# Temperature Sensitivities of the Sensitized Fluorescence Spectrum of Thallium†

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An investigation of the sensitized fluorescence of thallium and mercury mixtures using a photomultiplier type of detection is discussed. Data are given to indicate the variation of the intensity of the thallium lines as a function of the temperature of the excess mercury. Explanation of results requires the use of Winan's partial selection rule, $\Delta J=0$, in addition to generally accepted ideas concerning energy transfer, emission, and absorption.

## INTRODUCTION

COLLISIONS of the second kind were first suggested by Klein and Rosseland.[1] By thermodynamic reasoning it was deduced that excited atoms could collide with slow electrons and transfer their excitation energy to produce unexcited atoms and fast electrons without accompanying radiation. Franck[2] extended this theory to include a system which contained electrons, excited atoms, radiation, and normal atoms of a different element from that excited. From this extension Franck predicted that mercury atoms, excited by light emitted from mercury vapor at a wave length of 2537 A, could transfer their excitation energy during collision with normal atoms of a vapor which does not absorb the mercury radiation. The vapor atoms which are excited by such collisions could then emit their characteristic spectra from all states whose excitation energy is less than the exciting potential corresponding to the mercury 2537 A line. Experimental investigations by Cario and Franck[3] confirmed this prediction with a mixture of mercury and thallium vapors. Franck called the new phenomenon sensitized fluorescence.

Early investigators recognized that metastable mercury atoms probably played an important role in the phenomenon of sensitized fluorescence. Experimental investigations by Donat[4] and Loria[5] seemed to confirm the concept that metastable atoms can enhance thallium lines. Donat and Loria both used argon and nitrogen as foreign gases in mixtures of mercury and thallium and found that both caused enhancement of the thallium lines. It is well known that the presence of nitrogen in mercury vapor being irradiated by mercury 2537 A produces atoms in the metastable mercury $6^3P_0$ state. It is interesting to note that Loria found enhancement of thallium lines for small foreign gas pressures; but as the foreign gas pressure was increased, the intensity of thallium lines increased to a maximum and then fell off. The various thallium lines (see Fig. 1) reached their maxima at different foreign gas pressures. Donat did not find maxima for the lines 2768, 3776, and 5350 A.

That inconsistencies such as these could arise is apparent in considering the many difficulties which are encountered in obtaining data concerning sensitized fluorescence by spectrographic methods. A few of these may be listed as (a) obtaining a maximal focus for the ultraviolet light involved, (b) maintaining constant conditions in the gaseous mixture within the specimen tube over the necessarily long exposures, and (c) calibrating the photographic plate in terms of light intensity for the weak lines normally observed.

The purpose of this paper is to describe and discuss the variation of intensity of the sensitized fluorescence of thallium when the temperature controlling the vapor pressure of the mercury present in the mixture is varied. Other parameters are maintained constant by the use of controlled furnaces for heating and the use of electronic detection for maximal focusing and rapid determination of intensities for given temperatures.

## APPARATUS AND METHOD

The quartz experimental tubes were similar to those of Winans and co-workers. They were prepared by distilling small amounts of thallium and mercury into the tubes and then sealing them off under a vacuum of the order of $10^{-7}$ mm or better of mercury. The shape of the experimental tubes is shown in the diagram Fig. 2. The central bulb was about 25 mm in diameter.

The detection apparatus is shown also in the diagram of Fig. 2. The source of the 2537 A radiation was a four-watt General Electric germicidal lamp. This source was focused onto the inner surface of the central bulb of the experimental tube by a pair of quartz lenses. This region, in turn, became the source of the sensitized fluorescence. The visible fluorescent light always appeared in a very thin layer on the inner surface of the tube. It was focused onto the slit of a Bausch and Lomb grating monochromator. The slits of the monochromator were set for a width of 0.4 mm throughout the investigation. The output of the monochromator was received by a 1*P*28 photomultiplier tube. The output current of the photomultiplier tube was passed through a 3-megohm resistor to provide an input voltage for the twin-*t* amplifier. The twin-*t* amplifier was tuned

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[1] O. Klein and S. Rosseland, Z. Physik 4, 46 (1921).
[2] J. Franck, Z. Physik 9, 259 (1922).
[3] G. Cario and J. Franck, Z. Physik 17, 202 (1923).
[4] K. Donat, Z. Physik 29, 345 (1924).
[5] S. Loria, Phys. Rev. 26, 573 (1925).

