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WALTER ELLIOTT CHASE

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DENSITY SHIFTS OF THE HYPERFINE SPLITTING FREQUENCY OF SILVER OBTAINED BY HIGH TEMPERATURE OPTICAL PUMPING

by

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A THESIS

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# TABLE OF CONTENTS

**LIST OF TABLES** ........................................ vi
**LIST OF FIGURES** ....................................... viii
**ABSTRACT** ........................................... ix

I. **INTRODUCTION** ...................................... 1

II. **THEORY** ........................................... 4

1. Optical Pumping ...................................... 4
2. Detection of Magnetic Resonances ............... 8
3. Polarization of an Atomic Vapor by Spin Exchange Collisions .......................... 14
4. Inclusion of a Buffer Gas in a Vapor Cell ......... 16
5. Breit-Rabi Formula ................................ 20

III. **APPARATUS AND EXPERIMENTAL PROCEDURE** ......... 26

1. Sample Flask Manufacture ........................... 26
2. The Optical Pumping Apparatus ................... 29
3. Experimental Procedure ............................ 37
4. Errors ............................................. 42

IV. **HYPERFINE FREQUENCY DRIFTS** ...................... 53

1. Vapor Cells Containing Helium Buffer Gas ........ 53
2. Vapor Cells Containing Neon Buffer Gas ........... 55
3. Vapor Cells Containing Argon and Nitrogen Buffer Gases ................................. 57

V. **TREATMENT OF EXPERIMENTAL DATA** ............... 58

1. Introduction ........................................ 58
2. Density Shifts Caused by Neon, Argon, and Nitrogen................................. 58

3. Temperature Dependence of Density Shifts Due to Neon, Argon, and Nitrogen ....... 70

4. Density Shift Caused by Helium and Its Temperature Dependence ................. 75

5. Summary of Results and Conclusions ....... 85

6. Additional Data for Argon and Nitrogen Buffer Gases ................................. 89

BIBLIOGRAPHY ........................................ 99

APPENDIX A ........................................ 104

APPENDIX B ........................................ 106

APPENDIX C ........................................ 118
List of Tables

1. Grouping of Hyperfine Frequency Measurements ... 40
2. Summary of the Measurements from Which the Density Shift of Ag\textsuperscript{107} Due to Neon Buffer Gas May Be Determined ...................... 61
3. Hfs of Ag\textsuperscript{107} as a Function of Density at the Constant Temperature of 830° C. The Buffer Gas is Neon .............................. 64
4. Hfs of Ag\textsuperscript{107} as a Function of Density at the Constant Temperature of 830° C. The Buffer Gas is Neon. Only the Error in the Density Measurement Is Considered ...................... 68
5. Hfs Versus Density Curves for Ag\textsuperscript{107} in Neon, Argon, and Nitrogen ................................. 69
6. Temperature Versus Frequency Measurements for the 203.2 Torr Neon Flask ......................... 73
7. Summary of the Results of the Measurements of the Temperature Dependence of the Density Shift of Ag\textsuperscript{107} in Neon Buffer Gas ...................... 74
8. Temperature Dependence of the Ag\textsuperscript{107} Hfs in Various Buffer Gases .............................. 75
9. Partial Temperature Versus Time Record of the 100 Torr Helium Flask .......................... 78
10. Partial Temperature Versus Time Record of the 60 Torr Helium Flask ......................... 81
11. Frequency Versus Temperature Measurements for the 60 Torr Helium Flask .................. 82
12. Hfs of Ag\textsuperscript{107} as a Function of Density at the Constant Temperature of 794° C. The Buffer Gas is Helium ................................. 83
13. Density Shift and Its Temperature Dependence for the Hfs of Ag\textsuperscript{107} ......................... 86
15. Summary of the Measurements from Which the Density Shift of Ag$^{107}$ Due to Argon Buffer Gas May Be Determined ........................................ 90

16. Hfs of Ag$^{107}$ as a Function of Density at the Constant Temperature of 852° C. The Buffer Gas Is Argon ............................................... 91

17. Hfs of Ag$^{107}$ as a Function of Density at the Constant Temperature of 852° C. The Buffer Gas Is Argon. Only the Error in the Density Measurement Is Considered ........................................ 91

18. Summary of the Results of the Measurements of the Temperature Dependence of the Density Shift of Ag$^{107}$ in Argon Buffer Gas ................. 92

19. Summary of the Measurements from Which the Density Shift of Ag$^{107}$ Due to Nitrogen Buffer Gas May Be Determined .................................. 93

20. Hfs of Ag$^{107}$ as a Function of Density at the Constant Temperature of 820° C. The Buffer Gas Is Nitrogen ........................................ 95


22. Summary of the Results of the Measurements of the Temperature Dependence of the Density Shift of Ag$^{107}$ in Nitrogen Buffer Gas .......... 96

23. Measured Leak Rates of Helium Through Quartz ... 111

24. Thermal Relaxation Time Constant of a Number of Elements as a Function of Temperature. Complete Mixing in the Excited State Is Assumed \( \tau \) Is Given in Units of Seconds ............... 135
List of Figures

1. Basic Optical Pumping Arrangement ................. 6
2. Low Lying Energy Levels for an Alkali-like Atom with Zero Nuclear Spin .................... 6
3. Breit-Rabi Energy Level Diagram for Ag\textsuperscript{107} ... 22
4. Sample Flask Prior to Attachment to Vacuum System ............................................. 46
5. Sample Flask and Rubidium Sidearm on Vacuum System .............................................. 47
6. Block Diagram of Optical Pumping Apparatus .. 48
7. Detail of Oven and Magnetic Shields .......... 49
8. Light Bulb for Rubidium Light Source ............ 50
9. Circuit Diagram for Rubidium Light Source ... 51
10. Vapor Cell in Air Cooled Socket ................. 52
11. Hfs of Ag\textsuperscript{107} as a Function of Buffer Gas Density at the Constant Temperature of 830° C. The Buffer Gas Is Neon .................. 64
12. Temperature Versus Frequency Measurements for the 203.2 Torr Neon Flask .................. 73
13. Frequency Versus Temperature Data as Originally Measured for the 58.5 Torr Helium Flask ........................................... 80
14. Frequency Versus Temperature Data for the 58.5 Torr Helium Flask After Correcting for Leakage .................................................. 80
15. Density Shifts of Ag\textsuperscript{107} .................... 87
16. The Low Lying Energy Levels of an Alkali-like Atom with Zero Nuclear Spin ................. 121
17. Branching Ratios for Spontaneous Decay ...... 123
ABSTRACT

DENSITY SHIFTS OF THE HYperfine SPLITTING
FREQUENCY OF SILVER OBTAINED BY HIGH
TEMPERATURE OPTICAL PUMPING

by

WALTER E. CHASE

High temperature spin exchange optical pumping was used to measure the density shifts of the hyperfine splitting of Ag$^{107}$ in buffer gases of He, Ne, N$_2$ and Ar. The temperature dependence of the density shifts was also obtained.

The fractional density shifts for silver were found to be $40.6 \pm 1.4 \times 10^{-9}$ Torr$^{-1}$ in helium at 794°C, $26.2 \pm 0.24 \times 10^{-9}$ Torr$^{-1}$ in neon at 830°C, $33.6 \pm 2.6 \times 10^{-9}$ Torr$^{-1}$ in nitrogen at 825°C, $14.2 \pm 0.9 \times 10^{-9}$ Torr$^{-1}$ in argon at 852°C. Measurements within the temperature range of 791°C - 887°C yielded the temperature dependences of $2.27 \pm 0.26 \times 10^{-2}$ Hz °C$^{-1}$ Torr$^{-1}$ in helium, $8.6 \pm 1.1 \times 10^{-3}$ Hz °C$^{-1}$ Torr$^{-1}$ in neon, $-8.3 \pm 1.4 \times 10^{-3}$ Hz °C$^{-1}$ Torr$^{-1}$ in nitrogen, and $-1.1 \pm 0.2 \times 10^{-2}$ Hz °C$^{-1}$ Torr$^{-1}$ in argon.

All pressures were measured at 25°C.
CHAPTER I

INTRODUCTION

In optical pumping\(^1\) experiments in which the pumped atoms are immersed in a buffer gas,\(^2\) the high precision of the measurements permits the determination of the small perturbing effects due to the presence of the buffer gas atoms. These perturbations produce a shift in the atomic hyperfine splitting frequency (hfs) which is a linear function of the buffer gas density. The slope of this curve is, generally speaking, only a weak function of the temperature. Consequently, it would be apt to refer to this effect as a "density shift," since it is the buffer gas density which predominates in determining the shift. Unfortunately, the rather misleading term "pressure shift" has become commonplace in the literature. In this discussion, however, the term "density shift" will be used.

The hyperfine splitting frequency of the \(^2S_\frac{1}{2}\) ground state has been measured for the hydrogen isotopes and all of the stable alkali atoms. The density shifts caused by various buffer gases have also been measured,\(^3-12\) and, in addition, a fairly extensive literature on the theory of these density shifts has been produced. We have included some representative theoretical papers in our references.\(^13-18\)

Measured hyperfine splittings and density shifts
are of importance to physicists attempting to refine calculations of the structure and interactions of atoms. Because of the complexity of the computations involved, rigorous calculations of these quantities from the first principles of the theory of quantum mechanics, although possible in principle, are not possible in practice. Accordingly, a wide range of experimental guideposts is necessary to allow theoretical calculations to be compared to empirical data, and refined until adequate agreement is obtained. One of the most effective ways of obtaining this data has been through the use of optical pumping experiments.

As might be expected, the atoms which could be optically pumped most easily were the first to be studied. As experimental techniques improved, however, other atoms, the optical pumping of which presented greater technical difficulties, were studied in their turn. A recent important advance in experimental technique was made at the University of New Hampshire in 1969. This development, which we discuss more fully in Chapter III, greatly extended the temperature range over which optical pumping experiments could be performed, and thereby considerably increased the number of elements which could be successfully pumped.

Silver was one of the elements thus rendered amenable to study by means of optical pumping. Silver, like the alkalies, has a $^2S_{1/2}$ ground state. It was the object of this experiment to continue the study of the hyperfine
structure of the alkali-like atoms by measuring the density shifts of silver in buffer gases of neon, argon, nitrogen, and helium. The temperature dependence of the density shifts was also to be obtained.

It is the purpose of this report to present the results of this experiment, and to describe the methods used to obtain them. As an aid to the reader, the format of the report will now be briefly sketched. Chapter II provides an elementary introduction to spin exchange optical pumping, and presents the basic theoretical concepts necessary to understand the experiment. Chapter III describes the apparatus and its operation. In Chapter IV the problem of leakage of buffer gas from the vapor cells is considered. Such leakage is not ordinarily a problem, but at the elevated temperatures at which this experiment was conducted (\( \sim 800^\circ \text{C} \)) it can be an observable phenomenon. Chapter V describes the analysis of the data, and presents our final results and conclusions.

Following the main text there are three appendices. Appendix A explains one of the sign conventions used in this report. Appendix B covers, in greater detail than was possible in the text, the subject of leakage of buffer gas through the walls of the vapor cells. Appendix C contains a theoretical calculation of the relaxation of atomic polarization which may be expected from a background black body radiation field.
CHAPTER II

THEORY

1. Optical Pumping

Several excellent reviews of optical pumping have been written,\textsuperscript{20-25} and the reader wishing to obtain a deeper understanding of the subject than can be provided here will find it of benefit to consult them. In the present chapter, however, we shall sketch those elements of the theory which are necessary for an understanding of the present experiment. At the outset, the author would like to acknowledge the debt which he owes to Happer's comprehensive overview of optical pumping\textsuperscript{25} for his own understanding of the subject. Several sections of this chapter have drawn heavily from Happer's presentation.

We shall now illustrate the essentials of the optical pumping process itself by means of a simple example. Consider the experimental arrangement shown in Figure 1 and which is typical of one method, originally introduced by Dehmelt,\textsuperscript{26} of optically pumping alkali metal atoms. The vapor cell is illuminated by a spectral lamp which emits the D\textsubscript{1}, D\textsubscript{2} resonance doublet of the alkali metal atom being studied. The light is collimated by means of a lens, passed through an interference filter where the D\textsubscript{2} component is blocked, and then passed through a circular
polarizer. The circularly polarized $D_1$ light then passes through the vapor cell which contains the vapor of the alkali metal species. The vapor cell is placed in a weak magnetic field, $\hat{H}_0$, which is directed along the light path. The purpose of this weak static field is to provide a natural axis of quantization for the $z$ projections of the total angular momentum of the atoms in the vapor cell. It might at first be thought that the light beam itself would do this, but this is not the case as the weak time dependent magnetic fields which are always present in the laboratory are sufficient to disorient the polarized alkali atoms in the absence of the larger field, $\hat{H}_o$. After passing through the vapor cell, the intensity of the $D_1$ radiation can be measured with the phototube.

The effect which the circularly polarized $D_1$ radiation has on the alkali atoms in the vapor cell will now be described. If the nuclear spin is neglected, the relevant energy level structure of a typical alkali is as shown in Figure 2. It is well known that the presence of the circularly polarized $D_1$ resonance light will cause the alkali atoms to be excited to the $^2P_{\frac{1}{2}}$ state under the restriction of the selection rule $\Delta M_J = +1$. Furthermore, the selection rule will be either $+1$ or $-1$ but not both. Which one holds will depend on the direction of the quantization axis with respect to the direction of propagation of the light and the direction of circular polarization. We shall assume that the selection rule $\Delta M_J = +1$ holds.
Fig. 1.—Basic Optical Pumping Arrangement

Fig. 2.—Low lying energy levels for an alkali-like atom with zero nuclear spin.
In this case, ground state atoms in the \( +\frac{1}{2} \) sublevel cannot absorb light. Physically, this situation arises because the atom cannot absorb the additional angular momentum of the photon and simultaneously undergo excitation to the \( ^2P_{\frac{1}{2}} \) state. However, ground state atoms in the \( -\frac{1}{2} \) sublevel can absorb a photon and jump to the \( +\frac{1}{2} \) level of the excited state. Atoms in the \( +\frac{1}{2} \) excited state sublevel decay very quickly (~ 10^{-8} \text{ sec.}) and fall back to either the \( -\frac{1}{2} \) ground state sublevel or the \( +\frac{1}{2} \) ground state sublevel. The atom is twice as likely to fall to the \( -\frac{1}{2} \) sublevel as the \( +\frac{1}{2} \) sublevel, but nevertheless, in the absence of any relaxation mechanisms, all atoms will eventually be "pumped" into the \( +\frac{1}{2} \) sublevel. It is this transference of atomic population between energy levels, occasioned by the absorption of light, to which the term optical pumping refers.

An important property of the apparatus shown in Figure 1 is that the intensity of light passing through the vapor cell will be a function of the amount of orientation of the atoms in the cell. If all the atoms were optically pumped into the ground state \( +\frac{1}{2} \) sublevel the alkali metal vapor would no longer be able to absorb the \( D_1 \) radiation, and the flask would become transparent. The larger the concentration of atoms in the ground state \( -\frac{1}{2} \) sublevel, the more opaque the flask will be to the \( D_1 \) radiation. Thus the amount of \( D_1 \) radiation passing through the apparatus is a measure of the amount of atomic orientation in the vapor cell.
The optical pumping process just described is still essentially correct when nuclear spin is included in the atomic model. The magnetic sublevel structure becomes more complicated, however.

It should perhaps be mentioned that prior to the start of the optical pumping process the population of the atomic energy levels will be given by the usual Boltzmann distribution. Typical magnetic interaction energies are sufficiently small, however, so that at ordinary temperatures the magnetic sublevels of the atomic ground state may be assumed to be equally populated when thermal equilibrium prevails.

2. Detection of Magnetic Resonances

The interaction with an external magnetic field of the ground state of one of the alkali metal atoms discussed in the previous section is represented by the Hamiltonian

\[ H = - \hat{\mu} \cdot \hat{H}_o. \]

Here \( \hat{\mu} \), the magnetic moment of the atom, is related to the total atomic angular momentum, \( \hat{F} \), by the formula

\[ \hat{\mu} = -g_F \frac{\mu_B}{\hbar} \hat{F} \]

where \( g_F \) is a number on the order of unity (\( g_F = 2 \) for the present example of an alkali with nuclear spin neglected), and \( \mu_B \) is the Bohr magneton. 
\[ \nu_B = \frac{|e|}{2MC} \frac{\hbar}{c}. \]

When this problem is solved classically, the well known result is that the total angular momentum (or magnetic moment) maintains a constant projection on the static field, \( \vec{H}_0 \), but precesses around it at the Larmor frequency

\[ \nu_L = \frac{g_F \mu_N H_0}{\hbar}. \]

The same result is obtained quantum mechanically with the exception that now it is the expectation value of the magnetic moment which precesses about the static field.

The condition that the expectation value have a constant projection on the static field may be expressed as follows. If the state vector of the atom is written as a linear combination of spin up (+) and spin down (−) states, one obtains

\[ |\psi\rangle = a_+(t)|+\rangle + a_-(t)|-\rangle. \]

Conservation of probability requires that

\[ |a_+(t)|^2 + |a_-(t)|^2 = 1 \]

and the condition that the projection on the static magnetic field be constant requires further that the magnitude of each of the coefficients be separately constant.

We now consider the effect of applying at right angles to \( \vec{H}_0 \) an oscillating magnetic field.
\[ \dot{H}(t) = \dot{H}_1 \cos(\omega t + \phi). \]

The total Hamiltonian for the interaction of the atom with the external magnetic fields is then

\[ H = \mathbf{\hat{\mu}} \cdot \mathbf{H}_0 - \mathbf{\hat{\mu}} \cdot \dot{H}_1 \cos(\omega t + \phi). \]

The above Hamiltonian is usually solved within the framework of the rotating field approximation. This consists of expressing the field \( \dot{H}_1(t) \) as the sum of two fields, each of amplitude \( \frac{1}{2} H_1 \), rotating in opposite directions, and then dropping that term in the Hamiltonian which involves the field rotating contrary to the Larmor precession of the atom. When this term is kept it may be shown to lead to a shift in the observed resonant frequency for Zeeman transitions between the \( \pm \frac{1}{2} \) and \( \mp \frac{1}{2} \) magnetic sublevels. These transitions normally occur at the frequency of the classical Larmor precession. The apparent change in the resonant frequency induced by the counter rotating magnetic field is known as the Bloch-Siegert shift.\(^{27}\) It is generally negligibly small.

It may be easily shown\(^{28}\) that the effect of a rotating magnetic field is to give the magnitude of the coefficient \( a_+(t) \) a time dependence of the form

\[ |a_+(t)|^2 = 1 - \left[ \frac{\omega_1^2}{\omega_1^2 + (\omega_0 - \omega)^2} \right] \sin^2 \left( \frac{1}{2} \left[ \omega_1^2 + (\omega_0 - \omega_1)^2 \right]^{\frac{1}{2}} t \right) \]

where
and \( \omega \) is the angular frequency of the rotating field. The above formula corresponds to the condition that 
\[ |a_+(t = 0)|^2 = 1. \]
The time dependence of \( |a_-(t)|^2 \) can be found from the normalization condition on the state vector.

