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1963

The measurement of the life-time of the $6^2P_{3/2}$ state of thallium

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THE MEASUREMENT OF THE LIFETIME OF THE

$6^2P_{3/2}$ STATE OF THALLIUM

BY

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A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the requirement for the

Degree of

MASTER OF SCIENCE

Rolla, Missouri

1963

Approved by

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ABSTRACT

The measurement of the lifetime of the metastable $6^2P_{3/2}$ state of thallium is discussed. Time-sampling equipment techniques and instantaneous methods of display on an oscilloscope for measuring the lifetime are explained. The lifetime is measured as a function of mercury vapor pressure. The decay of the 5350 A thallium line is also measured to give an indication of the effect of the imprisonment of the 3776 A resonance line. This decay of the 5350 A line is also in a mercury atmosphere.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to his adviser, Dr. Richard A. Anderson, who suggested this problem. Dr. Anderson's suggestions and help with the theory and his patience and encouragement were essential to the completion of the problem.

The electronic equipment was designed by Mr. E. Stepp whose assistance with this equipment and whose discussion of the theory facilitated the completion of the problem.

The author also wishes to acknowledge the graduate students and the Physics Department Staff who were most helpful during the course of this work.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF PLATES

I. INTRODUCTION

If a current is passed through a gas, collisions occur between the gas atoms and the electrons. If these electrons have sufficient energies, the gas atoms are excited to higher states. Also, the atoms are ionized, and after electron recombination, they decay by spontaneous transitions to the ground state. It is possible, as in the case of thallium, that many of these atoms decay to a metastable state. From this metastable state the atom cannot decay to the ground state under normal conditions. In this way it is possible to build up a large population of metastable atoms. Other methods of producing metastable atoms are also employed.

Anderson, Schricker, and Patterson have investigated the r-f excitation of an Hg-Tl mixture.[1] In this work the Hg and Tl atoms were excited by r-f excitation. Collisions of the second kind between the resonance excited and metastable Hg atoms and the ground state Tl atoms produced additional excited Tl atoms above those Tl atoms excited by the discharge. The Hg atoms in the resonance and metastable states had excitation energies which were nearly the same as the excitation energies of lower Tl states. Therefore, these Tl energy states could be populated by such collisions. In their experiment, Anderson, Schricker, and Patterson, observed an enhancement of certain Tl lines which decayed into the Tl metastable state. It was suggested that a large population could be built up in the metastable

state of Tl. Earlier experiments by Swanson and McFarland[2] and by Anderson and McFarland[3] indicated similar effects. The sensitized fluorescence experiments of Anderson and McFarland involved excitation of the Hg vapor by a mercury light source. The excited Hg atoms transferred their energies to the Tl atoms by collisions of the second kind. The intensities of those Tl lines which decayed to the metastable state were observed at various foreign gas pressures and enhancement of these lines was observed at certain argon and helium pressures. Thus, it might be possible to build up a large population in the metastable state of Tl and maintain this population by using an inert gas as a buffer.

The interest in the building up of a large population in a metastable state is in a possible application toward the development of a laser. In order to obtain laser action between two energy states, the upper state must be more heavily populated than the lower state. Thus, the population in the Tl $6^2P_{3/2}$ metastable state must exceed that of the ground state in order to have laser action between them. However, in addition to the large population these atoms must remain in the particular state for a relatively long time for laser applications. This is the reason for interest in the lifetime of the state. It should be noted, however, that the lifetime of the state is of interest in itself purely to add to our knowledge of the Tl atom.

In the experiment performed we measured the lifetime of the $6^2P_{3/2}$ state of Tl and determined the factors affecting this

lifetime. Also, we investigated the effects of foreign gases on this lifetime, and in particular the effects of Hg as a buffer gas.

II. LITERATURE REVIEW

During the period from 1920 to 1935, investigations were made of the lifetimes of metastable atoms. The first measurements of the lifetime of a metastable atom were made by Meissner[4] and Dorgelo.[5] An inert gas was electrically excited, this excitation was shut off and an exciting light which the metastable atoms could absorb was passed through the cell and removed the atoms from the metastable state. When absorption was no longer apparent, the metastable atoms had all been removed from the state. The intensity of the absorbed light was measured photographically and gave an indication of the lifetime of the state. This method was inaccurate in that the time between cut off of the electrical excitation and the passage of light could not be determined accurately enough to obtain a reliable decay curve from the absorption curve as a function of time.

Improvements in the experimental method were made by Meissner and Graffunder.[6] They operated the electrical discharge in the gas and the exciting light which could be absorbed by the metastable atoms with an alternating current. This alternating current had a variable phase, so when the electric discharge in the gas was turned off, the exciting light was incident on the gas. This allowed the exciting light to be on at different times after the electrical discharge had been shut off. This made possible accurate time measurements and gave reliable results. However, the failure to take into account repopulation of the metastable

state due to spontaneous transitions to the state gave erroneous results and this was also true of the previously mentioned experiments. The above experiments were for the metastable atoms of neon and argon, and photographic measurements of the decay curve gave the lifetime of the state.

Many experiments have been performed to determine the lifetime of the 6^3P_0 metastable state of mercury. Pool[7] studied this lifetime in a nitrogen atmosphere. In this experiment Hg atoms were excited to the 6^3P_1 resonance state by optical excitation. This light was shut off and a light of wavelength corresponding to a transition to a higher energy state of Hg from the metastable state was shone on the cell. The absorption spectrum was photographed. The rate of decrease of the intensity of the spectral line was assumed to be the rate of decay of the 6^3P_0 metastable mercury state. From this curve the lifetime was measured and was found to be 4.2×10^{-4} seconds. Measurements of this lifetime were also made by Webb and Messenger[8] and by Samson.[9] Webb and Messenger used an alternating current excitation of Hg atoms in a tube containing an anode, cathode, and two grids. By proper cycling of the anode current and by adjusting the grid voltages the periods of excitation could be controlled. When the excitation was off, the photons emitted by the excited Hg atoms hit the plate of the tube and a current was produced by the photoelectric effect. This current was measured with an electrometer and the magnitude of it indicated the decay of the excited atoms. The preferred states were excited by applying different exciting

potentials across the elements. The lifetime of the metastable 6^3P_0 state was measured by observing the radiation after all other excited atoms had decayed to the ground state by spontaneous transitions. This additional radiation was produced by metastable Hg atoms being excited by collisions to the 6^3P_1 state from which they could decay by spontaneous emission to the ground state. Samson performed the same experiment as Webb and Messenger. His method of detection consisted of a rotating wheel and a slit. A photographic film was attached to the wheel and as it swept past the slit, during the time the atoms were not being excited, a circular trace was made on the photographic film. This trace gave an indication of the decay of the radiation. Additional investigations of the Hg metastable state were made by Gaviola[10] and by Foote.[11]

The only successful measurement of the lifetime of the $6^2P_{3/2}$ metastable thallium energy state was made in 1962 by Gallagher and Lurio.[12] Atoms were excited to the $7^2S_{1/2}$ state and some of the excited atoms decayed to the metastable state. The exciting radiation was of wavelength 3776 A. When this radiation was shut off, the atoms in the $6^2P_{3/2}$ state were exposed to the 5350 A line which pumped them to the $7^2S_{1/2}$ state. The resulting re-radiated or scattered 5350 A radiation was measured with phototubes as a function of time after cut off of the 3776 A line. This gave the lifetime of the $6^2P_{3/2}$ atom in a pure Tl system. Similar measurements were made after adding argon at low pressure to the system. The measured lifetime for the $6^2P_{3/2}$ state was 30

microseconds in a cell containing only Tl and a lifetime of

nearly one millisecond was measured with the addition of a few

cm of Hg of argon.

III. DISCUSSION OF THEORY

The lifetime of the $6^2P_{3/2}$ state of thallium was measured
for various Tl and Hg vapor pressures. The experimental method
was to pump Tl atoms from the $6^2P_{1/2}$ ground state to the $7^2S_{1/2}$
state using 3776 A radiation from a Tl lamp. (See Figure 1)
From the $7^2S_{1/2}$ state the atoms decayed to the ground state or
to the $6^2P_{3/2}$ metastable state. 5350 A radiation corresponding
to the transition $7^2S_{1/2} - 6^2P_{3/2}$ from a second Tl lamp was
radiated collinearly with the 3776 A line into the absorption
cell, and was absorbed by the atoms in the $6^2P_{3/2}$ state. When
the pumping light was shut off by a chopper, the 5350 A inci-
dent light excited the metastable $6^2P_{3/2}$ atoms to the $7^2S_{1/2}$
state, and the re-radiated or scattered 5350 A light was moni-
tored at 90° to the exciting light with a photomultiplier. The
intensity of the scattered 5350 A light was proportional to the
number of atoms in the $6^2P_{3/2}$ state. The population of the
state was detected as a function of time after cutting off the
pumping light by measuring the intensity of the scattered light
with time. Knowing this one can determine the lifetime of the
state. However, one must consider the relative number of atoms
which go to this metastable state after the excitation is shut
off.