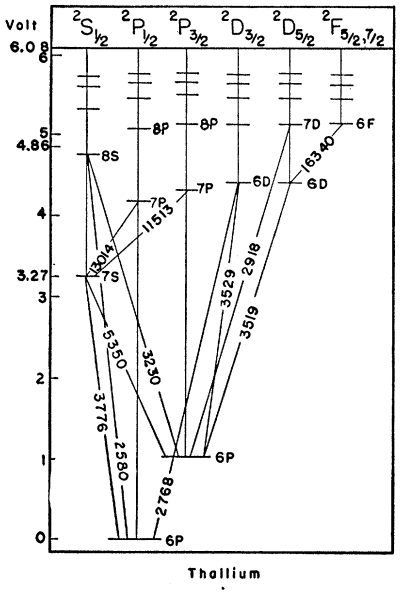


FIG. 1. An energy-level diagram of thallium.

to the 120-cycle signal supplied by the germicidal lamp. Below 80 cps or above 160 cps the output from the amplifier was less than 10 percent of that at 120 cps. The twin-*t* amplifier circuit was similar to that described by Kessler and Wolfe.[6] The output voltage of the amplifier was read with an RCA audio voltmeter.

Preliminary measurements had indicated that the maximum fluorescence was obtained with the extremity of the tube containing the excess mercury at a temperature between 200°C and 300°C and the central portion of the tube (the region of the thallium bead and source of fluorescence) at a temperature of approximately 900°C. This temperature of 900° was determined by the problem of retaining thallium in this region at higher temperatures rather than by any observed decrease of fluorescence with increasing temperatures. A main oven was designed and built to provide the high-temperature portion of this control. One end of the tube was allowed to protrude from the oven to provide the cool portion. Two quartz windows were installed in this oven to pass the incident and fluorescent light. The angle between the light paths was such as to reduce the effect of reflected light to a minimum. An auxiliary oven was designed to provide the temperature control of the portion of the tube which protruded from the main oven. The temperature of this protrusion will be called the mercury temperature since the mercury condensed in this region. The main oven temperature will be called the thallium temperature since an excess of thallium was maintained in the central bulb. The auxiliary oven could be placed around the protruding tube or removed without disturbing any focusing adjustments. The lower mercury temperatures were obtained by directing a jet of air against the end of the protruding tube.

The temperature of the main oven, the region of the thallium bead and source of fluorescence, determines the temperature of the thallium bead. The temperature of the thallium bead determines the vapor pressure in the immediate vicinity of the bead. The large temperature differential which existed between the central part of the tube and the part which protrudes from the main oven, however, makes it impossible to state precisely what the thallium vapor pressure is at the source of fluorescence. The vapor pressure of the thallium is undoubtedly at some value intermediate to those which would be determined by the two extremes of temperature. Experimental evidence obtained by Loria[5] indicates that the thallium vapor pressure is much closer to that determined by the high temperature of the thallium bead than that determined by the low temperature of the protrusion.

The experimental results to be presented were obtained by observing the intensities of the various thallium lines as the mercury temperature was varied, and the thallium temperature was kept constant. Observations were made at many different thallium temperatures.

