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SURFACE-INDUCED NUCLEAR SPIN RELAXATION IN
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IN GASEOUS HELIUM; THE INTERACTION POTENTIAL
AT LONG RANGE.

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Surface-Induced Nuclear Spin Relaxation in Gaseous He\(^3\)

and

Diffusion Studies of He\((2^3S_1)\) in Gaseous Helium; the Interaction Potential at Long Range

by

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Thesis Director's signature

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My wife, to whom this thesis is dedicated, for her patience and invaluable support.
**Introduction**

This thesis is the result of experimental and theoretical investigations of two independent physical phenomena. These phenomena are related, however, in that they are both important to the optical pumping process in He³.

The first part of this thesis is a study of surface-induced He³ nuclear spin relaxation. Past investigations of He³ spin relaxation have shown that the containing walls limit the observed relaxation times to values considerably less than expected for the bulk gas. The nuclear spin relaxation time for the bulk gas, due to the nuclear dipole-dipole coupling during atomic collisions, is estimated to be \( 4 \times 10^7 \; T^{1/2} \; p^{-1} \) seconds, where \( T \) is the absolute temperature and \( p \) the gas density in units equal to the sample pressure in torr at room temperature\(^1\). Relaxation times observed in the laboratory are typically of the order of \( 10^4 \) seconds or less. The importance of obtaining long He³ nuclear spin relaxation times has been stressed by many authors. Experiments requiring nuclear spin relaxation times in excess of several days have been proposed to measure the electric dipole moment of the He³ nucleus\(^2\). There is also considerable demand for dense polarized He³
He$^3$ nuclear targets and progress in this area depends on the reduction of surface relaxation effects. The investigation of surface relaxation to be discussed was undertaken in the hope that if the He$^3$-surface interaction was understood, then surface relaxation effects could be reduced. This program was successful and He$^3$ nuclear spin relaxation times in excess of $2 \times 10^5$ seconds (greater than 2 days) are now available with the proper selection of surface material and temperature.

As a result of this investigation, the experiments of Bouchiat et al. are being repeated$^3)$. In these experiments dense He$^3$ gas is used as the buffer gas in rubidium vapor optical pumping. The He$^3$ nuclei become polarized via collisions with the polarized Rb atoms, and the resulting He$^3$ nuclear polarization is directly proportional to the surface-induced nuclear spin relaxation time. With the long relaxation times now available, it is expected that He$^3$ nuclear polarizations of 10% in 1 atmospheric samples of He$^3$ are possible. This would be a significant advance in the field of polarized nuclear targets.

The second part of this thesis is an experimental and theoretical investigation of the He($2^3S_1$) - He($1^1S_0$) interaction. This interaction has been of particular interest because it is the connecting link for the optical pumping
of He$^3$ nuclei and furthermore exhibits an unusual repulsive behavior at intermediate nuclear separations. The existence of the repulsive barrier has been firmly established both experimentally and theoretically$^{4,21}$. However, collision cross-sections at thermal energies (less than 1000$^\circ$K) are determined by the repulsive interaction at large nuclear separations. This region of the interaction is not well known, as evidenced by the fact that the previous theoretical estimates of the potential functions are in poor agreement with experimental measurements. The experimental-theoretical investigation to be discussed consisted of measuring the diffusion cross-section for He($2^3S_1$) atoms in helium gas over the temperature range of 1$^\circ$K to 300$^\circ$K and then comparing the experimental results with cross-sections calculated on the basis of assumed interaction potential functions. As a result of this investigation, the He($2^3S_1$) - He($1^1S_0$) interaction at long range has been determined to an accuracy sufficient for the calculation of diffusion, excitation-transfer and total cross-sections to within the experimental uncertainties for a range of energies corresponding to 1$^\circ$K to 500$^\circ$K. A second very interesting result is that if the Van der Waals interaction is included, the long range repulsive interaction is cut off
at very large nuclear separations and a weak attractive potential well results in which a bound state may exist. If a bound state exists, the equilibrium nuclear separation would be roughly 10 Bohr radii. The nature of the repulsive interaction, as well as the existence or near existence of a bound state at large nuclear separations, is of particular interest in view of a planned program of research to study the behavior of He($2^3S_1$) atoms in liquid helium.
PART I

SURFACE-INDUCED NUCLEAR SPIN RELAXATION

IN GASEOUS $^3\text{He}$
PART I
SURFACE-INDUCED NUCLEAR SPIN RELAXATION
IN GASEOUS He³

I. Introduction

The temperature dependence of the surface-induced He³ nuclear spin relaxation time ($T_1$) was measured over the temperature range of 55°K to 350°K in an effort to elucidate the nature of the He³-surface interaction. The experiments were performed on low density samples of He³ gas contained in sealed pyrex and quartz vessels, and subsequently in aluminosilicate glass vessels. The nuclear spin relaxation times were measured by inducing a large (∼10%) nuclear polarization by the optical pumping method and then, by a conventional NMR technique, measuring the rate at which the polarization decayed to its thermal equilibrium value in a magnetic field of 225 gauss.

The He³ nuclear spin relaxation induced by pyrex and quartz surfaces exhibits a strong temperature dependence characterized by a relaxation time maximum near 125°K. This behavior suggests that the relaxation mechanism operative at low temperatures is distinctly different than the mechanism operative at high temperatures. The experimental results are
analyzed in terms of a phenomenological theory of surface relaxation. It is shown that the low temperature relaxation mechanism is the result of adsorption of the $^3\text{He}$ onto the surface, while the high temperature relaxation mechanism depends on the permeation of the $^3\text{He}$ into the wall material. Both these relaxation mechanisms have the common feature that the characteristic atom-surface interaction time (sticking time) is long compared to the gas-kinetic atom-wall collision time.

On the basis of the theoretical predictions, the high temperature relaxation mechanism is suppressed by constructing the sample containers of aluminosilicate glasses. These glasses are roughly three orders of magnitude less permeable to helium than either pyrex or quartz. The resulting $^3\text{He}$ nuclear spin relaxation times are typically in excess of $10^5$ seconds (greater than one day) at $300^\circ\text{K}$ and increase sharply with temperature. For pyrex surfaces the relaxation times at $300^\circ\text{K}$ are typically $10^4$ seconds and decrease with temperature.