The result shows that for \( \omega_1/\omega_0 \ll 1 \) and \( \omega \) very much different from the Zeeman transition frequency \( \omega_0 \), both \( |a_+(t)|^2 \) and \( |a_-(t)|^2 \) are essentially constant except for a low amplitude high frequency oscillation about their mean values. For \( \omega \) equal to \( \omega_0 \) both coefficients oscillate from zero to one with time averaged values

\[ \left< |a_+(t)|^2 \right> = \left< |a_-(t)|^2 \right> = 1/2. \]

We now consider such an oscillating magnetic field applied to the optically pumped alkali vapor previously discussed. If the frequency of the oscillating field is far removed from the Zeeman transition frequency, no change in the state of the vapor will be observed. If the field oscillates at the Zeeman frequency, and is intense enough to dominate the optical pumping process, the number of atoms occupying the \( +\frac{1}{2} \) and \( -\frac{1}{2} \) magnetic sublevels will be equalized on the time average.

We have been assuming that initially the atoms are predominately in the \( +\frac{1}{2} \) ground state magnetic sublevel. Since the application of the oscillating magnetic field causes the population of the \( -\frac{1}{2} \) sublevel to increase, more
D$_1$ radiation will be absorbed, and the vapor cell will transmit less of the pumping light. If the frequency of the oscillating field is varied and the intensity of D$_1$ light passing through the apparatus monitored, one will observe a curve of intensity versus frequency with a sharp minimum at the resonant frequency of transitions between the $+\frac{1}{2}$ and $-\frac{1}{2}$ sublevels. The above experiment, then, is a way of determining the frequencies of atomic magnetic transitions. This particular illustration shows how the Zeeman transitions of the atom in the static field $\hat{H}_0$ can be detected.

We shall now consider a more general case by removing the restriction that the magnetic moment of the nucleus be ignored. This will make the magnetic sublevels of the atomic electronic states somewhat more complicated. For an atom with a $^2S_{\frac{1}{2}}$ electronic ground state, the Hamiltonian for the ground state magnetic interactions with an external magnetic field is given by

$$\hat{H} = A\hat{I} \cdot \hat{J} + g_J \frac{\mu_B}{\hbar} \hat{J} \cdot \hat{H}_0 + g_I \frac{\mu_N}{\hbar} \hat{I} \cdot \hat{H}_0.$$  

The sign conventions employed in writing the Hamiltonian in this form are explained in Appendix A.

The first term in the above Hamiltonian arises from the fact that the energy of the atom now depends on the relative orientation of the nuclear angular momentum ($\hat{I}$) and the electronic angular momentum ($\hat{J}$). The second two terms represent the interaction of the electronic and...
nuclear magnetic moments with the external magnetic field. The constant $A$ can be calculated once the electronic wave function is known. This was first accomplished in 1930 by Fermi who employed the Dirac equation. Derivations employing non-relativistic quantum mechanics are also available. The result is

$$A = -\frac{8\pi}{3} \frac{g_J g_I \mu_B \mu_N}{\hbar^2} \left| \psi (0) \right|^2$$

for an atom whose single unpaired $S$ electron is described by the wave function $\psi (r)$. In the present case $g_J$ is just the electronic spin $g$ factor. To sufficient accuracy we may write

$$g_J = g_S = 2.$$

In the most common case $g_I$ is a negative number (under the sign convention explained in Appendix A), and in consequence $A$ is generally positive. A more complicated expression for $A$ is required if such effects as core polarization and configuration interaction are taken into account.

We shall not discuss the solution of this Hamiltonian in detail now. This is done in Section 5 where the Breit-Rabi formula is considered. Here we shall content ourselves with the observation that the Hamiltonian

$$H = A \mathbf{I} \cdot \mathbf{J}$$

has eigenstates which are also eigenstates of the total angular momentum $F^2$ and its z projection $F_z$. These
eigenstates are degenerate in $M_F$, the quantum number specifying the $z$ projection of the angular momentum. If a very weak magnetic field is applied along the $z$ axis, the quantum numbers of the atomic eigenstates remain unchanged but the degeneracy in $M_F$ is lifted. Optical pumping can now cause population differences between $M_F$ states and between $F$ states. There is now the opportunity of observing transitions between the $M_F$ states within a multiplet of constant $F$ (Zeeman transitions), and transitions between the $F$ levels themselves (hyperfine transitions). As before, this can be accomplished by applying an oscillating magnetic field of the correct frequency to the vapor cell, and observing the transmitted light intensity. If the direction along which the field oscillates is perpendicular to the static field, Zeeman transitions obeying the selection rule ($\Delta F = 0, \Delta M_F = \pm 1$) may be observed, while the selection rule for the hyperfine transitions is ($\Delta F = \pm 1, \Delta M_F = \pm 1$). If the direction of oscillation is parallel to the static field, no Zeeman transitions can be observed, but hyperfine transitions obeying the selection rule ($\Delta F = \pm 1, \Delta M_F = 0$) can be detected.

3. Polarization of an Atomic Vapor by Spin Exchange Collisions

In the previous section we considered the example of a vapor of alkali atoms which were polarized by interaction with a beam of circularly polarized $D_1$ radiation. This technique of polarizing the vapor is useful only when
a light source producing the required $D_1$ radiation is available. When technical difficulties prevent the construction of the necessary light source, the phenomenon of spin exchange collisions may often be utilized to produce the desired polarization.

The term spin exchange refers to the ability of two particles to transfer their spin orientation to one another upon making a collision. In optical pumping experiments employing spin exchange collisions, the vapor cell contains the vapor of two atomic species, say A and B. For one of the species, say A, a source of $D_1$ radiation is readily available, and it may be optically pumped in the manner previously described. Pumping of species B may then be produced by optically pumping A, the effect being transferred from A to B via spin exchange.

As in the case of direct optical pumping, Zeeman and hyperfine transitions of species B can be detected by the application to the vapor cell of an oscillating magnetic field of the correct frequency. The resulting depolarization of species B is transmitted to A via spin exchange, and the intensity of $D_1$ radiation passing through the flask is diminished.

For two spin $\frac{1}{2}$ systems, the spin exchange interaction arises from the difference between the lowest singlet and triplet potential energy curves of the molecular system AB. The potential responsible for spin exchange can be represented by an interaction of the form
Analogous but more complicated interaction potentials are required to describe the interaction between atoms with spins greater than $\frac{1}{2}$.

The original works on spin exchange collisions were semi-classical analyses carried out by Purcell and Field\textsuperscript{34} and by Dicke and Wittke.\textsuperscript{35} Subsequent work has been fully quantum mechanical. Balling, Hanson, and Pipkin,\textsuperscript{36} for example, used a partial wave analysis of the spin-exchange scattering process to derive a theory which predicts the density matrices describing two atoms after a spin exchange collision from the density matrices before the collision. A somewhat more detailed treatment of the effect of spin exchange collisions, also formulated in terms of the density matrix, was produced shortly thereafter by Grossetête.\textsuperscript{37}

4. \textbf{Inclusion of a Buffer Gas in the Vapor Cell}

Of importance in all optical pumping experiments is the ease with which polarization can be produced and maintained in the atomic vapor being pumped. The magnitude of the attainable polarization is critically limited by various relaxation mechanisms operating on the atomic ground state, and is effected to a lesser extent by the relaxation of the excited state.

The relaxation of the polarized atomic ground state
caused by collisions with the walls of the vapor cell can be a major limitation on the amount of polarization which can be produced. These collisions are highly disorienting, and a polarized alkali atom striking the walls of a quartz or pyrex container loses its polarization after essentially only one collision. The early optical pumping experiments attacked this problem either by eliminating the container - the first successful optical pumping experiments were done on atomic beams - or by making the container relatively large in order to increase the time of flight between collisions with the walls.

Two alternative methods for dealing with this problem have since become available. One method, developed by Dehmelt, Ensberg, and Robinson, is to coat the container walls with a nonrelaxing material. In such a treated container an atom may make thousands of collisions against the walls without loss of polarization. Unfortunately, these coatings cannot withstand high temperature, and for high temperature optical pumping another method of reducing the relaxation caused by wall collisions must be employed.

The second method, useful at both high and low temperatures, is to introduce a buffer gas into the vapor cell. Brossel was among the first to utilize this technique, which was based upon the discovery that the molecules of certain simple gases such as hydrogen, nitrogen, or the inert gases could make millions of collisions against polarized alkali atoms without destroying the polarization.
By introducing one, or possibly a combination of these gases into the vapor cell at pressures of a few Torr, the time for diffusion of the polarized atoms to the walls can be greatly increased and the relaxation caused by wall collisions can be accordingly reduced. The gas thus introduced into the vapor cell is known as a buffer gas, since it serves as a buffer between the polarized atoms and the walls.

Although the buffer gas was originally added to the vapor cell to reduce the relaxation caused by wall collisions, a totally different effect of the buffer gas quickly aroused much greater theoretical interest. This effect arose from the perturbation of the alkali atom wave functions caused by collisions with the atoms of the buffer gas. This perturbation causes a change in the hyperfine coupling constant, so that in the presence of a buffer gas the Hamiltonian responsible for the hyperfine interaction should read

\[ H = (A_o + \Delta A) \mathbf{I} \cdot \mathbf{J} \]

where \(A_o\) is the free atom hyperfine coupling constant and \(\Delta A\) is a perturbation caused by interactions with the atoms of the buffer gas.

From considerations of classical statistical mechanics, which may be shown\(^{13}\) to describe the present situation adequately, the following expression for the change in the hyperfine coupling constant may be derived.
\[ \Delta A = \rho \int \Delta A(\vec{R}) \ e^{-\frac{V(\vec{R})}{kT}} \ d^3\vec{R}. \]

In the above expression \( \rho \) is the number density of buffer gas atoms, \( \Delta A(\vec{R}) \) is the change in the hyperfine coupling constant of an atom of the atomic vapor located at the point \( \vec{R} \) relative to a buffer gas atom, and \( V(\vec{R}) \) is the interatomic potential energy of the system consisting of a buffer gas atom and an atom of the vapor.

The major problem in the calculation of the density shift, \( \Delta A \), is thus seen to be the determination of expressions for \( \Delta A(\vec{R}) \) and \( V(\vec{R}) \). Although it is a difficult calculational feat to obtain an accurate functional form for the dependence of \( \Delta A(\vec{R}) \) upon \( \vec{R} \), the general nature of the dependence is now understood, at least for the alkalis. At large interatomic separations, \( \Delta A \) is caused by the electrostatic Van de Waals forces which tend to pull the electron away from the nucleus of the alkali atom and thus decrease the magnitude of \( \Delta A \). For very small separations, exchange forces between the alkali valence electron and the buffer gas electrons tend to concentrate the valence electron more strongly at the nucleus, thus increasing the magnitude of \( \Delta A \). Heavy inert gases such as xenon or krypton produce negative density shifts since these gases are highly polarizable and have large Van der Waals interactions. Light inert gases such as helium and neon produce positive density shifts. These gases are not highly
polarizable, and exchange forces dominate during collisions.

The existence of an extensive literature on the theory of density shifts has previously been mentioned. A comprehensive bibliography on this subject may be found in the review article by Happer.

5. Breit-Rabi Formula

It is of interest to study somewhat more closely the energy levels of the electronic ground state of an alkali-like atom in an external magnetic field. The Hamiltonian for this system may be accurately represented by the operator

\[ H = \frac{\mathbf{\hat{A}}}{\hbar^2} \cdot \mathbf{\hat{J}} + g_J \frac{\mu_B}{\hbar} \mathbf{\hat{J}} \cdot \mathbf{\hat{H}} + g_I \frac{\mu_N}{\hbar} \mathbf{\hat{I}} \cdot \mathbf{\hat{H}} \]

where \( \hbar^2 \) has been inserted in the first term for later convenience. Here \( \mathbf{\hat{I}} \) and \( \mathbf{\hat{J}} \) are the operators for the nuclear and electronic total angular momentum. The Bohr and nuclear magnetons are positive numbers defined by

\[ \mu_B = \frac{e \hbar}{2M_e C} \quad \mu_N = \frac{e \hbar}{2M_p C} \approx \frac{e \hbar}{2M_n C} . \]

Most commonly the parameters \( A, g_J, \) and \( g_I \) are, respectively, positive, positive, and negative. For silver, both isotopes of which are anomalous in this regard, their values are negative, positive, and positive. This anomaly arises from the fact that the magnetic moment of the silver
nucleus is antiparallel to its angular momentum, while for most nuclei the magnetic moment and angular momentum are parallel.

For the case where either \( I = \frac{1}{2} \) or \( J = \frac{1}{2} \) and \( H_0 \) is a static magnetic field, the above Hamiltonian may be solved exactly. This was first done by G. Breit and I. Rabi\(^{42}\) and the result has accordingly come to be called the Breit-Rabi formula. Let \( \mathbf{H}_0 \) be along the \( z \) axis, \( I \) be arbitrary and \( J = \frac{1}{2} \). Using the notation of von Buttlar,\(^{43}\) one has

\[
E_\pm(M) = -\frac{A}{4} + g_{\mu N} M H_0 + \frac{A}{4} (2I + 1) \left[ 1 + \frac{4MX}{(2I + 1)} + X^2 \right]^{\frac{1}{2}}
\]

Where the abbreviations

\[
M = M_F = M_I + M_J
\]

and

\[
X = \frac{g_{J\mu B} - g_{I\mu N}}{\frac{1}{2}A(2I+1)} H_0
\]

have been used. The "+" ("-" ) sign gives the energy levels which evolve out of the degenerate zero field state with total angular momentum quantum number \( F = I + \frac{1}{2} \) (\( F = I - \frac{1}{2} \)). The energy levels for silver, computed from the Breit-Rabi formula, are shown in Figure 3. For zero magnetic field the state of highest \( F \) quantum number is lowest in energy because the hyperfine coupling constant is negative. Only the Breit-Rabi energy levels for Ag\(^{107}\) have been illustrated.
Fig. 3.—Breit-Rabi Energy Level Diagram for Ag$^{107}$
The structure of the energy levels for the other stable isotope of silver, Ag\textsuperscript{109}, is essentially the same, because the nuclear spins of these isotopes are identical (I = \(\frac{1}{2}\)), and because their magnetic moments are both negative and similar in magnitude. In units of the nuclear magneton \((\mu_n = 5.0505 \times 10^{-22} \text{ erg Gauss}^{-1})\), \(\mu = -0.113548\) and \(\mu = -0.130538\) for Ag\textsuperscript{107} and Ag\textsuperscript{109} respectively.\textsuperscript{44}

Specializing the Breit-Rabi formula to the case \(I = \frac{1}{2}\), expanding to second order in \(H_o\), and computing the frequencies of the hyperfine transitions from the formula

\[
\nu = \frac{E_- - E_+(M)}{\hbar}
\]

one obtains

\[
\nu = (\Delta \nu) - \frac{1}{2} \left[ g_J \frac{\mu_B}{\hbar} + g_I \frac{\mu_N}{\hbar} \right] MH_o + \frac{1}{4(\Delta \nu)} \left[ g_J \frac{\mu_B}{\hbar} - g_I \frac{\mu_N}{\hbar} \right]^2 (2-M^2)H_o^2
\]

where \((\Delta \nu)\) is the hyperfine frequency in the absence of the magnetic field.

To determine the hyperfine frequency which would characterize the atom in the absence of the magnetic field, the ideal transition to measure would be \((F = 1, M = 0 \leftrightarrow F = 0, M = 0)\), since this transition is independent of the field to first order. Unfortunately, the optical pumping process employed in this experiment does not produce a population difference between the two \(M = 0\) sublevels, and consequently this transition can not be observed by us. An alternative approach is to measure the two transitions
\( (F = 1, M = 1 \leftrightarrow F = 0, M = 0) \) and \( (F = 1, M = -1 \leftrightarrow F = 0, M = 0) \) and average them. The result is

\[
\bar{\nu} = (\Delta \nu) + \frac{1}{4(\Delta \nu)} \left[ g_J \frac{\mu_B}{\hbar} - g_I \frac{\mu_N}{\hbar} \right]^2 H_0^2
\]

which is also field independent to first order.

We shall now see how greatly \( \bar{\nu} \) is caused to deviate from \( (\Delta \nu) \) by the presence of the quadratic term. Since the nuclear magneton is 1836 times smaller than the Bohr magneton it is permissible to ignore the second term in the square brackets relative to the first. Then noting that for silver \( g_J = g_S = 2 \), and that accordingly the term in the square brackets times the magnetic field strength is just the Zeeman frequency of an electron in the field \( H_0 \), we obtain

\[
\bar{\nu} = (\Delta \nu) + \frac{(\nu_e)^2}{4(\Delta \nu)}
\]

In our experiment, the static field was always adjusted so that

\[
\nu_e \approx 1.2 \times 10^4 \text{ Hz}.
\]

Using

\[
(\Delta \nu) = 1.7 \times 10^9 \text{ Hz}
\]

for Ag\(^{107}\) yields

\[
\bar{\nu} = (\Delta \nu) + O(10^{-2})
\]
In the present experiment ($\Delta \nu$) for silver was obtained by measuring the two transitions ($F = 1, M = 1 \leftrightarrow F = 2, M = 0$) and ($F = 1, M = -1 \leftrightarrow F = 0, M = 0$) and averaging them. The above calculation shows that intrinsic to this method is a systematic error of about $10^{-2}$ Hz. This error, however, is negligible. It is about 300 times smaller than the typical error of $\pm 3$ Hz which remains after statistical treatment of our measurement data, and which arises primarily from random fluctuations in the intensity of the pumping light.
CHAPTER III

APPARATUS AND EXPERIMENTAL PROCEDURE

This chapter describes the apparatus employed and the procedure followed in the performance of the experiment. The discussion is divided into four sections. The first describes the manufacture of the sample flasks. The second describes the optical pumping apparatus. The third covers the experimental technique by which measurements were made, and the fourth discusses the sources of errors in these measurements.

1. Sample Flask Manufacture

The sample flasks were made from 300 cubic centimeter G. E. fused quartz spherical flasks, which had been reworked by a professional glass blower to the form shown in Figure 4. A sample was prepared on a vacuum system in the following manner. First, the sample was cleaned using a dilute solution of hydrofluoric acid, rinsed first with distilled water then with alcohol, and dried with a hot air gun. Powdered silver was then poured into the side-arm on the flask through a funnel inserted into the flask through the filling tube (shown in Figure 4). The flask was then attached to the vacuum system by the pyrex stem, and the filling tube removed. A sidearm containing an opened ampoule of rubidium was then connected to the
vacuum system near the spot where the sample was attached, and the vacuum system was then evacuated. Figure 5 illustrates the connection of the vapor cell and sidearm to the vacuum system. A firebrick oven which utilized heating elements made of Nichrome resistance wire was built around the sample, and the sample was baked out at approximately 800°C for an hour or so in order to clean it thoroughly. At the same time, the sidearm containing the ampoule of rubidium was gently heated with a Bunsen burner in order to drive off impurities. The heat to the oven was then turned off, and, after the flask had cooled, a small amount of rubidium was distilled into the tube at the base of the sample. The tube was then inserted into a water cooled socket and the sample was again baked out at approximately 850°C for roughly two hours. The exact temperature and time varied from sample to sample, but this appeared to have no effect on the ultimate performance of the sample. This second bake-out drove adsorbed rubidium off the walls of the sample flask and into the cooled tube at the base of the sample, and conditioned the sample for high temperature operation. Finally, the evacuated vacuum system with connected sample flask was sealed off from the vacuum pump, and buffer gas was admitted via a leak valve. The sample was then removed from the vacuum system.

