recent theory of Frish and Karaulinya[21] will be extended in this paper to a mercury thallium mixture without the addition of foreign gases. This theory was the first quantitative theory to explain the phenomenon of sensitized fluorescence.

THEORY OF FRISH AND KARAULINYA

The experimental apparatus for this discussion consisted of a resonance cell having three different reservoirs. One reservoir contained the mercury metal, another the thallium metal, and the central portion of the cell was used for fluorescence studies. Ovens were

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placed over each reservoir. The oven over the mercury reservoir was kept at a low temperature to reduce the production of metastable atoms and to reduce spectral reflection. The ovens over the thallium reservoir and the central portion of the cell were heated to between 600 and 900°C to produce thallium vapor. The central portion of the tube was irradiated with 2537 A mercury radiation so that $6\,^3P_1$ excited mercury atoms were produced. The excited mercury atoms may collide with the neutral thallium atoms, and the number of excited thallium atoms produced per unit volume is given by the relationship

$$\Delta N(\mathrm{Tl}) = N_0(\mathrm{Tl})N_m(\mathrm{Hg}^*)Q_{0k}\bar{v}, \tag{1}$$

where $N_0(\mathrm{Tl})$ and $N_m(\mathrm{Hg}^*)$ are the number of neutral thallium atoms and excited mercury atoms per unit volume, Q_{0k} is the collision cross section, and $\bar{v}$ is the relative velocity of the colliding particles. The kth thallium energy level will be considered in this theory.

The $6\,^3P_1$ mercury atoms will have a Maxwellian distribution of thermal energy determined by the temperature of the oven in addition to 4.86 electron volts excitation energy. Thus, all thalium energy states will be excited; and some atoms will even be ionized. The kth thallium energy level will be excited by direct energy exchange with the excited mercury atoms and by cascade transitions into the kth level from higher excited thallium levels. The kth level will be depopulated by radiation to the lowest allowed thallium states, and by collisions of the second kind with neutral mercury atoms. This can be represented by the following equations. Growth rate of kth thallium level equals the death rate of the kth level:

$$N_0(\mathrm{Tl})N_m(\mathrm{Hg}^*)Q_{0k}\bar{v} + \sum_{j=k+1}^{\infty} N_j(\mathrm{Tl}^*)A_{jk} = N_0(\mathrm{Hg})N_k(\mathrm{Tl}^*)Q_{k0}\bar{v} + N_k(\mathrm{Tl}^*)\sum_{i=k-1}^{0} A_{ki}, \tag{2}$$

where A_{ki}'s are the thallium transition probabilities. The following relation exists between Q_{0k} and Q_{k0},

$$g_0 p^2 Q_{0k} = g_k p'^2 Q_{k0}, \tag{3}$$

where g_0 and g_k are statistical weights of thallium energy states and p and p' are the initial and final momenta of the two atoms.

This experiment was carried out at low mercury and thallium vapor pressures, so the time between thallium and mercury collisions is long compared to the lifetime of the excited thallium state. Thus the first term on the right-hand side of Eq. (2) may be neglected. A relationship also exists between the concentration of thallium atoms in the kth energy state and the intensity of the spectral line, I_{kl}:

$$N_k(\mathrm{Tl}^*) = I_{kl}/h\nu_{kl}A_{kl}. \tag{4}$$

Neglecting the first term on the right-hand side of Eq. (2), substituting Eq. (4) into Eq. (2), and solving for the collision cross section, Q_{0k}, one obtains the following equation:

$$Q_{0k} = \frac{1}{N_0(\mathrm{Tl})N_m(\mathrm{Hg}^*)\bar{v}} \times \left[\frac{I_{kl}\sum_{i=k-1}^{0} A_{ki}}{h\nu_{kl}A_{kl}} - \sum_{j=k+1}^{\infty} N_j(\mathrm{Tl}^*)A_{jk}\right]. \tag{5}$$

Several simplifications can be made in the above equation. The term $1/[N_0(\mathrm{Tl})N_m(\mathrm{Hg}^*)\bar{v}]$ can be shown to be a function of the thallium and central oven temperature and is a constant term for each constant temperature. $N_0(\mathrm{Tl})$ will be a function of this temperature. $N_m(\mathrm{Hg}^*)$ is a function of the source intensity, which will be assumed to be constant during the experiment. The relative velocity $\bar{v}$ is also a function of the thallium and central tube temperature. The first term in the parenthesis accounts for all transitions from the kth thallium level to lower thallium levels. The summation, $\sum_{i=k-1}{}^{0}A_{ki}$, is the sum of the probabilities that an atom in the kth level will make transitions to lower levels and is equal to unity. The last term in the parenthesis considers all cascade transitions from higher thallium states into the kth state. The transition probabilities of these cascade transitions will be small compared to the direct transitions to the lowest thallium energy states and will be assumed to be negligible. Equation (5) then becomes

$$Q_{0k} = K(T)I_{kl}/h\nu_{kl}A_{kl}. \tag{6}$$

An approximate method proposed by Bates and Damgaard[22] will be used to calculate the thallium transition probabilities, A_{kl}. This method yields probabilities of the right order of magnitude for thallium.