The magnetic field dependence of the surface induced $^3\text{He}$ nuclear spin relaxation time was measured at a few temperatures for pyrex and aluminosilicate surfaces. In all cases the relaxation time exhibits a variation with the applied magnetic field, and the field dependence varies in
both magnitude and sign depending upon the temperature and surface under study. This is apparently due to the detailed nature of the unknown paramagnetic centers on or near the glass surface that cause the nuclear spin relaxation.
II. Experimental Procedure

The gaseous $^3\text{He}$ samples were contained in spherical bulbs, approximately 5 cm in diameter, blown from several glasses—pyrex, supracil quartz, and Corning 1720 and 1723 aluminosilicates. The containers were subjected to identical cleaning procedures starting with degreasing in strong laboratory detergent and thorough rinsing with distilled water. Then they were installed on an all glass vacuum and gas handling system and evacuated to a pressure of $10^{-7}$ torr at 800°K. The vacuum and gas handling system has been described by Byerly$^5)$. To further clean the inside surface, the bulbs were filled to 1 torr with a helium-hydrogen mixture in which an intense electrical discharge was ignited for about 30 minutes. After the discharge cleaning each vessel was re-evacuated and baked out to remove any residual $^4\text{He}$ or $\text{H}_2$. To check the surface cleanliness, each bulb was filled with reagent grade $^4\text{He}$ to a pressure of 1 torr and a bright discharge was ignited and viewed through a pocket spectrometer. In most cases no emission lines other than the helium spectra were observed. When the spectra indicated the presence of impurities, the above procedure of $^4\text{He}$ and $\text{H}_2$ discharge cleaning was repeated until no impurity lines could be seen. The discharge cleaning procedure never had to
be repeated more than once. After cleaning, the vessels were filled to the desired He$^3$ density by leaking reagent grade helium into the vacuum system through a densely packed copper foil cold trap immersed in liquid helium, and tipped off to yield permanently sealed samples. Sample densities varied between 2 and 20 torr at room temperature.

The experiment may be described with reference to Figure 1. The apparatus has three basic components:

1) The optical pumping system to initially polarize the He$^3$ gas. 2) A nuclear magnetic resonance spectrometer to detect and monitor the decay of the He$^3$ nuclear polarization. 3) A cryogenic system to control the temperature of the sample.

The glass bulb containing the He$^3$ is placed in a dewar with flat windows on the bottom. The windows provide an optical path for the circularly polarized 1.08μ optical pumping radiation emitted by a bright He$^4$ discharge lamp. The pumping radiation is incident on the He$^3$ along the direction of an external magnetic field provided by a co-axial and end-corrected solenoid. A weak electrode-less discharge ignited in the He$^3$ populates the $2^3S_1$ metastable state and the metastable atoms become polarized via absorption of the pumping radiation. Excitation transfer collisions between the metastable atoms and ground state
Figure 1  Apparatus for Surface Relaxation Studies
atoms transfer the optically induced spin polarization to the ground state nuclei in a manner described by Colegrove, Schearer and Walters, and more recently by Fitzsimmons\(^6,7\). Ground state polarizations between 5% and 15% are typical. After the sample is polarized, both the discharge in the sample and the pumping lamp are turned off for the remainder of the experiment and the decay of the nuclear polarization is monitored periodically by a slow-passage NMR technique. Larmor coils wound around the sample form one arm of a twin-T bridge. An R.F. generator operated at a frequency of 735 KHz and a radio receiver complete the magnetic resonance circuit\(^8\). The resonant absorption signals from a 12 torr sample of He\(^3\) with an initial nuclear polarization of approximately 6% is shown in Figure 2.

The external magnetic field of approximately 225 gauss provided by a \(^4\)th order end-corrected solenoid was homogeneous to a few parts in \(10^4\) over the sample volume of approximately 70 cm\(^3\). In these experiments good field homogeneity is important since the He\(^3\) nuclear spin polarization can be destroyed by gradients in the external magnetic field\(^9\). This effect will be discussed later.

Since the measured relaxation times were often very long, a means for introducing a standard signal was devised in order to correct for the day to day drift in the over-all
Figure 2: Decay of $^{3}$He NMR absorption signal with time.
Sample #111 - 12 torr He3, 300°K.
sensitivity of the spectrometer. The standard signal was generated by switching a very small fixed capacitor into the resistive side of the NMR bridge. Such a capacitor unbalances the bridge in a manner electrically equivalent to the unbalance caused by the nuclear resonance absorption.

The relaxation time was measured by periodically sweeping the spectrometer through the resonance condition, recording the strength of the absorption signal and the elapsed time between signals. The number of observations of the decaying polarization is limited in this experiment by the imperfect slow-passage conditions that result in the destruction of a small fraction (＜10%) of the signal during each pass through the resonance. The elapsed time between signals was chosen on the basis of a compromise between the desirability of observing large changes in polarization by waiting a long time between signals, and the deteriorating signal-to-noise as the polarization decayed. Best results were obtained by measuring the decaying polarization at three approximately equally spaced intervals with the elapsed time between the first and fourth measurement being somewhat longer than one relaxation time. After correcting for the imperfect passage conditions, the experimental data were plotted on semi-log paper to determine the relaxation time.
An important experimental requirement is temperature stability of the sample, at somewhat inconvenient temperatures, over time periods of two or three days. A set of commercially available non-toxic fluorocarbon compounds (Freons) span most of the desired temperature range. The pertinent physical properties of these Freons are shown in Table I. Liquid nitrogen and liquid argon were used also and are included for comparison. Temperature control of the sample is achieved in the standard way by immersing the sample in the cryogenic fluid, and regulating the fluid vapor pressure (hence temperature) by pumping on it.

The fluorocarbon compounds are readily available in the form of compressed gases and liquids and can be easily liquefied at atmospheric pressure with the apparatus shown in Figure 3. The liquefaction dewar is initially evacuated to remove any residual air and, depending upon the Freon to be liquefied, the metal can is filled with either liquid nitrogen or dry ice and acetone. Valve A is opened and expansion valve B is adjusted to keep the pressure in the dewar slightly less than atmospheric. The cooling upon expansion coupled with the cooling action of the cold metal surface in the dewar resulted in liquefaction rates of roughly two litres per hour. The use of cryogenic fluid
Figure 3  Apparatus for Liquefaction of Fluorocarbon Compounds.
Table I

Properties of cryogenic fluids that, as a group, almost continuously cover the temperature range of 277°K to 63°K.

<table>
<thead>
<tr>
<th>Freon 114</th>
<th>Freon 12</th>
<th>Freon 13</th>
<th>Freon 14</th>
<th>Argon</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling Point at 1 atm. °K</td>
<td>277</td>
<td>243</td>
<td>192</td>
<td>145</td>
<td>87</td>
</tr>
<tr>
<td>Freezing Point at 1 atm. °K</td>
<td>179</td>
<td>115</td>
<td>92</td>
<td>89</td>
<td>84</td>
</tr>
<tr>
<td>Density of Liquid g/cc</td>
<td>1.46</td>
<td>1.31</td>
<td>1.30</td>
<td>1.32</td>
<td>1.39</td>
</tr>
<tr>
<td>Heat of Vaporization at B.P. cal/g</td>
<td>32.5</td>
<td>39.5</td>
<td>35.5</td>
<td>32.5</td>
<td>37.6</td>
</tr>
</tbody>
</table>

vapor pressure regulation resulted in temperature stability of $\pm 1^\circ K$ over a two day period.

For measurements at temperatures higher than room temperature, hot water was circulated through copper coils that were thermally connected to the sample by a silicone fluid. Temperature stability for this method was $\pm 3^\circ K$ over a three day period.
III. Experimental Results and Interpretation

The experimental results for the surface-induced He\textsuperscript{3} nuclear spin relaxation time $T_1$ as a function of temperature are shown in Figure 4 for pyrex and quartz surfaces. Three curves for pyrex containers are shown to indicate the variation in absolute magnitude of the measured relaxation times from sample-to-sample. These variations are attributed to differences of an unknown nature in surface conditions from one sample to the next. No systematic dependence of the relaxation time on He\textsuperscript{3} density was observed over the density range corresponding to 2 to 20 torr at room temperature. This is to be expected for surface relaxation since the rate of wall collisions per atom is independent of density\textsuperscript{10}). Measurements on a given sample are reproducible, indicating that there are no significant effects due to aging (up to two years) or thermal cycling. The uncertainties in the measured relaxation times were typically 10\% to 15\%, and were determined principally by the signal-to-noise limitations of the NMR spectrometer. The experimental errors tended to be greater for the very long relaxation times because of spectrometer and thermal drift.