## EXPERIMENTAL RESULTS

The sensitized fluorescent lines which were observed in this investigation were the thallium lines 2580, 2768, 2918, 3230, 3519, 3529, 3776, and 5350 A. The 3519 and 3529 A lines were not resolved using the photomultiplier tube as a detector so they have been plotted together. Typical data curves are given in Figs. 3, 4, and 5. The relative intensities of the lines are plotted as functions of the mercury temperature. The relative intensity of one line as compared to another may be obtained from the curves. The 5350 A line has been corrected for phototube response since it is the only one with a correction of more than a few percent. Work by Engstrom[7] can be consulted for this photomultiplier

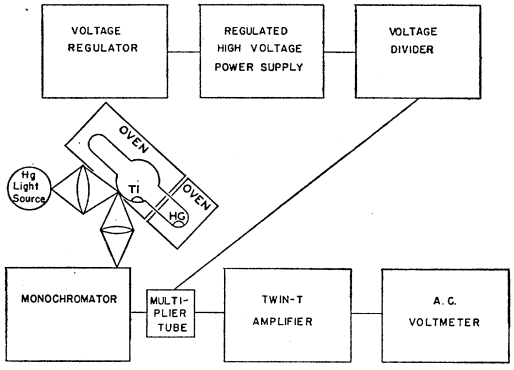


FIG. 2. Apparatus for determination of sensitized fluorescence intensities.

[6] K. G. Kessler and R. A. Wolfe, J. Opt. Soc. Am. **37**, 133 (1947).

[7] R. W. Engstrom, J. Opt. Soc. Am. **37**, 420 (1947).

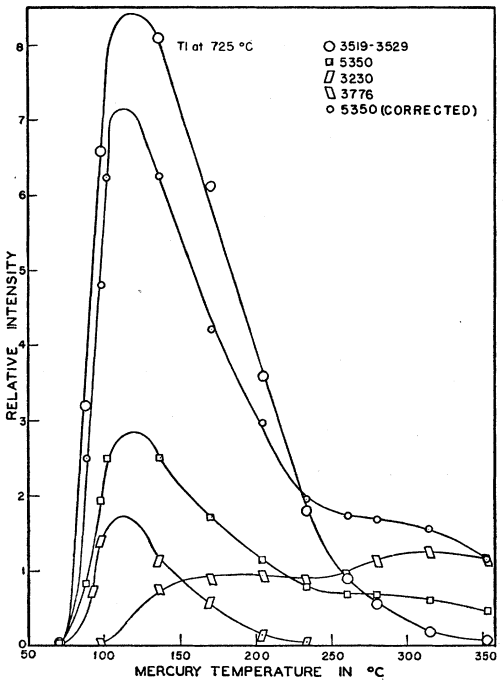


FIG. 3. Sensitized fluorescence intensities as a function of mercury temperatures with the thallium temperature at 725°C. (5350 line corrected for phototube response.)

tube response. Data taken at many different thallium temperatures gave curves having the same general appearance. Therefore, results from only two thallium temperatures are given. The large difference in the intensity scales of Figs. 3 and 4 is due to the difference in the thallium temperatures. Measurements made with transmission screens in an attempt to detect the existence of double absorption, in which an excited mercury atom absorbs a quantum of light, indicated that it was not a detectable process in the excitation of of the thallium levels.

## DISCUSSION

The general feature of the results which is most interesting is the variation of line intensities with mercury temperature. Not only does the intensity of a given line vary with mercury temperature, but also the ratio of the intensities of a given pair of lines may vary radically as the mercury temperature changes. Changes in thallium temperature, also, may be seen to cause changes in the intensity of the thallium lines but to a smaller extent and in a more direct fashion.

A feature of the results which warrants close investigation is the way in which the intensities of the thallium lines 5350 A and 3776 A vary. The ratio of their intensities as shown in Fig. 3 can vary widely in value and are dependent upon the mercury temperature.

The general features of these curves can be explained on the basis of a number of related phenomena which are occurring simultaneously within the experimental system. These include (a) an initial expected increase in sensitized fluorescence with increasing mercury vapor pressure, (b) an optimum intensity followed by decreasing intensity due to specular reflection in the mercury vapor and possibly to an unfavorable ratio in number of mercury atoms becoming available to thallium atoms, (c) a probability that metastable mercury states are more highly populated at the higher mercury temperatures and vapor pressures, and (d) the usual dependence of such a system on excitation and transition rules and the reabsorption of the emitted radiation.