APPARATUS AND METHOD

The quartz experimental tube was prepared in a fashion comparable to that described in previous work.[9,23,24] The experimental tube was left attached to the vacuum system. An Alpert valve, produced by the Consolidated Electrodynamics Corporation, was used to close the experimental tube during measurements. The experimental tube and Alpert valve were outgassed, and small amounts of mercury and thallium were introduced into the cell by vacuum distillation. Mass spectrographically pure gases protected against contamination were introduced into the vacuum system through stop cocks.

The detection apparatus was the same as used

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earlier[9,23] except that the source and lens were mounted rigidly in place on a modified nodal slide, so three degrees of freedom were obtained, to focus the system. The monochromator used was a Bausch and Lomb quartz 500 mm grating monochromator.

Swanson and McFarland[9] observed relationships between the intensity of the sensitized fluorescence lines and the mercury and thallium temperatures. Differential heating along the tube was obtained by two ovens. The thallium metal was heated by a small main oven which contained two quartz windows; so incident and fluorescent light could be passed. An auxiliary oven patterned after the Westinghouse outgassing ovens was placed over the Alpert valve and the protruding end of the experimental tube which acted as a mercury reservoir. The main oven temperature was called the thallium temperature, and the temperature of the mercury reservoir was called the mercury temperature.

The 2537 A output of the source varied as much as 30% under controlled conditions. This fluctuation was overcome by monitoring the source as the experimental readings were taken. The monitor consisted of an internally silvered tube, a camera shutter to open and close the tube, and an ultraviolet filter. This filter was an improved filter of Hoshina and Yoshida type which the authors have described previously[25] and which virtually isolated the 2537 A line, for the intensity of all other lines was less than 1% of the 2537 A intensity.

After the vacuum system was pumped down to less than 1×10^{-6} mm of mercury the main stopcock above the diffusion pumps was closed, and zero argon pressure readings were taken. Argon gas was added to a maximum pressure as shown in the results and readings were taken. The gas pressure was reduced and additional readings were taken. This procedure was continued until the gas pressure was reduced to the lowest reading. During each series of readings involving a single quenching gas pressure, the Alpert valve was closed.

After the argon readings were taken, the tube was outgassed prior to a final series of zero pressure argon gas readings; for the argon diffused into the metals when the tube cooled down. The maximum pressure of argon gas was initially introduced into the cell because of this diffusion of the gases into the metals. This procedure gave reproducible results with some lack of knowledge concerning the absolute gas pressures. Quenching gas pressures as indicated in the results are room temperature measured pressures.

Helium readings were taken in a similar manner.

The experimental apparatus and methods used without the addition of foreign gases were the same as used above.

EXPERIMENTAL RESULTS

The sensitized fluorescence lines, which were observed with the addition of argon and helium, were the 2768, 3229, 3519, 3529, 3776, and 5350 A thallium lines. The 2537 A mercury line was also observed. Figures 1 through 6 show representative sets of curves plotted as a function of argon and helium pressures with a fixed thallium and three mercury temperatures.

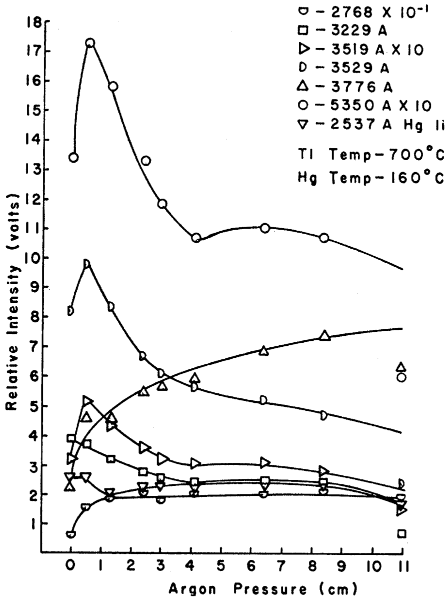

FIG. 1. Relative intensity of selected thallium lines versus argon pressures.

The relative intensities of selected thallium lines without the addition of foreign gases plotted as a function of mercury temperature are shown in Fig. 7. Since the majority of the thallium lines have maximal in-

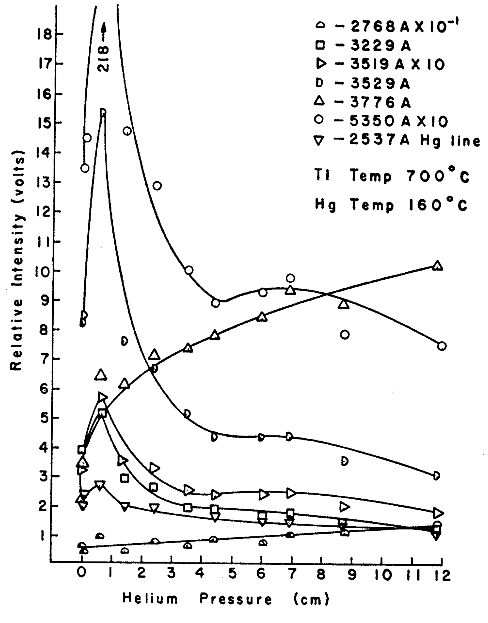

FIG. 2. Relative intensity of selected thallium lines versus helium pressures.