The most interesting feature of the data shown in Figure 4 is the characteristic relaxation time maximum
Figure 4  Surface-induced He$^3$ nuclear spin relaxation time versus temperature for pyrex and quartz surfaces. Curves 1, 2, and 3 represent measurements on three samples in different pyrex containers with He$^3$ pressures at room temperature of 10, 20, and 20 torr respectively. Curve 4 represents the data taken on a single 10 torr sample in a fused quartz container.
occurring for all samples near 125°K. This behavior suggests that distinctly different surface relaxation mechanisms are operative at low and high temperatures respectively.

The probability of a $\text{He}^3$ nuclear spin flip during an atomic collision with the container wall should be proportional to the collision duration or sticking time. Therefore one is led to seek an explanation of the relaxation time data in terms of the (presumably different) sticking mechanisms that predominate at low and high temperatures. The obvious candidates are adsorption due to Van der Waals forces at lower temperatures, and the well known permeation of helium into pyrex and quartz at higher temperatures. In the next section a quantitative phenomenological theory incorporating these ideas is developed and shown to be in good agreement with the experimental results.

Since quartz is known to be several times more permeable to helium than pyrex, it can be seen from Figure 4 that the high temperature mechanism is consistent with the experimental results—the more permeable glass exhibits the smaller $T_1$. In order to test the high temperature mechanism further, $\text{He}^3$ samples were prepared in containers made of nearly impermeable glasses (Corning 1720 and 1723). Norten\textsuperscript{11} and Altemose\textsuperscript{12} have shown that glasses composed of a high percentage of glass-forming oxides, or network
formers (principally SiO₂), have a chain-like structure with openings large enough for small gas atoms to permeate; hence, pyrex and quartz are relatively permeable to helium. In the aluminosilicate glasses, Al₂O₃ acts as a network modifier, with aluminum ions filling the openings in the glass network. As a consequence the Corning 1720 and 1723 aluminosilicate glasses are about three orders of magnitude less permeable to helium at room temperature than pyrex.

Nuclear spin relaxation times for He³ samples in a number of aluminosilicate glass bulbs are shown in Figure 5, along with a representative pyrex curve for comparison. As with pyrex and quartz containers, there is a reproducible relaxation time variation from sample-to-sample, presumably indicating different surface areas or varying densities of surface paramagnetic centers that induce He³ nuclear spin relaxation. However, with the exception of curve 5, it is clear that, in contrast to the results for pyrex and quartz, there is no evidence of a T₁ maximum. This is regarded as strong experimental support for a permeation-controlled high temperature relaxation mechanism in the cases of pyrex and quartz surfaces. The slight turn-over of curve 5 at high temperatures is not due to any surface property but can be attributed to the magnetic-gradient relaxation mechanism discussed by Schearer and Walters⁹). At helium densities
Figure 5 Surface-induced $^3\text{He}$ nuclear spin relaxation time versus temperature for aluminosilicate surfaces. Curves 6 and 7 and the point labeled 8 represent data taken on three samples in different Corning 1723 containers. Curve 5 is data taken on a single Corning 1720 container. Curve 2 is representative pyrex data included for comparison.
of the order of 10 torr at 300°K and for a magnetic field of 225 gauss, the circular Larmor frequency times the time between gas atom collisions is much less than 1. In the limit \( w_L \gamma_c \ll 1 \), these authors obtain the expression

\[
T_1 = \frac{3}{2} \left( \frac{H_0}{\Delta H_0} \right)^2 \left( \frac{1}{\gamma_c \langle U^2 \rangle} \right)
\]

\[
\approx 2.7 \times 10^{-3} \left( \frac{H_0}{\Delta H_0} \right)^2
\]

for \( \langle U^2 \rangle = 2.5 \times 10^{10} \text{ (cm/sec)}^2 \) is the mean-square velocity corresponding to 300°K, and \( \gamma_c = 2.2 \times 10^{-8} \) seconds corresponding to a pressure of 10 torr\(^9\). \( H_0 \) and \( \Delta H_0 \) are the average magnetic field and the variation in this field over the sample volume respectively. By measuring the line width of the proton resonance from water samples of the same size as the He\(^3\) samples, as well as measuring the magnetic field variation in the neighborhood of the sample with a magnetometer, \( H_0/\Delta H_0 \) is estimated to be between 1.3 and 0.6 \( \times 10^4 \) cm. Thus the magnetic-gradient relaxation time limit of the apparatus is between 1 and 5 \( \times 10^5 \) seconds. It can be seen from Figure 5 that the longer relaxation times are in the range where gradient effects are expected to become important. In a homogeneous magnetic environment, the relaxation times of samples 5 and 8 could be expected to be much longer at the higher temperatures than the values
indicated in the figure.

An attempt was made to measure the surface relaxation time at 4.2°K in a few samples contained in pyrex and in one sample contained in Corning 1723 aluminosilicate glass (curve 6 of Figure 5). The optical pumping method for producing the initial polarization will not work at low temperatures because the metastable–ground state excitation–transfer cross-section becomes very small\textsuperscript{4}). Thus the experimental approach consisted of initially polarizing the sample at 77°K and then cooling it as quickly as possible in the hope that the polarization decay could be monitored at 4.2°K. In all attempts the time required to cool the sample to 4.2°K was 5 minutes or less, but no NMR signal was detected. This places an upper limit of about 2 minutes on the He\textsuperscript{3} surface relaxation time for all samples at 4.2°K.

The magnetic field dependence of surface-induced nuclear spin relaxation was measured at several temperatures for He\textsuperscript{3} samples in both pyrex and aluminosilicate containers. Because of the long relaxation times, it is a simple matter to monitor the polarization decay at any accessible field strength. This is accomplished by periodically turning the field to the 225 gauss value required for NMR, then quickly returning the field to the desired value, all in a time
short compared to $T_1$. The experimental results are shown in Figure 6. The maximum magnetic field of 225 gauss is the highest the solenoid can produce without overheating. The lower field limit of approximately 10 gauss was established to avoid relaxation due to gradients in the ambient laboratory field.

The magnetic field dependence of the surface-induced $^3$He nuclear spin relaxation cannot be adequately interpreted because of the very limited information available on the details of the surface relaxation mechanism. It is probably safe to assume that the relaxing agents are paramagnetic centers on or near the glass container surface. However, these experiments provide no information on the nature of the paramagnetic centers, or on their locations in the glass network. About all that can be said about the magnetic field dependence of $T_1$ is that it probably reflects a field dependence of the paramagnetic relaxation of the surface centers. A few additional comments about this are made at the end of the next section.
Figure 6  Magnetic field dependence of surface-induced $^3$He nuclear spin relaxation times. Curves are labeled according to surface material and temperature at which the measurements were carried out.
IV. Phenomenological Theory

The surface-induced relaxation behavior of gaseous $^3\text{He}$ can be described quantitatively by consideration of the average collision duration (or sticking time) $t_s$ characterizing the $^3\text{He}$-surface interaction. A rather general expression relating the observed $^3\text{He}$ relaxation time $T_1$ to $t_s$ is first derived in a manner paralleling that of Torrey et al. in their treatment of magnetic spin pumping of fluids contained in porous media\textsuperscript{13}). The behavior of $T_1$ at low and high temperature limits is then analyzed by evaluating $t_s$ and the steady-state number $n$ of $^3\text{He}$ atoms under the influence of the surface, in terms of $^3\text{He}$ adsorption and permeation properties, respectively.