In a system free from interactions of various forms the
$7^2S_{1/2}$ atoms of thallium will under go spontaneous transitions
to either the ground state or the metastable state. The spon-
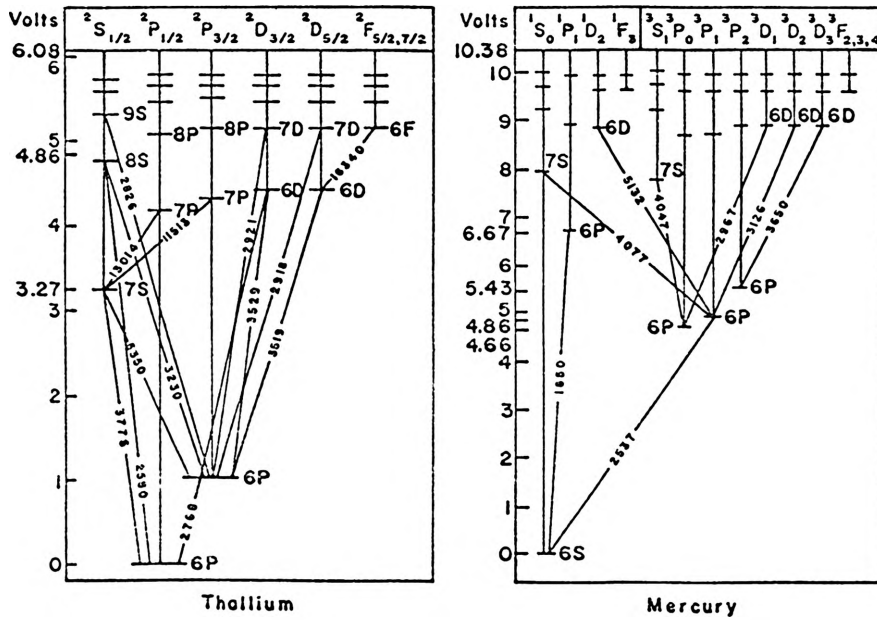taneous transition probabilities for these transitions are

Figure I - Energy Level Diagram[2]

$$7\,^2S_{1/2} - 6\,^2P_{3/2} \qquad A = 0.370 \text{ x } 10^{-8} \text{ sec}^{-1}$$

$$7\,^2S_{1/2} - 6\,^2P_{1/2} \qquad A = 0.197 \text{ x } 10^{-8} \text{ sec}^{-1};$$

therefore, the atom is more likely to go to the $6\,^2P_{3/2}$ state.
The relative number of atoms going to the $6\,^2P_{1/2}$ state is fur-
ther reduced by imprisonment of the resonance line; that is,
the net number of atoms leaving the state by way of the $7\,^2S_{1/2}$ -
$6\,^2P_{1/2}$ transition appears small due to repeated emission and re-
absorption of the 3776 A line. The effects of imprisonment are
very pronounced for higher vapor pressures of Tl. The presence
of more atoms increases the probability for the 3776 A line to
be re-absorbed. From the results of our investigations the
probability of the transition $7\,^2S_{1/2}$ - $6\,^2P_{1/2}$ was of the order
of 10^5 sec^{-1}. These transition probabilities are for electric
dipole transitions which obey the following selection rules:
the change in the orbital quantum number, 1, is $\Delta 1 = \pm 1$ and
the change in the total angular momentum quantum number, J, is
$\Delta J = 0, \pm 1$, but the transition where $J = 0 \rightarrow J = 0$ is for-
bidden. Transitions from the $6\,^2P_{3/2}$ state to the ground state
are not allowed by these selection rules. The electric dipole
transition probabilities are given by the relation[13]

$$A = \frac{64 \, \pi^4 \sigma^3}{3h} \sum_{m_J, \, m_J'} |< n,L,J,m_J|\vec{P}|n',L',J',m_J' >|^2$$

where σ is the wave number of the transition, the last term is
the electric dipole moment matrix element squared, and $\vec{P} = -e\vec{r}$

is the electric dipole moment. The evaluation of the angular portions of the term $|< n,L,J,m_J|\vec{P}|n',L',J',m_J' >|$ can be performed immediately since the angular dependence of the wave functions for the $7^2S_{1/2}$, $6^2P_{3/2}$, and $6^2P_{1/2}$ states are known. They are the usual hydrogen-like spherical harmonics. The radial integrals of the matrix components of the form $< n,L|\vec{P}|n',L' >$ can only be evaluated approximately. Their evaluation involves a knowledge of the radial wave functions of Tl for these states. Bates and Damgaard[14] have given a Coulombic approximation method which was used to evaluate the above transition probabilities.

The transition probability for the transition from the $6^2P_{3/2}$ state to the ground state is proportional to the absolute square of the matrix elements of the spin and orbital magnetic moments. If these matrix elements are zero, the transition is forbidden by magnetic dipole selection rules. The selection rules for the magnetic dipole transitions apply to the $6^2P_{3/2}$ - $6^2P_{1/2}$ transition. These rules are: $\Delta l = 0$, $\Delta J = \pm 1$, and for the $6^2P_{3/2}$ - $6^2P_{1/2}$ transition $\Delta l = 0$ and $\Delta J = 1$.

The magnetic dipole transition probability[15] is given by

$$A_m = \frac{64 \pi^4 \sigma^3}{3h} \sum_{m_J, m_J'} |< n,L,J,m_J|\vec{M}|n',L',J',m_J' >|^2$$

where σ is the wave number of the transition, $< n,L,J,m_J|$ are the wave functions for the $6^2P_{3/2}$ state, $|n',L',J',m_J' >$ are the

wave functions for the $6^2P_{1/2}$ state, and $\vec{M}$ is given by $e/2mc$ $(\vec{L} + 2\vec{S})$, where $\vec{L}$ is the orbital angular momentum operator and $\vec{S}$ is the spin angular momentum operator. Since the magnetic dipole operator $\vec{M}$ does not involve the radial portions of the wave functions for the $6^2P_{3/2}$ and $6^2P_{1/2}$ states, the sum of the magnetic dipole matrix elements above can be evaluated without knowing them. The radial integrals can be performed and are equal to unity because the wave functions are normalized. The angular dependence of the Tl $6^2P_{3/2}$, $m_J = 3/2, 1/2, -1/2, -3/2$ and $6^2P_{1/2}$, $m_J = 1/2, -1/2$ wave functions are hydrogen-like, since they are products of spin functions and spherical harmonics. The following matrix elements will appear in the above sum:

$$
\begin{aligned}
< J, m_J |\vec{M}| J', m_J' > &= \ < 3/2, 3/2 |\vec{M}| 1/2, 1/2 > \\
&= \ < 3/2, 1/2 |\vec{M}| 1/2, 1/2 > \\
&= \ < 3/2, 1/2 |\vec{M}| 1/2, -1/2 > \\
&= \ < 3/2, -1/2 |\vec{M}| 1/2, 1/2 > \\
&= \ < 3/2, -1/2 |\vec{M}| 1/2, -1/2 > \\
&= \ < 3/2, -3/2 |\vec{M}| 1/2, -1/2 >
\end{aligned}
$$

The matrix elements when evaluated give the following values:

$$
\begin{aligned}
< 3/2, 3/2 |\vec{M}| 1/2, 1/2 > &= -2.568 \ e\hbar/2mc \\
< 3/2, 1/2 |\vec{M}| 1/2, 1/2 > &= 0 \\
< 3/2, 1/2 |\vec{M}| 1/2, -1/2 > &= 1.483 \ e\hbar/2mc \\
< 3/2, -1/2 |\vec{M}| 1/2, 1/2 > &= 1.483 \ e\hbar/2mc \\
< 3/2, -1/2 |\vec{M}| 1/2, -1/2 > &= 0 \\
< 3/2, -3/2 |\vec{M}| 1/2, -1/2 > &= -2.568 \ e\hbar/2mc
\end{aligned}
$$

Finally, one has

$$\sum_{m_J,\ m_J'} |< n,L,J,m_J|\vec{M}|n',L',J',m_J' >|^2 = 17.56 \ (e\hbar/2mc)^2$$

and a magnetic dipole transition probability for the transition $6^2P_{3/2} - 6^2P_{1/2}$ of

$$A_m = \frac{64 \ \pi^4 \sigma^3}{3h} \ (e\hbar/2mc)^2 \ (17.56) \ sec^{-1}.$$

The lifetime of the metastable state is $\tau = 1/A_m$ and for the transition $6^2P_{3/2} - 6^2P_{1/2}$ the lifetime is 0.078 seconds. Thus, the lifetime of the $6^2P_{3/2}$ state is very long compared to electric dipole transition lifetimes and the Tl atoms are trapped in the metastable state.