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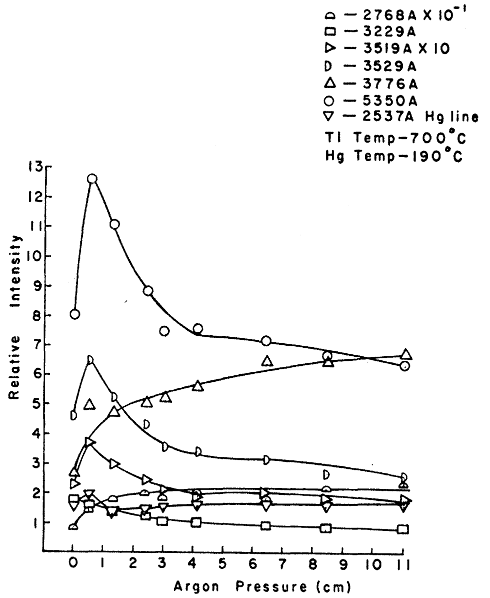

FIG. 3. Relative intensity of selected thallium lines versus argon pressures.

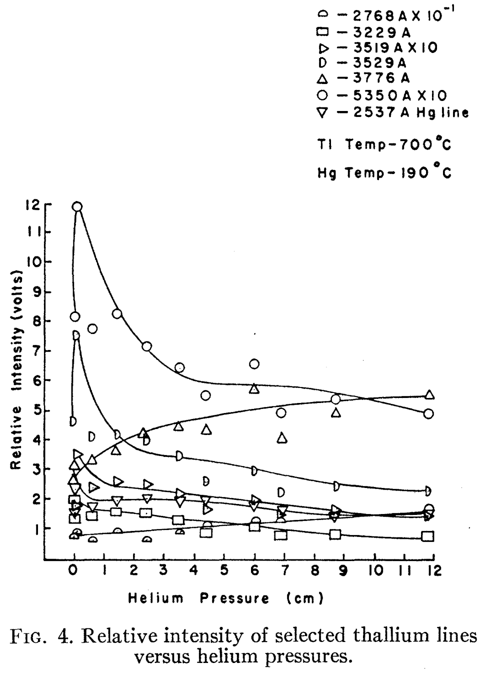

FIG. 4. Relative intensity of selected thallium lines versus helium pressures.

tensities at mercury temperatures of 120°C, calculations which follow have utilized this mercury temperature and a thallium temperature of 703°C.

Table I shows the relative measured intensities of the various selected lines as taken from Fig. 7. The intensities of the 2379 and 2316 A thallium lines could not be detected, and the 2921/18, 2826, 2768, and 2580 A lines were barely detectable.

Table II summarized the transition probabilities calculated for cascade, stepwise, and direct transitions of thallium as calculated by the method proposed by Bates and Damgaard.[22] Relative collision cross sections can be calculated by Eq. (6) for the 3529, 3519, 3229, 2921/18, and 2826 A thallium lines with negligible errors introduced by neglecting cascade transitions. These are summarized in Table III. Relative effective collision cross sections calculated for the 5350, 3776,

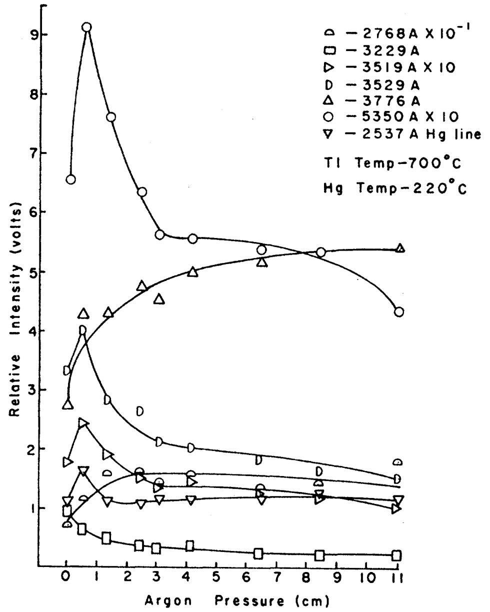

FIG. 5. Relative intensity of selected thallium lines versus argon pressures.

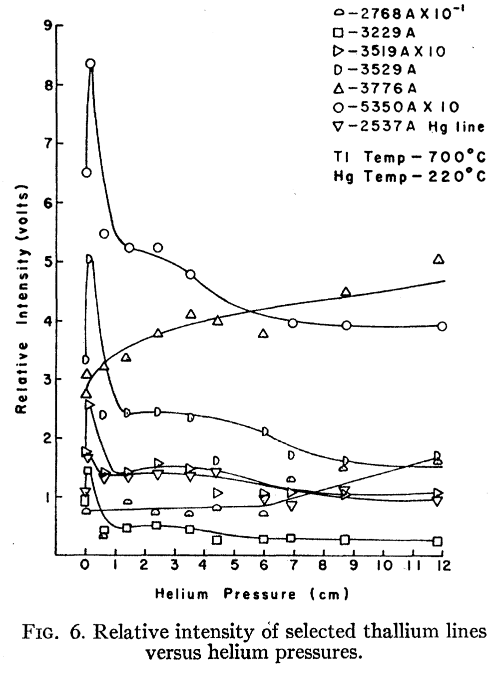

FIG. 6. Relative intensity of selected thallium lines versus helium pressures.