A. Basic Equations

Consider a sample of $N$ $^3\text{He}$ atoms in a container of volume $V$ and surface area $A$. The relatively small number $n$ of these atoms in interaction with the container surface at any time can be regarded as continually interchanging at the rate $n/t_s$ with atoms of the bulk gas. If $T_s$ is the characteristic relaxation time for the atoms under the influence of the surface, then the rate equations describing the relaxation process are
a) \( \frac{dn_+}{dt} = -\frac{1}{2T_s} (n_+ - n_-) - \frac{1}{Nt_s} (n_{+N} - n_{-N}) \)

(1)

b) \( \frac{dN_+}{dt} = \frac{1}{Nt_s} (n_{+N} - n_{-N}) \),

where the intrinsic relaxation in the bulk gas and the small population difference due to the thermal Boltzmann factor are neglected. \( N_+ \) and \( N_- \) are the numbers of \( ^3\)He atoms in the gas with magnetic quantum numbers \( m = +\frac{1}{2} \) and \( -\frac{1}{2} \), respectively; \( n_+ \) and \( n_- \) are the corresponding quantities for the atoms interacting with the surface.

Equations 1 can be rewritten in terms of the gas and surface atom polarizations, \( P = (N_+ - N_-)/N \) and \( p = (n_+ - n_-)/n \), using \( N_+ + N_- = N \) and \( n_+ + n_- = n \):

a) \( \frac{dp}{dt} = -(1/T_s + 1/t_s_p) p + P/t_s \)

(2)

b) \( \frac{dP}{dt} = n/Nt_s (p - P) \)

The solutions of Equations 2 are the form \( P = \alpha_i \exp(-\lambda_i t) \) and \( p = \beta_i \exp(-\lambda_i t) \). Using \( n < < N \), the rate constants \( \lambda_i \) are

a) \( \lambda_1 = 1/T_s + 1/t_s + n/Nt_s \)

(3)

b) \( \lambda_2 = n/N(t_s + T_s) \)
The decay to zero of the observable polarization $P$ from its initial value is characterized by the slower rate $\lambda_2$. Thus

$$T_1 = \frac{N}{n}(t_s + T_s) \quad \text{for } n \ll N.$$  

This expression for $T_1$ has been derived without reference to a specific atom-surface interaction and is therefore a suitable point of departure for the discussion of particular models of surface relaxation. The quantities $N/n$, $t_s$ and $T_s$ will depend on the details of the atom-surface interaction. With suitable approximations these quantities can be estimated for surface relaxation involving adsorption and permeation of $\text{He}^3$.

B. Adsorption-Controlled Relaxation

Helium is known to adsorb on glass surfaces with an energy of adsorption $E \approx 0.01 \text{ eV}^{14) \text{.}}$ Frenkel showed that the sticking time per collision is related to $E$ by the expression $t_s = t_s^0 \exp(E/KT)$, where $t_s^0 \approx 10^{-13}$ seconds, $T$ is the absolute temperature and $K$ is Boltzmann's constant$^{15) \text{.}}$. At very high temperatures $t_s \approx t_s^0 \approx 10^{-13}$ seconds, corresponding roughly to simple reflection of the incident gas atoms at the surface.

The number $n$ of gas atoms adsorbed at any instant is just the product of $t_s$ and the rate at which atoms strike the wall,
\[ n = \left( \frac{\bar{v}A}{4V} \right) t_s \]

where \( \bar{v} \) is the mean thermal velocity of the He\(^3\) atoms\(^{16}\).

One can say very little about the relaxation time \( T_s \) for adsorbed atoms. Relaxation is presumably induced by paramagnetic centers on or near the container surface, but their nature, density and exact locations are unknown. However, we may reasonably expect that \( T_s \gg t_s \) at the temperatures of interest, because \( t_s \) is very short; much shorter than typical nuclear relaxation times in highly paramagnetic substances\(^{17}\). In this limit \( T_s \) can be expressed in terms of the probability \( W \approx (E_i t_s/\hbar)^2 \) of a nuclear spin flip per collision with the surface, where \( E_i \) is the average magnetic interaction energy during the atom-surface interaction. The result is \( T_s = t_s/2W \)\(^{18}\).

Substituting the expressions for \( T_s \), \( t_s \) and \( n \) into Equation 4, the He\(^3\) adsorption-controlled relaxation time \( T_{1A} \) is

\[
T_{1A} = \frac{2V/Av}{\bar{v}} \left( \frac{\hbar}{E_i t_s^0} \right)^2 \exp(-2E/\kappa T)
\]

under the assumption \( T_s \gg t_s \). (Note that the opposite limit, \( T_s \ll t_s \), leads, independent of \( T_s \), to \( T_{1A} = 2V/Av \), in violent disagreement with the experimental behavior described in Section III.)
The form of $T_{1A}$ suggests that a plot of $\ln(T_{1A}/T_{1})$ versus $1/RT$ should be linear with slope $-2E$. Figure 7 is such a plot of the low temperature $T_1$ data for pyrex surfaces, taken from Figure 4. The data for each of the three samples separately exhibit the predicted linear behavior and, averaging the slopes for the three cases, the adsorption energy is about 0.01 eV with an uncertainty of roughly 0.003 eV. This is quite close to the published experimental values for helium adsorption onto pyrex which lie between about 0.01 and 0.015 eV$^{14}$.

The expression for $T_{1A}$ is based on the assumed existence of local magnetic fields associated with the surface. These fields presumably arise from paramagnetic centers on or near the surface. From a naive point of view, a surface may be pictured as resulting from the cleavage of the bulk material and thus could be paramagnetic due to the unpaired chemical bonds. On the other hand, surfaces are rarely clean as evidenced by the copious out-gassing when heated under vacuum, and the nature of the surface paramagnetic centers is unknown. Thus the observed magnetic field dependence of $T_1$, which is attributable to the detailed nature of the surface paramagnetic centers, is presently beyond the scope of this investigation.
Figure 7  The $\bullet$, $\circ$, and $\triangle$ points correspond to the low temperature pyrex data shown in Figure 4, Curves 1, 2 and 3.
C. Permeation-Controlled Surface Relaxation

It is well-known that at moderate temperatures helium readily permeates fused quartz and glasses of high SiO₂ content. The maximum in the surface-induced He³ relaxation time at about 125°K and its rapid decline at higher temperatures, for quartz and pyrex surfaces, suggest the onset of a permeation-controlled relaxation mechanism²⁰. The solubility of helium, as well as its permeation and diffusion characteristics, have been well-established by previous work and may be used to evaluate n and tₛ in Equation 4¹¹,¹².

