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ABSTRACT

Progress in the measurement of the total quenching cross section of thallium on mercury fluorescence is described. Preliminary results of an experimental determination of the total quenching cross section are given and an analysis of the data is presented. Plans for the direction of experimental work for the next quarter are outlined.

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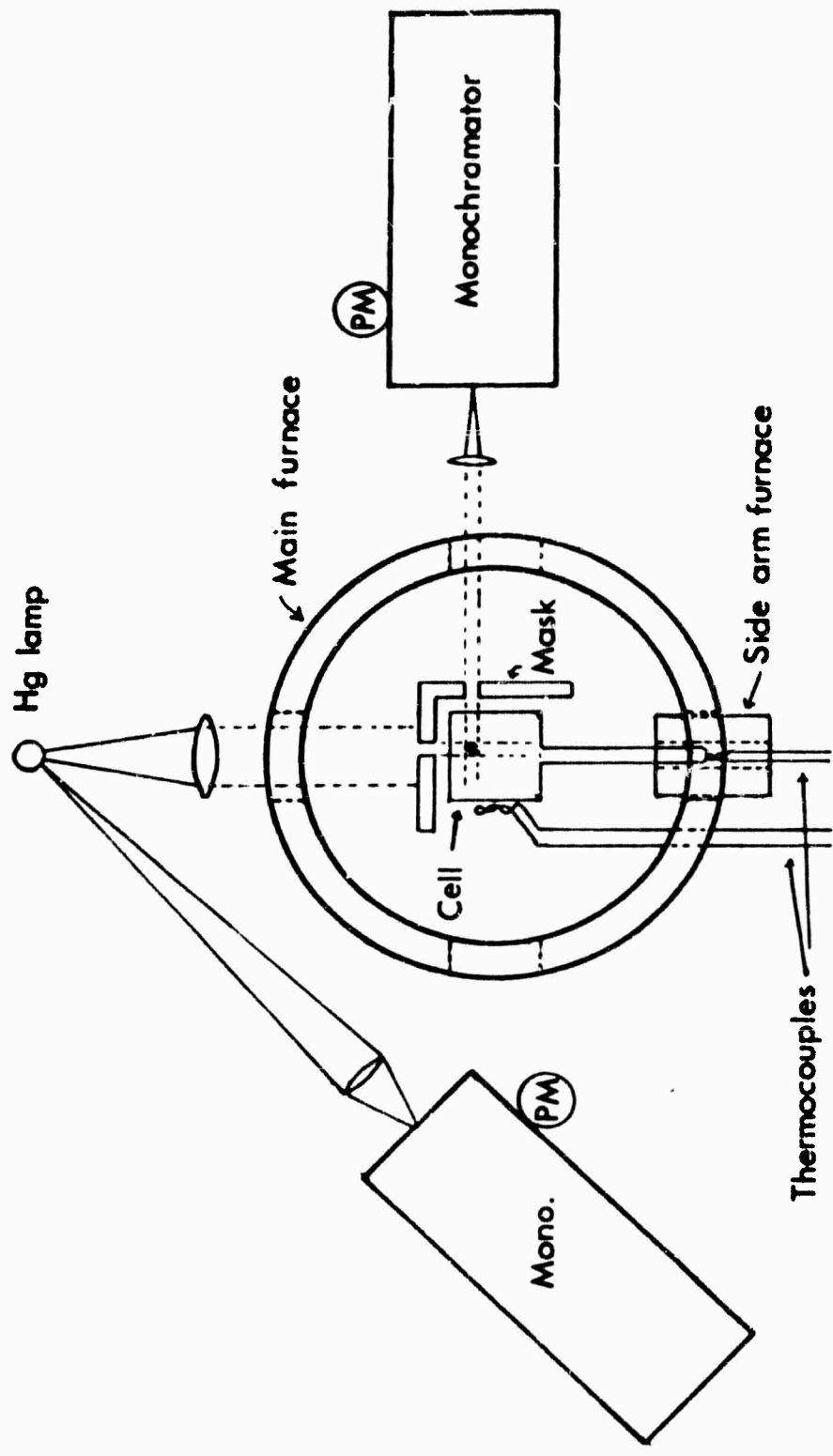
EXPERIMENTAL