2768, and 2580 A thallium lines were calculated neglecting cascade transitions and imprisonment of these lines. Since absolute intensities measurements were not made, all cross sections are relative values compared with an assigned value of unity to the 3519 A transition.

TABLE I. Relative intensities of the various selected thallium lines.

Transition	Wavelength (A)	Intensity (volts)
$9\,{}^2S_{\frac12}$–$6\,{}^2P_{\frac32}$	2826	0.018
$7\,{}^2D_{\frac52,\frac32}$–$6\,{}^2P_{\frac32}$	2921/18	0.216
$8\,{}^2S_{\frac12}$–$6\,{}^2P_{\frac32}$	3229	10.8
$8\,{}^2S_{\frac12}$–$6\,{}^2P_{\frac12}$	2580	0.152
$6\,{}^2D_{\frac52}$–$6\,{}^2P_{\frac32}$	3519	57.0
$6\,{}^2D_{\frac32}$–$6\,{}^2P_{\frac32}$	3529	16.3
$6\,{}^2D_{\frac32}$–$6\,{}^2P_{\frac12}$	2768	0.186
$7\,{}^2S_{\frac12}$–$6\,{}^2P_{\frac32}$	5350	188.0
$7\,{}^2S_{\frac12}$–$6\,{}^2P_{\frac12}$	3776	2.70

TABLE II. Comparison of cascade, stepwise, and direct transition probabilities calculated by method of Bates and Damgaard.

Cascade transitions	Wavelength (A)	Theoretical transition probability (A_{kl})
$8\,{}^2P_{\frac32}$–$6\,{}^2D_{\frac52}$	18 047	0.141×10^8
$8\,{}^2P_{\frac32}$–$6\,{}^2D_{\frac32}$	17 754	0.711×10^5
$8\,{}^2P_{\frac12}$–$6\,{}^2D_{\frac32}$	19 047	0.116×10^7
$8\,{}^2P_{\frac32}$–$8\,{}^2S_{\frac12}$	33 388	0.402×10^7
$8\,{}^2P_{\frac12}$–$8\,{}^2S_{\frac12}$	38 133	0.260×10^7
$8\,{}^2P_{\frac32}$–$7\,{}^2S_{\frac12}$	6549	0.508×10^7
$8\,{}^2P_{\frac12}$–$7\,{}^2S_{\frac12}$	6114	0.504×10^7
$7\,{}^2P_{\frac32}$–$7\,{}^2S_{\frac12}$	11 513	0.132×10^8
$7\,{}^2P_{\frac12}$–$7\,{}^2S_{\frac12}$	13 014	0.110×10^8
Stepwise transition	**Wavelength (A)**	**Theoretical transition probability (A_{kl})**
$7\,{}^2D_{\frac52}$–$8\,{}^2P_{\frac32}$	324 675	0.916×10^4
$7\,{}^2D_{\frac52}$–$7\,{}^2P_{\frac32}$	14 518	0.733×10^7
$6\,{}^2D_{\frac52}$–$7\,{}^2P_{\frac32}$	24 757	0.654×10^7
$7\,{}^2D_{\frac32}$–$8\,{}^2P_{\frac32}$	369 822	0.102×10^4
$7\,{}^2D_{\frac32}$–$8\,{}^2P_{\frac12}$	155 496	0.680×10^5
$7\,{}^2D_{\frac32}$–$7\,{}^2P_{\frac32}$	14 597	0.381×10^7
$7\,{}^2D_{\frac32}$–$7\,{}^2P_{\frac12}$	12 736	0.505×10^7
$6\,{}^2D_{\frac32}$–$7\,{}^2P_{\frac32}$	104 417	0.926×10^4
$6\,{}^2D_{\frac32}$–$7\,{}^2P_{\frac12}$	51 062	0.393×10^6
$9\,{}^2S_{\frac12}$–$8\,{}^2P_{\frac32}$	70 175	0.116×10^7
$9\,{}^2S_{\frac12}$–$8\,{}^2P_{\frac12}$	55 626	0.864×10^6
$9\,{}^2S_{\frac12}$–$7\,{}^2P_{\frac32}$	12 492	0.125×10^7
$9\,{}^2S_{\frac12}$–$7\,{}^2P_{\frac12}$	11 103	0.106×10^7
$8\,{}^2S_{\frac12}$–$7\,{}^2P_{\frac32}$	27 893	0.460×10^7
$8\,{}^2S_{\frac12}$–$7\,{}^2P_{\frac12}$	21 804	0.330×10^7
Direct transition	**Wavelength (A)**	**Theoretical transition probability (A_{kl})**
$7\,{}^2D_{\frac52}$–$6\,{}^2P_{\frac32}$	2918	0.449×10^8
$6\,{}^2D_{\frac52}$–$6\,{}^2P_{\frac32}$	3519	0.117×10^8
$7\,{}^2D_{\frac32}$–$6\,{}^2P_{\frac32}$	2921	0.494×10^7
$7\,{}^2D_{\frac32}$–$6\,{}^2P_{\frac12}$	2379	0.263×10^8
$6\,{}^2D_{\frac32}$–$6\,{}^2P_{\frac32}$	3529	0.165×10^8
$6\,{}^2D_{\frac32}$–$6\,{}^2P_{\frac12}$	2768	0.489×10^8
$9\,{}^2S_{\frac12}$–$6\,{}^2P_{\frac32}$	2826	0.286×10^7
$9\,{}^2S_{\frac12}$–$6\,{}^2P_{\frac12}$	2316	0.122×10^7
$8\,{}^2S_{\frac12}$–$6\,{}^2P_{\frac32}$	3229	0.660×10^7
$8\,{}^2S_{\frac12}$–$6\,{}^2P_{\frac12}$	2580	0.306×10^7
$7\,{}^2S_{\frac12}$–$6\,{}^2P_{\frac32}$	5350	0.370×10^8
$7\,{}^2S_{\frac12}$–$6\,{}^2P_{\frac12}$	3776	0.197×10^8