If there is a weak 5350 A light incident on the absorption cell when the 3776 A pumping light is shut off, atoms in the $6^2P_{3/2}$ state are excited to the $7^2S_{1/2}$ state. Since the transition probability to the ground state (10^5 sec^{-1}) is small compared with that back to the $6^2P_{3/2}$ state (0.370×10^8 sec^{-1}), one can measure the intensity of the re-emitted 5350 A light at various times and determine the lifetime of the $6^2P_{3/2}$ state. All the atoms in the $7^2S_{1/2}$ state are from the $6^2P_{3/2}$ state, since the pumping light has been shut off and no ground state atoms are excited. This gives an approximation to the lifetime and should be of the order of magnitude of the calculated lifetime if there are no outside factors reducing the number of

metastable atoms.

In an actual experiment the lifetime of the metastable atom is affected by various mechanisms. The number of metastable atoms can be decreased by collisions with the walls of the experimental cell in which the metastable atom's energy and angular momentum are given up to the wall which is effectively an infinite barrier to the metastable atom. Any reduction of the number of metastable atoms shortens the lifetime of the state.

If metastable atoms of thallium, designated by Tl* are diffusing in a pure thallium vapor, wall collisions will be a major factor reducing the number of Tl* atoms. Due to the electron configuration of the Tl* and ground state Tl atoms, it is possible that on a close approach of the atoms an interaction can occur resulting in a spin flip or exchange. This process does not change the relative number of Tl* atoms but it facilitates the diffusion process, when the vapor pressure of Tl increases and more Tl*-Tl collisions occur. In this discussion collision is used in reference to any interaction which occurs as two atoms approach each other.

Even though the spin flip does not directly affect the number of Tl* atoms it is an important phenomena. As a Tl* atom approaches a Tl ground state atom, there is a small resultant attractive interaction energy. A short-lived quasi-molecule is formed because of magnetic dipole-dipole and spin-orbit interactions. The Tl* atom in the $6\,^2P_{3/2}$ state has a p-electron with a spin of +1/2 and the ground state $6\,^2P_{1/2}$ atom has a p-electron with spin of -1/2.

On formation of a molecule the resultant spin is zero and since the binding energy is small, the molecule dissociates easily. As the molecule dissociates, the original atoms can exchange outer electrons. This results in the original $6^2P_{3/2}$ Tl atom going to the ground state and the original ground state atom going to the metastable state, so the number of Tl* atoms has not changed.

A buffer gas can be added to the system to reduce the number of wall collisions. Collisions between the buffer gas atoms and Tl* atoms occur which inhibit the number of wall collisions. The mean free path[16] for Tl*-Tl collisions and Tl*-Buffer Gas collisions is

$$L_{1-2} = 1/\sqrt{2}\ \pi N_2 d_2^2 \quad \text{and} \quad L_{1-3} = 1/\pi N_3 S^2_{1-3} \sqrt{1 + m_1/m_3}\ ,$$

where N_2 is the number of Tl atoms per unit volume, d_2 is the diameter of a Tl atom, N_3 is the density of buffer gas atoms, m_1 is the mass of the Tl atom, m_3 is the mass of the buffer gas atom, and S_{1-3} is the mean collision radius given by

$$S_{1-3} = (r_1 + r_3)/2$$

where r_1 is the radius of the Tl atom and r_3 is the radius of the buffer gas atom. L_{1-2} and L_{1-3} are the mean free paths of Tl* atoms in Tl and buffer gas atmospheres, respectively. In an actual experiment the Tl atom density is low, and therefore, the mean free path is large. If the buffer gas is at a high density, the mean free path for Tl*-Buffer Gas collisions will be small.

Therefore, the number of Tl*-Buffer Gas collisions can be varied by changing the vapor pressure of the buffer gas. This will reduce the rate of diffusion of Tl* atoms to the cell walls and the lifetime of the Tl* state will be extended.

As a Tl* atom makes a close approach to a thallium ground state atom, there is a magnetic dipole-dipole interaction due to interaction between the total magnetic moments of the valence electrons. The interaction of the nuclear magnetic moment of the thallium atoms on close approach can be neglected, for this energy is proportional to the nuclear magneton squared and is small compared to the interaction of the magnetic moments of the valence electrons. From classical electrodynamics the magnetic dipole-dipole energy of the valence electrons is

$$H_{12} = \frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{r_{12}^3} - 3 \frac{\vec{\mu}_1 \cdot \vec{r}_{12} \ \vec{\mu}_2 \cdot \vec{r}_{12}}{r_{12}^5}$$

where $\vec{\mu}_1$ and $\vec{\mu}_2$ are the total magnetic moments of the valence electrons and $\vec{r}_{12}$ is the separation distance of the electrons. $\vec{\mu}_1$ and $\vec{\mu}_2$ are of the form

$$\vec{\mu}_k = e/2mc \ (\vec{L}_k + 2\vec{S}_k)$$

where $\vec{L}_k$ is the orbital angular momentum of the valence electron and $\vec{S}_k$ is the spin angular momentum. In addition to this interaction energy there is also a spin-orbit interaction energy due to the relative motion of the electrons and nuclei. The orbital motion of each valence electron about the other gives rise to a

magnetic field at the position of the other electron. This field interacts with the spin magnetic moment of this valence electron. The nuclei and their electrons in the filled shells also are in motion with respect to the valence electrons. The field produced by this motion also interacts with the spin magnetic moment of the valence electrons. These interactions are attractive and cause the formation of a weakly bound molecule which can result in an exchange of valence electrons on dissociation.

The spin-orbit interaction is discussed more fully in a paper by Van Vleck.[17] The form of the spin-orbit energy as given by Van Vleck is

$$H_{so} = -1/c \sum_K \sum_j (Z_K e/r_{jK}^3) (\vec{r}_j - \vec{r}_K) \times (1/2\vec{v}_j - \vec{v}_K) \cdot \vec{\mu}_{sj}$$

$$-1/c \sum_{k>j} (-e/r_{jk}^3) (\vec{r}_j - \vec{r}_k) \times (1/2\vec{v}_j - \vec{v}_k) \cdot \vec{\mu}_{sj}$$

where the capital and lower case subscripts refer to the nuclei and electrons, respectively. The magnetic field at the jth electron produced by the orbital motion of the nuclei is

$$1/c \sum_K (Z_K e/r_{jK}^3) (\vec{r}_j - \vec{r}_K) \times (1/2\vec{v}_j - \vec{v}_K)$$

where K is summed over each nucleus forming the molecule, $\vec{r}_{jK} = (\vec{r}_j - \vec{r}_K)$ is the separation distance of the Kth nucleus from the

j^{th} electron, and $(1/2\vec{v}_j - \vec{v}_K)$ is the relative velocity of the jth electron with respect to the Kth nucleus with the 1/2 factor being the Thomas correction. The field due to the orbital motion of the remaining electrons on the jth electron is

$$1/c \sum_k (-e/r_{jk}^3) \; (\vec{r}_j - \vec{r}_k) \times (1/2\vec{v}_j - \vec{v}_k)$$

where the symbols have the same meaning as above, except the summation is over electrons rather than nuclei. These fields are coupled to the spin magnetic moment of the electrons, $\vec{\mu}_{sj}$, giving the resultant spin-orbit energy. This energy is attractive or positive because the nuclear interaction energy is positive and is the dominating term.

In an atmosphere of an inert gas or Hg, Tl* collisions with these atoms can occur. One can see for the case of Hg from the energy level diagram, Figure 1, that there is a large energy difference between excited states of these atoms. The metastable $6^2P_{3/2}$ Tl atom has an excitation energy of 0.96 ev while the lowest state of Hg has an excitation energy of 4.66 ev. For this reason there will not be an exchange of excitation energies, and therefore, no Tl* atoms will be lost by collisions. It is possible for thallium and mercury or inert gas atoms in the ground state to collide and the Tl can eventually receive enough energy to become excited. In experiments, however, the total thermal energy of the two atoms was 0.22 ev and the Tl excitation

energy was 0.96 ev. Since there was this large energy difference, the collisions will appear to be elastic and the concentration of Tl* atoms will not change.

A closer examination of the interaction between a Tl* and buffer gas atom shows there can be a decrease in the number of Tl* atoms. As the Tl* atom approaches the buffer gas atom in the ground state, there is a spin-orbit interaction. Due to the electron configuration of the buffer gas atom, or the Hg atom, there is no magnetic dipole-dipole interaction. In the actual experiment Hg was used as a buffer gas. The ground state Hg atom has two s-electrons in the outer shell and this shell is filled as in an inert gas. The electrons in this shell have a net spin magnetic moment of zero, since the electrons possess opposite spins and magnetic moments. Thus the total magnetic dipole moment of the ground state inert gas or Hg atom is zero and is not available to interact with the total magnetic moment of the Tl* atom. The term H_{12} is then zero. On the other hand on a close approach of the atoms, the individual electrons of the Tl*-Buffer Gas system can be seen by the nuclei as they move with respect to the electrons. This gives rise to a nuclear-valence electron spin-orbit energy. Also on a close approach the valence electrons individually will be in motion with respect to each other giving rise to an electron-electron spin-orbit energy. It is this weak spin-orbit attractive interaction energy which produces the quasi-molecule.