In removing the sample from the vacuum system it was necessary to heat the neck of the sample to the melting point of quartz. This raised the temperature of the sample as a whole, and this in turn drove buffer gas from the
sample into the vacuum system. Thus, when the sample was removed from the vacuum system, the density of buffer gas in the sample was lower than it had been prior to removal. By measuring the pressure in the vacuum system-sample flask combination prior to the removal of the sample, and the pressure in the vacuum system after removal of the sample, it was possible to compute the amount of buffer gas which had been driven from the sample into the vacuum system. From this it was possible to determine the pressure in the sample flask after its removal from the vacuum system. This calculation was effected by means of the following formula, which may be derived by appropriately applying the ideal gas law to the vacuum system-sample flask combination.

\[ P_f = P_o + (P_o - P_{sf}) \left( \frac{V_s}{V_b} \right) \]

In the above formula \( P_f \) is the pressure in the sample after removal from the vacuum system, \( P_o \) is the pressure in the vacuum system-sample flask combination prior to removal of the sample, \( P_{sf} \) is the pressure in the vacuum system after removal of the sample, and \( V_s \) and \( V_b \) are respectively the volumes of the vacuum system and the sample flask. All the pressures are measured at that room temperature which prevailed at the time of the sample's removal. After removal, the ideal gas law was used to compute the pressure which would exist in the sample at 298° K (25°C). Thereafter, unless otherwise indicated, the sample flask pressure was
always considered to be that pressure which would prevail in the sample at 25\(^\circ\) C. In this way all pressures were in effect measured at a common temperature.

2. The Optical Pumping Apparatus

Figure 6 is a block diagram of the apparatus used to perform the experiment. Figure 7 shows some details of the apparatus which are omitted in Figure 6. We shall now briefly discuss this equipment.

The rubidium light source was a standard electrodeless discharge,\(^{49,50}\) The light bulb was made from a 25 c.c. pyrex flask whose filler neck had been removed and replaced with a hollow pyrex tube .6 centimeters in o.d. and approximately 3 centimeters in length. This reworked flask was then attached to a vacuum system, evacuated, and a small amount of rubidium distilled into it. Finally, the bulb was filled with approximately 1 to 2 Torr of argon, and removed from the vacuum system. The finished product is illustrated in Figure 8.

The electronic circuitry for the light followed, with slight modifications, a design for a 50 MHz transmitter found in the ARRL Handbook.\(^{51}\) A circuit diagram for the light source is shown in Figure 9. In operation, the light bulb, whose construction has just been described, was placed inside the inductor labeled \(L_5\) in Figure 9, with its 3 centimeter long glass stem pointing straight down and extending outside the circumference of the inductor, which consisted of 2 turns of 3/16 inch copper tubing.
The stem was inserted in a glass socket, which could be heated by passing a current through a coil of resistance wire surrounding it. By controlling the temperature of the stem, into which all the rubidium had initially been distilled, it was possible to control the density of rubidium atoms in the bulb for optimum light intensity. As can be seen from Figure 9, the inductor containing the light bulb was part of the output circuit of the radio transmitter. The intense electromagnetic fields generated inside this inductor when the transmitter was operating caused the atoms in the flask to be raised to excited energy levels, and, in the subsequent decay of these atoms to lower energy levels, light was emitted. This light was then collimated into a beam by means of a lens, and passed through an interference filter which transmitted the $D_1$ rubidium line (7,948 Å) while blocking the $D_2$ line (7,800 Å). The light was then circularly polarized, and allowed to pass through the sample flask where the optical pumping process took place.

The sample flask itself was contained inside an oven manufactured from non-magnetic firebrick. The oven was heated by means of three resistance heating rods at the top and a coil of non-magnetic resistance wire at the bottom. Care had to be taken to construct the oven only from materials which exhibited no ferro-magnetism, in order to prevent excessive magnetic field inhomogeneity. The optical pumping beam entered and left the oven through two pyrex windows (4 inches in diameter by 1/4 inch thick)
in the front and rear of the oven.  

The entire oven was enclosed by two concentric magnetic shields, designed to isolate the sample from external magnetic fields. The outer shield was 106.4 centimeters long and 47 centimeters in diameter. The inner shield was 102 centimeters long and 42.5 centimeters in diameter. End caps on the outer shield completed the enclosure. A hole, 11.4 centimeters in diameter, was cut in the center of each end cap. The optical pumping beam entered and exited through these holes which also provided a means of making connections between the laboratory and the magnetically shielded area.

There were six connections made from the laboratory to the interior of the shields. One connection was for the electricity by which the oven was heated, another was for the three thermocouples (to be discussed later) by which the temperature and temperature gradients in the oven were determined, a third was for an air hose the purpose of which will presently be discussed, and a fourth connection was for a pair of hoses admitting a flow of water into a coil of copper tubing wrapped around the interior of the inner shield at each end of the oven and in contact with the shield. This flow of water was necessary to keep the shields from overheating when the oven was operating at high temperature. Another connection admitted a steady direct current to a pair of Helmholtz coils connected in parallel and situated with one at the front of the oven and the other at the rear. These Helmholtz coils were used
to generate a static magnetic field of about seven milligauss. The final connection was electrical and went to a loop of non-magnetic conducting wire surrounding the sample in such a way that the plane of the loop was parallel to the oven floor. This loop was used to generate an oscillating magnetic field at right angles to the direction of the light beam.

In operation, the oven was heated to around 800°C in order to obtain a density of silver vapor in the sample flask high enough for the (spin exchange) optical pumping process to take place. The silver in the sample was in the form of a powder and contained in a sidearm, while the rubidium was contained in a hollow tube .6 centimeters in diameter and approximately 3 centimeters long. This tube extended straight down from the base of the flask. When the oven was heated, the amount of silver vapor in the sample was determined by the vapor pressure of silver at the temperature of the oven. The amount of rubidium vapor in the flask was controlled independently of the temperature of the oven by inserting the tube containing the rubidium into a pyrex socket which was cooled by blowing air through it. The temperature of the tube was then controlled by varying the rate of air flow. The amount of rubidium vapor in the flask was thus determined primarily by the temperature of the rubidium in the tube and not by the temperature of the flask itself. By adjusting the temperature of the oven and the temperature of the tube, it was possible to control the density of silver and rubidium atoms in the
sample independently. Figure 10 shows a typical sample flask with its air cooled socket. The method of high temperature control briefly sketched above has been discussed in greater detail by Balling, Lambert, Wright, and Weiss. 19

As mentioned earlier, the temperature and temperature gradients in the oven were monitored by means of three thermocouples. These thermocouples entered through the rear of the oven inside ceramic feed-throughs, and extended far enough forward so that the junction of each could be placed in physical contact with the sample flask. One thermocouple was placed in contact with the sample flask midway down its side, and the other two were symmetrically placed near the top and bottom. Typically, the top and bottom of the sample were about 20° C hotter than the midpoint. The thermocouples were of the platinum-platinum, 20% rhodium type. They were used in conjunction with tables of temperature versus voltage accurate to ±.5° C without interpolation. The validity of temperature measurements made using the thermocouples was checked experimentally by using the thermocouples to measure the temperature of a solution of water and ice and the temperature of boiling water. Answers within a degree of 0° C and 100° C were obtained.

When in operation for the making of measurements, the oven, as mentioned earlier, was heated to around 800° C. At this temperature the oven glowed red-orange, and the changes in thermal radiation intensity which occurred when the heat to the oven was turned on and off were of such
amplitude that they completely saturated the Tektronix 122 preamplifier and rendered it incapable of amplifying the optical pumping signals. In order to shield the light detection apparatus from thermal radiation from the oven, an interference filter was placed in the light path between the oven and the light detector. This filter passed the rubidium $D_1$ line, had a bandpass of $50 \, \text{Å}$, and was blocked from x-rays to microwaves. With this filter in place, only minimal thermal radiation reached the light detector from the oven, and the problem of saturating the electronics was eliminated.

The light detector consisted of a 6953 gas photodiode. This phototube has its maximum response in the infrared near the rubidium $D_1$ line. The phototube was connected in series with a 67 1/2 volt battery, a 1 megohm resistor, and a microammeter. This circuit biased the phototube and allowed a change in light intensity at the phototube to be detected as a change in voltage across the resistor. The microammeter measured the direct current through the phototube. By adjusting the rubidium light source until this current was maximized, it was possible to adjust the rubidium lamp for maximum light output. The voltage across the resistor was coupled into the Tektronix 122 preamplifier through a 5 microfarad capacitor. Thus only changes in the voltage across the resistor were detected and amplified. The output of the preamplifier was coupled directly into a Tektronix 504 oscilloscope and a Princeton Applied Research JB-5 lock-in amplifier. The
oscilloscope allowed the visual observation of the waveform of the larger signals, while the lock-in amplifier allowed the detection of the integrated amplitude of the smaller signals.

The remainder of the apparatus shown in Figure 6 will now be briefly discussed. The technical details of the equipment and its operation will not be covered here, as this information may be found in the appropriate manuals published by the various manufacturers. Here we shall be concerned only with the essentials of the operation of the equipment as they pertain to this experiment.

The operation of the circuitry shown in Figure 6 may easily be understood. Essentially, the output of a sine wave generator is coupled into the r.f. coil in the oven through an adjustable attenuator and a chopper. This creates in the oven, at right angles to the light path, an oscillating magnetic field which is square wave modulated at the frequency of the chopper, and whose amplitude may be varied by adjusting the attenuator. In operation, the attenuator was adjusted to minimize r.f. broadening of the observed signal, while still maintaining a readable signal amplitude. The frequency of the chopper was determined by the frequency of a reference signal put out by the lock-in. The two frequencies were equal and were set at around 13 Hz. When the output of the frequency generator was tuned to an atomic resonance, the oscillating magnetic field in the oven reduced the atomic polarization previously induced by the optical pumping light. When the chopper
turned off the oscillating field, the atomic polarization again built up to its original value. Since the absorption of optical pumping light by the flask is a function of the degree of polarization of the rubidium vapor, the intensity of the light transmitted through the flask was accordingly altered, producing a signal which was detected by the phototube and preamplifier down the light path. This signal was modulated at the reference frequency of the lock-in, since it was produced by an oscillating magnetic field which was itself modulated at this frequency. The frequency of the signal observed at the phototube was thus exactly the frequency which the lock-in was tuned to detect. By sweeping the frequency of the oscillating magnetic field until a signal was detected by the lock-in, it was possible to observe atomic Zeeman and hyperfine transitions.

Figure 6 has two circuits like that just described above. The one associated with the Hewlett Packard wide range oscillator produced low frequency signals useful for observing atomic Zeeman resonances. The one associated with the PRD signal generator produced .95 to 1 GHz microwaves which were used to observe the hyperfine transitions in Ag$^{107}$ and Ag$^{109}$. It was possible to replace the PRD L712-B signal generator with the S712-B signal generator. This signal generator operated in the range of 1.9 to 4 GHz and was used to observe the hyperfine transitions in Rb$^{85}$.

Either the low frequency circuit or the microwave circuit could be coupled into the oven by means of the Transco r.f. switch. It was thus possible to go directly
from an observation of a Zeeman resonance to an observation of a hyperfine resonance merely by throwing a switch.

The frequencies of both the low frequency generator and the microwave generator were measured by means of a Hewlett Packard 5245L frequency counter. The frequency counter read directly from 0 to 50 MHz, but the use of the 5254A (5255A) plug-in unit was necessary to measure frequencies in the .3 to 3 (3 to 12.4) GHz range. The accuracy of the frequency counter was maintained by the use of the Hewlett Packard 117A comparator. This unit compares the frequency of the 1 MHz crystal in the frequency counter with the 60 KHz standard signal broadcast by WWVB (NBS, Boulder, Colorado). The comparator provides what is essentially a written record of the discrepancy between the ideal crystal frequency of 1 MHz and the actual frequency of the crystal in the counter. By tuning the frequency of this crystal it was possible to reduce this discrepancy and thus increase the accuracy of the counter. During this experiment the accuracy of the counter was maintained at better than 2 parts in $10^9$ for all measurements.

3. Experimental Procedure

Prior to using the apparatus to make measurements, the rubidium resonance lamp was turned on and its intensity maximized. A sample was then inserted in the air cooled socket in the oven, the access hole to the oven closed, the cooling air turned on, and the oven heated to around 800° C. The rubidium Zeeman signals were measured to make sure that
there was rubidium vapor in the sample flask, and the flow of cooling air adjusted until these signals were maximized. The silver Zeeman signals were then measured and the oven temperature and cooling air velocity adjusted until these signals were maximized. The Hewlett Packard frequency generator was then disconnected from the oven and the microwave generator connected, by throwing the Transco r.f. switch. If previous measurements had indicated approximately where the density and Zeeman shifted Ag\textsuperscript{107} hyperfine transitions would be observed, these transitions were quickly found and their frequencies noted. If no previous measurements for the particular buffer gas being used had been made, the hyperfine transitions were found by sweeping the microwave band in the vicinity of one of the Zeeman shifted hfs transitions. The free atom hfs was taken to be 1,712,512,111(18) Hz from the measurements of Dahmen and Penselin.\textsuperscript{45} Once the transitions had been found and their frequencies noted, we were ready to make a careful measurement of the Ag\textsuperscript{107} hyperfine frequency and determine the temperature to which it corresponded.

The determination of the Ag\textsuperscript{107} hfs at some temperature, T\textsubscript{m'}, was made as follows. First the oven was heated up to 10°C above the temperature at which it was desired to know the Ag\textsuperscript{107} hfs. The heat to the oven was then turned off and one of the Zeeman shifted hfs transitions was measured. This measurement was made by slowly sweeping the microwave frequency around the vicinity of the frequency of the desired transition until the maximum signal strength
was obtained on the lock-in. The frequency at which the maximum signal occurred was read off the frequency counter and recorded. During the process of finding the maximum signal, the temperature in the oven was being continuously monitored. At the moment the maximum signal was found, the temperature in the oven was noted and recorded. This is the temperature which was assigned to the frequency measurement. If, during the process of finding the maximum signal, the oven temperature fell more than 10° C below the desired temperature, no measurement was made. In this case the oven was heated again, and the measurement was made over. The other Zeeman transition was measured in a like manner.

In measurements made using vapor cells containing helium buffer gas one minor change was made in the procedure just described. For helium the vapor cells were initially heated to 5° C above the temperature at which it was desired to know the hfs, and were allowed to fall to only 5° C below this temperature. This change was made in an effort to define the temperature of the helium cells somewhat more precisely, in partial compensation for the additional source of error represented by the rapid rate of leakage of helium buffer gas from the vapor cell. The subject of buffer gas leakage is covered in more detail in Chapter IV.

We illustrate below in Table 1 the manner in which the measurements of the Ag\textsuperscript{107} hfs were grouped and analysed. The subscripts on the entries in the table indicate the order in which the measurements were taken. The method of analysis is reasonably clear from the table. Essentially,
<table>
<thead>
<tr>
<th>Upper (Lower)</th>
<th>Lower (Upper)</th>
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<td>Temperature</td>
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<tr>
<td>hfs</td>
<td>hfs</td>
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<td>hfs</td>
</tr>
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<td>$f_1$ : $T_1$ : $f_3$ : $T_3$ : $\frac{4}{4}$</td>
<td>$\sum f_i$ : $\sum T_i$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$f_2$ : $T_2$ : $f_4$ : $T_4$ : $\frac{i = 1}{4}$</td>
<td>$\frac{i = 1}{4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$f_7$ : $T_7$ : $f_5$ : $T_5$ : $\frac{8}{8}$</td>
<td>$\sum f_i$ : $\sum T_i$</td>
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</tr>
<tr>
<td>$f_8$ : $T_8$ : $f_6$ : $T_6$ : $\frac{i = 5}{4}$</td>
<td>$\frac{i = 5}{4}$</td>
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<tr>
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<td>$\sum f_i$ : $\sum T_i$</td>
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<tr>
<td>$f_{10}$ : $T_{10}$ : $f_{12}$ : $T_{12}$ : $\frac{4}{4}$</td>
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</tr>
</tbody>
</table>
two measurements of one Zeeman shifted hfs transition were averaged with two measurements of the oppositely shifted transition to average out the effect of the magnetic field. We thus obtained one measurement of the pressure and temperature (but not Zeeman) shifted hfs. The temperature which is assigned to each such measurement is the average of the temperatures of the individual magnetic field shifted measurements. Each group of four measurements was composed of measurements made in the opposite order from those in the immediately preceding group. That is, if in one group the two measurements of the hfs transition shifted upward by the static magnetic field were made first, in the next group these measurements were made second. This method of measuring tends in the long run to average out the effect of drift of the static magnetic field, $H_o$.

In order to standardize the measurement process we generally attempted to make a total of 40 measurements of the magnetic field shifted hfs transitions. When averaged in groups of 4, the result was 10 measurements of the pressure and temperature shifted hfs, with the effect of the magnetic field averaged out. The final measurement and its associated error were taken to be the mean and standard deviation of the mean of these 10 measurements. The temperature assigned to this determination of the hfs was the average of the temperatures of the 10 individual measurements. All the temperature measurements were made using the thermocouple in contact with the bulb midway
down its side. The thermocouples in contact with the bulb near its top and bottom were used to measure the temperature gradients across the bulb, and thus allow them to be minimized by appropriate adjustment of the current in the heating elements at the top and bottom of the oven.

4. Errors

As described above, in a determination of the Ag$^{107}$ hfs the error caused by random errors in the individual measurements was found by computing the standard deviation of the mean using the ordinary formulae of statistical analysis. Typical standard deviations lay in the range of 3 to 5 Hz. It is clearly of interest to consider the existence of other sources of error and to estimate their magnitude.

A check was made to find out if the measured value of the hfs depended on the direction or magnitude of the static magnetic field, $\mathbf{H}_0$. A flask containing neon buffer gas at 50.6 Torr was placed in the oven, and the Ag$^{107}$ hfs measured at the temperature of $850^\circ$C. The result was

$$v = 1,712,514,251.3(2.2) \text{ Hz}.$$ 

The direction of the static magnetic field was then reversed by reversing the direction of the current in the Helmholtz coils which created it. Because of residual magnetism in the shields, the magnitude of the new magnetic field was different from that of the old. The Ag$^{107}$ hfs was then measured at the temperature of $850^\circ$C. The
result of

\[ v = 1,712,514,247.0(1.3) \text{ Hz} \]

was clearly in experimental agreement with the earlier measurement. We concluded that in this experiment the measured value of the Ag\textsuperscript{107} hfs was not significantly dependent on the magnitude or direction of the static magnetic field.

An experiment was performed to determine if the measured Ag\textsuperscript{107} hfs depended noticeably on whether the optical pumping light was right or left circularly polarized. Two measurements were made of the Ag\textsuperscript{107} hfs using the flask containing neon buffer gas at 50.6 Torr. The circular polarization was opposite for the two cases. The two measurements were in experimental agreement. The standard deviation of each measurement was about 2 Hz, but the two measurements differed by only 0.8 Hz.