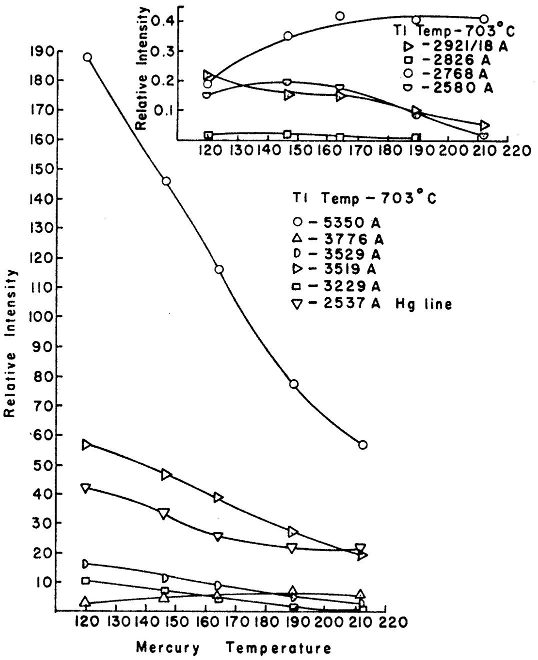

FIG. 7. Relative intensity of selected thallium lines versus mercury temperatures without the addition of gases.

TABLE III. Relative collision cross sections as calculated from Fig. 7 for the 3529, 3519, 3229, 2921/18, and 2826 A thallium lines.

Transition	Wavelength (A)	Cross section (arbitrary units)
$6\,{}^2D_{\frac32}$–$6\,{}^2P_{\frac32}$	3529	0.20
$6\,{}^2D_{\frac52}$–$6\,{}^2P_{\frac32}$	3519	1.00
$8\,{}^2S_{\frac12}$–$6\,{}^2P_{\frac32}$	3229	0.31
$7\,{}^2D_{\frac52,\frac32}$–$6\,{}^2P_{\frac32}$	2921/18	0.00082
$9\,{}^2S_{\frac12}$–$6\,{}^2P_{\frac32}$	2826	0.00105
Relative collision cross section for the 5350 A thallium line neglecting cascade transitions		
		Maximum
$7\,{}^2S_{\frac12}$–$6\,{}^2P_{\frac32}$	5350	1.59
Relative collision cross section for the 3776 A thallium line neglecting cascade transitions and imprisonment of this line.		
$7\,{}^2S_{\frac12}$–$6\,{}^2P_{\frac12}$	3776	0.030
Relative collision cross section for the 2768 and 2580 A thallium lines neglecting imprisonment of these lines.		
$6\,{}^2D_{\frac32}$–$6\,{}^2P_{\frac12}$	2768	0.00061
$8\,{}^2S_{\frac12}$–$6\,{}^2P_{\frac12}$	2580	0.00750

DISCUSSION

The results of the present experiment with the addition of foreign gases did not agree in all details with the results obtained by Donat[4] and Loria.[5] Common trends for intensity of the thallium lines through the addition of both argon and helium are noted in Figs. 1 through 6. The 5350, 3529, 3519, and 3229 A thallium lines initially increase in intensity to a maximum value and then decrease with the addition of more gas. The 3776 A

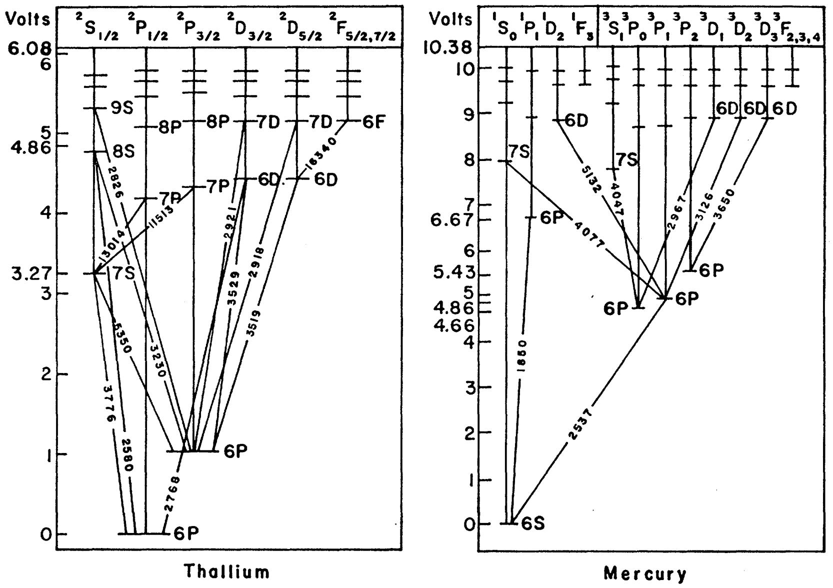

FIG. 8. Energy level diagram.

thallium line exhibits a continuous increase in intensity with the addition of both gases after a sharp initial rise.