The quasi-molecule easily dissociates and a spin exchange

cannot occur since this would allow both valence electrons of the Hg or inert gas atom to have identical spins and energy states. Therefore, as the molecule dissociates there are two possible results. The Tl* atom and the ground state Hg or inert gas atom are the dissociation products with no change in the number of metastable atoms, or the Tl* atom goes to the ground state in the dissociation with energy and angular momentum conserved by the resulting motion of the Tl and Hg or inert gas ground state atoms on separation. This last dissociation process may occur and will lead to a loss of metastable atoms.

Another mechanism reducing the number of metastable atoms is produced by the intensity of the exciting light. If the exciting light is too intense, an excess of metastable atoms is produced. It was experimentally observed that generally a collision between two metastable thallium atoms results in both atoms going to the ground state.[10] As the intensity of the illumination increases, the number of metastable atoms increases linearly with the incident intensity and the probability of a Tl*-Tl* collision increases as the square of the intensity.[18] In this experiment the 3776 A Tl line is relatively weak and thus the density of Tl* atoms is negligible compared to the density of ground state atoms. Therefore, Tl*-Tl* collisions are negligible and this is not an important process with regard to the lifetime of the metastable atom.

The above discussion points out the importance of wall collisions, Tl*-Tl collisions, and Tl*-Buffer Gas collisions as

factors reducing the lifetime of the metastable thallium atom. Experiments can be performed to determine which of these mechanisms are more important.

An experiment measuring the lifetime of the metastable thallium atom in a pure thallium atmosphere at various vapor pressures would add to one's knowledge of the importance of these factors. Tl* atoms would be lost by wall collisions, Tl*-Tl collisions, and spontaneous magnetic dipole transitions to the ground state. The rate of decrease in the number of Tl* atoms is given by the equation

$$\frac{\partial n_1}{\partial t} = D_2 \nabla^2 n_1 - k n_1$$

where D_2 is the diffusion coefficient for Tl* in a pure Tl vapor, n_1 is the density of Tl* atoms, and k is a constant for the given system. k is given by

$$k = n_2 \sigma \vec{v}_{rel} + A_m$$

where n_2 is the density of Tl atoms for few metastable atoms are produced, σ is the disorientation cross section for Tl*-Tl collisions, $\vec{v}_{rel}$ is the relative velocity of the metastable and ground state Tl atoms, and A_m is the spontaneous magnetic dipole transition probability for the $6^2 P_{3/2} - 6^2 P_{1/2}$ transition. The diffusion coefficient is given by

$$D_2 = D_o (p_o / p)$$

where D_o is the diffusion coefficient at some specified condition, p_o is the specified Tl pressure, and p is the actual Tl pressure of the system.

For an experimental cell with cylindrical geometry and where all metastable atoms are assumed lost on reaching the wall, Franzen[19] has given a solution to the diffusion equation of the form

$$n_1(r,z,t) = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} C_{ij} \exp - [(\mu_i^2 + \nu_j^2)D_2 + k]\, t$$

$$\times J_o(\mu_i r) \cos(\nu_j z)$$

where $\nu_j = (2j-1)\pi/L$, L is the length of the cell; μ_i is defined by $J_o(\mu_i a) = 0$, a is the radius of the cell; J_o is the zero order Bessel function and C_{ij} is a constant to be determined by the boundary conditions.

The simplest approximation that can be made for the above equation in the absence of a detailed knowledge of the initial distribution of n_1 is to consider only the first term of the expansion for n_1. Using this approximation, the lifetime of the metastable atom is given by

$$\tau = 1/[(\mu_1^2 + \nu_1^2)D_2 + k] = 1/[(\mu_1^2 + \nu_1^2)D_2 + n_2\sigma \vec{v}_{rel} + A_m]\ .$$

One can measure the lifetime experimentally and plot the lifetime of the metastable state as a function of thallium vapor pressure. By fitting the above expression for the lifetime to the

experimentally obtained curve, values of D_2 and σ are determined. If the disorientation cross section for Tl*-Tl collisions is small, this verifies the hypothesis that a Tl*-Tl collision causes an electron spin exchange and the number of thallium metastable atoms is not meterially reduced by these collisions.

A second experiment can be performed to determine the life-time of the Tl metastable atom in a cell containing a buffer gas at various pressures. In this atmosphere the lifetime of the Tl* atom will be reduced by wall collisions, Tl*-Tl collisions, Tl*-Buffer Gas collisions, and by spontaneous magnetic dipole transitions to the ground state. If from the previous experiment σ is small for Tl*-Tl collisions and the Tl vapor pressure is small, then the Tl*-Tl collision term and the diffusion term of Tl* atoms in a Tl atmosphere can be neglected. Therefore, the rate of decrease of Tl* atoms in a buffer gas atmosphere is given by

$$\frac{\partial n_1}{\partial t} = D_3 \nabla^2 n_1 - k_3 n_1$$

where D_3 is the diffusion coefficient for Tl* in the buffer gas and is given by

$$D_3 = D_o(p_o/p)$$

where p_o and p are the buffer gas pressures, D_o and p_o are defined at some specified condition, and k_3 is a constant for the system. k_3 is given by

$$k_3 = n_3 \sigma_3 \vec{v}'_{rel} + A_m$$

where n_3 is the density of buffer gas atoms, σ_3 is the disorientation cross section for Tl*-Buffer Gas collisions, $\vec{v}'_{rel}$ is the relative velocity of the Tl* and buffer gas atoms, and A_m is the spontaneous magnetic dipole transition probability for the Tl* atoms to the ground state. The solution is again of the same form as for Tl* atoms in a Tl atmosphere with the lifetime given by

$$\tau = 1/[(\mu_1^2 + \nu_1^2)D_3 + n_3\sigma_3\vec{v}'_{rel} + A_m] \ .$$

Again by determining τ experimentally as a function of buffer gas pressure and fitting this expression to the resulting curve, D_3 and σ_3 can be determined.

Bernheim,[20] by means of optical pumping experiments, has shown for optically oriented rubidium colliding with certain inert gases that the cross section for disorientation varies as the cube of the atomic number of the inert gas. The same results should also hold in our experiments. The spin-orbit interaction energy term of buffer gas nuclei with the electrons is of the form

$$H_{so} = -1/c \sum_j (Z'_K e/r_{jK}^3) \ (\vec{r}_j - \vec{r}_K) \times (1/2\vec{v}_j - \vec{v}_K) \cdot \vec{\mu}_{sj}$$

$$= 2\beta/c \sum_j (Z'_K e/r_{jK}^3) \ (\vec{r}_j - \vec{r}_K) \times (1/2\vec{v}_j - \vec{v}_K) \cdot \vec{s}_j$$

where Z_K is the effective atomic number of the buffer gas nucleus, $\vec{s}_j$ is the electron spin operator with $\hbar$ grouped in β, and β is the Bohr magneton. We can rewrite the last equation in the form

$$H_{so} = 2\beta/M_K c \sum_j (Z_K' e/r_{jK}^3) M_K (\vec{r}_j - \vec{r}_K) \times (1/2\vec{v}_j - \vec{v}_K) \cdot \vec{s}_j$$

where M_K is the mass of the buffer gas nucleus. The term $M_K(\vec{r}_j - \vec{r}_K) \times (1/2\vec{v}_j - \vec{v}_K)$ is an effective orbital angular momentum of the nucleus about the jth electron and will be designated as $\vec{L}_{j\,eff}$. This will be a constant of the motion independent of the atomic number of the nucleus, for $\vec{r}_{jK}$ can be shown to be proportional to $1/Z_{eff}^{21}$ and $\vec{v}_{jK} = (1/2\vec{v}_j - \vec{v}_K)$ can be shown to be proportional to Z_{eff}^{21}, where Z_{eff} is the effective charge of all nuclei as seen by the electrons and is proportional to the atomic number of the buffer gas atom. The spin-orbit energy becomes

$$H_{so} = 2\beta/M_K c \sum_j (Z_K e/r_{jK}^3) \vec{L}_{j\,eff} \cdot \vec{s}_j .$$

Only the term $Z_K/M_K r_{jK}^3$ will involve the atomic number of the buffer gas atom. The nuclear mass M_K is directly proportional to Z_K and, from extending the results of the hydrogen-like atom, $1/r_{jK}^3$ can be shown to be proportional to $Z_{eff}^3 \approx Z_K^3$. Thus the spin-orbit energy is proportional to Z_K^3.

By using different inert gases and Hg in the above experiment one could establish this atomic number dependence. This would substantiate the hypothesis of spin-orbit interaction giving rise to disorientation effects in thallium-buffer gas collisions.