As before, the rate at which atoms dissolved in the glass exchange with atoms impinging on the surface from the gas is n/tₛ. In this case, n is identified as the number of atoms dissolved within an average diffusion jump distance ⟨Δx⟩ of the surface. The characteristic exchange, or sticking, time in the assumed model is tₛ ≈ αζ, where ζ is the mean time between diffusive jumps for a dissolved He³ atom, and α ≈ 6 is a geometric factor required because the dissolved He³ atoms may jump in directions other than toward the surface. ζ and ⟨Δx⟩ are related through the known diffusion coefficient D of helium in the glass of interest, D = ⟨Δx²⟩ /6ζ. For diffusion with activation
energy \( Q, \zeta = \zeta_0 \exp(Q/\kT) \), where \( \zeta_0 \) is a constant for a given glass.

The solubility \( S \) of helium in all the glasses used in the present experiments has been determined by previous workers. \( S \) is characteristically temperature independent, suggesting that the heat of solution for helium is very low, and therefore that the activation energies for permeation and diffusion are approximately equal. The solubilities and diffusion activation energies for the glasses of interest are shown in Table II, as are the values for \( \zeta_0 \) for an assumed jump distance \( \langle \Delta x \rangle \) of about 3\( \AA \) (roughly the spacing between the "holes" in the quartz lattice).

In terms of \( S \), the number of dissolved atoms within a diffusion jump distance of the surface is

\[
n = SA \langle \Delta x \rangle \frac{NKT}{V}
\]

Substituting for \( n \) and \( t_s \) in Equation 4 yields the expression for diffusion, or permeation, controlled relaxation,

\[
T_{lp} = \frac{V/A \langle \Delta x \rangle}{SKT}[T_s + \zeta_0 \exp(Q/\kT)]
\]

where \( t_s = \zeta_0 \exp(Q/\kT) \) and \( T_s \) is the characteristic nuclear spin relaxation time for the \( \text{He}^3 \) atoms dissolved in the glass. For this case, the relative values of \( T_s \) and \( t_s \) are uncertain. It is nevertheless tempting to attribute the
Table II

Solubilities $S$, diffusion activation energies $Q$, and $\tau_0$ for glasses studied in this experiment.

<table>
<thead>
<tr>
<th></th>
<th>SiO$_2$</th>
<th>Pyrex</th>
<th>Aluminosilicate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S$ (CC-STP/CC-Atmos pres)</td>
<td>0.01</td>
<td>0.0056</td>
<td>0.0016</td>
</tr>
<tr>
<td>(He atom/CC-mm Hg)</td>
<td>$3.5 \times 10^{14}$</td>
<td>$2.0 \times 10^{14}$</td>
<td>$5.6 \times 10^{13}$</td>
</tr>
<tr>
<td>$Q$ (cal/mole)</td>
<td>4800</td>
<td>6400</td>
<td>12,000</td>
</tr>
<tr>
<td>ev</td>
<td>0.21</td>
<td>0.28</td>
<td>0.523</td>
</tr>
<tr>
<td>$\tau_0$ (seconds)</td>
<td>$3 \times 10^{-10}$</td>
<td>$3 \times 10^{-12}$</td>
<td>-----</td>
</tr>
</tbody>
</table>

Ref. V. O. Altemose, *Helium Diffusion through Glass*  
rapid decline of $T_1$ above 125°K, observed for pyrex and fused quartz surfaces, to the exponential term in the expression for $T_{1p}$. Indeed, the much shorter relaxation times observed for fused quartz in comparison to pyrex surfaces are consistent with the greater permeability of quartz to helium. This possible interpretation can be explored by assuming $T_s < t_s$, and plotting $\ln(TT_1)$ versus $1/KT$ to extract a value for $Q$. The result for pyrex is a straight line yielding $Q \approx 0.05$ eV, which is roughly 5.5 times less than the reported diffusion activation energy for helium in pyrex. This may reflect the fact that reported values of $Q$ are characteristic of diffusion through the bulk glass, while it is predominantly diffusion within a few atomic distances of the surface that determines $T_{1p}$. Since the glass surface may reasonably be expected to have chemical composition and structure properties that are somewhat different from the bulk glass, the factor of 5.5 is not surprising. On the other hand, the assumption that $T_s < t_s$ is certainly open to question, particularly in view of the observed magnetic field dependence of $T_1$ for pyrex surfaces at high temperatures shown in Figure 6. While an explanation of this effect is beyond the scope of the model presented here, it might reasonably be attributed, through $T_s$, to the relaxation properties of the surface paramagnetic centers.
In summary, the prediction of the model for the overall dependence of $T_1$ on temperature for the case of pyrex and quartz surfaces is

$$T_1^{-1} = T_{1A}^{-1} + T_{1P}^{-1},$$

suggesting a relaxation time maximum at intermediate temperatures in agreement with the experimental results of Section III. In principle, the expressions for $T_{1A}$ and $T_{1P}$ can be used to make quantitative estimates of the surface-induced relaxation time. However, the reliability of such estimates would be questionable because many of the quantities determining $T_1$ are not well-known. For example, the surface area $A$ should be considered the microscopic surface area available to the $\text{He}^3$ atoms and this is not known. Furthermore, the nature and surface density of the paramagnetic centers, as well as the motion relative to these centers of the $\text{He}^3$ atoms, is uncertain. Thus quantitative estimates of $T_1$ would require several a priori assumptions concerning the details of the $\text{He}^3$ surface interaction. On the other hand, the qualitative behavior of $T_1$ with respect to temperature and surface permeability has been determined without detailed knowledge of the $\text{He}^3$-surface interaction, and this is, in fact, a favorable aspect of the model.
V. Conclusions

The surface-induced He\(^3\) nuclear spin relaxation time was measured as a function of temperature for pyrex, quartz and aluminosilicate surfaces. The observed reproducible temperature dependence is interpreted in terms of two surface relaxation mechanisms. The first, or low temperature mechanism, involves the adsorption of the He\(^3\) atoms onto the surface where the adsorbed atoms are relaxed by some, as yet unknown, magnetic coupling with the surface and the continuous exchange of these adsorbed atoms with the gas. The second, or high temperature mechanism, in the case of pyrex and quartz, involves the permeative exchange of the atoms dissolved in the glass and the atoms in the gas; again, the dissolved atoms are relaxed by some unknown magnetic interaction. The temperature dependence of the adsorption model can be estimated without detailed knowledge of the coupling between the He\(^3\) nucleus and the glass and it is shown that good agreement exists between experiment and theory in terms of the known adsorption energies. Although the temperature dependence of the permeation model cannot be reliably estimated, the usefulness of this model was demonstrated by the fact that the relaxation time changes in a manner consistent with the model as the permeability of the
surface material to helium is changed.

Of the samples contained in the impermeable glass (Corning 1720 and 1723 aluminosilicates), more than half exhibited relaxation times longer than $10^5$ seconds at room temperature; for these samples only a lower limit is established for the surface controlled relaxation times because magnetic gradient relaxation determines the measured $T_1$ in the apparatus for $T_1 \geq (1 \text{ to } 5) \times 10^5$ seconds. There is every indication that much longer relaxation times can be realized at higher temperatures in a magnetic environment where gradients are minimized.