The initial rapid increase in intensity of the 5350, 3529, 3519, and 3229 A thallium lines may be caused by an enhanced formation of HgTl quasi-molecule through the addition of small amounts of argon or helium gases. These gases may act as third bodies which accept some of the excitation energy of the excited mercury atoms and thallium atoms, so they can combine and remain combined to emit radiation. This would cause an increased interaction between $6\,^3P_1$ excited mercury atoms and thallium atoms, and cause the enhancement of these lines, for all of these lines are selectively excited by $6\,^3P_1$ atoms. The 3519 and 3529 A thallium lines, originating from the $6\,^3D_{\frac{5}{2}}$ and $6\,^2D_{\frac{3}{2}}$ levels, are selectively excited by the $6\,^3P_1$ mercury atoms by Winans' partial selection rule. The 3229 A line, originating from the $8\,^2S_{\frac{1}{2}}$ level, is excited by the $6\,^3P_1$ mercury atoms because of near energy resonance; and the 5350 A line, originating from the $7\,^2S_{\frac{1}{2}}$ level, is excited by the $6\,^3P_1$ atom because of cascade transitions to this level from higher thallium levels. The reader may refer to Fig. 8 to follow these transitions.

A second effect which may also be active is that the addition of argon and helium gases reduces the rate of diffusion of metastable $6\,^3P_0$ mercury atoms to the walls of the container. Calculations were made to determine the argon and helium pressures for which the mean free paths of the mercury atoms were reduced to the order of the radius of the tube. These pressures were 0.3 and 0.2 microns, respectively.

The largest initial enhancement of these lines is observed for helium. An explanation may be that argon produced some metastable atoms, thus reducing the population of the $6\,^3P_1$ level. Also, argon is more massive and is more effective in stopping the thallium vapor from pumping mercury out of the cell. This would result in a higher effective mercury vapor pressure and a greater destruction rate of the $6\,^3P_1$ mercury atoms.[9] Both of the above effects reduce the number of $6\,^3P_1$ atoms in the cell, and the reduction results in the loss of intensity of the thallium lines excited by these atoms.

At gas pressure of 0.6 cm the intensity of these lines drops abruptly. It may be assumed that through the addition of these gases there is an enhanced formation of mercury molecules, and this becomes a competing process. These gases act as a third body to form the $Hg_2(^31_u)$ and $Hg_2(^30_u^-)$ molecules formed between the $6\,^3P_1$ and $6\,^3P_0$ mercury atoms and neutral mercury atoms, respectively. Berberet and Clark[13] have observed the enhanced formation of $Hg_2(^30_u^-)$ molecules through the addition of nitrogen to a resonance cell. These two molecules both possess about 4 electron volts of excitation energy and can excite only the $7\,^2S_{\frac{1}{2}}$ thallium level. This molecular formation reduces the number of $6\,^3P_1$ and $6\,^3P_0$ mercury atoms, and the intensities of the 5350, 3529, 3519, and 3229 A lines decrease.

The leveling off of intensity of these lines between 3 and 6 cm of argon or helium gas pressure seems to be real and be the result of a number of competitive processes. One such would involve the formation of $Hg_2(^30_u^+)$ mercury molecules, which have an excitation energy comparable with that of the excited $6\,^3P_1$ mercury atoms.

The intensity of these thallium lines again decrease above 6 or 7 cm for both gases.

The variation of intensity of the 3776 A thallium line can be explained in a similar manner. The initial rise in intensity of this line might be explained by the enhanced formation of the HgTl, quasi-molecule, and the reduction of the loss rate of metastable mercury atoms. The 3776 A thallium line is a resonance line and is reabsorbed in the cell. This line is also selectively excited by $6\,^3P_0$ mercury atoms.[18,9] The reduction of the loss of metastable atoms would cause the initial rise in intensity of the 3776 A line, for if they excite the $7\,^2S_{\frac{1}{2}}$ level, there would be a Doppler broadening of this line; so only the central portion is reabsorbed and the line is enhanced. Argon causes the greatest enhancement of this line, for argon produces metastable atoms and reduces the pumping action of the thallium vapor.

The intensity of this line continues to increase when mercury molecules are formed. The mercury molecules can excite the $7\,^2S_{\frac{1}{2}}$ thallium level, and 0.73 electron volt of excitation energy is shared as kinetic energy of the colliding particles. Thus the 3776 A line exhibits Doppler broadening when it is excited by mercury molecules and is enhanced.

The intensity of the 2768 A line is barely above background and no conclusions could be drawn about it.