Considerable progress has been made in the past six months in improving the reproducibility of the measurements of the fluorescent intensity from the sample chambers. Two major difficulties have been identified and improvements have been made to reduce their effect. One of the difficulties was uneven temperature distribution over the sample chamber. This resulted in the condensation of thallium vapor on the entrance and exit windows of the cell causing variable and erroneous readings of scattered light. The sample chamber furnace was redesigned so that each face of the sample chamber was exposed to the same area of window and furnace wall and the temperature variation over the cell was reduced to less than 10°C.

The second difficulty was in the control of the intensity of the source of radiation. Although the temperature was controlled we found that the variation of intensity of the incident 2537Å radiation still fluctuated by about 30% and have remedied this by monitoring the radiation and manually controlling the source during measurements.

The measurements of the total quenching cross section of thallium on mercury have progressed to the point where we can now give preliminary results and are gathering the data to complete this phase of the experiment.

The preparation of sample cells for the mercury-thallium experiment has been described in the first semi-annual technical report on the project. For each set of measurements a pair of quartz cells has been constructed, one having a fixed quantity of mercury and an excess



Experimental arrangement

Figure 1

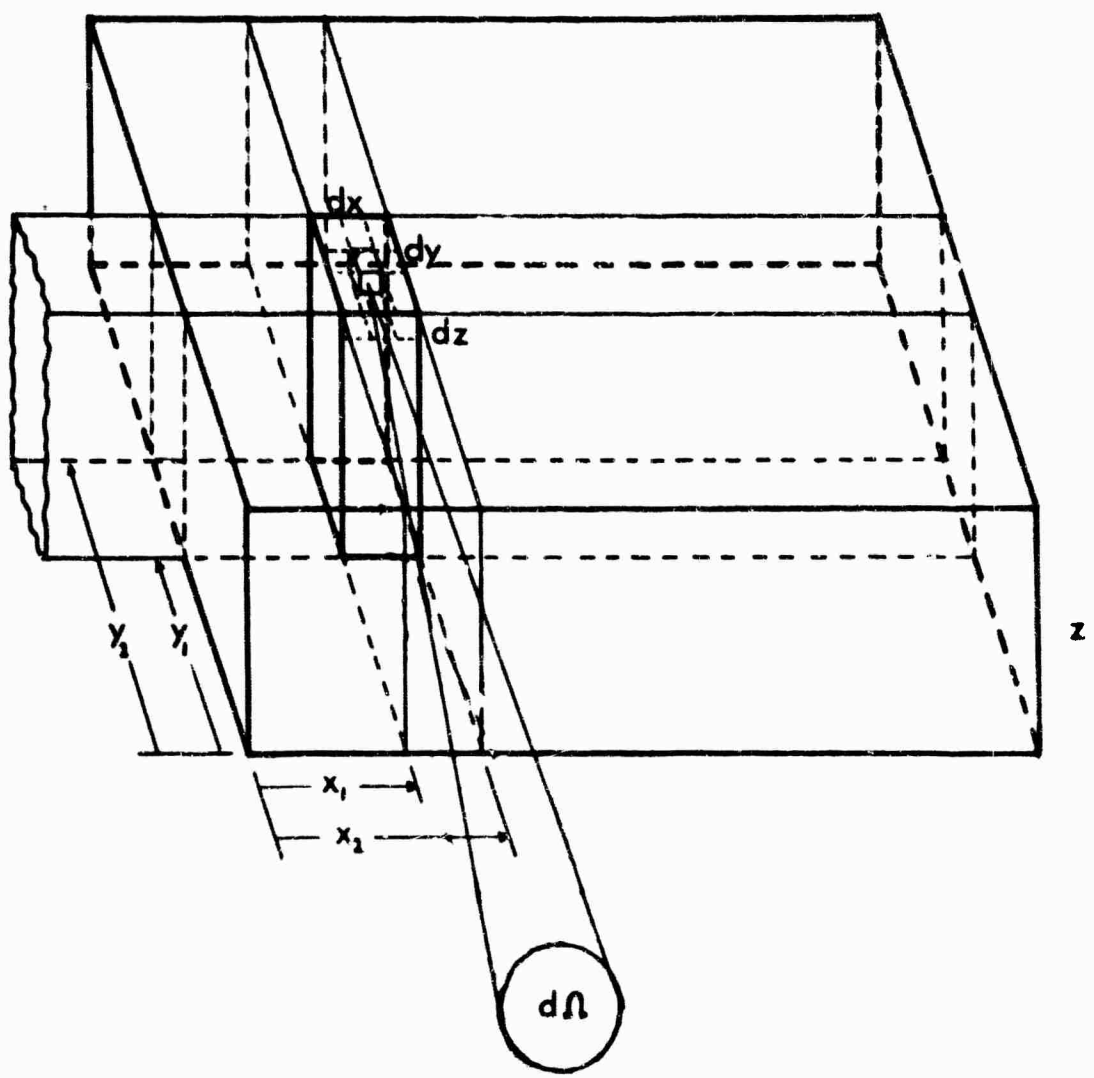


Diagram showing geometry of scattering volume in fluorescence cell.

Figure 2

of thallium, the other having mercury only, each having less than 5×10^{-9} mm Hg of impurities present at 1000°C .

Each of the pair of cells is placed in a furnace and carefully aligned with a mask having two narrow windows for incident radiation and fluorescent radiation. Nearly parallel light from a mercury germicidal lamp falls on the incident window while fluorescent radiation from the other window is collected by a Bausch and Lomb 500 mm grating monochromator. A schematic diagram of the experimental arrangement is shown as figure 1.