IV. EXPERIMENTAL PROCEDURES

A Wood's type absorption cell was constructed of quartz
tubing. The main cell was one inch in diameter and four inches
long with reservoirs constructed of smaller tubing connected to
the cell. One reservoir was perpendicular to the cell and the
other was aligned with it. This construction was necessary to
accommodate the ovens which will be discussed later. This cell
was attached to a pyrex vacuum system (Plate I) having the fol-
lowing components:

1. Mercury diffusion pump,

2. Fore pump,

3. Consolidated Electrodynamic Ionization Vacuum Gauge,
   Type GIC-110,

4. Dewar cold traps containing dry ice and acetone.

The cell was enclosed in ovens and outgassed at 800°C for several
days to remove impurities from the glass. (Plate II) A Leeds
and Northrup potentiometer and chromel-alumel thermocouples were
used to measure temperatures in the various ovens. After a vacuum
of approximately 10^{-5} mm of Hg was reached, the oven over one
reservoir was removed. The reservoir was opened and small pieces
of thallium metal were introduced. The reservoir was resealed
and the oven replaced. Thallium was distilled under vacuum into
the main cell and the reservoir with some thallium oxides still
present was severed from the cell. The system was pumped down
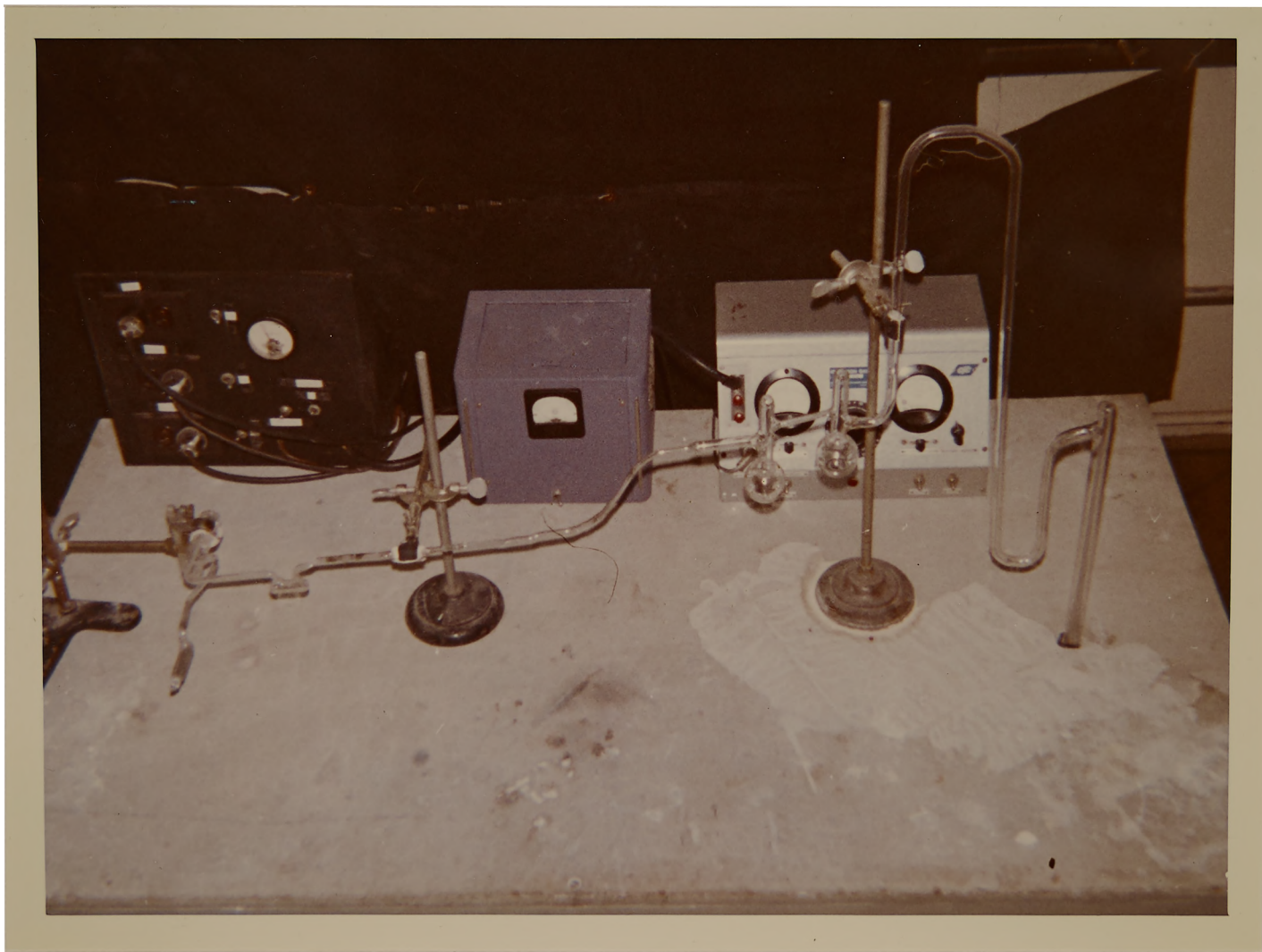to a vacuum of 5.9×10^{-6} mm of Hg. Hg was distilled into the

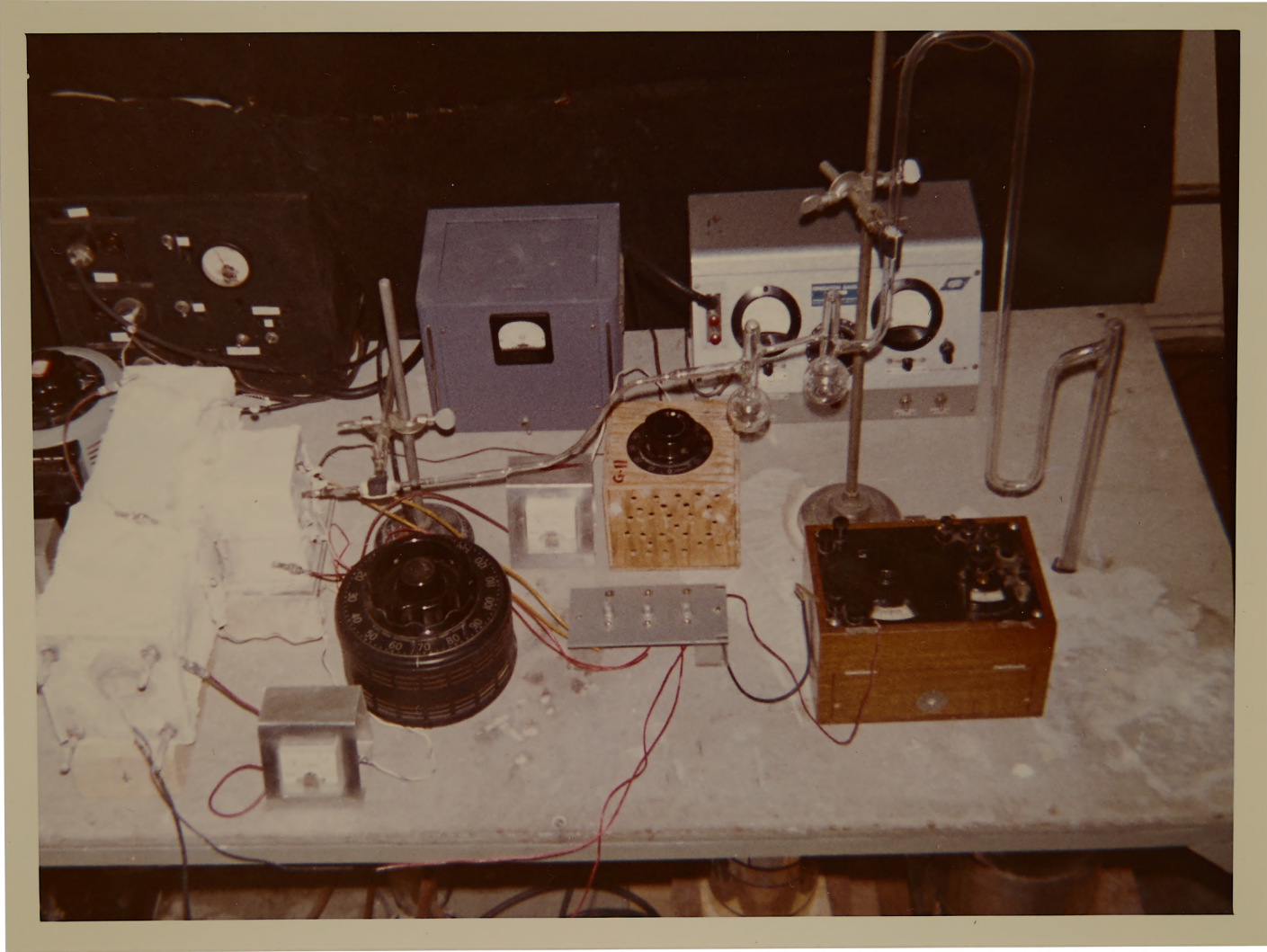Plate I. Vacuum system, with cell attached

Plate II. Vacuum system, with cell being outgassed

29

cell and the entire cell was removed from the vacuum system.