The possible error due to temperature gradients across the bulb was small, but not negligible. The largest temperature dependence of the Ag\textsuperscript{107} hfs was in helium buffer gas, and had the value of \(2.27 \times 10^{-2} \text{ Hz } ^\circ\text{C}^{-1} \text{ Torr}^{-1}\). For temperature differentials of about 20\(^\circ\)C (the size of those encountered in this experiment) and a sample flask containing 10 Torr of buffer gas, the temperature dependence yields a frequency differential of 4.5 Hz.

The lineshapes of the Ag\textsuperscript{107} hfs transitions were observed to be essentially symmetrical.

The magnetic shields surrounding the oven had the capacity to acquire permanent magnetization. In order to
allow their demagnetization, the shields were assembled with several turns of #18 insulated copper wire wound around the outside of the inner shield, while 18 turns of #12 copper manget wire were bundled together to form a single large toroidal loop wound to enclose both shields longitudinally. The portion of this loop which was inside the shields was pressed up against the inside surface of the inner shield, and ran parallel to the axis of the shields. In order to demagnetize the shields, about 30 Amperes of 60 Hz AC was passed through these coils, first one and then the other. The current was turned up suddenly and then decreased slowly to zero using a 20 Ampere Variac. This process disoriented the magnetic domains and thus destroyed any permanent magnetization which might have built up in the metal of the shields. Following this method the shields were periodically demagnetized. This was not observed to have any effect on the location of the hfs transitions once the average which removed the first order dependence on the magnetic field was performed.

During the course of this experiment the Hewlett Packard 5245L frequency counter was held to an accuracy of better than 2 parts in $10^9$. For frequencies (like the Ag$^{107}$ hfs) in the 1.7 GHz range, this translated into an error of 3.4 Hz or less.

No attempt was made in this experiment to check for the possible existence of measurable shifts of the Rb$^{85}$ and Ag$^{107}$ hyperfine frequencies due to the presence of the optical pumping light itself. Such light shifts are not
expected to be a significant source of error. Several at-
tempts have been made in this laboratory to detect such
shifts using optical pumping apparatuses similar to the one
employed in this experiment. The shifts have always
proven to be too small to observe using our methods of de-
tection.

All measurements were made using the lowest r.f.
power which would produce a readable signal, in order to
minimize possible frequency shifts due to the Bloch-Siegert
effect. No dependence of the hfs on r.f. power level was
observed during this experiment.
Fig. 4.—Sample Flask Prior to Attachment to Vacuum System
Fig. 5.—Sample Flask and Rubidium Sidearm on Vacuum System
Fig. 6.—Block Diagram of Optical Pumping Apparatus
Fig. 7.—Detail of Oven and Magnetic Shields
Light bulb contains ~1 to 2 Torr of argon.

Fig. 8.—Light Bulb for Rubidium Light Source
Capacitors are ceramic unless specified. Values under .001 are in μuf. Resistors ½ watt unless specified.

- \( C_1 \) - 50 μuf. variable.
- \( C_2 \) - 25 μuf. variable.
- \( C_3 \) - 0.5 to 3 μuf. ceramic trimmer.
- \( C_4 \) - 25 μuf. variable.
- \( L_1 \) - 14 t. No. 20 tinned, 1/2 inch diam., 7/8 in. long, tapped 4 1/2 t. from crystal end.
- \( L_2 \) - 6 1/2 t., 7/16 in. long, similar to \( L_1 \).
- \( L_3 \) - 7 1/4 t., 1/2 in. long, similar to \( L_2 \).
- \( L_4 \) - 5 t. No. 20 wound on and spaced to fill 100 ohm 1 watt resistor.
- \( L_5 \) - 2 t. 3/16 in. copper tubing, 1 5/8 in. diam., 3/4 in. long.
- \( R_1 \) - 37,500 ohms, 4 watts (4 150,000 ohm 1 watt resistors in parallel).
- \( RFC_1 \) - Single layer v.h.f. choke, 2 to 7 μh.

Fig. 9.-- Circuit Diagram for Rubidium Light Source
Fig. 10.—Vapor Cell in Air Cooled Socket
CHAPTER IV

HYPERFINE FREQUENCY DRIFTS

For each of the vapor cells containing helium and neon buffer gas, the silver hyperfine frequency - measured at a constant temperature - tended to change somewhat over the course of the experiment. These changes were small compared to the total pressure shift, but were large enough to influence measurements of the temperature dependence of the shift. For flasks which were run several times, the frequency change was a monotonic function of the number of runs. In addition to the frequency changes which occurred in cells buffered with helium and neon, a frequency drift was observed in one of the cells buffered with argon. The present chapter discusses the nature of the frequency drift observed for each of the four buffer gases used in this experiment.

1. Vapor Cells Containing Helium Buffer Gas

For the vapor cells containing helium buffer gas, the frequency drift may be understood entirely in terms of leakage of helium from the vapor cell. From the known properties of the diffusion of helium through fused quartz\textsuperscript{59,61} it is possible to predict a loss of helium from the cell of about two percent per hour at 800° C. This rate of loss is great enough so that in order to correlate
a measurement of the silver hfs density shift with the appropriate buffer gas density, an explicit correction for leakage must be made. This correction can be made once the behavior of the helium leakage is understood. Diffusion of helium through fused quartz is discussed in greater detail in Appendix B. Here we shall merely state the most pertinent facts.

At constant temperature, the equation for the rate of decrease of helium density in a vapor cell is given by

\[ \frac{d\rho}{dt} = -R\rho. \]

Here \( R \) is a parameter characterizing the leak rate. It is shown in Appendix B that \( R \) is inversely proportional to the wall thickness of the vapor cell, and that it depends on the temperature of the cell in a complicated way. When the dependence of \( R \) upon wall thickness and temperature is taken into account, the leakage equation may be written as

\[ \frac{1}{\rho} \frac{d\rho}{dt} = -\frac{C}{T} \frac{d}{d Te}. \]

If the temperature is considered to be a function of the time, this equation may be integrated to give

\[ \ln \left( \frac{\rho(t)}{\rho} \right) = -\int_{t_0}^{t} \frac{C}{T(x)} e^{-\frac{C}{T(x)}} dx. \]
The values of $K$ and $C$ are determined in Appendix B. When $t$ is measured in minutes and $d$ in millimeters, the final equation is

$$
\ln \frac{\rho(t)}{\rho_0} = - \left[ \frac{5.023 \times 10^{-6}}{d} \right] \int_{t_0}^{t} \frac{2491}{T(x)} e^{- \frac{T(x)}{T}} dx.
$$

By utilizing this equation it is possible to correct the measured hyperfine frequencies for the effect of leakage of helium from the vapor cell. The details of how this correction can be effected are contained in Chapter V.

2. Vapor Cells Containing Neon Buffer Gas

The frequency drift occurring in cells buffered with neon is fully explainable in terms of leakage of neon from the cells. The equation describing the diffusion of neon through quartz has exactly the same functional form as that describing the leakage of helium. It differs from the latter only in the values to be assigned to the parameters $K$ and $C$ in the leakage equation written on the previous page. Using the results of the measurements of T'sai and Hogness$^{60}$ the following equation for the leakage of neon from a vapor cell may be derived

$$
\frac{1}{\rho} \frac{d\rho}{dt} = - \left[ \frac{8.815 \times 10^{-7}}{d} \right] T e^{- \frac{T}{T}}
$$

where $t$ is the time in minutes, $d$ is the thickness of the
vapor cell wall in millimeters, and $T$ is the absolute temperature.

The above equation may be used to justify the assertion that the frequency drift may be explained in terms of neon leakage. A careful temperature versus time record was kept for one of the neon buffered vapor cells. In one period of 5 hours and 25 minutes, during which the cell was held at an average temperature of 829° C, the measured silver hfs frequency drifted downward by 19.2 Hz. This works out to an average drop of 3.54 Hz per hour. Since the hfs pressure shift for this cell (which contained neon at 115.5 Torr) was approximately 5,100 Hz, the pressure shift diminished at the rate of .07 percent per hour.

The wall thickness of a vapor cell was originally estimated to be about 1.5 mm, and the measurements on helium leakage reported in Chapter V have essentially confirmed this estimate. Assuming a wall thickness of 1.5 mm, the differential equation for the leakage of neon predicts a loss rate of approximately .05 percent per hour, in excellent agreement with the measured rate of decrease of the hfs pressure shift. These results were substantially confirmed by measurements on a second vapor cell (containing neon at 203.2 Torr) which yielded a decrease in the hfs pressure shift of .06 percent per hour at 855° C. The calculated value for the leak rate, again under the assumption that $d = 1.5$ mm, is .06 percent per hour. This is in exact agreement with the measured rate of change of the pressure shift.
3. **Vapor Cells Containing Argon and Nitrogen Buffer Gases**

Only one argon filled cell was measured long enough for a consistent frequency drift to become apparent. The temperature dependence of the silver hfs shift was determined from this cell by two sets of measurements taken over an extended temperature range. During the course of these measurements, the measured silver hfs frequency drifted upward at an average rate of about 2.3 Hz per hour. We do not have an explanation for this shift. Leakage of atmospheric nitrogen (which would induce a positive pressure shift) could cause it, but an explanation based on leakage does not appear likely since the leak rates of the three gases involved - argon, atmospheric nitrogen and oxygen - are all extremely slow.\(^{59}\) Liberation of adsorbed gases from the interior surface of the sample is also a possibility.

No consistent frequency drifts were observed for the nitrogen filled vapor cells. These cells, however, were among the last to be measured, and our technique had improved to the point where measurements were made fairly rapidly. Frequency drifts which would require several measurements runs to become apparent would not have been detected.
CHAPTER V

TREATMENT OF EXPERIMENTAL DATA

1. Introduction

The purpose of this experiment was to obtain the density shift of the Ag$^{107}$ hfs in each of several buffer gases. The temperature dependence of the density shift was also to be found. In this chapter the manner in which these quantities were obtained from the experimental data is discussed. The buffer gases considered are neon, argon, nitrogen, and helium. Due to the fact that the leakage of helium through the walls of the vessel containing it was great enough to require special attention, the data for this buffer gas is analysed separately from that for the other three.

2. Density Shifts Caused by Neon, Argon, and Nitrogen

Basically, what is required for a determination of the density shift is a series of measurements of the hfs at different buffer gas densities but at the same temperature. Except for quite high pressures (on the order of several atmospheres at room temperature), the hfs is a linear function of buffer gas density. Accordingly, the measurements of the hfs versus buffer gas density may be fitted to a straight line by the method of least squares.
The slope of this line is then the quantity designated the "density shift."

For historical reasons we shall measure buffer gas density in units of pressure. The ideal gas law written in the form

$$P = \rho kT$$

constitutes a relation between pressure, number density, temperature and Boltzmann's constant. If \( T \) is assigned some specific value, say \( T_o \), then \( kT_o \) represents, in effect, a conversion factor relating the density measured in particles per unit volume to the density measured in units of pressure. In this paper \( T_o \) will be set equal to 298° k (25° C). Thus, regardless of the actual temperature of the gas in question, its density will be specified by stating the pressure which that density of gas would exert at room temperature (25° C).

For each of the buffer gases now being considered three flasks were made, each containing a different buffer gas pressure from the other two. For each flask the density shifted hfs of Ag\(^{107}\) was measured for several different temperatures in the range 775° C to 875° C. These measured points were then fitted to a straight line by the method of least squares, yielding for each flask a curve of hfs versus temperature. For each buffer gas the three curves of hfs versus temperature were evaluated for the same value of the temperature. This yielded three points on the curve of hfs versus density. The curve of hfs
versus density was then determined by least squares fitting a straight line to these three points. The density shift is then given by the slope of this curve.

For purposes of illustration we shall now provide a detailed discussion of this procedure for the case of neon buffer gas. The results for argon and nitrogen will merely be stated. However, a more detailed discussion of these buffer gases may be found in the last section of this chapter.

For neon three flasks were made containing densities of 50.6, 115.7, and 203.5 Torr. Each flask was heated until good signals were obtained and a series of runs made in which the silver hfs was measured for different values of the temperature. At the temperatures at which the measurements were made, the leakage of neon through the walls of the sample flask was small (\~{}1 percent per hour) but not negligible. Accordingly, only the earliest of the various measurements made on each flask were used in determining the density shift. For these first measurements the buffer gas density in each flask had not had time enough to be significantly altered by leakage. Table 2 summarizes the measurements from which the density shift of $^{107}$Ag due to neon buffer gas may be determined.

It should be noted that in Table 2 no error has been quoted on the temperature measurement. At first this might appear obviously valid since the thermocouple which took the measurement was calibrated accurately enough so that the temperature of the thermocouple junction itself


**TABLE 2**

SUMMARY OF THE MEASUREMENTS FROM WHICH THE DENSITY SHIFT OF \(^{107}\text{Ag}\) DUE TO NEON BUFFER GAS MAY BE DETERMINED

<table>
<thead>
<tr>
<th>Density (Torr)</th>
<th>Temperature (°C)</th>
<th>Frequency ((\nu-1,712,500,000) Hz)</th>
<th>Straight Line Fit (\nu-1,712,500,000 = MT + B)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(M (\text{Hz} \text{°C}^{-1}))</td>
</tr>
<tr>
<td>50.6</td>
<td>858</td>
<td>14,326.5(4.1)</td>
<td>.41860</td>
</tr>
<tr>
<td></td>
<td>772</td>
<td>14,290.5(3.9)</td>
<td></td>
</tr>
<tr>
<td>115.7</td>
<td>807</td>
<td>17,210.2(2.9)</td>
<td>.83782</td>
</tr>
<tr>
<td></td>
<td>832</td>
<td>17,229.0(4.0)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>859</td>
<td>17,254.0(3.7)</td>
<td></td>
</tr>
<tr>
<td>203.5</td>
<td>816</td>
<td>21,156.2(4.4)</td>
<td>1.47955</td>
</tr>
<tr>
<td></td>
<td>860</td>
<td>21,221.3(4.3)</td>
<td></td>
</tr>
</tbody>
</table>
could be determined to better than ±0.5°C. This is a totally negligible error. A problem arises, however, due to the fact that the thermocouple measured the temperature of only one point on the bulb, and a point on the outside of the bulb at that. As the upper and lower extremities of the bulb were approximately 20°C hotter than the point midway down the side of the bulb at which the temperature was measured, it is clear that temperature differences of this magnitude could reasonably be expected to have existed within the gas inside the bulb. This is not a serious problem when it comes to determining the density shift, however. The temperature dependence of the silver density shift is so small for all the buffer gases used in this experiment that essentially the same density shift would be obtained at (say) 850°C as 870°C.

The question of the accuracy of the temperature measurement acquires greater cogency, however, when the experimental data is used to determine the temperature dependence of the density shift. Actually the question is not so much one of the accuracy of the temperature measurement, for as noted earlier the thermocouple provides a highly accurate measurement of the temperature of the point on the side of the bulb with which it is in contact. The question rather is one of the appropriateness of the measurement. Clearly a more appropriate temperature to assign to each frequency measurement would be the average temperature of the gas inside the bulb. Unfortunately this average temperature is not very accessible to direct measurement.
Accordingly, in order to be able to use the measured temperature to determine the temperature dependence of the hfs shift, we shall make the following plausible assumption. We shall assume that when the measured temperature changes by T degrees the average temperature changes by T degrees also. If this is correct the slope of the curve of hfs versus measured temperature will be the same as the slope of the curve of hfs versus average temperature.

The truth of this assumption cannot be checked directly. Rather, its validity is to be inferred from the consistency of the results obtained by employing it as a working hypothesis.

Returning now to the problem of determining the density shift, we have evaluated at $T = 830^\circ C$ the curve of frequency versus temperature obtained for each of the flasks in Table 2. The results are presented in Table 3 which records frequency versus density. The same data is displayed in Figure 11.

The straight line fits in Tables 2 and 3 were made from formulae derived in the discussion on least squares fitting in Mathews and Walker. The errors quoted on the entries in the second, third, and fourth columns of Table 3 were computed following the method of error analysis contained in this discussion. In the analysis so far the density has been treated as though its value were known precisely, as is indicated by the lack of any quoted errors on the density entries in Table 3. This defect will be remedied presently.
TABLE 3

HFS of Ag$^{107}$ as a function of density at the constant temperature of 830° C. The buffer gas is neon. The densities quoted in this table have been corrected for the thermal expansion of the sample flask. They thus differ slightly from the densities recorded in Table 5.1.

<table>
<thead>
<tr>
<th>Density (Torr)</th>
<th>Frequency ($\nu - 1,712,500,000$ Hz)</th>
<th>Straight Line Fit $\nu - 1,712,500,000 = M \rho + B$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$M$ (Hz Torr$^{-1}$)</td>
</tr>
<tr>
<td>50.5</td>
<td>14,314.8(3.0)</td>
<td>44.941(.029)</td>
</tr>
<tr>
<td>115.5</td>
<td>17,229.0(2.0)</td>
<td></td>
</tr>
<tr>
<td>203.2</td>
<td>21,176.9(3.3)</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 11.—Hfs of Ag$^{107}$ as a function of buffer gas density at the constant temperature of 830° C. The buffer gas is neon.
It should be noted that the densities recorded in Table 3 differ slightly from those in Table 2. The density entries in Table 3 have been corrected for the thermal expansion of the volume of the sample flask. This expansion is given by the formula

\[ \frac{V}{V_r} = 1 + 3\beta (T - T_r) \]

where \( V_r \) is the volume of the sample flask at room temperature, \( T_r \) is room temperature (25°C), \( V \) is the volume of the flask at temperature \( T \), and \( \beta (=5.46 \times 10^{-7}) \) is the coefficient of linear thermal expansion of fused quartz. As the buffer gas density is inversely proportional to the volume of the sample flask, the densities in Table 3 are obtained by multiplying those in Table 2 by the factor

\[ \frac{V_r}{V} = \frac{1}{1 + 3\beta (T - T_r)} \cdot \]

The \( \rho = 0 \) intercept of the hyperfine frequency versus density curve is the free atom hfs. From Table 3 one finds for Ag\(^{107}\)

\[ \nu_o = 1,712,512,041.3 \pm 3.7. \]

Dahmen and Penselin\(^{45}\) have measured the Ag\(^{107}\) free atom hfs using an atomic beam method. They obtained the result

\[ \nu_o = 1,712,512,111 \pm 18. \]

These results are not in experimental agreement. This lack
of agreement has arisen from the failure thus far to take into account the uncertainty in the measured buffer gas densities. We shall now remedy this omission.