For the experimental arrangement shown we may derive some relationships from which we may calculate the quenching cross reaction. Let a beam of incident nearly monochromatic radiation of width $\Delta y = y_2 - y_1$, fall on a resonance cell containing n_1 atoms of mercury per unit volume in the ground state and n_4 atoms of thallium per unit volume in the ground state as indicated in Figure 2. If the intensity of the radiation is not extremely high the numbers n_1 and n_4 will be very nearly constant. In any infinitesimal volume element the production of excited mercury atoms will be constant and will depend on the intensity of the radiation reaching the volume and the number n_1 , let this rate of production be called R_{12} , and let the equilibrium number of mercury atoms per unit volume in the 6^3P_1 state be called n_2 . Assuming that no stimulated emission occurs, the fluorescence radiation will be emitted uniformly in all directions and the amount of energy per unit time emitted in a small solid angle $d\Omega$, in the frequency interval du is given by,

$$n_2 \frac{h\nu}{\tau} \frac{d\Omega}{4\pi} F(\nu) d\nu dx dy dz = I(\nu) d\Omega dx dz d\nu, \quad (1)$$

where τ is the lifetime of the excited state.

Equation (1) gives the energy per unit time per unit frequency interval in the solid angle $d\Omega$ leaving the infinitesimal volume element of cross section $dx dz$. Not all this energy reaches the detector since some of it is reabsorbed. Let $I(\nu) = I F(\nu)$ with $\int_{\nu} F(\nu) d\nu = 1$, thus describing the emitted radiation as having a spectral line shape. If $k(\nu)$ is the absorption coefficient of the vapor in the cell then the amount of energy per unit time per unit frequency interval reaching the detector from $dx dy dz$ is:

$$I(\nu) e^{-k(\nu)y} dx dz d\Omega d\nu = F(\nu) n_2 \frac{h\nu}{\tau} dx dy dz d\nu \frac{\Omega}{4\pi} \times e^{-k(\nu)y} . \quad (2)$$

The total energy per unit time reaching the detector is then

$$\int_{\nu} \int_{y_1}^{y_2} \int_{x_1}^{x_2} n_2 F(\nu) e^{-k(\nu)y} \frac{h\nu}{4\pi\tau} dy dx dz d\Omega d\nu = \text{const.} \times I_m , \quad (3)$$

where I_m = meter reading of detector, assuming the detector sensitivity does not change appreciably over the width of $F(\nu)$.