Three ovens were constructed for the experiment, each was a different size to accommodate the particular portion of the cell to be enclosed. The ovens were constructed using a Norton Alumina core would with nichrome wire. This wire was covered with Metaldam, a refractory mortar, to protect the nichrome from alkali damage from the 85% magnesia cement used as an insulator. The core was placed between slabs of transite and the area sur- rounding the core was filled with the magnesia cement. The oven enclosing the main observation cell was constructed with two quartz windows. One window was placed in the side of the oven to allow detection of the scattered light. This was necessary to eliminate the detection of reflected incident light. The window areas were kept at the same temperature as the main cell to prevent condensation of thallium on the walls of the main cell near the windows.

The exciting light was produced by an Osram Spectral lamp, and the 3776 A line was isolated using an interference filter. This light was focused on a rotating wheel which served as a shut- ter. The shutter consisted of a disk, which was divided into four equal sections with two of the sections removed. This wheel was driven by a motor at approximately 3460 revolutions per minute. The exciting light passed through the top of the wheel and simul- taneously another light passed through the bottom. The light pass- ing through the bottom was focused on a photomultiplier. This photomultiplier passed a signal to a low voltage pulser. This

shaped the pulse and it entered a delay circuit. The delay could be varied by changing an external capacitance. A decade capacitance box and several small capacitors were timed on the circuit by measuring the pulse width with a Tektronix Type 531A oscilloscope. This allowed the pulse to be delayed from 3.6 microseconds to any value desired. This delayed pulse entered a high voltage pulser which amplified the pulse. The outgoing pulse was approximately 1200 volts. This high voltage pulse fired the detecting photomultiplier at prescribed times after the 3776 A light was shut off. The photo-current from the photomultiplier was stored in a capacitor. A timer allowed the sampling time to be varied. If data were taken for one minute this would correspond to over 6000 readings of the same point of the decay curve. In this way random fluctuations could be averaged and an integrated value for each point on the curve was obtained. The data stored in the capacitor was measured using a Keithley Electrometer, Model 200B. (Plate III)

In order to perform the measurement of the lifetime of the metastable state, the atoms in the $6^2P_{3/2}$ state must be pumped to the $7^2S_{1/2}$ state. In order to do this an additional lamp was used, this lamp provided excitation radiation of wavelength of 5350 A. This light and the 3776 A light entered the cell collinearly. Since there were no atoms being pumped to the resonance state from the ground state after the 3776 A line was shut off by the rotating wheel, all the atoms in the $7^2S_{1/2}$ state were from the $6^2P_{3/2}$ state. The decay from the $7^2S_{1/2}$ state to the ground
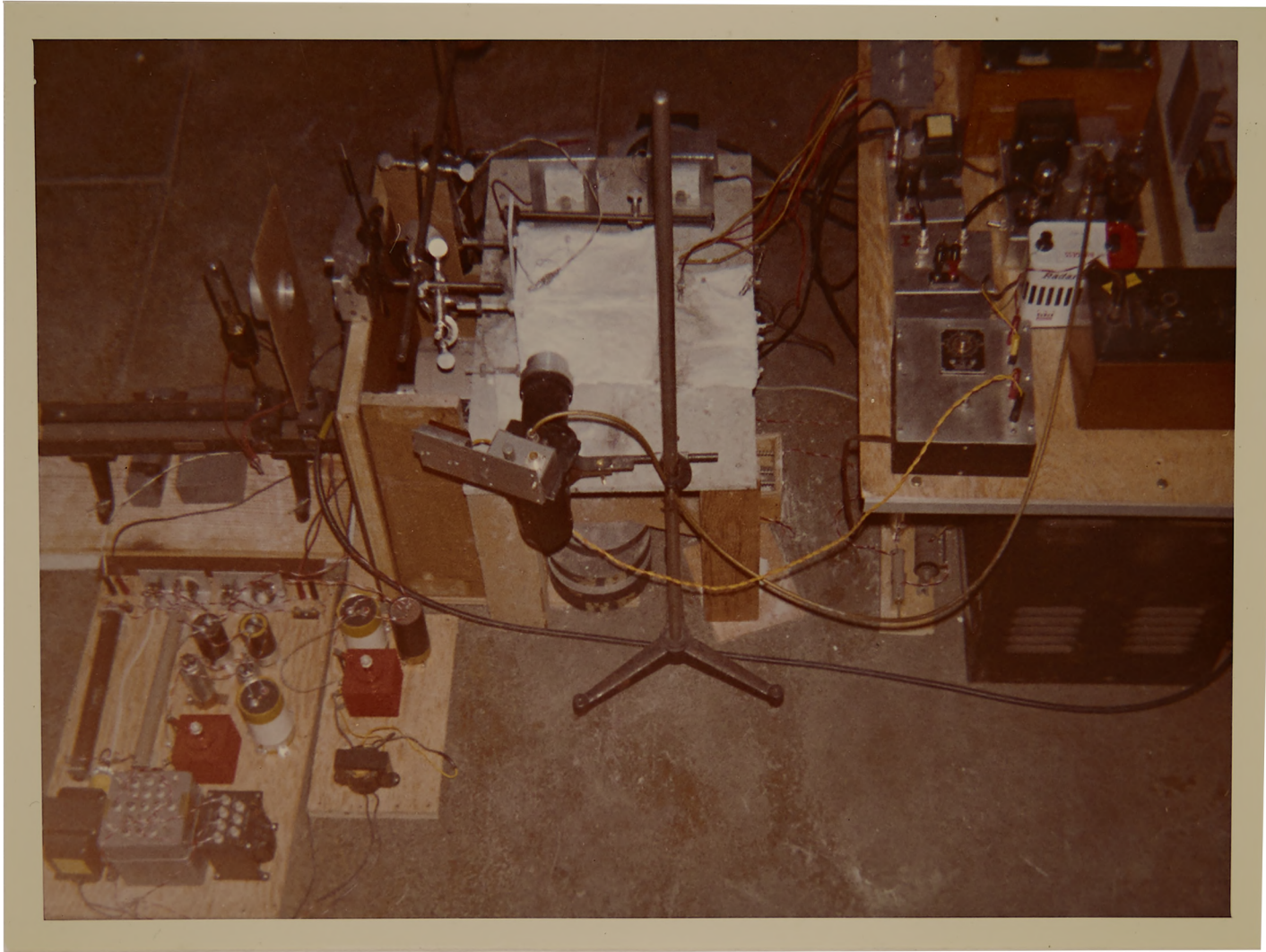
Plate III. Experimental set-up, time-sampling equipment

state is approximately 1000 times less likely than the transition

to the metastable state. The intensity of the re-emitted 5350 A

line as the atoms decayed back to the metastable state from the

$7^2S_{1/2}$ state should be proportional to the number of atoms orig-

inally in the metastable state. From the intensity of the re-

emitted 5350 A light the lifetime of the metastable state could

be determined.