The 2537 A light as measured is made up of two components, the resonant radiation from the cell and the reflected light from the cell walls and thallium bead. There were indications that the 2537 A light intensity depended on the size of the thallium bead in the cell which varied in size during the experiment. Thus no conclusions were made about the intensity variation of this line.

Certain simplifications must be justified in the theory of Frish and Karaulinya[21] to extend it to a mercury thallium mixture. The mercury in the central portion of the cell was at a temperature of 703°C, so the excited mercury atoms had their energies distributed from 4.86 electron volts to infinity. The following thallium energy levels with energies above 4.86 volts are of interest, the $9\,^2S_{\frac{1}{2}}$, $7\,^2D_{\frac{5}{2}}$, $7\,^2D_{\frac{3}{2}}$, $8\,^2P_{\frac{3}{2}}$, and $8\,^2P_{\frac{1}{2}}$ levels with energies of 5.25, 5.20, 5.20, 5.16, and 5.10 ev, respectively. For simplification, it may be assumed that only the $6\,^3P_1$ excited mercury atoms with total energies above 5.25 ev will excite the $9\,^2S_{\frac{1}{2}}$ level, only the mercury atoms with energies lying between 5.20 and 5.25 ev will excite the two $7\,^2D$ levels, only the mercury atoms with energies between 5.16 and 5.20 ev will excite the $8\,^2P_{\frac{3}{2}}$ level, and only the mercury atoms with their energies between 5.10 and 5.16 ev will excite the $8\,^2P_{\frac{1}{2}}$ level. With the further assumption the mercury atoms follow a Maxwellian distribution of energies, it can be determined that only 2% of all of the excited mercury atoms excite the $9\,^2S_{\frac{1}{2}}$, $8\,^2P_{\frac{3}{2}}$ and the two $7\,^2D$ levels and that only 5% of all of the excited mercury atoms excite the $8\,^2P_{\frac{1}{2}}$ level.

The 2836 A line and the 2921/18 A doublet, which correspond to transitions from the $9\,^2S_{\frac{1}{2}}$, and the $7\,^2D_{\frac{5}{2}}$ and $_{\frac{3}{2}}$ levels to the $6\,^2P_{\frac{3}{2}}$ level, could just be detected. Thus it required at least 2% of the excited mercury atoms to populate a level heavily enough to yield measurable radiation, and the highest thallium levels excited to a detectable limit were the $9\,^2S_{\frac{1}{2}}$ and the two $7\,^2D$ levels.

The transitions which were measured in this experiment and shown in Fig. 8 were those of the following series sequences, the $n\,^2S_{\frac{1}{2}}$, $n\,^2D_{\frac{5}{2}}$, and $n\,^2D_{\frac{3}{2}}$ transitions to the $6\,^2P_{\frac{3}{2}}$ and $6\,^2P_{\frac{1}{2}}$ levels. The $9\,^2S_{\frac{1}{2}}$ and two $7\,^2D$ levels are the highest energy terms of these series.

It can be assumed that all cascade transitions from the thallium energy levels above 4.86 ev to lower thallium levels, except the $6\,^2P_{\frac{3}{2}}$ and $6\,^2P_{\frac{1}{2}}$ levels, can be neglected. In justification of this assumption, the $9\,^2S_{\frac{1}{2}}$ level is sparsely populated, and the only line observed is the 2826 A line which is the direct transition to the $6\,^2P_{\frac{3}{2}}$ level. This transition has the highest probability, so all other transitions with smaller probabilities can be neglected. By comparable reasoning and the observation that the intensity of 2921/18 A doublet is weak, the populating action due to transitions from the $7\,^2D$ levels may be neglected.

The $8\,^2P_{\frac{3}{2}}$ thallium level would be populated by direct energy exchange with the mercury atoms to the same extent as the $9\,^2S_{\frac{1}{2}}$ and the $7\,^2D$ levels, for cascade transitions from higher thallium levels may be neglected. Since the $8\,^2P_{\frac{3}{2}}$ level is sparsely populated and has four modes of decay, this level should not lead to a measurable population of these lower levels.

The $8\,^2P_{\frac{1}{2}}$ level is excited by 5% of all of the excited mercury atoms so that this level is populated 2½ times more heavily than the $9\,^2S_{\frac{1}{2}}$, $8\,^2P_{\frac{3}{2}}$ and the two $7\,^2D$ levels by direct energy exchange. The $8\,^2P_{\frac{1}{2}}$ level has three modes of decay, and by considering the transition probabilities, this level will lead to a detectable population of the $8\,^2D_{\frac{3}{2}}$ and $7\,^2S_{\frac{1}{2}}$ levels. For the transition from the $8\,^2P_{\frac{1}{2}}$ level to the $8\,^2S_{\frac{1}{2}}$ level, the transition probability is of the same order of magnitude as the transition probability for the $9\,^2S_{\frac{1}{2}}$–$6\,^2P_{\frac{3}{2}}$ transition. Thus the intensity of the line corresponding to the transition $8\,^2P_{\frac{1}{2}}$–$8\,^2S_{\frac{1}{2}}$ should be approximately 2½ times the intensity of the 2826 A line or a few tenths of a volt. Since the intensity of the 3229 A line is several volts, this increase in intensity caused by the cascade transition from the $8\,^2P_{\frac{1}{2}}$ level may be neglected. Since the transition probability for the transition, $8\,^2P_{\frac{1}{2}}$–$6\,^2D_{\frac{3}{2}}$ is ½ of the probability for the $9\,^2S_{\frac{1}{2}}$–$6\,^2P_{\frac{3}{2}}$ transition, by similar reasoning any cascade transition to the $6\,^2D_{\frac{3}{2}}$ level may be neglected.