It is known that the metastable mercury atom $6^3P_0$ is produced by collisions of $6^3P_1$ atoms with nitrogen molecules. The number of atoms in the metastable state increases with increasing nitrogen pressures, at least at low nitrogen pressures. It seems probable, therefore, that collisions of the $6^3P_1$ atom with other mercury atoms and molecules may produce metastable $6^3P_0$ atoms. There are indications in the literature that this does happen.[8–10] Results of the present investigation show an increasing absorption of the 2967 A line in a mercury absorption cell as the vapor pressure is increased and the cell is irradiated with unfiltered mercury light. This implies the presence of $6^3P_0$ atoms. Thus it seems reasonable to assume that an increase in the mercury vapor pressure while the vapor is being irradiated by the mercury 2537 A line would bring about an increase in the number of metastable mercury atoms.

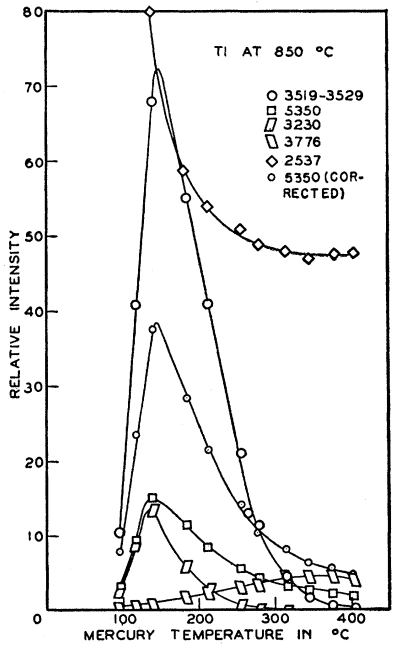


FIG. 4. Sensitized fluorescence intensities as a function of mercury temperatures with the thallium temperature at 850°C. (5350 line corrected for phototube response.)

[8] J. G. Winans, Revs. Modern Phys. **16**, 175 (1944).
[9] W. Orthmann and P. Pringsheim, Z. Physik **35**, 626 (1926).
[10] H. Beutler and B. Josephy, Z. Physik **53**, 747 (1929).

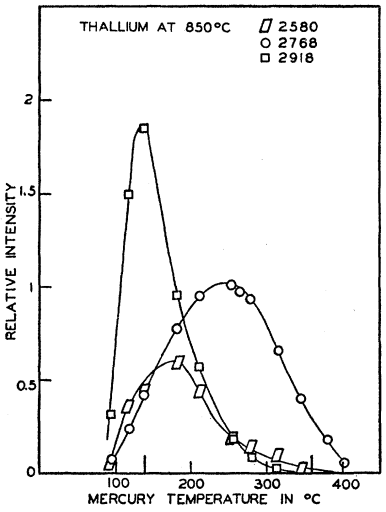


FIG. 5. Sensitized fluorescence intensities of the three least intense lines observed.

The change of intensity of the thallium 3519–3529 A lines is probably the least complex of those observed. Build-up of initial intensity follows the build-up of Hg vapor pressure. Fall-off occurs at approximately the same temperatures as does that for mercury fluorescence and is probably due primarily to specular reflection. A secondary factor contributing to this fall-off must correspond to the dilution effect of the increasing number of mercury atoms present in comparison to a relatively small and constant number of thallium atoms.

The causes of the observed intensities of the thallium 3776 A and 5350 A lines are more complex. If Winan's partial selection rule, $\Delta J=0$,[8] is applied, the most probable transfer of energy at low temperatures and low mercury vapor pressures would be from the $6^3P_1$ mercury atom, to leave the thallium atom in the $7^2P_{\frac{3}{2}}$, $8^2P_{\frac{3}{2}}$, and other $j=\frac{3}{2}$ states. These may decay to leave the atom in the $7^2S_{\frac{1}{2}}$ state. Subsequent emission should produce a 3776 A thallium line which should be roughly three times as intense as the 5350 A line. That it does not is an indication of the role that reabsorption plays in determining the intensity of the thallium lines 2580, 2768, and 3776 A which correspond to transitions to the ground state in the thallium atom.