Due to imperfections in the machining of the wheel and in

alignment of both beams of light passing through the wheel, the

actual time required for the wheel to close was determined by

the electronic equipment in the detection circuit. This was done

by shining the light through both slits and reflecting that going

through the upper slit into the detecting photomultiplier. A

"decay curve" was determined, and an average shut off time was

found to be 23 microseconds. (Figure 2) Therefore, this was the

lower limit on the lifetime which was capable of being measured

with this equipment. Due to the intensity of scattered light and

the instability of the electrometer, measurement of the lifetime

of the $6^2P_{3/2}$ state was not possible. Also, on checking the

stability of the light sources variations in output were observed

so the time sampling detection method was not feasible. The

pulse circuitry and the electrometer were eliminated. The 5350 A

Tl line was detected using an EMI/US type 6256B photomultiplier

with a quartz window and a solid state photo-cathode having max-

imum efficiency for wavelengths of the order of 5000 A. The

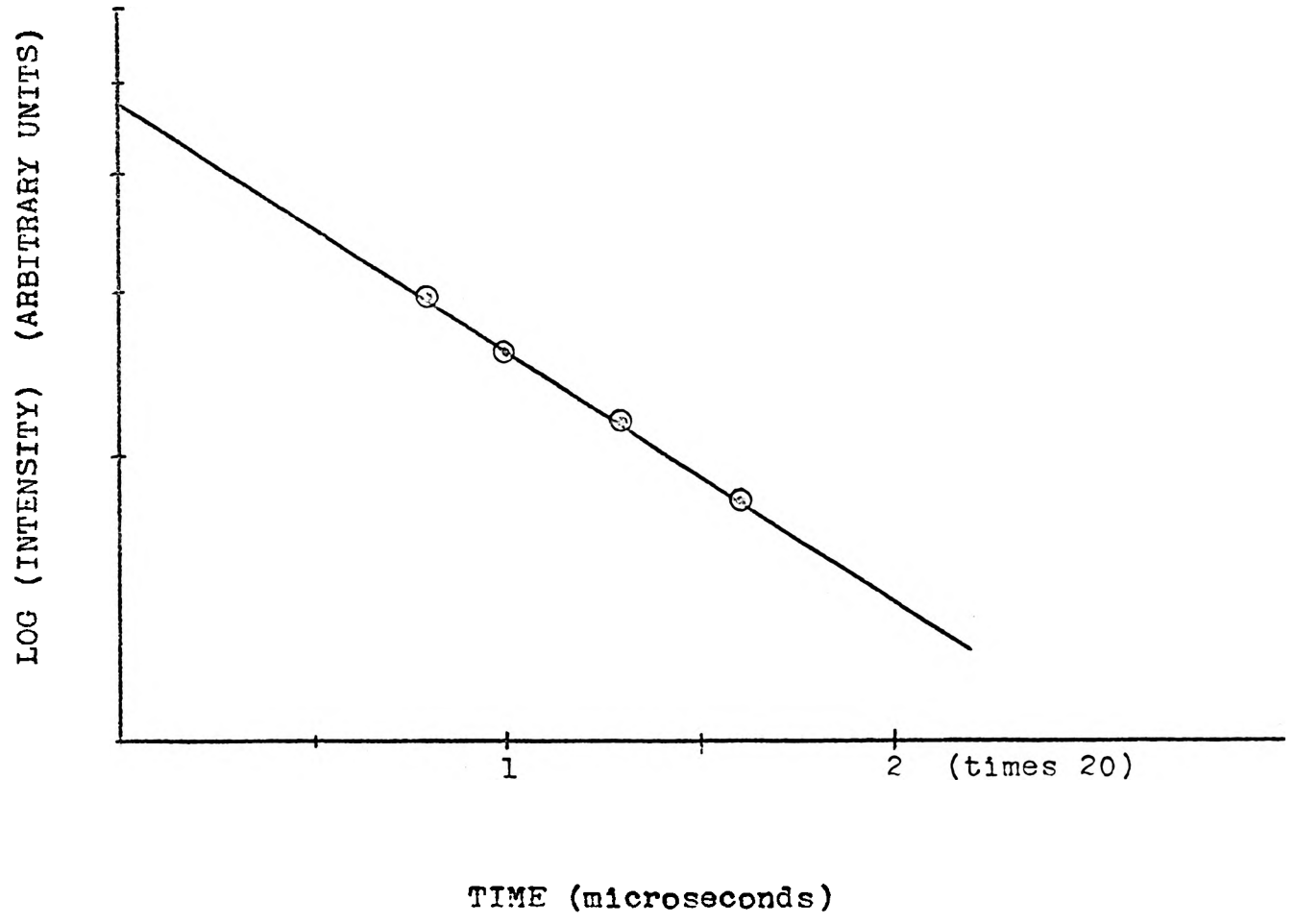output of the photomultiplier was applied to a Tektronix Type

FIGURE 2. CUT OFF OF WHEEL

531A oscilloscope. The oscilloscope was triggered by the bottom light source and photomultiplier mentioned earlier. When the 3776 A exciting light was shut off, the decay curve of the 5350 A line was displayed on the oscilloscope. The trace of this curve was photographed with a Tektronix oscilloscope camera, type C-12. (Plate IV) By knowing the sweep speed of the exposure the average lifetime of the state could be determined. Corrections to the average lifetime were made using the "decay time" of the chopper.

Data were taken for different values for the thallium vapor pressures and observation cell temperatures. The mercury vapor pressure was also varied to study the effect of mercury as a buffer gas.
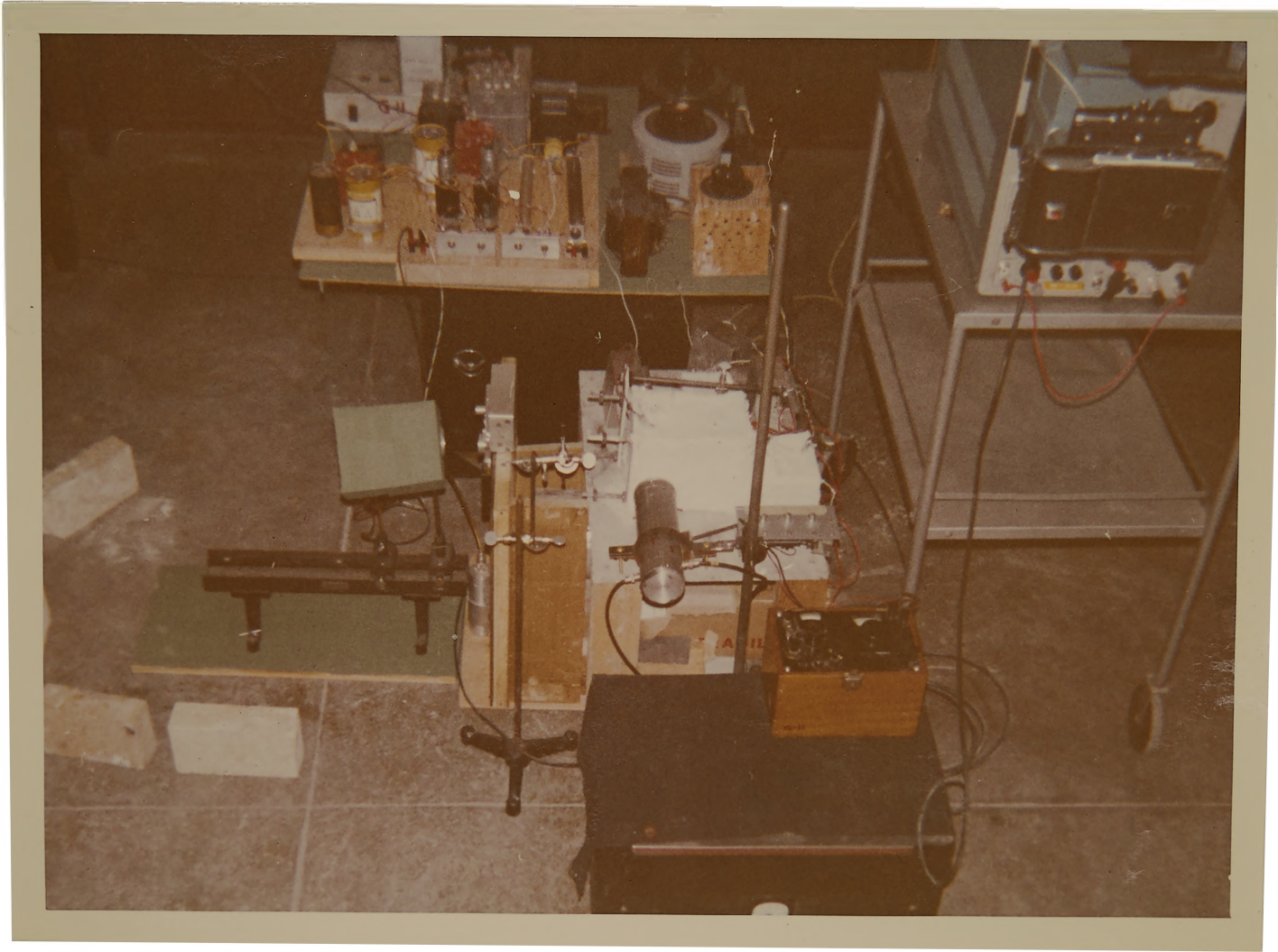
Plate IV. Experimental set-up, oscilloscope method