As was discussed earlier, the pressure in a sample after its removal from the vacuum system was computed from the formula

\[ P_f = P_o + (P_o - P_{sf}) \frac{V_s}{V_b} \]

All of the sample flasks containing neon buffer gas were manufactured on a vacuum system for which the ratio

\[ \frac{V_s}{V_b} \approx 2 \]

was always true. The buffer gas pressure was measured using a mercury manometer. The formula for \( P_f \) may now be written in the approximate form

\[ P_f \approx P_o + 2(P_o - P_{sf}) = 3P_o - 2P_{sf} \]

If the standard deviation of \( P_o \) is \( \sigma \) and of \( P_{sf} \) is \( \sigma_{sf} \), then from ordinary error analysis we obtain the following formula for the standard deviation of \( P_f \)

\[ \sigma_f = \left[ (3\sigma_o)^2 + (2\sigma_{sf})^2 \right]^{1/2} \]

The height of the mercury in the arms of the manometer was measured using an ordinary meter stick with hash marks every .1 centimeter. Assuming that the meter stick
can be read to an accuracy of ±0.02 centimeters, it follows that each measurement of the pressure should be accurate to ±0.03 centimeters. This last figure follows from the fact that each measurement of the pressure involves measuring the height of the mercury in both arms of the manometer, and the errors in these measured heights combine as the square root of the sum of the squares. Thus letting

\[ \sigma_o = \sigma_{sf} = 0.03 \text{ centimeter} \]

there follows

\[ \sigma_f = 0.1 \text{ centimeters} = 1 \text{ Torr} \]

It is now possible to remedy our earlier neglect of the uncertainty in the density measurements. Table 4 records the same frequency versus density data as was earlier presented in Table 3. The straight line fit in Table 4, however, was made treating the frequencies as precisely known and taking into account only the errors in the density measurements. It is thus in a sense complimentary to Table 3 where only the errors in the frequency measurements were considered.

From Tables 3 and 4 it is at once apparent that by far the greater source of error in both the slope of the frequency versus density curve and its \( \rho = 0 \) intercept arises from the uncertainty in the measured density of buffer gas in the sample flask. Following Beers\(^66\) we choose the averages of \( M \) and \( B \) as given on Tables 3 and 4 to be the
TABLE 4

<table>
<thead>
<tr>
<th>Density (Torr)</th>
<th>Frequency ( (v-1,712,500,000) )Hz</th>
<th>Straight Line Fit ( v-1,712,500,000 = M_p + B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.5(1.0)</td>
<td>14,314.8</td>
<td></td>
</tr>
<tr>
<td>115.5(1.0)</td>
<td>17,229.0</td>
<td>44.94(.41) 12,043(57)</td>
</tr>
<tr>
<td>203.2(1.0)</td>
<td>21,176.9</td>
<td></td>
</tr>
</tbody>
</table>

final estimates of the values of these quantities. The errors in \( M \) and \( B \) will be taken from Table 4 since it is from the uncertainty in the density measurements that almost all the error in these quantities arises.

Calculations similar to those for neon buffer gas have been performed for buffer gases of argon and nitrogen. The results of these calculations are summarized in Table 5 below. This table presents the hyperfine frequency versus density curves for \( \text{Ag}^{107} \) as determined for the buffer gases listed. The density shifts are graphed in Figure 15 at the end of this chapter. The density shift caused by helium buffer gas is included in this graph.

The \( \rho = 0 \) intercepts recorded in Table 5 can be regarded as three independent measurements of the \( \text{Ag}^{107} \)}
free atom hfs. We have computed the mean of these three

TABLE 5

HFS VERSUS DENSITY CURVES FOR Ag^{107}
IN NEON, ARGON, AND NITROGEN

<table>
<thead>
<tr>
<th>Gas</th>
<th>Temp(°C)</th>
<th>Density Shift Hz Torr^{-1}</th>
<th>ρ = 0 Intercept (ν-1,712,500,000)Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neon</td>
<td>830</td>
<td>44.94(.41)</td>
<td>12,042 (57)</td>
</tr>
<tr>
<td>Argon</td>
<td>852</td>
<td>24.3 (1.5)</td>
<td>12,115 (49)</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>825</td>
<td>57.5 (4.4)</td>
<td>12,350 (200)</td>
</tr>
</tbody>
</table>

measurements, and we have taken its associated error to be the standard deviation of the mean

\[ \sigma_m = \left[ \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n(n - 1)} \right]^{1/2} \]

The result is

\[ \nu_0 = 1,712,512,169 (93). \]

This estimate of the Ag^{107} free atom hfs is in full experimental agreement with the measurement of Dahmen and Penselin cited earlier.
3. Temperature Dependence of Density Shifts Due to Neon, Argon, and Nitrogen

We shall write the following equation for the hyperfine frequency as a function of temperature and density.

\[ v = \left[ m + \alpha (T - T_0) \right] \rho + v_0 \]

This equation expresses the fact that at constant temperature the hfs shift is essentially linear in buffer gas density. Similarly, for constant buffer gas density the hfs shift is essentially linear in the temperature for small variations about the temperature \( T_0 \). The quantity represented by \( \alpha \) will be designated the temperature dependence of the density shift. It is easy to see that

\[ \alpha = \frac{1}{\rho} \left( \frac{\partial v}{\partial T} \right)_{\rho} \]

For purposes of illustration we shall now provide a detailed discussion of the procedure by which \( \alpha \) was found for Ag\(^{107}\) in neon buffer gas. The values for \( \alpha \) for Ag\(^{107}\) in buffer gases of argon and nitrogen will merely be stated. More detailed information regarding these buffer gases may be found in the last section of this chapter.

As was noted earlier, three flasks containing neon buffer gas were made containing densities of 50.6, 115.7, and 203.5 torr. For each of these flasks the hyperfine frequency was measured for several different temperatures.
and a straight line fitted to these measurements by the method of least squares. In order to compensate for the effects of leakage of buffer gas through the walls of the flask, the measurements were made in a manner now to be described.

A typical set of measurements of the hfs would be one composed of measurements taken at the following temperatures in the following order: $810^\circ C$, $840^\circ C$, $870^\circ C$, $840^\circ C$, $810^\circ C$. The first three measurements were thus made in the order of the lowest temperature first and the highest temperature last. The second three measurements (the one at $870^\circ C$ is counted twice) reverse the order but are taken at the same temperatures. By least squares fitting straight lines to the first three and the second three measurements, two curves of frequency versus temperature were obtained. It is fairly easy to see that leakage of buffer gas will cause the slopes of these two curves to be shifted in opposite directions from the slope which would be measured in the absence of leakage. Accordingly, when determining the temperature dependence of the density shift the slopes of the two curves were averaged and the result taken as a leakage-corrected measurement of the slope of the frequency versus temperature curve for the flask being measured. For a slow and essentially constant leak rate this method of correcting for leakage is highly accurate, provided that the time required to make the measurements running from low to high temperature is
essentially equal to the time required to make the same measurements in reverse order.

Table 6 presents a complete set of frequency versus temperature measurements for the 203.2 Torr flask. The data in this table are displayed graphically in Figure 12 where the effect of leakage on the measured temperature shift is clearly visible. Table 7 shows the results of several measurements of the temperature dependence of the density shift of Ag$^{107}$ in neon buffer gas. The entries in this table are explained below.

Column 1. Buffer gas density corrected for thermal expansion of the sample flask.

Column 2. Slope of curve of frequency versus temperature when the measurements are made in the order of lowest temperature first and highest temperature last.

Column 3. Slope of curve of frequency versus temperature when the measurements are made in the order of highest temperature first and lowest temperature last.

Column 4. Average of previous two columns.

Column 5. Temperature range over which the measurements were made.

Column 6. Entry in Column 4 divided by entry in Column 1.

The best estimate for the temperature dependence ($\alpha$) and its associated error are given respectively by the mean and standard deviation of the entries in the final column.
**TABLE 6**

TEMPERATURE VERSUS FREQUENCY MEASUREMENTS
FOR THE 203.2 TORR NEON FLASK

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>(ν-1,712,500,000)Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>819</td>
<td>21,133.4 (2.2)</td>
</tr>
<tr>
<td>843</td>
<td>21,176.2 (2.8)</td>
</tr>
<tr>
<td>867</td>
<td>21,211.9 (2.0)</td>
</tr>
<tr>
<td>843</td>
<td>21,167.6 (3.0)</td>
</tr>
<tr>
<td>819</td>
<td>21,123.1 (3.5)</td>
</tr>
</tbody>
</table>

Fig. 12.—Temperature versus frequency measurements for the 203.2 Torr neon flask.
### TABLE 7

**SUMMARY OF THE RESULTS OF THE MEASUREMENTS OF THE TEMPERATURE DEPENDENCE OF THE DENSITY SHIFT OF \(^{107}\text{Ag}\) IN NEON BUFFER GAS**

<table>
<thead>
<tr>
<th>Density (Torr)</th>
<th>Slope (L - H) (Hz °C⁻¹)</th>
<th>Slope (H - L) (Hz °C⁻¹)</th>
<th>Average Slope (Hz °C⁻¹)</th>
<th>Temperature Range (°C)</th>
<th>Slope/Density (Hz °C⁻¹ Torr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.5</td>
<td>0.400</td>
<td>0.336</td>
<td>0.368</td>
<td>817 - 887</td>
<td>7.29 x 10⁻³</td>
</tr>
<tr>
<td>115.5</td>
<td>0.838</td>
<td>1.155</td>
<td>0.997</td>
<td>807 - 859</td>
<td>8.63 x 10⁻³</td>
</tr>
<tr>
<td></td>
<td>1.08</td>
<td>1.24</td>
<td>1.16</td>
<td>809 - 861</td>
<td>10.04 x 10⁻³</td>
</tr>
<tr>
<td>203.2</td>
<td>1.63</td>
<td>1.85</td>
<td>1.74</td>
<td>819 - 867</td>
<td>8.56 x 10⁻³</td>
</tr>
</tbody>
</table>

**Estimate of temperature dependence (\(\alpha\)) is obtained by averaging entries in last column**

\[ \alpha = 8.6 \times 10^{-3} \text{ Hz °C}^{-1} \text{ Torr}^{-1} \]
Measurements similar to those made for neon buffer gas have been made for buffer gases of argon and nitrogen. In Table 8 are presented the final results of the measurements of the temperature dependence of the $^{107}\text{Ag}$ hfs in buffer gases of neon, argon, and nitrogen. More detailed tables of measurements for the last two buffer gases may be found in the last section of this chapter.

**TABLE 8**

**TEMPERATURE DEPENDENCE OF THE $^{107}\text{Ag}$ HFS IN VARIOUS BUFFER GASES**

<table>
<thead>
<tr>
<th>Buffer Gas</th>
<th>Temperature Range Over Which Measurements Were Made (in °C)</th>
<th>Temperature Dependence ($\alpha$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neon</td>
<td>807 - 887</td>
<td>8.6(1.1) x 10^{-3}</td>
</tr>
<tr>
<td>Argon</td>
<td>811 - 868</td>
<td>-1.1(0.2) x 10^{-2}</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>791 - 862</td>
<td>-8.3(1.4) x 10^{-3}</td>
</tr>
</tbody>
</table>

4. **Density Shift Caused By Helium and Its Temperature Dependence**

The leak rate of helium from a typical sample flask at 800°C was about two percent per hour. This is clearly a significant rate of loss. In the course of a series of measurements lasting from three to four hours, some six to eight percent of the helium in the flask would be lost.
through leakage. When measuring the Ag$^{107}$ hfs in helium buffer gas, it was necessary to correct the measured frequency for the effect of the leakage. This was done by keeping a careful temperature versus time log for each bulb from the time it was made until the time it was discarded. With this temperature versus time record, it was then possible to integrate the equation

$$\ln \frac{\rho(t)}{\rho_0} = -\frac{5.023 \times 10^{-6}}{d} \int_{t_0}^{t} \frac{2491}{T(x)} e^{-\frac{2491}{T(x)}} dx$$

and thus determine the density in the sample flask at any given time. Actually the procedure is slightly more complicated than just indicated. The thickness parameter for the flask (d) is an unknown number whose value must be determined before the indicated integration can be performed. We shall discuss shortly the method by which this value was obtained.

Assuming that the integration has been performed, the correction for leakage is made as follows. Since the hfs shift is linear in the buffer gas density, the ratio of the hfs shift at time t to the hfs shift which would have been measured in the absence of leakage is the same as the ratio of the density at time t to the original density. Thus we have

$$\frac{\Delta f(t)}{\Delta f_0} = \frac{\rho(t)}{\rho_0}.$$
Solving for $\Delta f_o$ we obtain

$$\Delta f_o = \frac{\rho_o}{\rho(t)} \Delta f(t).$$

The hfs shift which would have been measured if no leakage were present has thus been found in terms of the measured hfs shift and the ratio $\rho_o/\rho(t)$ which is computed by integrating the leak rate equation. Once $\Delta f_o$ has been found we may forget about leakage and proceed normally.

The hfs shift was obtained from our measured value of the hfs and the value of the free atom hfs

$$\nu_o = 1,712,512,111(18)$$

measured by Dahem and Penselin.45

The density shift of Ag$^{107}$ in helium buffer gas was determined by measurements made on two sample flasks. One of these sample flasks was measured over an extended temperature range, and from this data the temperature dependence of the density shift was obtained. The two sample flasks contained initial helium densities of 58.5 and 104.5 Torr. For consistency, the two flasks will be referred to by their initial densities even though the density in each flask diminished over the course of the experiment.

Table 9 is a partial temperature versus time record of the 104.5 Torr flask. The zero of time for this record is the start of the measurement run, defined as the moment at which the heat in the oven was turned on. Three
### TABLE 9

**PARTIAL TEMPERATURE VERSUS TIME RECORD OF THE 100 TORR HELIUM FLASK**

<table>
<thead>
<tr>
<th>Time (Minutes)</th>
<th>Temp (°K)</th>
<th>Element</th>
<th>Measured Frequency (Hz)</th>
<th>Frequency Shift (Hz)</th>
<th>Corrected Frequency Shift (Hz)</th>
<th>Corrected Frequency (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>103</td>
<td>1067</td>
<td>Rb$^{85}$</td>
<td>78,083 (43)</td>
<td>45,644 (43)</td>
<td>46,904 (43)</td>
<td>79,343 (43)</td>
</tr>
<tr>
<td>165</td>
<td>1067</td>
<td>Ag$^{107}$</td>
<td>19,064.9 (5.4)</td>
<td>6,953.9 (5.4)</td>
<td>7,295.3 (5.4)</td>
<td>19,406.3 (5.4)</td>
</tr>
<tr>
<td>196</td>
<td>1067</td>
<td>Rb$^{85}$</td>
<td>76,691.3 (8.8)</td>
<td>44,252.3 (8.8)</td>
<td>46,903.4 (8.8)</td>
<td>79,342.4 (8.8)</td>
</tr>
</tbody>
</table>

Thickness parameter (computed by requiring agreement between the two measurements of the Rb$^{85}$ hfs) = 1.57 mm

Density in bulb at start of measurement run = 104.1 Torr
frequency measurements were made from this flask. The first and third measurements were of the Rb\(^{85}\) hfs; the second was of the Ag\(^{107}\) hfs. The unknown thickness parameter \(d\) in the leak rate equation was determined by requiring the two measurements of the Rb\(^{85}\) hfs to be the same when the effects of leakage were taken into account. A thickness parameter was guessed and the leak rate equation integrated to find the correction for the effect of leakage. The two corrected measurements of the Rb\(^{85}\) hfs were compared, and the process repeated using different thickness parameters until the two corrected measurements were the same. Using this value of the thickness parameter the leak rate equation was integrated from the time the bulb was made until the time the measurement run was started. This determined the buffer gas density in the bulb at the start of the run.

Figure 13 shows the Ag\(^{107}\) data from the 58.4 Torr flask as originally measured while Figure 14 shows the data as corrected for the effect of leakage. This same data is presented numerically in Table 10. The result of fitting a straight line to the data (corrected for the effect of leakage) is presented in Table 11. If this straight line fit is evaluated at a temperature of 194\(^{\circ}\) C and the result combined with the value of the Ag\(^{107}\) hfs measured using the 104.5 Torr flask, we obtain Table 14. From this table the density shift of the hfs of Ag\(^{107}\) in helium buffer gas
Fig. 13.—Frequency versus temperature data as originally measured for the 58.5 Torr helium flask. The average slope of the two lines is $\bar{m}$.

Fig. 14.—Frequency versus temperature data for the 58.5 Torr helium flask after correcting for leakage.
### TABLE 10
PARTIAL TEMPERATURE VERSUS TIME RECORD
OF THE 60 TORR HELIUM FLASK

<table>
<thead>
<tr>
<th>Time (Minutes)</th>
<th>Temp (°K)</th>
<th>Element</th>
<th>Measured Frequency Hz</th>
<th>Frequency Shift Hz</th>
<th>Corrected Frequency Shift Hz</th>
<th>Corrected Frequency Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1076</td>
<td>Rb$^{85}$</td>
<td>57,970.8 (5.4)</td>
<td>25,531.8 (5.4)</td>
<td>26,230.4 (5.4)</td>
<td>58,669.4 (5.4)</td>
</tr>
<tr>
<td>147</td>
<td>1077</td>
<td>Ag$^{107}$</td>
<td>16,061.0 (3.1)</td>
<td>3,950.0 (3.1)</td>
<td>4,126.0 (3.1)</td>
<td>16,237.0 (3.1)</td>
</tr>
<tr>
<td>179</td>
<td>1106</td>
<td>Ag$^{107}$</td>
<td>16,048.0 (2.6)</td>
<td>3,937.0 (2.6)</td>
<td>4,159.0 (2.6)</td>
<td>16,270.0 (2.6)</td>
</tr>
<tr>
<td>211</td>
<td>1135</td>
<td>Ag$^{107}$</td>
<td>16,034.2 (6.1)</td>
<td>3,923.2 (6.1)</td>
<td>4,196.0 (6.1)</td>
<td>16,307.0 (6.1)</td>
</tr>
<tr>
<td>246</td>
<td>1107</td>
<td>Ag$^{107}$</td>
<td>15,958.9 (4.0)</td>
<td>3,847.8 (4.0)</td>
<td>4,171.8 (4.0)</td>
<td>16,282.8 (4.0)</td>
</tr>
<tr>
<td>264</td>
<td>1078</td>
<td>Ag$^{107}$</td>
<td>15,884.8 (4.2)</td>
<td>3,773.8 (4.2)</td>
<td>4,117.6 (4.2)</td>
<td>16,228.6 (4.2)</td>
</tr>
<tr>
<td>309</td>
<td>1078</td>
<td>Rb$^{85}$</td>
<td>56,174 (14)</td>
<td>23,735 (14)</td>
<td>26,230 (14)</td>
<td>58,669 (14)</td>
</tr>
</tbody>
</table>

Thickness parameter (computed from Ag$^{107}$ data only) = 1.58 mm
Thickness parameter (computed from Rb$^{85}$ data only) = 1.62 mm
Density in bulb at start of measurement run = 58.3 Torr
### TABLE 11
FREQUENCY VERSUS TEMPERATURE MEASUREMENTS FOR THE 60 TORR HELIUM FLASK

| Density (Torr) | Temperature (°C) | Frequency (ν-1,712,500,000 Hz) | Straight Line Fit  
\[ \nu - 1,712,500,000 = MT + B \] | Temperature Dependence  
\[ \text{Hz }^\circ C^{-1} \] |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>58.3</td>
<td>804</td>
<td>16,237.0 (3.1)</td>
<td>M (Hz °C^{-1}) : 1.32223</td>
<td></td>
</tr>
<tr>
<td></td>
<td>833</td>
<td>16,270.0 (2.6)</td>
<td>B (Hz) : 15,170.80</td>
<td></td>
</tr>
<tr>
<td></td>
<td>862</td>
<td>16,307.0 (6.1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>834</td>
<td>16,282.8 (4.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>805</td>
<td>16,228.6 (4.2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: The values in parentheses are uncertainties.
TABLE 12

HFS OF Ag\textsuperscript{107} AS A FUNCTION OF DENSITY
AT THE CONSTANT TEMPERATURE OF 794° C.
THE BUFFER GAS IS HELIUM. ONLY THE
ERRORS IN THE DENSITY MEASUREMENTS
HAVE BEEN CONSIDERED.