At higher mercury temperatures, an increasingly greater abundance of mercury $6^3P_0$ atoms are postulated. Collision of this atom with neutral thallium atoms are most likely to produce excited thallium $7^2S_{\frac{1}{2}}$, $7^2P_{\frac{1}{2}}$, $8^2S_{\frac{1}{2}}$ and other $j=\frac{1}{2}$ atomic states.[8] Thus at higher mercury temperatures, the thallium $7^2S_{\frac{1}{2}}$ state may be excited directly by collision or by transitions from upper states. Under the condition of a direct collision, the colliding atoms must convert to kinetic energy and share the one and four-tenths volt excess excitation energy. The resultant Doppler broadening of the 3776 A thallium line has been observed to be sufficient so that only its central portion is reabsorbed. This effect has been postulated by other investigators[3] to explain the difference in intensity between the thallium lines 2768 A and 3776 A. The postulation of increased excitation of the thallium $7^2S_{\frac{1}{2}}$ level at higher mercury temperatures by the mercury $6^3P_0$ atom serves to explain the greater intensity of the thallium 5350 A over that of the thallium 3519–29 lines. For while the thallium $7^2S_{\frac{1}{2}}$ state may be excited by either mercury $6^3P_0$ or $6^3P_1$ mercury atoms, the probability is greater for an excitation of the thallium $6^2D_{\frac{3}{2},\frac{5}{2}}$ states by $6^3P_1$ mercury atom than the $6^3P_0$.

A secondary effect which may contribute toward a general increase in the observed thallium 3776 intensity may result from the dilution of the thallium vapor by the increasing mercury vapor. Thus more resonance radiation could conceivably escape. While this is masked by the Doppler effect in the thallium 3776 A line, it becomes more apparent with the other thallium resonance lines.

As evidence of this effect, thallium 2768 A should not be affected appreciably by Doppler broadening. Neither should it be excited preferentially by the mercury $6^3P_0$ atom. It may be observed however, that its intensity maximum as compared with thallium 3529 A is shifted toward higher mercury temperatures. Thallium 2580 A arising from an excitation of thallium $8^2S_{\frac{1}{2}}$ state, is, also, observed to exhibit a similar shift. It is probable that this shift is influenced at least in part by the $8^2S_{\frac{1}{2}}$ state being excited by collision with both the mercury $6^3P_0$ and $6^3P_1$ states due to the $8^2S_{\frac{1}{2}}$ state lying only slightly below the mercury $6^3P_1$ state and above the $6^3P_0$ state. The intensity variation of thallium 3230 A may be used to indicate the relative extent of the role that these two mercury states play in exciting the thallium $8^2S_{\frac{1}{2}}$ state.

## CONCLUSION

The photomultiplier method of detection in the measurement of fluorescence has proved to be sensitive and convenient.

The observations made on the intensity of the sensitized fluorescence of thallium as a function of mercury temperature agree in general with those made by Loria and are in disagreement with those of Donat[4] and Orthmann and Pringsheim.[9] The results given in this paper show that the sensitized fluorescence disappears at sufficiently high mercury pressures. This is to be expected in terms of the dilution of the thallium by the mercury vapor and specular reflection of the mercury vapor. Donat and Orthmann and Pringsheim found a leveling off of the intensity of some lines. The comparison of the results of this investigation with those of Donat and Loria where a foreign gas pressure is the parameter, assumes that collisions of the mercury $6^3P_1$ atom with either certain foreign gas molecules or

other mercury atoms produce the metastable mercury $6^3P_0$ atom.

An interpretation of the experimental results made with the application of Winan's partial selection rule $\Delta J=0$ gives good explanation of the results. This work seems to give support to this selection rule.