These measurements suggest that surface-induced nuclear spin relaxation in gaseous $\text{He}^3$ can be suppressed to the extent desired by controlling the sample temperature and impermeable container materials. It is not unreasonable to expect that intrinsic $\text{He}^3$ spin relaxation times of the order of weeks to years (depending on sample density) can be achieved. Furthermore, such samples can be highly spin-polarized by optical pumping to yield appreciable macroscopic nuclear magnetizations even in low density $\text{He}^3$ gas. These properties should be useful in applications requiring very low friction gyroscopes (e.g. tests of Einstein's theory of relativity$^{19}$), search for a $\text{He}^3$ nuclear electric dipole moment$^2$).
Suppression of surface relaxation effects also opens new possibilities for producing sizeable nuclear polarizations in dense He\textsuperscript{3} gas. A number of years ago Bouchiat, Carver and Varnum attempted to polarize He\textsuperscript{3} gas at 50°C and 3 atmospheres pressure by spin exchange with optically pumped rubidium vapor\textsuperscript{3).} Though an effect was noted, the method failed to yield useful values of polarization because of the short-circuiting effect of He\textsuperscript{3} spin relaxation at the container walls. For these experiments $T_1$ was about $10^3$ seconds. It is estimated that with the much slower wall relaxation to be expected from impermeable container materials, a polarization of the order of 10% might now be possible by this method. Such estimates are based on the results of experimental measurements which reveal that the presence of rubidium on the walls does not significantly effect the very long relaxation times observed for alumino-silicate containers.
PART II

DIFFUSION STUDIES OF He(2^3S_1) IN GASEOUS HELIUM;

THE INTERACTION POTENTIAL AT LONG RANGE
PART II

DIFFUSION STUDIES OF He\(^{2\,3}S_1\) IN GASEOUS HELIUM;

THE INTERACTION POTENTIAL AT LONG RANGE

I. Introduction

The interaction potentials between helium atoms in the excited \(2\,3\,S_1\) state and the \(1\,S_0\) ground state have been the subject of considerable theoretical and experimental investigation. The interest in this interaction stems from the fact that both the \(3\Sigma_u^+\) and the \(3\Sigma_g^+\) molecular potential functions, though attractive at shorter range, exhibit repulsive barriers at intermediate nuclear separations.

This behavior was first predicted on theoretical grounds for the \(3\Sigma_u^+\) state by Buckingham and Dalgarno\(^{21}\). Their calculations indicated a binding minimum for an internuclear separation \(R\) of about \(2a_o\), and a repulsive maximum at \(R = 4a_o\) with a barrier height of 0.29 eV. The long range repulsive character of the interaction was attributed to the dominance over the Van der Waals attraction of the repulsive electron-exchange contribution to the interaction energy. Buckingham and Dalgarno also pointed out that the presence of the barrier would have the effect of reducing the diffusion coefficient of \(2\,3\,S_1\) atoms at low temperatures,
and would lead to a $2^3S_1 - 1^1S_0$ excitation-transfer cross section that falls off rapidly at low (thermal) energies in contrast to that expected for attractive interactions.

More sophisticated theoretical calculations of the $3^+ \Sigma^+_g,u$ molecular potentials in helium were undertaken by Matsen and co-workers (1961--)\(^{22,23,24}\). These calculations were intended to reconfirm the theoretical basis of the repulsive interaction and to accurately determine the interaction energies in the region of the potential maxima and minima. Their results have shown that both the $3^+ \Sigma^+_u$ and $3^+ \Sigma^+_g$ interactions have attractive minima near $2a_0$ with repulsive barriers in the neighborhood of $4.5a_0$. The predicted barrier heights have tended to decrease slightly as these calculations were improved, the latest estimate of the $3^+ \Sigma^+_u$ barrier height being about 0.14 eV.

Strong experimental evidence for the existence of the barrier was provided by Colegrove, Shearer, and Walters\(^4)\). They used an optical pumping technique on discharge-excited He\(^3\) to study excitation transfer in $2^3S_1 - 1^1S_0$ collisions, and found that the reaction rate falls off rapidly as the temperature is decreased below 300\(^0\)K. This is in qualitative agreement with the predictions of Buckingham and Dalgarno, though the measured rates are substantially larger than were predicted.
The present investigation was undertaken in an effort to determine the long-range interaction appropriate to the calculation of cross-section at thermal energies. The experimental study consisted of measuring the diffusion cross-section for triplet metastable helium atoms in helium gas over the temperature range of 1°K to 300°K. These results were compared with diffusion cross-sections calculated on the basis of assumed long-range repulsive potentials. The interaction potentials were parameterized in a manner consistent with the previous theoretical calculations, and the parameters were varied until the calculated and experimentally determined diffusion cross-sections were in agreement. As a check, the long-range repulsive interaction determined on the basis of the diffusion data was used to calculate total and excitation-transfer cross-sections and the results were found to be in excellent agreement with previous and independent experimental measurements.
II. Experimental Procedure

A conventional discharge after-glow technique is used to measure the temperature dependence of the diffusion coefficient of metastable $^3S_1$ helium atoms in helium gas. At low helium densities, the average lifetime of the discharge excited $^3S_1$ state is determined by their rates of diffusion to the container walls where de-excitation occurs.

The sample cleaning procedure is the same as described in Part I of this thesis. However, since the experimental diffusion coefficient depends on the sample density, the sample densities were carefully measured prior to sealing by using a liquid nitrogen trapped McLeod gauge and measuring the pressure three times at fifteen minute intervals to insure that the equilibrium density was being determined.

After each vessel had been filled to the desired He$^4$ density, the small filling tube connecting the bulb to the vacuum system was tipped off to yield a permanently sealed sample. Since the glass vessels must be heated locally in order to tip off the filling tube, there is a small systematic difference between the actual He$^4$ density in the closed bulb and the density measured prior to sealing. If
it is assumed that $1 \text{ cm}^2$ of the spherical surface ($80 \text{ cm}^2$ total area) is heated to a temperature of $1400^\circ \text{K}$ before the filling tube is closed, the average temperature of the entire bulb has been raised by roughly $15^\circ \text{K}$. This would correspond to a systematic decrease in the final density of the sample of no more than 5% below that measured prior to sealing. The above estimate is a realistic upper limit on the possible systematic error in the density because the filling tubes were small (roughly 4 mm O.D.) and were tipped off a short distance from the spherical surface. Since the actual error is not known and since an error of this magnitude does not significantly change the final conclusions, the experimental results have been analyzed on the basis of the density measured prior to sealing.

The experimental apparatus may be described briefly with reference to Figure 8. The external electrodes support the sample near the bottom of the inside dewar of a double dewar arrangement. Both dewars are provided with unsilvered strips to allow an optical path through the absorption cell. A weak discharge is ignited periodically in the sample by the application of a $100 \mu \text{sec}$ pulse of 200 KHz high voltage to the electrodes. At the end of the pulsed discharge, the $\text{He} (2^3 S_1)$ atom concentration was between $5 \times 10^9$ and $1 \times 10^{10}$
Figure 8  Apparatus for $\text{He}(^3S_1)$ diffusion measurements.
triplet metastable atoms per cm$^3$. The discharge repetition rate varied between 2 and 250 pulses per second depending upon sample density and temperature.