<table>
<thead>
<tr>
<th>Density (Torr)</th>
<th>Frequency (ν-1,712,500,000)Hz</th>
<th>Straight Line Fit ν-1,712,500,000 = M_0 + B</th>
</tr>
</thead>
<tbody>
<tr>
<td>58.2 (1.2)</td>
<td>16,220.7</td>
<td>:M(Hz Torr^{-1}) : B (Hz)</td>
</tr>
<tr>
<td>104.0 (1.0)</td>
<td>19,406.3</td>
<td>:</td>
</tr>
</tbody>
</table>

may be read off. The temperature dependence of the density shift (α) is contained in the last column of Table 11.

The thickness parameter for the 58.5 Torr bulb was chosen so as to minimize the quantity

\[ I(d) = \left[ f_1(d) - f_5(d) \right]^2 + \left[ f_2(d) - f_4(d) \right]^2. \]

Here the \( f_i(d) \) stand for the various measurements of the Ag\textsuperscript{107} hfs shift after the correction for leakage has been made. Thus the final values of the \( f_i(d) \) are

\[ f_1 = 4,126.0 \quad f_2 = 4,159.0 \]
\[ f_3 = 4,196.0 \quad f_4 = 4,171.8 \]
\[ f_5 = 4,117.6. \]

Clearly since the measurements \( f_1 \) and \( f_5 \) were taken at essentially the same temperature they should be the same (up to the measurement accuracy) once the effect of leakage is
taken into account. This is also true for $f_2$ and $f_4$, and constitutes the justification for finding $d$ by minimizing $I$. The thickness parameter obtained in this fashion was

$$d = 1.58 \text{ mm}.$$  

Prior to making the five measurements of the Ag$^{107}$ hfs a measurement of the Rb$^{85}$ hfs was made. A second measurement of the Rb$^{85}$ hfs was made after the measurements on Ag$^{107}$ were completed. All these measurements may be found in Table 10. The Rb$^{85}$ hfs shift was obtained from our measured value of the hfs and the value of the free atom hfs

$$v_o = 3,035,732,439(5)$$

measured by Penselin, Moran, Cohen, and Winkler.$^{68}$

The value of the thickness parameter which brings the two measurements of the Rb$^{85}$ hfs shift into coincidence once the effect of leakage is taken into account is

$$d = 1.62 \text{ mm}.$$  

This value differs by less than 3% from the value obtained using the Ag$^{107}$ measurements. The agreement between these two independent determinations of the thickness parameter for the 58.5 Torr flask is thus quite good.
5. Summary of Results and Conclusions

The density shift of the hfs of Ag$^{107}$ and its temperature dependence are presented in Table 13 for buffer gases of neon, argon, nitrogen, and helium. The hfs as a function of density is plotted in Figure 15 for the same buffer gases.

The fractional density shifts for silver are compared with the fractional density shifts for hydrogen and the alkalies in Table 14. It is apparent that the density shifts for silver are comparable in magnitude with those of the alkalies, and that they vary in essentially the same fashion from buffer gas to buffer gas as one reads from left to right across the table. This similarity indicates that the general behavior of the silver density shifts can probably be explained, as can those of the alkalies, by a competition between long range Van der Waals and short range exchange forces. This result is not surprising in view of the similarity in electronic structure of silver to the alkalies.

Among the specific details of the silver density shifts which an adequate theory must explain is the somewhat surprising positive shift in argon. Another is the fact that the change in the density shift between buffer gases clearly tends to be smaller for silver than for the alkalies.
TABLE 13
DENSITY SHIFT AND ITS TEMPERATURE DEPENDENCE FOR THE HFS OF AG\textsuperscript{107}

<table>
<thead>
<tr>
<th>Buffer Gas</th>
<th>Temperature at Which Pressure Shift Measured °C</th>
<th>Pressure Shift Hz Torr(^{-1})</th>
<th>Temperature Range Over Which Temperature Dependence Measured °C</th>
<th>Temperature Dependence Hz °C(^{-1}) Torr(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neon</td>
<td>830</td>
<td>44.94 (.41)</td>
<td>807 - 887</td>
<td>8.6 (1.1) \times 10^{-3}</td>
</tr>
<tr>
<td>Argon</td>
<td>852</td>
<td>24.3 (1.5)</td>
<td>811 - 868</td>
<td>-1.1 (0.2) \times 10^{-2}</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>825</td>
<td>57.5 (4.4)</td>
<td>791 - 862</td>
<td>-8.3 (1.4) \times 10^{-3}</td>
</tr>
<tr>
<td>Helium</td>
<td>794</td>
<td>69.6 (2.4)</td>
<td>804 - 862</td>
<td>2.27 (.26) \times 10^{-2}</td>
</tr>
</tbody>
</table>
Fig. 15.—Density Shifts of Ag$^{107}$
### TABLE 14

THE FRACTIONAL DENSITY SHIFTS OF THE HYDROGEN-LIKE ATOMS*

<table>
<thead>
<tr>
<th>Element</th>
<th>Fractional Density Shifts (Torr$^{-1} \times 10^9$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>He</td>
<td>N$_2$</td>
</tr>
<tr>
<td>H</td>
<td>4.80</td>
<td>2.88</td>
</tr>
<tr>
<td>Li</td>
<td>77.7</td>
<td>40.5</td>
</tr>
<tr>
<td>Na</td>
<td>73.4</td>
<td>49</td>
</tr>
<tr>
<td>K</td>
<td>94</td>
<td>66.6</td>
</tr>
<tr>
<td>Rb</td>
<td>105.3</td>
<td>76.1</td>
</tr>
<tr>
<td>Cs</td>
<td>114.2</td>
<td>96.8</td>
</tr>
<tr>
<td>Ag</td>
<td>40.6</td>
<td>33.6</td>
</tr>
</tbody>
</table>

*The numbers listed here are taken directly from the references given at the end of each row. They have not been adjusted for differences in gas filling temperatures or operating temperatures.
6. Additional Data for Argon and Nitrogen Buffer Gases

Table 15 summarizes the measurements from which the density shift of Ag\textsuperscript{107} due to argon buffer gas may be determined. The curve of frequency versus temperature obtained for each of the flasks in Table 15 has been evaluated for T = 852° C, and the results presented in Tables 16 and 18. In Table 16 only the errors in the measured frequencies were taken into account when fitting a straight line to the measured points by the method of least squares. In Table 17 only the errors in the measured density were considered. Table 18 presents the results of several measurements of the temperature dependence of the hfs of Ag\textsuperscript{107} in argon buffer gas. This table contains measurements for only two flasks. The third argon flask at 41.4 Torr could not be measured over an extended temperature range due to the poor quality of the signals obtained from it. Due to an accident the flask at 30.4 Torr was broken before a series of measurements going from high to low temperature could be taken. This was not considered too serious, however, both because of the good agreement with the 17.2 Torr sample from which two complete series of measurements were taken and because in previous measurements the 30.4 Torr flask showed no signs of leakage.

Tables 19 through 22 are for nitrogen buffer gas and are analogous to Tables 15 through 18.

A brief word of explanation is now in order
### TABLE 15
SUMMARY OF THE MEASUREMENTS FROM WHICH THE DENSITY SHIFT OF AG$^{107}$ DUE TO ARGON BUFFER GAS MAY BE DETERMINED

<table>
<thead>
<tr>
<th>Density (Torr)</th>
<th>Temperature (°C)</th>
<th>Frequency ($v-1,712,500,000$ Hz)</th>
<th>Straight Line Fit $v-1,712,500,000 = MT + B$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>M (Hz °C$^{-1}$)</td>
</tr>
<tr>
<td>17.2</td>
<td>823</td>
<td>12,592.5 (4.4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>832</td>
<td>12,522.7 (3.4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>842</td>
<td>12,527.1 (2.0)</td>
<td>$-0.11365$</td>
</tr>
<tr>
<td></td>
<td>851</td>
<td>12,530.8 (4.9)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>861</td>
<td>12,519.3 (4.3)</td>
<td></td>
</tr>
<tr>
<td>30.4</td>
<td>811</td>
<td>12,872.2 (3.3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>821</td>
<td>12,874.5 (2.0)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>831</td>
<td>12,878.7 (2.2)</td>
<td>$-0.36046$</td>
</tr>
<tr>
<td></td>
<td>840</td>
<td>12,861.6 (3.3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>12,862.3 (3.6)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>861</td>
<td>12,858.3 (4.0)</td>
<td></td>
</tr>
<tr>
<td>41.4</td>
<td>852</td>
<td>13,085.5 (7.8)</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 16

HFS of Ag\(^{107}\) as a function of density at the constant temperature of 852° C. The buffer gas is argon.

<table>
<thead>
<tr>
<th>Density (Torr)</th>
<th>Frequency ((v-1,712,500,000)\text{Hz})</th>
<th>Straight Line Fit (v-1,712,500,000 = M\rho + B)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(M) (Hz Torr(^{-1}))</td>
<td>(B) (Hz)</td>
</tr>
<tr>
<td>17.2</td>
<td>12,524.8(2.1)</td>
<td></td>
</tr>
<tr>
<td>30.4</td>
<td>12,867.7(2.1)</td>
<td>25.30(0.20) : 12,092.8(5.1)</td>
</tr>
<tr>
<td>41.3</td>
<td>13,085.5(7.8)</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 17

HFS of Ag\(^{107}\) as a function of density at the constant temperature of 852° C. The buffer gas is argon. Only the error in the density measurement is considered.

<table>
<thead>
<tr>
<th>Density (Torr)</th>
<th>Frequency ((v-1,712,500,000)\text{Hz})</th>
<th>Straight Line Fit (v-1,712,500,000 = M\rho + B)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(M) (Hz Torr(^{-1}))</td>
<td>(B) (Hz)</td>
</tr>
<tr>
<td>17.2(1.2)</td>
<td>12,524.8</td>
<td></td>
</tr>
<tr>
<td>30.4(1.0)</td>
<td>12,867.7</td>
<td>23.3(1.5) : 12,137(49)</td>
</tr>
<tr>
<td>41.3(1.0)</td>
<td>13,085.5</td>
<td></td>
</tr>
<tr>
<td>Density (Torr)</td>
<td>Slope(L - H) (Hz °C⁻¹)</td>
<td>Slope(H - L) (Hz °C⁻¹)</td>
</tr>
<tr>
<td>---------------</td>
<td>------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>17.2</td>
<td>-.11</td>
<td>-.29</td>
</tr>
<tr>
<td></td>
<td>.05</td>
<td>-.37</td>
</tr>
<tr>
<td>30.4</td>
<td>-.36</td>
<td>-.36</td>
</tr>
</tbody>
</table>

Estimate of temperature dependence (α) is obtained by averaging entries in last column

\[ \alpha = -1.1(0.2) \times 10^{-2} \, \text{Hz °C}^{-1} \, \text{Torr}^{-1} \]
TABLE 19

SUMMARY OF THE MEASUREMENTS FROM WHICH THE DENSITY SHIFT OF Ag$^{107}$ DUE TO NITROGEN BUFFER GAS MAY BE DETERMINED

<table>
<thead>
<tr>
<th>Density (Torr)</th>
<th>Temperature (°C)</th>
<th>Frequency ($\nu-1,712,500,000$ Hz)</th>
<th>Straight Line Fit $\nu-1,712,500,000 = MT + B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.9</td>
<td>862</td>
<td>14,131(10)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>836</td>
<td>14,139.9(7.4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>825</td>
<td>14,135.7(7.4)</td>
<td>-.28966</td>
</tr>
<tr>
<td></td>
<td>813</td>
<td>14,144.1(5.9)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>804</td>
<td>14,167(22)</td>
<td></td>
</tr>
<tr>
<td>46.8</td>
<td>833</td>
<td>15,104.8(8.6)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>824</td>
<td>15,110.0(5.3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>816</td>
<td>15,109.3(3.7)</td>
<td>-.40524</td>
</tr>
<tr>
<td></td>
<td>804</td>
<td>15,123.2(5.7)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>794</td>
<td>15,118.8(4.4)</td>
<td></td>
</tr>
<tr>
<td>Density (Torr)</td>
<td>Temperature (°C)</td>
<td>Frequency (ν-1,712,500,000)Hz</td>
<td>Straight Line Fit (v-1,712,500,000 = MT + B)</td>
</tr>
<tr>
<td>---------------</td>
<td>------------------</td>
<td>-------------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>54.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>844</td>
<td>15,406.5(3.8)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>836</td>
<td>15,395.2(4.7)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>826</td>
<td>15,411.8(5.3)</td>
<td>-.29506 15,652.44</td>
</tr>
<tr>
<td></td>
<td>816</td>
<td>15,419.9(4.5)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>806</td>
<td>15,407.6(5.3)</td>
<td></td>
</tr>
<tr>
<td>Density (Torr)</td>
<td>Frequency (v-1,712,500,000)Hz</td>
<td>Straight Line Fit v-1,712,500,000 = M₀ + B</td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>-------------------------------</td>
<td>------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>31.9</td>
<td>14,142.2(3.9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>46.7</td>
<td>15,110.0(2.7)</td>
<td>56.24(.20) : 12,403.9(9.9)</td>
<td></td>
</tr>
<tr>
<td>54.2</td>
<td>15,410.5(2.4)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 21**

HFS of Ag₁⁰⁷ as a function of density at the constant temperature of 820°C. The buffer gas is Nitrogen. Only the error in the density measurement is considered.

<table>
<thead>
<tr>
<th>Density (Torr)</th>
<th>Frequency (v-1,712,500,000)Hz</th>
<th>Straight Line Fit v-1,712,500,000 = M₀ + B</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.9(1.2)</td>
<td>14,142.2</td>
<td></td>
</tr>
<tr>
<td>46.7(1.2)</td>
<td>15,110.0</td>
<td>58.8(4.4) : 12,290(200)</td>
</tr>
<tr>
<td>54.2(1.2)</td>
<td>15,410.5</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 22

SUMMARY OF THE RESULTS OF THE MEASUREMENTS OF THE TEMPERATURE DEPENDENCE OF THE DENSITY SHIFT OF Ag\textsuperscript{107} IN NITROGEN BUFFER GAS

<table>
<thead>
<tr>
<th>Density (Torr)</th>
<th>Slope(L - H) (Hz °C\textsuperscript{-1})</th>
<th>Slope(H - L) (Hz °C\textsuperscript{-1})</th>
<th>Average Slope (Hz °C\textsuperscript{-1})</th>
<th>Temperature Range (°C)</th>
<th>Slope/Density (Hz °C\textsuperscript{-1} Torr\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.9</td>
<td>-.33</td>
<td>-.29</td>
<td>-.31</td>
<td>791 - 862</td>
<td>-9.7 x 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>46.7</td>
<td>-.34</td>
<td>-.41</td>
<td>-.38</td>
<td>793 - 834</td>
<td>-8.1 x 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>54.2</td>
<td>-.45</td>
<td>-.30</td>
<td>-.38</td>
<td>803 - 844</td>
<td>-7.0 x 10\textsuperscript{-3}</td>
</tr>
</tbody>
</table>

Estimate of temperature dependence (\(\alpha\)) is obtained by averaging entries in last column

\[ \alpha = -8.3(1.4) \times 10^{-3} \text{ Hz °C}^{-1} \text{ Torr}^{-1} \]
concerning the errors quoted on the density measurements in Tables 17 and 21. The samples used in this experiment were made on two different vacuum systems. One system was equipped with a mercury manometer and the other with an oil manometer. It is to be expected that the error in the measured density of buffer gas in a sample will depend on which system was used in the manufacture of the sample. An estimate was made earlier of the anticipated error in a density measurement made using the mercury manometer, and the result of +1.0 Torr obtained. With regard to the oil manometer, it was not until the experiment was nearly completed that it was realized that the accuracy of the oil manometer was being reduced by an effect which had not been anticipated. The effect in question is the tendency of the manometer oil to absorb gas from the atmosphere at times when the vacuum system is not in use, and subsequently to emit these gases when the system is under vacuum. When these gases are emitted into the sealed and evacuated manometer arm, the vacuum in this arm is degraded and the accuracy of the manometer diminished. We have estimated the probable error in a density measurement made on the oil manometer as +1.2 Torr. This is the minimum error in the oil manometer measurements which will bring the zero density intercepts of all the frequency versus density curves into experimental agreement. Had it been realized that this outgassing problem was present, its effect could have been minimized by evacuating both arms of the manometer and
forcibly outgassing the oil prior to using the manometer to make a measurement. This forcible outgassing can be accomplished by gently heating the manometer with a hot air gun.

In Tables 17 and 21 an error of 1.0 Torr quoted on a density measurement identifies a sample prepared using the mercury manometer, while a quoted error of 1.2 Torr indicated a sample whose density was measured using the oil manometer. The densities recorded in Tables 16, 17, 20, and 21 have been corrected for the thermal expansion of the sample flask.
BIBLIOGRAPHY


23. R. A. Bernheim, Optical Pumping (Benjamin, New York, 1965).


46. The powdered silver was supplied by Dr. Harry Hall of the University of New Hampshire.

47. Rb (99.9% purity) purchased from Leico Industries, Inc., 250 W. 57th St., New York, New York.

48. Research grade gas manufactured in one liter pyrex flasks by the Union Carbide Corporation, Linde Division, Industrial Highway, Keasbey, New Jersey.


53. The resistance heating rods were "Globar", type LL Delta electric heating elements, size 28 x 8 x 5/8 inches, 1.07 ohms (±10%). Purchased from the Carborundum Co., Refractories & Electronics Division, Dept. TR 72, Box 337, Niagara Falls, New York 14302.
54. The non-magnetic resistance heating wire was #20 Chromel "A" purchased from The Malin Co., Cleveland, Ohio.

55. Pyrex windows purchased through the Anderson Glass Co., Old Turnpike Road, Fitzwilliam, New Hampshire.

56. Moly permalloy hydrogen annealed shields, 0.050 inches thick, purchased from Allegheny Ludlum Steel Corp., Wellesley, Massachusetts.


58. Dr. Bruce Bean (Private Communication).


62. The estimate was made in conversation with the author by Mr. Robert Anderson, the professional glass blower who prepared our vapor cells.


APPENDIX A

Because of the variety of sign and notation conventions in use, the formula relating the magnetic dipole moment of a quantum mechanical system to its angular momentum may be written in several different ways. It is the purpose of this appendix to explain the convention used in this report.