Since, n_2 is a function of x , and $k(\nu)$ is a constant in the space of the cell,

$$I_m = \text{const.} \times (x_2 - x_1) z \left[\int_{\nu} \frac{h\nu}{4\pi\tau} F(\nu) \left[\frac{e^{-k(\nu)y_1} - e^{-k(\nu)y_2}}{k(\nu)} \right] d\nu \right] \frac{n_2(\text{ave})}{\tau} \quad (4)$$

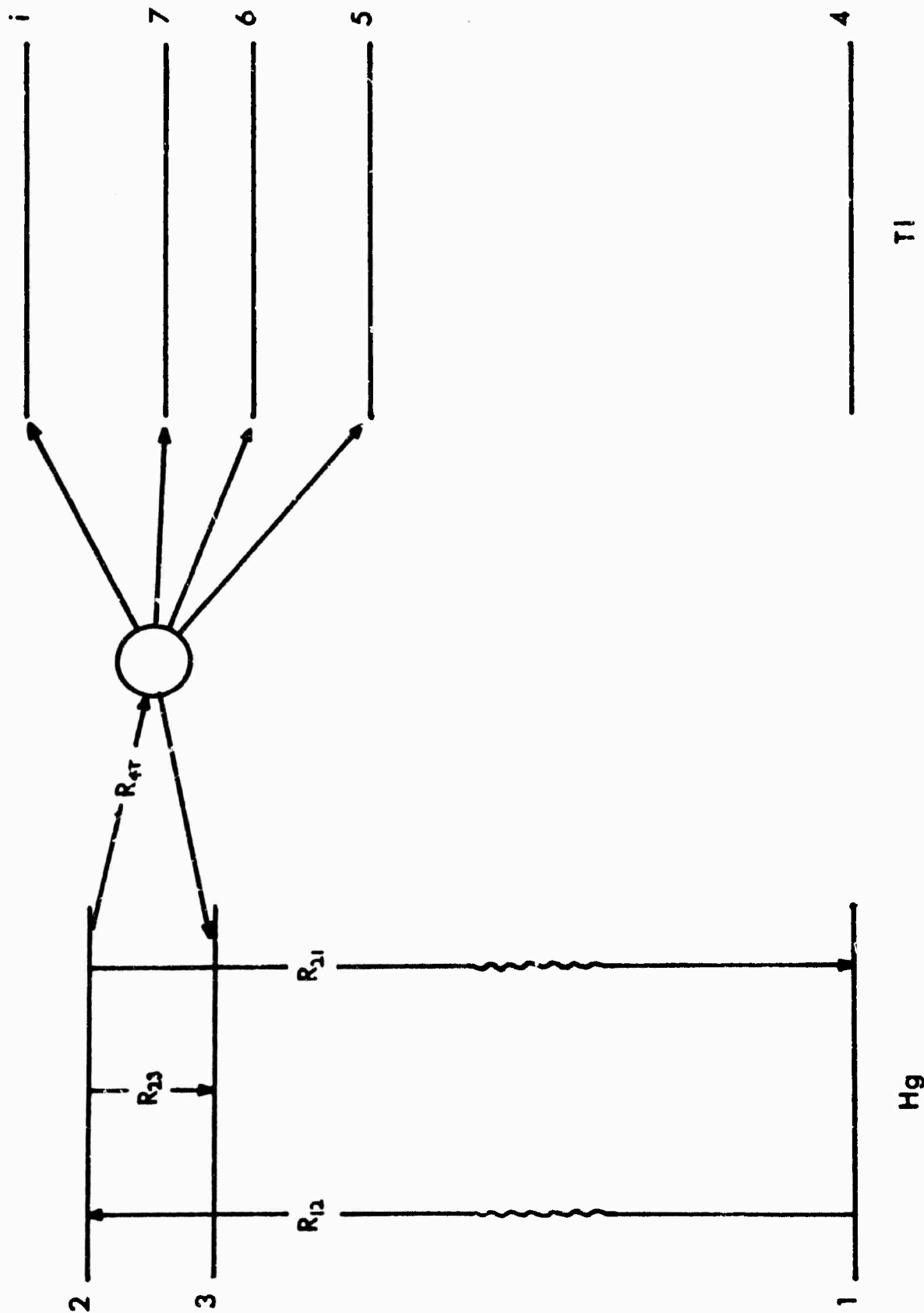
The integral in brackets is a constant as long as n_1 , and T , remain constant. It will change rather rapidly with n_1 but slowly with T . The integral is independent of n_2 .