The He($^2S_1$) atoms are detected by monitoring the absorption of the 10,830 Å line emitted during $^2P-^2S$ transitions in a bright He$^4$ discharge lamp. The absorption of this radiation does not constitute a triplet metastable atom loss mechanism. The 10,830 Å line is separated from the radiation of the lamp by an interference filter, passed through the absorption cell and focused on a photo detector. The detector used was a silicon photo diode with a response time of 60μ seconds.

The periodic absorption signal was averaged over many signals (1000 to 2000) by the use of a P.A.R. Waveform Eductor resulting in a considerable enhancement of signal-to-noise. The averaged absorption signals were read out on an X-Y recorder and later plotted on semi-log paper to extract the characteristic decay time. The time base of each measurement was calibrated with a time-mark generator to better than 1%.

The sample temperature was controlled by immersing the glass bulb in various cryogenic fluids and pumping on the fluids through a vapor pressure regulator. The temperature
was determined by measuring the vapor pressure of the fluid with trapped mercury and oil manometers. The cryogenic fluids were Freon 12, liquid nitrogen, liquid hydrogen and liquid helium. In situations where liquid nitrogen was in the outer dewar, it was super-cooled to avoid bubbling in the optical path.

In experiments of this nature, the temperature of the gaseous sample is usually uncertain because of the periodic heating due to the discharge. This problem is of particular importance at low temperatures. The experimental results to be presented, the results at liquid helium temperatures in particular, were found to be independent of discharge pulse length over the range of 100μ seconds to 1000μ seconds. This indicates that there is no significant rise in the gas temperature due to the pulsed discharge. Quantitative estimates of the temperature rise were obtained from measurements of the power dissipated in one sample during continuous 200 KHz R.F. discharges at 4.2°K. These measurements were carried out by immersing a sample in liquid helium and measuring the liquid helium boil-off rates with and without a CW discharge. The discharge intensity was characterized by the equilibrium density of triplet metastable atoms. The results of measurements on a sample with a He\textsuperscript{4} density corresponding to 2.5 Torr at 300°K are shown in Figure 9.
Figure 9  Thermal power dissipated in gaseous sample of He$^4$ at 4.2$^\circ$K during R.F. discharge versus equilibrium He(2$^3$S$_1$) density. He$^4$ density corresponds to 2.5 torr at 300$^\circ$K. Sample volume 70 cc.
For metastable densities of the order of $10^{10}/\text{cm}^3$, the dissipated power is roughly $5\times10^{-3}$ watts and for a 100$\mu$s second pulsed discharge of this intensity the total energy per pulse could raise the gas temperature by no more than $10^{-2}$°K. The results shown in Figure 9 indicate that the dissipated power increases sharply with the triplet metastable density, and it is for this reason that particularly weak pulsed discharges were used in this experiment. Under the conditions of this experiment, it may be concluded that there is no significant difference between the $\text{He}^4$ gas temperature and the temperature of the cryogenic bath.
III. Experimental Results

At the instant the discharge excitation is removed, called the beginning of the after-glow, the $^3S_1$ metastable state population begins to change rapidly with time and ultimately decreases monotonically toward zero. As regards the He($^3S_1$) atoms, the after-glow time period can be separated into two parts characterized by different mechanisms for changing the triplet metastable atom concentration. In the first part, or early after-glow, the changes in the He($^3S_1$) concentration are due, for the most part, to the reactions:

$$\text{He}(2^1S_0) + e^- \rightarrow \text{He}(2^3S_1) + e^- + 0.8 \text{ eV}$$

and

$$\text{He}(2^3S_1) + \text{He}(2^3S_1) \rightarrow \text{He}(1^1S_0) + \text{He}^+ + e^-$$

Neither of the above reactions will lead to an exponential-ly decaying triplet metastable atom concentration$^{26})$. Furthermore, the effects of these reactions last for only a short time (typically a few milliseconds) and can be avoided by taking data in the late after-glow only. In the late after-glow, the He($^3S_1$) population is determined by the rate of diffusion of metastable atoms to the container walls, three body collisions involving two ground state
atoms and de-excitation during collisions with impurity atoms\(^{25,26}\). For this experiment, the sample densities were selected so that three body collisional de-excitation would be negligible compared to the diffusion loss mechanism. The sample impurity content is estimated to be less than 1 part in \(10^5\) and concentrations of this magnitude would not be expected to give rise to the observed He\((2^3S_1)\) lifetimes\(^ {27}\). Furthermore, the diffusion loss mechanism can be demonstrated by showing that sample density divided by the observed He\((2^3S_1)\) decay time is a constant. This would not be true for an impurity loss mechanism. Thus, in the late after-glow the He\((2^3S_1)\) concentration \(M\) obeys the relation

\[
\frac{dM}{dt} = D \nabla^2 M
\]

where \(D\) is the diffusion coefficient in \(\text{cm}^2/\text{sec}\). It is shown in Appendix I that under the conditions of this experiment, this equation may be solved to sufficient accuracy by requiring \(M(r_o,t) = 0\) where \(r_o\) is the inside radius of the spherical container. Assuming spherical symmetry the solution is

\[
M(r,t) = \sum_k \left( \frac{B_k}{r} \right) \sin\left( \frac{r}{\Lambda_k} \right) \exp\left( -\frac{Dt}{\Lambda_k^2} \right), \quad k = 1, 2, 3-\]
In the late after-flow only the fundamental diffusion mode (k = 1) is observed and the triplet metastable concentration is characterized by a single time constant 
\[ \tau = \left( \frac{\Lambda_1^2}{D} \right), \]  
where \( \Lambda_1 = \frac{r_0}{\pi} \) is the diffusion length.  
\[ \Lambda_1^2 = 0.61 \] for the samples used in this experiment. Figure 10 is a log plot of representative lifetime data, showing clearly the single-exponential \( 2^3S_1 \) decay in the late after-glow period.

The quantity \( DP \) (cm\(^2\)/sec)(density in units corresponding to a pressure of 1 torr at 300\(^\circ\)K) is shown as a function of the temperature in Figure 11. Figure 12 shows the low temperature data with an expanded temperature scale. The quantity \( DP \) is a constant to within \( \pm \) 5\% over the range of sample densities of 0.57, 1.5 and 2.5 torr at 300\(^\circ\)K. This confirms that diffusion is in fact the observed metastable loss mechanism. The uncertainty in \( DP \) at all temperatures is estimated to be \( \pm \) 5\%.

The result at 300\(^\circ\)K, \( DP = 490 \pm 25 \) (cm\(^2\)/sec)(torr), is in good agreement with the early measurements of Phelps\(^{26}\). However, the results at liquid helium temperatures are in gross disagreement with the values reported by Fugol and Pakhomov\(^{28}\). They have reported an anomalously large \( 2^3S_1 \) diffusion coefficient measured by similar techniques.
Figure 10  $\text{He}(2^3S_1)$ concentration versus time in after-glow of pulsed R.F. discharge. Curves 1, 2 and 3 correspond to sample densities of 2.5, 2.5 and 1.5 torr at 300°C and measurements made at 1.0, 3.0 and 1.5°C respectively.
Figure 11  Product He(2^3S_1) diffusion coefficient and helium gas density versus temperature.
Figure 12  \( \text{He}(2^3S_1) \) diffusion coefficient \( D \) and \( D_\text{x(density)} \) vs. temperature. Curves 1, 2 and 3 are for gas densities of 0.57, 1.5 and 2.5 torr at 300°K.
Their measurements are believed to be in error, either because of sample heating or because their data were taken too early in the after-glow period.