For the relation between the magnetic moment and the angular momentum of an electron we shall employ the formula

$$\vec{\mu} = -g_J \frac{\mu_B}{\hbar} \hat{J}.$$ 

In the above expression $\mu_B$ is the Bohr magneton (a positive number), $2\pi \hbar$ equals Planck's constant, and $\hat{J}$ is the total angular momentum of the electron. Since the magnetic moment of an electron is always antiparallel to its angular momentum, the explicit presence of the negative sign in this formula implies that $g_J$ will always be positive.

For the relation between the magnetic moment and angular momentum of a nucleus we shall employ an analogous formula. We shall write

$$\vec{\mu} = -g_I \frac{\mu_N}{\hbar} \hat{I}.$$
In this formula $\mu_N$ is the nuclear magneton (a positive number) and $\hat{I}$ is the total angular momentum of the nucleus. Since the magnetic moments of most nuclei are parallel to the nuclear angular momentum, the presence of the negative sign implies that for most nuclei $g_I$ will be negative. Although this sign convention differs from the usual one employed in nuclear physics in which $g_I$ is positive, it is still used occasionally in that subject. It is, for example, the sign convention employed in the textbook by Von Buttlar.\textsuperscript{43}
APPENDIX B

THE LEAKAGE OF HELIUM THROUGH QUARTZ

It has been observed that thin-walled vessels of quarts or glass are permeable to helium, hydrogen, and a few other gases, especially at higher temperatures.\(^{59}\)

At the temperatures at which the present experiment was conducted the leakage of helium buffer gas through the walls of the quarts sample flasks was large enough to be significant. Consequently it was necessary to correct our data for the effect of this leakage. At the same temperatures the leakage of neon, argon, and nitrogen was small enough to present no real problem.\(^{59}\)

In this section we define the basic concepts involved in the quantitative analysis of leak rates, and we derive the basic equations which will enable us to effect such an analysis for our present experimental situation.

We shall customarily measure an amount of gas by stating its PV product at some temperature, for theoretical discussions usually standard temperature (0°C). We shall assume the gas density to be low enough so that the ideal gas law for fixed temperature holds. Then

\[ PV = K \]

where \( K \) is a constant (parametrized by the temperature of the gas). The PV product of a sample of gas at some
temperature is simply the value of the constant $K$ at that temperature.

Once the product of $P$ and $V$ is known at some stated temperature for a sample of gas, assumed to be composed of atoms or molecules of a single species, we have an unambiguous measure of the amount of gas present. This may easily be seen by noting that if $P$ is measured in atmospheres then the $PV$ product of a sample of gas at standard temperature is numerically equal to the volume which the gas would occupy at STP. Due to the relation

$$1 \text{ mole (of gas)} = 22.4 \text{ liters (at STP)}$$

knowledge of the $PV$ product at standard temperature makes possible a determination of the number of moles of gas present in the sample. From Avogadro's number

$$N = 6.023 \times 10^{23} \text{ particles/mole}$$

the number of atoms or molecules present in the gas may then be found. If the $PV$ product is not given at standard temperature use of the general gas law

$$\frac{PV}{T} = \frac{P'V'}{T'}$$

allows the $PV$ product at STP to be determined. The $PV$ product will typically be given in units of atmosphere $\cdot$ cm$^3$ or micron $\cdot$ liters.

We shall now discuss some phenomenological facts about leak rates in a fashion closely paralleling the
treatment by Dushman. Consider a glass slab suffering a differential gas pressure of $P$ across its surface. Let $q$ denote the amount of gas in atmosphere $\cdot \text{cm}^3$ (at $0^\circ C$) flowing through the wall per square centimeter per second. If $P$ is one atmosphere then $PV = V$ and thus $q$ is also the volume in cubic centimeters (at STP) flowing through the slab per square centimeter per second. It has been experimentally determined that $q$ varies linearly with the pressure of the gas, and inversely with the wall thickness $d$. Thus we may write

$$q = k \frac{P}{d}$$

where $k$ is called the permeability of the substance in question. In the literature $P$ is usually expressed in centimeters of mercury and $d$ in millimeters. Hence $k$ denotes the volume in cubic centimeters (at STP) per second which would flow through a slab of glass one square centimeter in area and one millimeter in thickness, assuming a differential gas pressure of one centimeter of mercury.

It is important to note that in the above equation $q$ is the volume of gas leaking through the glass per second, assuming that the measurement of the volume is made at STP. This, of course, will in general not be the temperature and pressure of the space into which the gas actually diffuses. In contrast, on the right hand side of the equation $k$, $P$, and $d$ all refer to quantities which are in fact
measured at the temperature and pressure at which the diffusion actually takes place.

The value of $k$ increases rapidly with increasing $T$. Dushman\textsuperscript{59} indicates that the functional dependence of $k$ upon $T$ is accurately given by the expression

$$k = k_o e^{-\frac{E}{RT}}.$$  

Here $E$ is a constant characteristic of the type of glass and the diffusing gas. It is designated the "activation energy" and is generally expressed in calories per mole. The constant $R$ is the universal gas constant

$$R = 1.986 \text{ cal/mole } ^0\text{K}.$$  

Frequently one deals with the logarithm of the equation for $k(T)$. For historical reasons it is customary to take the base ten logarithm. Doing this yields

$$\log k = A - \frac{B}{T}$$

which has the advantage of being a linear relationship between $\log k$ and the reciprocal temperature. In the above expression

$$A = \log k_o$$

and

$$B = (\log e) \frac{E}{R_o} = \frac{E}{4.574}$$
When the rate of flow is expressed in units of atmosphere \( \cdot \) \( \text{cm}^3 \) per second the magnitude of \( k \) is generally on the order of \( 10^{-8} \) to \( 10^{-10} \) or less. In practice, therefore, it is more convenient to express the flow rate in terms of \( Q' \) micron \( \cdot \) liters (at \( 0^\circ\text{C} \)) per hour through a slab of glass one square centimeter in area, one millimeter thick, suffering a differential gas pressure of 76 centimeters. The conversion is

\[
Q' = 3,600 \times 760 \times 76k = 2.08 \times 10^8 k.
\]

To obtain the above result we first multiplied \( k \) by 76 to get the rate of flow in atmosphere \( \cdot \) \( \text{cm}^3 \) per second for a pressure differential of 76 cm. We then reexpressed this flow rate in terms of micron \( \cdot \) liters per hour by multiplying by the conversion factors

\[
3,600 \text{ sec/hr} \ , \ 76 \times 10^4 \text{ microns/atm} \ , \ 10^{-3} \text{ liters/cm}.
\]

In the present experiment the pressure in each sample flask was measured at \( 25^\circ\text{C} \). Accordingly, for us it will be more convenient to work with the leak rate \( Q \) in micron \( \cdot \) liters at \( 25^\circ\text{C} \). This is obtained by multiplying the leak rate at \( 0^\circ\text{C} \) by the factor

\[
\frac{298}{273} = 1.091.
\]

Then the log of the leak rate at \( 0^\circ\text{C} \) and at \( 25^\circ\text{C} \) is given by

\[
\log Q' = \log (2.08 \times 10^8 k) = 8.318 + A - \frac{B}{T}
\]
and

\[ \log Q = \log (1.091 \times 2.08 \times 10^8 k) = 8.356 + A - \frac{B}{T} \]

respectively.

The leak rates of helium through G. E. fused quartz as measured by Altemose are presented in Table 23. When the log of these measured leak rates is least square fitted to the formula

\[ \log k = A - \frac{B}{T} \]

the values

\[ A = -6.38 \]
\[ B = 1081 \]

are obtained. From these values the formula

\[ k(T) = 4.2 \times 10^{-7} \cdot e^{-\frac{2491}{T}} \]

follows easily. This formula reproduces the measured values of \( k \) to within ten percent.

**TABLE 23**

**MEASURED LEAK RATES OF HELIUM THROUGH QUARTZ**

<table>
<thead>
<tr>
<th>( T(°K) )</th>
<th>( k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>( 1.0 \times 10^{-10} )</td>
</tr>
<tr>
<td>434</td>
<td>( 1.3 \times 10^{-9} )</td>
</tr>
<tr>
<td>606</td>
<td>( 6.4 \times 10^{-9} )</td>
</tr>
<tr>
<td>758</td>
<td>( 1.7 \times 10^{-8} )</td>
</tr>
</tbody>
</table>
So far our considerations pertaining to the leakage of helium through quartz have been completely general. We shall now apply the results of the preceding discussion to our specific physical situation. The basic problem may be formulated as follows. Given an essentially spherical quartz flask of thickness $d$ and volume $V$ initially containing helium at some specified pressure $P_0$, find the pressure in the flask at any later time assuming that the temperature of the flask at any later time is known.

Let $Q(T)$ be the permeability of the quartz as defined earlier. Then the total rate of leakage from the bulb in micron $^3$ liters per hour is

$$R(T) = Q(T) \frac{A}{d} \frac{P(T)}{d}$$

where $P$ is in atmospheres, $d$ is in millimeters, and $A$ is the surface area of the bulb in square centimeters. Since the area of a sphere is related to its volume by

$$A = 4\pi \left[ \frac{3V}{4\pi} \right]^{2/3}$$

we obtain

$$R(T) = 4\pi \left[ \frac{3V}{4\pi} \right]^{2/3} Q(T) \frac{P(T)}{d}$$

In this formula $V$ and $d$ are very weak functions of the temperature due to the thermal expansion of the sample flask. It may easily be shown, however, that thermal expansion has only negligible influence upon the leak.
rate. Accordingly, from now on $V$ and $d$ will be treated as constants.

To find the temperature dependence of $P(T)$ we apply the ideal gas law in the form

$$\frac{PV}{T} = \frac{P_0 V_0}{T_0}$$

Here $P_0$ and $V_0$ are the pressure and volume of the sample flask at the normalization temperature ($T_0 = 298 \, ^\circ$K), while $P$ and $V$ are the pressure and volume at the temperature $T$. Since $V$ is being treated as a constant it follows that

$$V = V_0$$

and

$$P(T) = P_0 \frac{T}{T_0}$$

Therefore,

$$R(T) = 4\pi \left[ \frac{3V}{4\pi} \right]^{2/3} \frac{P_0}{d \frac{T}{T_0}} T Q(T)$$

In the above formula $P_0$ is the pressure (measured in atmospheres) in the sample flask at room temperature. It is more appropriate for us to measure the pressure in centimeters of mercury. Accordingly we make the transformation

$$P_0 \rightarrow \frac{P_0}{76}$$
Similarly we shall change the units of the leak rate \( R(T) \) from micron \cdot\) liters (at 25\(^\circ\)C) per hour to cm \cdot\) liters (at 25\(^\circ\)C) per hour. Since one micron equals \( 10^{-4} \) centimeters this transformation is effected by multiplying the right hand side of the expression for \( R(T) \) by \( 10^{-4} \). We now have

\[
R(T) = \frac{4\pi (10^{-4})}{76} \left[ \frac{3V}{4\pi} \right]^{2/3} \frac{P_o}{d} \frac{1}{T_o} TQ(T).
\]

In the above expression \( R(T) \) is the leak rate in cm \cdot\) liters (at 25\(^\circ\)C) per hour, \( P_o \) is measured in centimeters of mercury and is the (instantaneous) pressure which would exist in the flask at 25\(^\circ\)C, \( d \) is in millimeters, \( V \) is in cubic centimeters, and \( T_o \) is the normalization temperature measured on the Kelvin scale (298\(^\circ\)k). The instantaneous temperature \( T \) is also measured on the Kelvin scale.

The quantity of actual interest to us is the rate of decrease of the pressure in the sample flask \( (P_o) \). This may easily be found in terms of \( R(T) \). Since \( R(T) \) is the leak rate in cm \cdot\) liters (at 25\(^\circ\)C) it is numerically equal to the rate of increase of the pressure in centimeters of mercury if it is imagined that the leaked gas is confined in a one liter container at 25\(^\circ\)C. If instead we imagine the leaked gas to be confined in a container of volume \( V \) equal to the volume of the container in which it was originally confined, the rate of increase of pressure in the new container will be just
\[
\frac{dP_o}{dt} = \frac{R(T)}{V}.
\]

In the above expression \( P_o \) is in centimeters of mercury and \( V \) must be measured in liters. In order to be consistent with the earlier discussion \( V \) should be measured in cubic centimeters. Accordingly we make the transformation

\[ V \rightarrow \frac{V}{1000} \]

Then

\[
\frac{dP_o}{dt} = (10^3) \frac{R(T)}{V}.
\]

Since the leaked gas is being confined in a container equal in volume to the original container, it follows that the rate of increase of density in the one is equal to the rate of decrease of density in the other. Accordingly, the rate of decrease in the pressure (referred to 25\(^\circ\) C) of the sample flask is

\[
\frac{dP_o}{dt} = -(10^3) \frac{R(T)}{V}.
\]

Then by substituting in for \( R(T) \), there results

\[
\frac{dP_o}{dt} = \frac{-4\pi P_o}{760d T_o V} \left[ \frac{3V}{4\pi} \right]^{2/3} TQ(T).
\]

It has already been shown that \( Q(T) \) is of the form

\[
Q(T) = Q_o e^{-\frac{C}{T}}
\]
with
\[ Q = 94.6 \quad C = 2591. \]

Substituting this expression into the equation for \( \frac{dP_Q}{dt} \) yields
\[
\frac{dP_Q}{dt} = \frac{-4\pi P_0 Q_o}{760d} \left(\frac{3V}{4\pi}\right)^{2/3} T e^{-\frac{C}{T}}.
\]

In the above expression for the rate of loss of pressure the unit of time is the hour. For our purposes it will be more convenient to deal with the rate of pressure loss per minute. This is given by
\[
\frac{dP_Q}{dt} = \frac{-4\pi P_0 Q_o}{760d} \left(\frac{3V}{4\pi}\right)^{2/3} T e^{-\frac{C}{T}}.
\]

Thus we now have determined an expression for the rate of loss of pressure (normalized to 298° k) from the sample at temperature T. In this equation the value of all the constants are known except for the thickness parameter d. We call that
\[ Q_o = 94.6 \quad V = 300 \]
\[ T_o = 298 \quad C = 2491 \]

Substituting in these values and dividing by \( P_o \) yields
\[
\frac{1}{P_o} \frac{dP_o}{dt} = -5.023 \times 10^{-6} \frac{d}{T} e^{-\frac{2491}{T}}.
\]
Let $\rho$ be the density of helium in the sample. Since $P_0$ is proportional to $\rho$, the above equation may be written as

$$\frac{1}{\rho} \frac{d\rho}{dt} = -5.023 \times 10^{-6} \frac{1}{T} e^{-\frac{2491}{T}}.$$

The above form expresses the equation for helium leakage in the same notation as is employed in Chapter IV.

It is perhaps worth noting at this point that the equation describing the leakage of neon has the same functional form as that describing the leakage of helium. The two equations differ only in the values assigned to $Q_0$ and $C$. From the measurements of T'sai and Hogness as summarized by Dushman, the values of

$$Q_0 = 16.6 \quad C = 4822$$

may be derived for the case of neon leakage. Substituting these values yields

$$\frac{1}{\rho} \frac{d\rho}{dt} = -8.815 \times 10^{-7} \frac{1}{T} e^{-\frac{4822}{T}}.$$

where $T$ is in minutes and $d$ in millimeters. The above form of the equation for neon leakage is the one employed in Chapter IV.
APPENDIX C

THE RELAXATION OF ATOMIC POLARIZATION
BY THERMAL RADIATION

INTRODUCTION

The optical pumping of silver via spin exchange has necessitated the performing of the optical pumping process at higher temperatures than ever previously attempted. While performing this experiment a sharp drop in signal strength as a function of temperature was observed to occur for sample flask temperatures above 750°C. This was true for signals obtained from both the directly pumped rubidium and the spin-exchange oriented silver. Above 900°C our measurement apparatus was incapable of obtaining useful signals.

It was speculated that at these elevated temperatures the thermal radiation field might have become intense enough to compete with the optical pumping light and thus constitute a relaxation mechanism significant enough to cause the observed reduction in signal strength. In order to check the validity of this hypothesis, the relaxation rate due to thermal relaxation was calculated for the hypothetical case of a "spinless" alkali-like atom. It was possible to do this using quite elementary methods. The purpose of this appendix is to present the results of this calculation.
We shall consider a polarized ensemble of non-interacting atoms and analyze the manner in which a background thermal radiation field relaxes it to an unpolarized ensemble. The ensemble will be supposed to exist in an isotropic space. That is, we do not consider an optical pumping light beam or a static of r.f. magnetic field to be present. The situation being considered is thus considerably more simple than that which would exist in most actual optical pumping experiments. However, our model will be quite adequate to obtain an estimate of the magnitude of the relaxation rate caused by thermal radiation.

At the outset we shall impose some restrictions upon our investigation.

1. First, the only type of atom which we shall consider is one whose ground state possesses zero orbital angular momentum \((L = 0)\) and whose first excited state possesses one unit of orbital angular momentum \((L = 1)\). This restriction to atoms whose ground and first excited states are \(S\) and \(P\) states respectively is not fundamental, and we made it only because by doing so we shall be confining our attention to the type of atom most frequently encountered in optical pumping experiments.

2. Second, in analyzing the process of relaxation we shall consider only the ground state and the first excited state, ignoring the existence of higher energy levels. We shall further assume that the temperature of our ensemble of atoms is low enough so that at any instant
the number of atoms in the ground state is overwhelmingly larger than the number of atoms in the excited states. The occupation probabilities for the various energy levels can, of course, be computed from the Boltzmann probability distribution. Although we shall not do so here, it is easy to show that the restrictions expressed above in 2 in fact correspond to the situation actually encountered in practice in the optical pumping of alkali-like atoms.

THE RELAXATION OF ATOMS WITH ZERO NUCLEAR SPIN

1. Derivation of the Rate of Transfer of Polarization Between Ground State Sublevels.

Let us now consider a hypothetical atom possessing zero nuclear spin (I = 0) and an electronic intrinsic spin which is one-half (S = 1/2) in both the ground and first excited states. The energy level diagram for such an atom is given in Figure 16. In this diagram the states are labeled by the letters A, B, etc. as well as by the usual quantum numbers of each state J and M. Instead of referring to a particular state by listing all its quantum numbers we shall, for conciseness of expression, frequently refer to a state by its single letter designation.

The question which we now pose for ourselves is as follows. Given that initially our ensemble is essentially totally polarized with virtually all the atoms in (say) the state A, how long will it take for the ensemble
Fig. 16.--The low lying energy levels of an alkali-like atom with zero nuclear spin.

to relax to the unpolarized condition in which half the atoms are in state A and half in state B? We will assume that relaxation occurs via absorption of a photon from the radiation field (and consequent excitation to the P state) followed by emission of a photon and consequent decay back down to the S state. The total rate at which polarization is transferred from state A to state B will then be the total rate at which atoms in state A are excited up to the P level times the fraction of atoms in the P level which decay down to state B. We shall now compute this rate.