Thus we may write:

$$I_m = C(n_1, T) \frac{n_2}{\tau} \quad (5)$$

and we see that the meter reading of the detector is proportional to the number of excited atoms per unit volume provided the temperature is held nearly constant and the number density n_1 is held constant. This will

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Schematic energy level diagram indicating processes of interest in sensitized fluorescence

Figure 3

provide the basis for our measurements.

Consider now the equilibrium situation in an infinitesimal volume element such as we have just described when it is exposed to resonance radiation. A schematic energy level diagram is given in figure 3.

If resonance radiation of constant intensity is present let R_{12} be the rate of formation of excited atoms, which will depend on I_0 , n_1 , and only slightly on temperature.

Let the following rate processes be considered:

- (a) the rate of production of excited atoms per unit volume per unit time, R_{12} , by absorption of resonance radiation,
- (b) the rate of de-excitation of excited atoms to the lower state by collision with ground state atoms, which depends on the cross section for the process, σ_{23}^2 , and the number of n_1 , n_2 , collisions per unit time per unit volume,

$$R_{23} = 2n_2n_1\sigma_{23}^2\sqrt{2\pi RT\left(\frac{1}{m_1} + \frac{1}{m_2}\right)}, \quad (6)$$

- (c) the rate of reradiation of fluorescence radiation, which depends on the number of excited atoms and the lifetime of the state,

$$R_{21} = n_2/\tau,$$

- (d) the rate of de-excitation by collision of the second kind exciting one of the states n_i ($i = 4, 5, 6, \dots$),

$$R_{4T} = \sum_i 2n_2n_i\sigma_{4i}^2\sqrt{2\pi RT\left(\frac{1}{m_1} + \frac{1}{m_i}\right)}, \quad (7)$$

where σ_{4i}^2 is the cross section for transfer of excitation from mercury to thallium atoms.

We can write in general for equilibrium that

$$R_{12} = R_{21} + R_{23} + R_{4T}, \text{ or}$$

$$R_{12} = 2n_2n_1\sigma_{23}^2 \sqrt{2\pi RT \left(\frac{1}{m_1} + \frac{1}{m_1} \right)} + \sum_i 2n_2n_4\sigma_{4i}^2 \sqrt{2\pi RT \left(\frac{1}{m_1} + \frac{1}{m_2} \right)} + n_2/\tau \quad (9)$$

Now, call

$$\sum_i \sigma_{4i}^2 = \sigma_{4T}^2, \text{ then}$$

$$R_{12} = 2n_2n_1\sigma_{23}^2 \sqrt{4\pi RT/m_1} + 2n_2n_4\sigma_{4T}^2 \sqrt{2\pi RT \left(\frac{1}{m_1} + \frac{1}{m_2} \right)} + n_2/\tau \quad (10)$$

Consider two cells each having identical values for n_1 and T but one having $n_4 = 0$, if these cells are exposed to the same incident radiation and the same volume is observed then the rate of production of excited atoms in the volume under observation is the same.

$$R_{12} = R'_{12}$$

Let n_2' be the number density of excited atoms in the presence of $n_4 \neq 0$ then we may write:

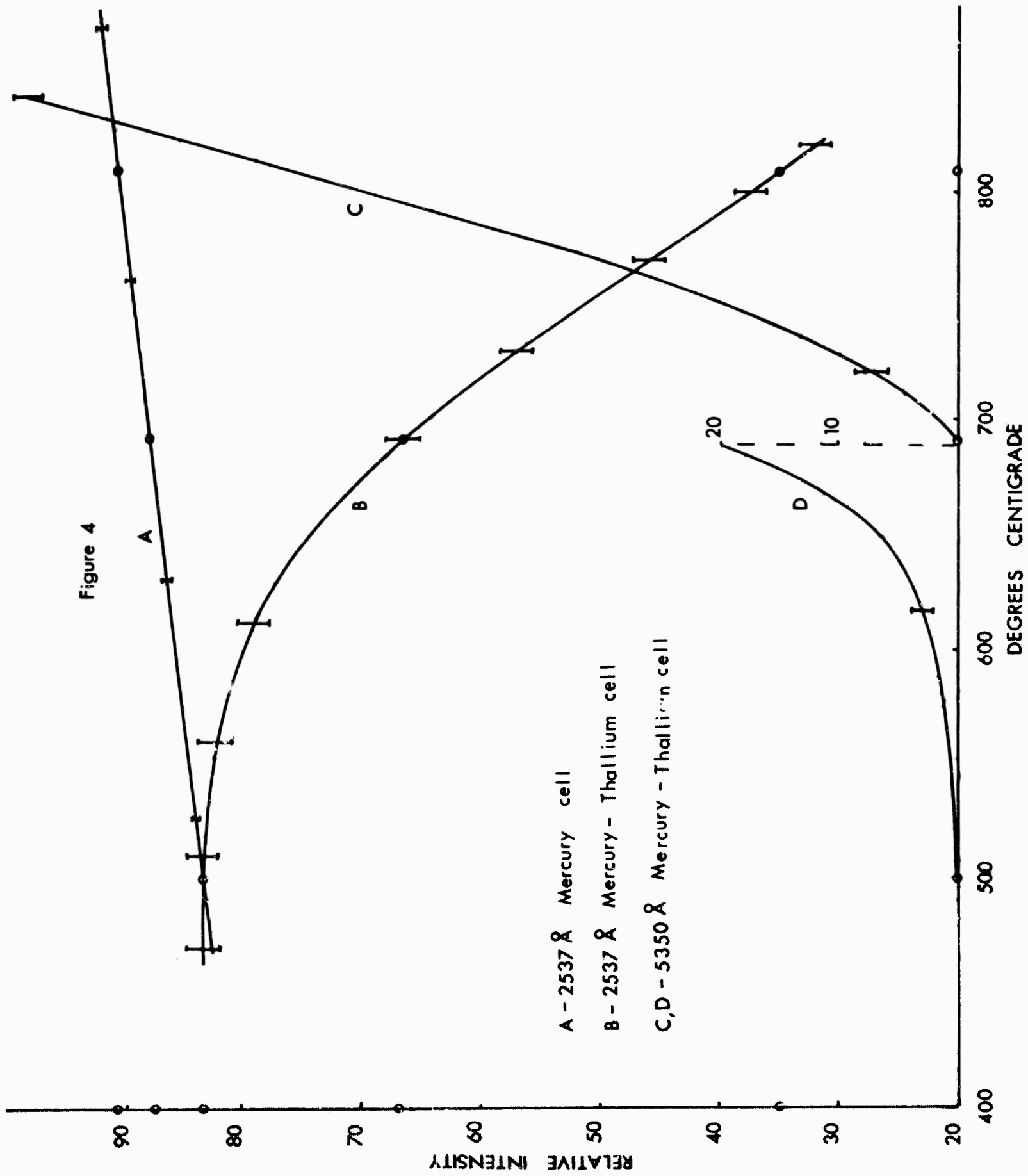
$$2n_2n_1\sigma_{23}^2 \sqrt{4\pi RT/m_1} + n_2/\tau = 2n_2'n_1\sigma_{23}^2 \sqrt{4\pi RT/m_1} + 2n_2'n_4\sigma_{4T}^2 \sqrt{2\pi RT \left(\frac{1}{m_1} + \frac{1}{m_2} \right)} + n_2'/\tau \quad (11)$$