V. DISCUSSION OF RESULTS

As was stated in the previous section, the time-sampling technique proved to be impractical. However, a change of detection equipment did not alleviate the situation. The trace displayed on the oscilloscope was due to fluctuations in the wheel and the scattered 5350 A light from the source which overshadowed the decay. It was assumed that some information could be obtained concerning the actual decay of the 5350 A line from the $7^2S_{1/2}$ state. In order to do this the 5350 A line which was used initially to excite the metastable atoms was removed. Data were taken on the decay of the 5350 A line from the $7^2S_{1/2}$ state when the 3776 A line was shuttered, but no conclusions could be drawn from these graphs, as shown in Figures 3 and 4. Later work by E. Stepp[22] has indicated that this decay was less than 7 microseconds for thallium at a temperature of 900° C. This short time would be impossible to measure with this equipment since the wheel does not shut off for more than 23 microseconds. A more recent communication with Dr. H. Okaya[23] of the Quantum Electrodynamics Division of Westinghouse Electric Corporation has verified that the decay time is short. Dr. Okaya electrically excited a Hg-Tl mixture and found the decay time of the 5350 A line to be one microsecond.
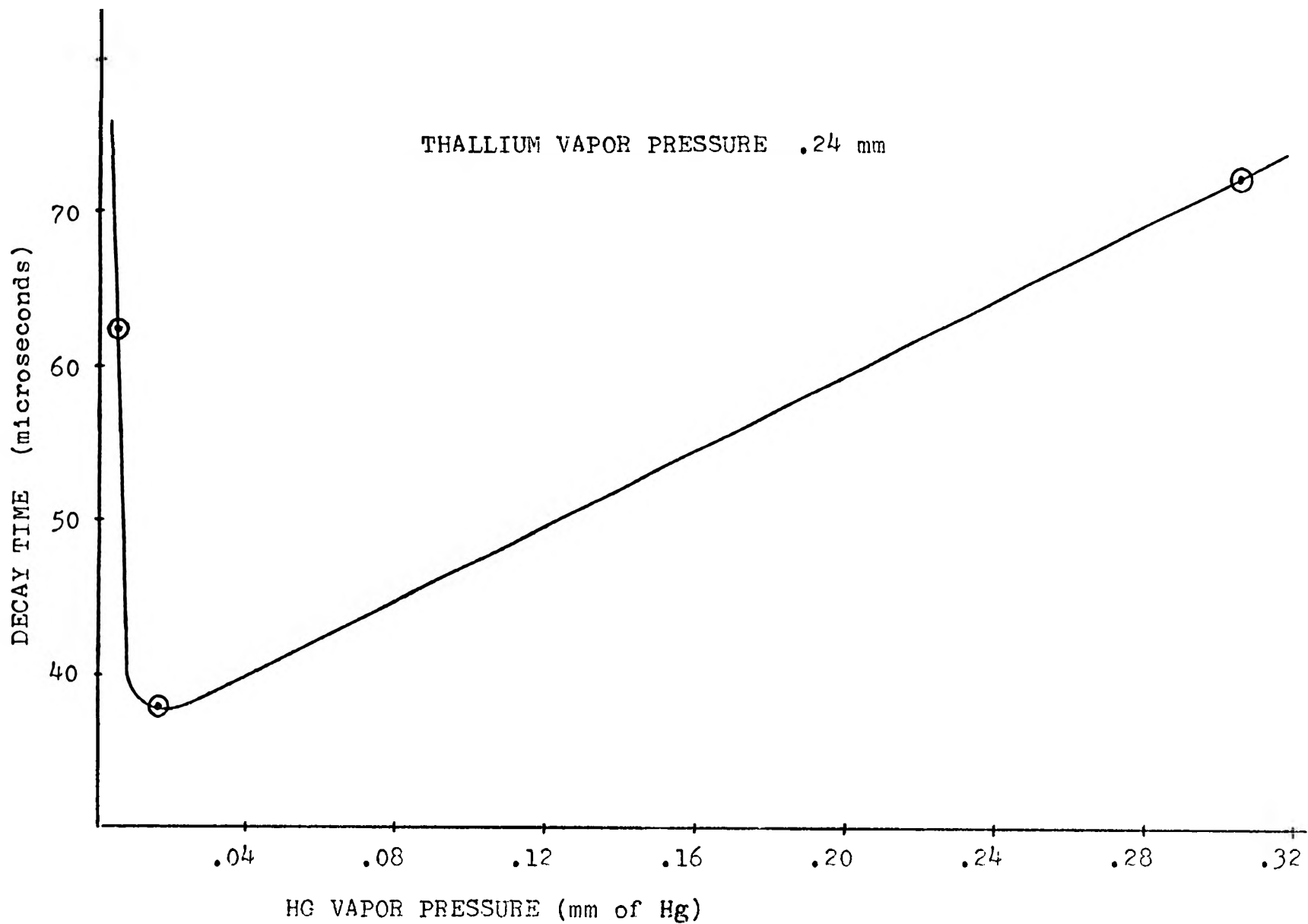
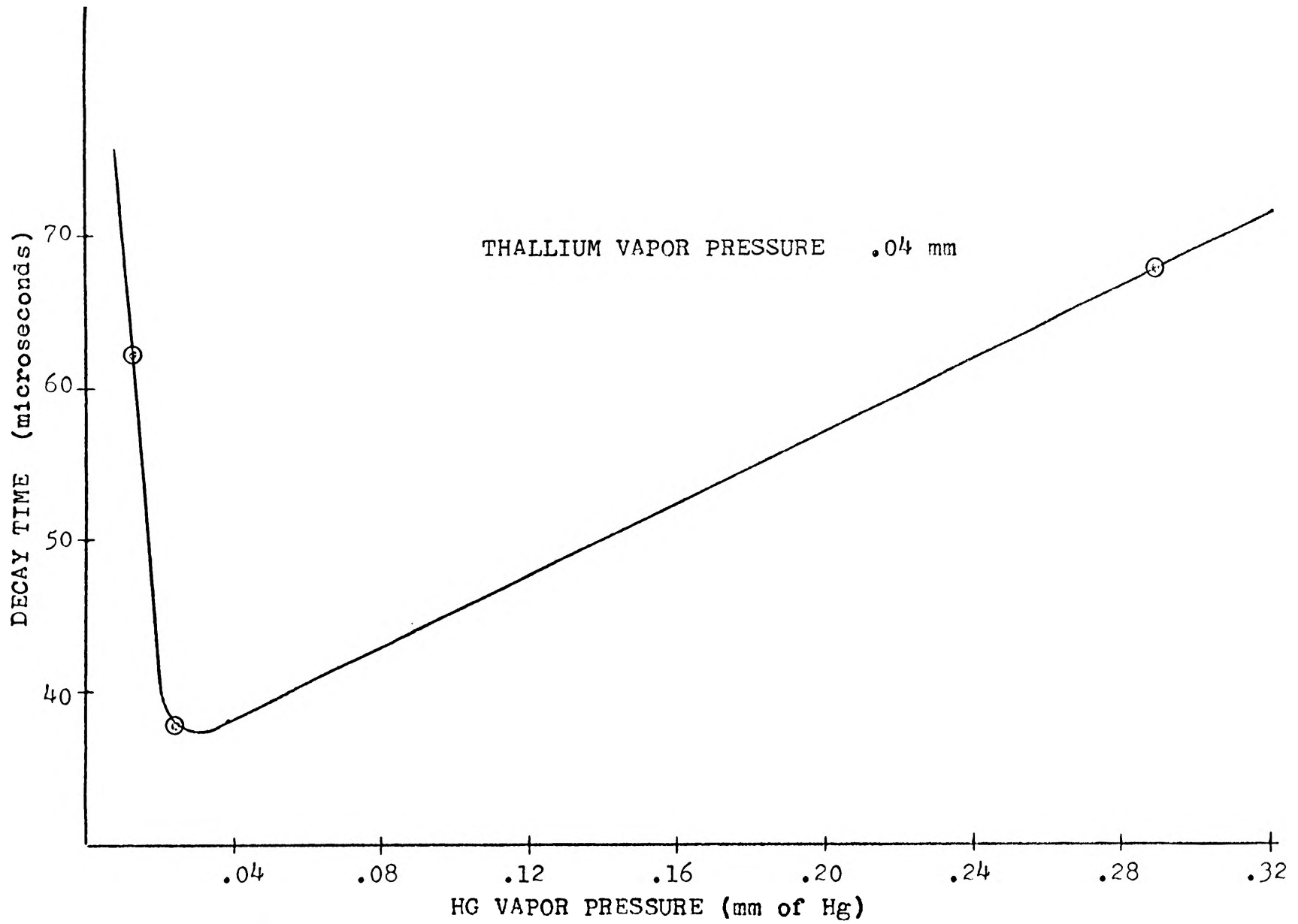FIGURE 3. DECAY OF THE 5350 A LINE AS A FUNCTION OF HG AND TL VAPOR PRESSURES

FIGURE 4. DECAY OF THE 5350 A LINE AS A FUNCTION OF HG AND TL VAPOR PRESSURES

38

VI. CONCLUSIONS

In the measurements of the lifetime of the $6^2P_{3/2}$ state of Tl some improvements could be made in the equipment. First, a more intense and stable light source should be constructed. This would create a higher population in the $6^2P_{3/2}$ state and the resultant decay of the 5350 A line would be more easily detected. The chopper should be replaced by an electro-optical device which will cut off the incident 3776 A radiation and trigger the oscilloscope. The oscilloscope method seems more feasible, but the time-sampling method could be employed if measures are taken to stabilize the light sources. The 5350 A pumping light must be monitored for stability and this light must be better aligned and collimnated in order to reduce reflections. It will also be necessary to build an observation cell in the form of an exponential horn. This will collect the reflected incident 5350 A light and eliminate the problem of this light overshadowing the actual decay of the re-emitted 5350 A light.

The measurements of the decay of the 5350 A line when Tl is excited to the $7^2S_{1/2}$ state can be performed if some method were found to shutter the incident 3776 A light in times less than a microsecond. The only change in the experiment will be the elimination of the 5350 A pumping light.

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