For an atom in a radiation field it is possible to derive the following formula for the rate at which the atom is excited from its ground state \( a \) to an excited state \( b \).\(^{70}\)

\[
R(b\rightarrow a) = \frac{2\pi e^2}{3\hbar^2} \rho \langle \nu_{ba} \rangle \left| \langle b | \hat{\tau} | a \rangle \right|^2
\]
Putting in for \( \rho(\nu) \) the Planck formula for thermal radiation

\[
\rho(\nu) = \frac{16\pi^2h\nu^3}{c^3} \frac{1}{e^{h\nu/kt-1}}
\]

we obtain

\[
R(b+a) = \frac{1}{e^{h\nu/kt-1}} W(a+b)
\]

where \( W(a+b) \) given by the expression

\[
W(a+b) = \frac{32c^2\pi^3\nu^3ab}{3hc^3} \left| \langle a|\not r|b\rangle \right|^2
\]

is the rate of spontaneous decay from the excited state "b" to the ground state "a." This formula for \( W(a+b) \) may be computed either from quantum electrodynamics or from Einstein's theory of spontaneous emission.

It is possible to express \( W(a+b) \) in terms of the measured lifetime of the excited state if one knows the branching ratios for decay of the various excited state sublevels to the various ground state sublevels. These are shown in Figure 17. The branching ratios (BR) not shown may be determined from the relation

\[
BR\left[ P_j(m) \rightarrow S_j, (m') \right] = BR\left[ P_j(-m) \rightarrow S_j, (-m') \right]
\]

Essentially, Figure 17 is left-right symmetric and to avoid a cluttered diagram we have shown the transitions on the
Fig. 17.—Branching Ratios for Spontaneous Decay

left hand side of the diagram only. Figure 17 implies the following results.

\[ W(C \rightarrow A) = W_{3/2} \]
\[ W(G \rightarrow A) = 1/3W_{1/2} \]
\[ W(D \rightarrow A) = 2/3W_{3/2} \]
\[ W(G \rightarrow B) = 2/3W_{1/2} \]
\[ W(D \rightarrow B) = 1/3W_{3/2} \]

Here \( W_{3/2} = \frac{1}{\tau_{3/2}} \) and \( W_{1/2} = \frac{1}{\tau_{1/2}} \), where \( \tau_{3/2} \) and \( \tau_{1/2} \) are the lifetimes of the \( P_{3/2} \) and \( P_{1/2} \) states respectively.

The above equations follow from a knowledge of three things:

(1) the branching ratios, (2) the fact that the rate of spontaneous decay of any \( P_{\frac{j}{2}} \) state sublevel is independent of its \( m \) value, and (3) the fact that the spontaneous decay rate of any \( P_{\frac{j}{2}} (m) \) state is the sum of the rates of spontaneous decay to each ground state sublevel.

We are now able to express the upward rate of
excitation induced by a thermal radiation field in terms of the rates of spontaneous decay of the \( P_{3/2} \) state and the \( P_{1/2} \) state. This is significant since these lifetimes have been measured and are well known. Using the abbreviation

\[
B_j(T) = \frac{1}{e^{E_j/KT} - 1}
\]

we obtain

\[
R(A \rightarrow C) = B_{3/2}(T) W_{3/2} \quad R(A \rightarrow G) = 1/3 B_{1/2}(T) W_{1/2}
\]

\[
R(A \rightarrow D) = 2/3 B_{3/2}(T) W_{3/2} \quad R(A \rightarrow H) = 2/3 B_{1/2}(T) W_{1/2}
\]

\[
R(A \rightarrow E) = 1/3 B_{3/2}(T) W_{3/2}
\]

In computing the rate of transfer of polarization from one ground state sublevel to the other there are two distinct cases which we may consider. One is the case in which there is complete mixing of the excited state sublevels prior to the spontaneous decay to the ground state. The other, clearly, is the case in which there is no such mixing. We shall first consider the case in which complete mixing occurs.

a) Relaxation Under the Assumption of Complete Excited State Mixing. We shall now compute the rate of transfer of polarization from sublevel A to sublevel B under the assumption of complete mixing in the excited state. Clearly this will also be the rate of transfer of polarization going in the other direction (from B to A).
When complete mixing in the excited state occurs all the excited state sublevels become equally populated prior to the decay of the atom back down to the ground state. The occupation of the excited state sublevels thus becomes totally symmetric and in consequence the atom decays down to states A and B with equal probability. The total rate at which atoms are transferred from state A to state B is then one-half the rate at which atoms are excited out of state A, the one-half being the fraction of atoms excited out of state A which subsequently decay down to state B. The total rate at which atoms are excited out of state A by a thermal radiation field is

\[ R' = R(A\rightarrow C) + R(A\rightarrow D) + R(A\rightarrow E) + R(A\rightarrow F) + R(A\rightarrow G) + R(A\rightarrow H) \]

or

\[ R' = \frac{2}{3} B^{3/2}(T) W^{3/2} + \frac{1}{3} B^{3/2}(T) W^{3/2} + 0 \]

\[ + \frac{1}{3} B^{1/2}(T) W^{1/2} + \frac{2}{3} B^{1/2}(T) W^{1/2} \]

This becomes

\[ R' = 2B^{3/2}(T) W^{3/2} + B^{1/2}(T) W^{1/2} \]

Multiplying by one half yields

\[ R = B^{3/2}(T) W^{3/2} + \frac{1}{2} B^{1/2}(T) W^{1/2} \]

where R is the rate at which atoms are transferred from state A to state B in the presence of a radiation field.
at temperature $T$. Writing out this formula in more detail and expressing it in terms of times rather than rates, we obtain

$$\frac{1}{T} = \frac{1}{2} \left[ \frac{1}{e^{\frac{E_{1/2}}{KT}} - 1} \right] \frac{1}{\tau_{1/2}} + \left[ \frac{1}{e^{\frac{E_{3/2}}{KT}} - 1} \right] \frac{1}{\tau_{3/2}}$$

We now turn our attention to the calculation of the analogous formulae for the case of no mixing in the excited state.

b) Relaxation Under the Assumption of No Excited State Mixing. When no excited state mixing occurs the rate at which atoms are transferred from state $A$ to state $B$ is given by

$$R = \sum_{I} f_{I} R(A \rightarrow I)$$

where $R(A \rightarrow I)$ is the rate at which atoms are excited from state $A$ to state $I$, and $f_{I}$ is the fraction of atoms in state $I$ which decay down to state $B$. Expanding this formula out yields

$$R = \frac{4}{9} B_{3/2}(T) W_{3/2} + \frac{4}{9} B_{3/2}(T) W_{1/2}$$

If we again write out this formula in more detail and express it in terms of times, we obtain

$$\frac{1}{T} = \frac{4}{9} \left[ \frac{1}{e^{\frac{E_{1/2}}{KT}} - 1} \right] \frac{1}{\tau_{1/2}} + \frac{4}{9} \left[ \frac{1}{e^{\frac{E_{3/2}}{KT}} - 1} \right] \frac{1}{\tau_{3/2}}$$
THE DIFFERENTIAL EQUATIONS OF THE RELAXATION

1. The Relaxation Equations for the Populations

We shall now derive the equations of motion for the populations of the S state sublevels. Let us employ standard density matrix notation and denote the probability of finding an atom in state A or B by $P_{11}$ and $P_{22}$ respectively. Then we have

$$\frac{dP_{11}}{dt} = -\frac{1}{T} P_{11} + \frac{1}{T} P_{22}$$

$$\frac{dP_{22}}{dt} = -\frac{1}{T} P_{22} + \frac{1}{T} P_{11}.$$ 

These equations may be put in a more illuminating form by some simple algebraic manipulation. It is easy to see that the above two equations may be written in the form

$$\frac{dP_{11}}{dt} = -\frac{2}{T} \left[ P_{11} - \frac{1}{2} (P_{11} + P_{22}) \right]$$

$$\frac{dP_{22}}{dt} = -\frac{2}{T} \left[ P_{22} - \frac{1}{2} (P_{11} + P_{22}) \right]$$

Clearly if, as we have assumed, most of the atoms in our ensemble at any given time are in the ground state then we must have

$$P_{11} + P_{22} = 1$$
We may use this relation in the equations given directly above. When this is done we may use matrix notation to write the equation for the relaxation of the diagonal terms of the density matrix as follows

\[
\begin{pmatrix}
\frac{dP_{11}}{dt} & 0 \\
0 & \frac{dP_{22}}{dt}
\end{pmatrix} = \begin{pmatrix}
\frac{1}{2} - \frac{P_{11}}{\tau} & 0 \\
0 & \frac{1}{2} - \frac{P_{22}}{\tau}
\end{pmatrix}
\]

Here

\[
\frac{1}{\tau} = \frac{2}{T}
\]

and expressions for \(1/T\) have previously been calculated under the assumptions of complete excited state mixing and no excited state mixing. From the above equation it is obvious that all the diagonal elements of the density matrix relax independently and with the same time constant to their equilibrium value of one-half.

2. The Relaxation Equations for the Coherences

We have obtained above the equations of motion for the diagonal elements of the density matrix. We now obtain the equations of motion for the off diagonal elements. To do this we shall first show that any arbitrary density matrix for a spin one-half particle may always be diagonalized by a simple rotation of the underlying Cartesian coordinate system. However, we know the complete equations of motion in a coordinate system in which the density
matrix is diagonal. They are as given directly above. We then argue that we may find the equations of motion in the original coordinate system by rotating back to it from the system in which the density matrix is diagonal and the equations of motion known.

The proof that the density matrix for a spin one-half particle can always be diagonalized by a rotation is simple. We first note that we may always make a rotation to a coordinate system in which the expectation value of the spin lies solely along the z axis. Using

\[
P = \begin{bmatrix}
P_{11} & P_{12} \\
P_{21} & P_{22}
\end{bmatrix}
\]

The Hermiticity condition

\[
P_{12} = P_{21}^*
\]

and the relations

\[
S_x = 1/2 \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad S_y = 1/2 \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad S_z = 1/2 \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}
\]

we may make use of the equation

\[
\langle S_i \rangle = \text{tr}(PS_i)
\]

to obtain the following relations (valid in any Cartesian coordinate system).
\[
\langle S_x \rangle = \frac{1}{2} (P_{12} + P_{21}) = \frac{1}{2} (P_{12} + P_{12}^*) = \text{Re } P_{12}
\]

\[
\langle S_y \rangle = \frac{i}{2} (P_{12} - P_{21}) = \frac{i}{2} (P_{12} - P_{12}^*) = -\text{Im } P_{12}
\]

\[
\langle S_z \rangle = \frac{1}{2} (P_{11} - P_{22})
\]

Thus in the coordinate system in which

\[
\langle S_x \rangle = \langle S_y \rangle = 0
\]

the above equations imply

\[
\text{Re } P_{12} = \text{Im } P_{12} = 0
\]

and consequently

\[
P_{12} = P_{21} = 0
\]

Therefore, the coordinate system in which \( P \) is diagonal is the coordinate system in which the expectation value of the spin lies solely along the z axis. Clearly this system can always be reached by making a rotation.

We now consider the way in which the equation of motion for the density matrix transforms under rotations. As we have seen, in the coordinate system in which the density matrix is diagonal we have
This equation may also be written in the form

\[
\frac{d}{dt} \begin{bmatrix} P_{11} & 0 \\ 0 & P_{22} \end{bmatrix} = \begin{bmatrix} \frac{1}{2} - \frac{P_{11}}{\tau} & 0 \\ 0 & \frac{1}{2} - \frac{P_{22}}{\tau} \end{bmatrix}
\]

or, more compactly,

\[
\frac{d}{dt} P = \frac{1}{2\tau} I - \frac{1}{\tau} P
\]

In this last form, however, the equation is clearly invariant under a rotation. To see this we note that the density matrix expressed in a rotated coordinate system (P') is related to the density matrix prior to the rotation (P) by a unitary transformation. Thus

\[
P' = R^+ P R
\]

where, of course,

\[
R^+ R = R R^+ = I
\]

If we apply this transformation to the equation of motion for the diagonal density matrix we obtain

\[
\frac{d}{dt} (R^+ P R) = \frac{1}{2\tau} R^+ I R - \frac{1}{\tau} R^+ P R
\]
or

\[
\frac{d}{dt} \mathbf{p}' = \frac{1}{2\tau} \mathbf{I} - \frac{1}{\tau} \mathbf{p}'
\]

We may write this last equation in matrix form. If we consider \( R \) to be the rotation which transforms back to the original coordinate system in which the density matrix was not diagonal we shall obtain

\[
\frac{d}{dt} \begin{bmatrix}
    p'_{11} & p'_{12} \\
    p'_{21} & p'_{22}
\end{bmatrix} = \frac{1}{2\tau} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} - \frac{1}{\tau} \begin{bmatrix}
    p'_{11} & p'_{12} \\
    p'_{21} & p'_{22}
\end{bmatrix}
\]

as the equation of motion for the density matrix in the original coordinate system. Dropping the primes and writing the above more compactly we obtain

\[
\frac{d}{dt} \begin{bmatrix}
    p_{11} & p_{12} \\
    p_{21} & p_{22}
\end{bmatrix} = \begin{bmatrix}
    1/2 - \frac{p_{11}}{\tau} & -\frac{p_{12}}{\tau} \\
    -\frac{p_{21}}{\tau} & 1/2 - \frac{p_{22}}{\tau}
\end{bmatrix}
\]

as the general form of the relaxation equations for the density matrix describing our ensemble of atoms. We recall that \( \tau \) can be computed for a given atom and temperature from the expressions derived earlier in this paper. For the case of complete mixing in the excited state we obtained
\[
\frac{1}{\tau} = \left[ \frac{1}{e^{E_{1/2}/KT-1}} \right] \frac{1}{\tau_{1/2}} + 2 \left[ \frac{1}{e^{E_{3/2}/KT-1}} \right] \frac{1}{\tau_{3/2}}
\]

while in the absence of excited state mixing we derived

\[
\frac{1}{\tau} = \frac{8}{9} \left[ \frac{1}{e^{E_{1/2}/KT-1}} \right] \frac{1}{\tau_{1/2}} + \frac{8}{9} \left[ \frac{1}{e^{E_{3/2}/KT-1}} \right] \frac{1}{\tau_{3/2}}
\]

As a final calculation we shall compare the magnitudes of the relaxation rates computed under the assumption of complete mixing in the excited state and no mixing in the excited state. It is always a good approximation to assume

\[E_{1/2} = E_{3/2} = E_P\quad \tau_{1/2} = \tau_{3/2} = \tau_P\]

Then for the case of complete mixing we obtain

\[
\frac{1}{\tau_c} = 3 \left[ \frac{1}{e^{E_P/KT-1}} \right] \frac{1}{\tau_P}
\]

while for the case of no mixing we obtain

\[
\frac{1}{\tau_n} = \frac{16}{9} \left[ \frac{1}{e^{E_P/KT-1}} \right] \frac{1}{\tau_P}
\]

We can now compute the ratio
\[ \frac{\tau_n}{\tau_c} = \frac{27}{16} = 1.7 \]

This says that if we assume no mixing in the excited state our polarized ensemble will take approximately 1.7 times longer to relax to the unpolarized state than it will if complete mixing in the excited state occurs. Table 24 compares the thermally induced relaxation for the number of elements.

CONCLUSIONS

From the foregoing analysis several results emerge.

1. At the temperatures attained in this experiment relaxation caused by thermal radiation is clearly significant. Rates are comparable to those observed in more traditional experiments. Bouchiat, \cite{71,72} for example, observed the relaxation of \( \langle S_z \rangle \) for \( \text{Rb}^{87} \) in a paraffin coated cell. She observed the decay to be the sum of two exponentials with time constants

\[ \tau_e = 0.34 \text{ sec.} \quad \tau_n = 1.03 \text{ sec.} \]

Her value for \( \tau_e \) may be compared with the relaxation rate of "spinless" rubidium at 827° C.

2. Thermal relaxation is probably not, by itself, sufficient to account for the sharp drop in signal intensity observed above 750° C. Optical pumping rates attained with conventional lamps are generally on the order of a thousand photon absorptions per second. Relaxation rates
**TABLE 24**

THERMAL RELAXATION TIME CONSTANT ($\tau$) OF A NUMBER OF ELEMENTS AS A FUNCTION OF TEMPERATURE

COMPLETE MIXING IN THE EXCITED STATE IS ASSUMED

$\tau$ IS GIVEN IN UNITS OF SECONDS.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>527</th>
<th>627</th>
<th>727</th>
<th>827</th>
<th>927</th>
<th>1,027</th>
<th>1,127</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>3,950</td>
<td>200</td>
<td>19</td>
<td>2.6</td>
<td>.52</td>
<td>.13</td>
<td>.040</td>
</tr>
<tr>
<td>Na</td>
<td>(9.6 \times 10^4)</td>
<td>3,200</td>
<td>210</td>
<td>23</td>
<td>3.6</td>
<td>0.76</td>
<td>0.20</td>
</tr>
<tr>
<td>K</td>
<td>130</td>
<td>9.6</td>
<td>1.2</td>
<td>0.22</td>
<td>0.052</td>
<td>0.016</td>
<td>0.0057</td>
</tr>
<tr>
<td>Rb</td>
<td>79</td>
<td>6.2</td>
<td>0.81</td>
<td>0.15</td>
<td>0.038</td>
<td>0.012</td>
<td>0.0043</td>
</tr>
<tr>
<td>Cs</td>
<td>10</td>
<td>1.0</td>
<td>.71</td>
<td>0.038</td>
<td>0.011</td>
<td>0.0038</td>
<td>0.0015</td>
</tr>
<tr>
<td>Cu</td>
<td>(2.3 \times 10^{15})</td>
<td>(4.9 \times 10^{12})</td>
<td>(3.7 \times 10^{10})</td>
<td>(6.6 \times 10^8)</td>
<td>(2.3 \times 10^7)</td>
<td>(1.4 \times 10^6)</td>
<td>(1.2 \times 10^5)</td>
</tr>
<tr>
<td>Ag</td>
<td>(6.5 \times 10^{14})</td>
<td>(1.7 \times 10^{12})</td>
<td>(1.4 \times 10^{10})</td>
<td>(2.8 \times 10^8)</td>
<td>(1.1 \times 10^7)</td>
<td>(6.7 \times 10^5)</td>
<td>(6.3 \times 10^4)</td>
</tr>
<tr>
<td>H</td>
<td>(9.0 \times 10^{54})</td>
<td>(6.7 \times 10^{47})</td>
<td>(1.3 \times 10^{42})</td>
<td>(2.7 \times 10^{37})</td>
<td>(3.4 \times 10^{33})</td>
<td>(1.7 \times 10^{30})</td>
<td>(2.6 \times 10^{27})</td>
</tr>
</tbody>
</table>
of a millisecond or less are therefore required in order to prevent the development of appreciable polarization. Thermal relaxation rates of this magnitude are not obtained at present operating temperatures.

3. The problem of greatly enhanced relaxation at high temperature will be a crucial one in any attempt to polarize gold or copper by spin exchange. Because of their low vapor pressures, it appears that operating temperatures of at least 100° C higher than those necessary in the case of silver will be needed. The relatively slow thermal relaxation rate of sodium suggests that it might be possible at these temperatures to polarize gold or copper by spin exchange with polarized sodium. The thermal relaxation of sodium will be negligible, and it is possible that other relaxation mechanisms which involve transfer through the excited state may also be reduced. The polarization of sodium by conventional means may thus be possible at temperatures higher than those at which appreciable polarization may be produced in any of the other alkalies.