It has been shown, that all cascade transitions from levels above 4.86 electron volts of energy, can be neglected to the $8\,^2S_{\frac{1}{2}}$, $6\,^2D_{\frac{5}{2}}$, and $6\,^2D_{\frac{3}{2}}$ levels. Thus these levels with energies of 4.70, 4.42, and 4.50 ev, respectively, are excited almost entirely by direct energy exchange with the excited mercury atoms. The relative effective collision cross sections may be calculated for these levels, as well as, the $9\,^2S_{\frac{1}{2}}$ and the two $7\,^2D$ levels to the $6\,^2P_{\frac{3}{2}}$ level by Eq. (6). These transitions correspond to the lines 3529, 3519, 3229, 2921/18, and 2826 A and are shown in the first group of lines of Table III. Transitions to the $6\,^2P_{\frac{1}{2}}$ level are resonance transitions, and this radiation is imprisoned in the cell. Thus the 2768 and 2580 A lines are resonance lines and cross sections are calculated by Eq. (6) neglecting this imprisonment of radiation. These cross sections are those of the last group of lines in Table III.

The final two transitions which must be considered are the $7\,^2S_{\frac{1}{2}}$–$6\,^2P_{\frac{3}{2}}$ and $7\,^2S_{\frac{1}{2}}$–$6\,^2P_{\frac{1}{2}}$, which correspond to the thallium lines 5350 and 3776 A, respectively. The $7\,^2S_{\frac{1}{2}}$ level has an energy of 3.27 ev and may be populated by both cascade transitions and by collisions with mercury atoms. This level is heavily populated by cascade transitions from the $7\,^2P_{\frac{3}{2}}$ and $7\,^2P_{\frac{1}{2}}$ thallium levels, as well as, a slight population from the $8\,^2P_{\frac{3}{2}}$ and $8\,^2P_{\frac{1}{2}}$ levels. The $7\,^2P_{\frac{3}{2}}$ and $7\,^2P_{\frac{1}{2}}$ levels are populated by energy exchange and by cascade transitions from the heavily populated $6\,^2D_{\frac{5}{2}}$ and $6\,^2D_{\frac{3}{2}}$ thallium levels. In calculating a collision cross section for the $7\,^2S_{\frac{1}{2}}$ level, cascade transitions cannot be neglected. The cross section calculated for the 5350 A thallium line by Eq. (6) is a maximum cross section calculated neglecting all the cascade transitions. The 3776 A thallium line is a resonance line, and the cross section, calculated for this line, is calculated neglecting cascade transitions and imprisoned radiation.

The cross section calculated for the $6\,^2D_{\frac{5}{2}}$ level, corresponding to the transition, $6\,^2D_{\frac{5}{2}}$–$6\,^2P_{\frac{3}{2}}$, or the 3519 A line, had the largest value of those lines of the first group. The $8\,^2S_{\frac{1}{2}}$ level would be expected to have the largest cross section for the lines of the group, for this level was in closest energy resonance with the excited mercury atoms. A possible explanation, for this discrepancy with the law of energy resonance, is that a third neutral mercury atom may be necessary to form the HgTl, quasi-molecule.

CONCLUSIONS

The results of the experiment with added gases indicated that the 5350, 3529, 3519, and 3229 A thallium lines reach a maximum intensity below 0.6 cm of added gas. The intensity of these lines decreased with the addition of added argon or helium. The 3776 A line showed a continuous increase in intensity for the addition of both argon or helium.

The initial increase in intensity of the thallium lines was explained by the reduction of the loss of metastable atoms to the walls of the cell and an enhanced formation of HgTl, quasi-molecules, formed at low gas pressures. Argon also reduced the pumping action of the thallium vapor which carried mercury vapor from the cell.

A competing process, the enhanced formation of mercury molecules caused by the addition of more gas, occurred in the cell. The mercury molecules could only excite the $7\,^2S_{\frac{1}{2}}$ level of thallium. These caused a reduction in the number of excited mercury atoms and a reduction in the intensities of the 5350, 3529, 3519, and 3229 A lines.

The 3776 A thallium line increased in intensity at all pressures because of Doppler broadening of this line when it was excited by mercury metastable atoms and to a lesser extent by mercury molecules.

In the extension of the theory of Frish and Karaulinya[21] to a mercury thallium mixture, it was observed that the $6\,^2D_{\frac{5}{2}}$ thallium level had the largest cross section. The $8\,^2S_{\frac{1}{2}}$ level should have had the largest cross section, from the assumption that in energy resonance there should be the highest probability of energy exchange. The hypothesis, presented to explain this effect, was that a third neutral mercury atom was involved in the formation of the HgTl, quasi-molecule.

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