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# Helium Wave Equation

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The wave function for the ground state of helium has been obtained by a method which involves iterating in one direction only, the values of the function in any one plane being made mutually consistent by solving 30 simultaneous equations in 30 unknowns. The local energy value $(H\phi)/\phi$ is approximately constant over most of space, the maximum deviations occurring at large distances between electron and nucleus. The present accuracy is not sufficient to give a good determination of the eigenvalue, but it appears to be at least within 0.5 percent of the experimental value.

DETERMINATION of the form of the wave function for the ground state of the helium atom has been a baffling problem.[1] However, rather powerful methods have now been developed, as a result of which a fairly good wave function has been obtained. It seems, therefore, appropriate to report briefly on the above methods.

The wave equation is

$$\nabla^2\psi+\frac{1}{z}\frac{\partial\psi}{\partial z}+\frac{1}{4r}(E-V)\psi=0, \tag{1}$$

where, if $r_1$ and $r_2$ are the electron-nucleus distances and $\theta$ is the angle between the corresponding radius vectors, then $4x=2r_1r_2\cos\theta$, $4y=r_1^2-r_2^2$, $4z=2r_1r_2\sin\theta$ and $4r=r_1^2+r_2^2$. The potential energy $V$ is such that

$$-\tfrac{1}{4}V=[2(r+y)]^{-\frac{1}{2}}+[2(r-y)]^{-\frac{1}{2}}-\tfrac{1}{4}(r-x)^{-\frac{1}{2}}. \tag{2}$$

Since the wave function for zero electron interaction is exponential in form, i.e., $\psi=e^{-\frac{1}{2}(r_1+r_2)}$, we make the substitution $\psi=e^F$ and consider the function $F$. This satisfies the nonlinear equation

$$\nabla^2F+\frac{1}{z}\frac{\partial F}{\partial z}+|\nabla F|^2+\frac{1}{4r}(E-V)=0. \tag{3}$$

The boundary conditions are $F(y)=F(-y)$, $F(z)=F(-z)$, $F\to-\infty$ as $r\to\infty$.

Now the function

$$F^{(0)}=-\tfrac{1}{2}\sqrt{2}[(r+y)^{\frac{1}{2}}+(r-y)^{\frac{1}{2}}]+\tfrac{1}{4}(r-x)^{\frac{1}{2}}$$

satisfies the equation

$$\left(\nabla^2+\frac{1}{z}\frac{\partial}{\partial z}\right)F^{(0)}-\frac{V}{4r}=0. \tag{4}$$

Subtracting (4) from (3), and letting $G=F-F^{(0)}$, the equation for $G$ is

$$\nabla^2G+\frac{1}{z}\frac{\partial G}{\partial z}+|\nabla G|^2+2(\nabla F^{(0)}\cdot\nabla G)+|\nabla F^{(0)}|^2+\frac{E}{4r}=0. \tag{5}$$

Previous work[1] had shown that the Laplacian must be approximated by an adequate difference operator. To this end, we have assumed that $G$ at any point may be represented by a fourth-degree polynomial in $x$, $y$, and $z$. If $G$ be given at five successive mesh points in, say, the $x$-direction, then the coefficients of the polynomial may be determined. Also, the derivatives of $G$ may be found by differentiating the polynomial.

For the early work, it was necessary to choose a mesh with variable intervals, and this mesh has been retained. At first the boundary was taken to be defined by $|x|=31$, $|y|=31$, $|z|=31$, and $G$ was assumed to be zero there. Later work with the boundary at 63 gives much the same result and this will be reported here. The present mesh points are at $x=\pm63$, $\pm31$, $\pm15$, $\pm7$, $\pm3$, $\pm1$, and 0; $y=0$, 3, 7, 15, 31, and 63; and $z=0$, 1, 3, 7, 15, 31, and 63.

When Eq. (5) is approximated by a difference equation, it relates the value of $G$ at a given point to values at surrounding points. An attempt was made to use

[1] J. H. Bartlett, Phys. Rev. **88**, 525 (1952).