From which we may write,

$$\sigma_{4T}^2 = \left[\left(\frac{n_2 - n_2'}{n_2'} \right) / n_4 \right] \left\{ \frac{1/\tau}{\sqrt{8\pi RT \left(\frac{1}{m_1} + \frac{1}{m_2} \right)}} + n_1\sigma_{23}^2 \sqrt{\frac{2m_2}{m_1 + m_2}} \right\} \quad (12)$$

From our considerations of the reading of the detector we see that,

$$\left(\frac{n_2 - n_2'}{n_2'} \right) = \frac{I_m - I_m'}{I_m'}, \text{ an experimentally determined quantity. Also we see}$$



that we can determine the total quenching cross section and the quenching cross section to the metastable state if the determination of the resonance fluorescence intensity is made for several values of n_1 .

For the first pair of sample chambers the cells were sealed off with the mercury at a temperature of 26°C and the main body of the cell at a temperature of 318°C. Assuming an equilibrium to be reached between the effusion of the mercury from the cold end (T') to the hot end (T) we find, $n_1 = \frac{p'}{kT'} \frac{T'}{T}$, which yields for this set of cells $n_1 = 46.0 \times 10^{14}$ atoms/cm³. An independent check on this number is planned using absorption techniques.

For the data reported here a sample cell was placed in the furnace and the furnace temperature was raised using a temperature controller to avoid overshoot in coming up to temperature. As soon as the readings stabilized, the temperature of the main body of the cell, the temperature of the cell stem, the intensity of the fluorescence, and the intensity of the source were recorded. This procedure was followed for about eight temperatures from 450°C to 825°C. This procedure was reversed and data obtained by decreasing the temperature from about 825°C to 450°C.

Throughout the experiment the temperature of the stem was maintained 50°C lower than the main body of the cell to reduce the possibility of Thallium condensation on the windows of the cell, and the intensity of the source was maintained at a constant value manually.

Figure 4, presents graphically the results of four such runs on the mercury-thallium cell, and two such runs on the mercury cell. The results of Figure 4 are also tabulated in Table I.

Table I

T(°C)	I ₂	I ₂ '	$\frac{I_2 - I_2'}{I_2'}$	N ₄
500	83.5	83.5	0	24.4 X 10 ¹²
600	85.8	79.1	.08	149 X 10 ¹²
700	88.0	64.8	.36	874 X 10 ¹²
750	89.3	50.5	.77	2630 X 10 ¹²
775	90.0	44.1	1.04	3320 X 10 ¹²
800	90.1	37.1	1.43	5680 X 10 ¹²

The data for the n₄ column in Table I was obtained from a vapor pressure curve for thallium and the ideal gas equation.

The values of Table I may be substituted into equation (12) to find the total quenching cross section of mercury by thallium and yields the results given in Table II.

Table II

T(°C)	$\sigma^2 (\times 10^{16} \text{ cm}^2)$
500	indeterminate
600	360 + 50 -
700	260 + 40 -
800	150 + 40 -

In calculating the above cross sections it has been assumed that σ_{23}^2 is less than $1000 \times 10^{-16} \text{ cm}^2$ which makes the contribution of this term to the quenching negligible. The mercury pressure would have to be increased about 100 times before the effect of σ_{23}^2 would become apparent. We plan to examine one set of cells with pressures in this region.

From the theory of slow collision cross sections it is expected that

the cross section should vary as the reciprocal of the velocity, or as $1/\sqrt{T}$. The uncertainty in the data does not permit a check of the linear variation of σ_{4T}^2 with $1/\sqrt{T}$.

Future Plans

We plan to continue measurements on the mercury-thallium system during the next quarter to verify the results of our preliminary measurements and to evaluate the cross section for the production of metastable mercury atoms. We also plan to make measurements on the relative intensity of the thallium fluorescent lines to evaluate the cross sections for excitation to specific thallium levels. We will also begin preparation of cesium-potassium sample cells for a similar study of collision cross sections in this system.

We have concentrated on the experimental aspects of the problem for the past quarter and expect to continue this during the next quarter.