The theory of diffusion, as developed by Chapman and Enskog, relates the diffusion coefficient $D$ to the averaged diffusion cross-section $\bar{Q}_D(T)$ through the relations:

$$D = \frac{3kT}{16\pi M_NN_0}$$

where $\Omega_D$ is called the diffusion collision integral

$$\Omega_D = \left(\frac{kT}{2\pi M_r}\right)^{\frac{3}{2}} \bar{Q}_D(T)$$

with

$$\bar{Q}_D(T) = \int_0^\infty \exp(-g^2) Q_D(v) g^5 dg$$

$g = (M_r v^2/2kT)^{\frac{1}{2}}$, $k$ is Boltzmann's constant, $T$ the absolute temperature, $M_r$ the reduced mass or twice the proton mass, $N$ the gas density in atoms/cm$^3$ and $v$ the relative velocity in cm/sec. The averaged diffusion cross-section $\bar{Q}_D(T)$ will be the point of comparison between the experimental results shown in Figures 11 and 12 and the calculated diffusion cross-sections $Q_D(v)$ averaged over the distribution integral in Equation 9.
IV. Theory

The quantum mechanical treatment of collisions between atoms having identical nuclei has been given by Massey and Smith\(^{30}\). They employed the standard adiabatic approximation in which the electronic problem is solved first for all fixed nuclear separations. The relative nuclear motion is then determined by the electronic energies plus the nuclear coulomb repulsion. The two electronic states arising from the separated He\((2^3S_1)\) and He\((1^1S_0)\) atoms are the lowest \(3\Sigma^+_g\) and \(3\Sigma^+_u\) states of He\(_2\). The respective electronic wave functions are denoted by \(\chi(3\Sigma^+_g)\) and \(\chi(3\Sigma^+_u)\) and energies (including nuclear repulsion) by \(V_+(R)\) and \(V_-(R)\), where \(R\) designates the relative positions of the nuclei. In the case of He\(^{4}(^3S)\)-He\(^{4}(^1S)\) scattering, the total wave function must be symmetric with respect to interchange of the nuclei and, in this two-state approximation, the total wave function takes the form:

\[
\Psi^+(R) = \phi(R) + \tilde{\phi}(-R)
\]

where

\[
\phi(R) = \chi(3\Sigma^+_g)F_+(R) + \chi(3\Sigma^+_u)F_-(R)
\]

in which \(F_+(R)\) and \(F_-(R)\) represent the relative motion of the nuclei and, in the adiabatic approximation, are solutions
of the following uncoupled differential equations (atomic units are used throughout):

\[ \nabla^2_{R} F^\pm_+(R) + [k^2 - (2\mu/m)\nu^\pm_+(R)] F^\pm_+(R) = 0 \]

(11)

\[ \nabla^2_{R} F^\pm_-(R) + [k^2 - (2\mu/m)\nu^\pm_-(R)] F^\pm_-(R) = 0 \]

where \( \nabla^2_{R} \) is the Laplacian operator in the relative nuclear coordinate \( R \), \( \mu \) is the reduced mass of the helium nuclei, \( m \) is the mass of the electron and \( k/a_0 = \mu \nu/\hbar \), where \( \nu \) is the relative velocity. The solutions of Eqs. 11 represent the scattering process and for large \( R \) have the asymptotic form:

(12) \[ F^\pm_+(R) = \alpha^\pm_+ \left[ \exp(ikZ) + R^{-1} \exp(ikR) f^\pm_+(\theta) \right] \]

The coefficients \( \alpha^\pm_+ \) are determined by requiring that the incident \( \text{He}(2^3S_1) \) atoms be described by a plane wave of unit amplitude moving in the positive \( Z \) direction. The resulting asymptotic expression for the total wave function \( \Psi^+(R) \) yields the total scattering amplitude

(13) \[ f(\theta) = \frac{1}{2} \left[ f^+_+(\theta) + f^+_+(\pi - \theta) + f^-_-(\theta) - f^-_-(\pi - \theta) \right]. \]

The partial scattering amplitudes \( f^\pm_+(\theta) \) can be expressed in terms of the scattering phase shifts \( \eta^+_L \) and \( \eta^-_L \) appropriate to the interaction potentials \( V^+_+(R) \) and \( V^-_-(R) \) respectively:
\[ f_{\pm}(\theta) = \frac{1}{2i k} \sum_{L} (2L+1) (\exp 2i \eta_{L}^{\pm} - 1) P_{L}(\cos \theta) \]

The total and diffusion cross-sections are given by

\[ Q_{\text{total}} = 2\pi \int_{0}^{\pi} |f(\theta)|^2 \sin \theta \, d\theta = \frac{4\pi}{k^2} \sum_{L} (2L+1) \sin^2 \delta_{L} \]

\[ Q_{D} = 2\pi \int_{0}^{\pi} |f(\theta)|^2 (1-\cos \theta) \sin \theta \, d\theta 
= \frac{4\pi}{k^2} \sum_{L} (L+1) \sin^2 (\delta_{L+1} - \delta_{L}) \]

where \[ \delta_{L} = \eta_{L}^{+} \quad \delta_{L+1} = \eta_{L+1}^{-} \quad L \text{ even} \]
\[ \delta_{L} = \eta_{L}^{-} \quad \delta_{L+1} = \eta_{L+1}^{+} \quad L \text{ odd} \]

Equations 15 and 16 include the effects of nuclear symmetry and were used to calculate the scattering cross-sections; in particular the cross-sections at low energies where symmetry effects are important.

At high incident energies the amplitudes \( f_{+}(\theta) \) and \( f_{-}(\theta) \) are strongly peaked in the forward direction. In this case the cross terms in the scattering intensity may be neglected and \( |f(\theta)|^2 \) takes the following form independent of nuclear symmetry

\[ |f(\theta)|^2 = \frac{1}{4} \left\{ |f_{+}(\theta) + f_{-}(\theta)|^2 + |f_{+}(\pi - \theta) - f_{-}(\pi - \theta)|^2 \right\} \]
The first term on the right hand side of Equation (17) is interpreted as the direct elastic scattering of the incident metastable atoms from the target ground state atoms. By analogy with non-resonance transfer collisions, the second term or large angle contribution to the scattering intensity is interpreted as being due to the transfer of excitation between the projectile and target atoms. The second term, when integrated over all angles, is the excitation-transfer cross-section

\begin{equation}
Q_{\text{trans.}} = \frac{\pi}{k^2} \sum \frac{(2L+1)\sin^2 (\eta_L^+ - \eta_L^-)}{L}.
\end{equation}

In this approximation

\begin{equation}
Q_{\text{total}} = Q_{\text{elastic}} + Q_{\text{trans}}.
\end{equation}

where \( Q_{\text{elastic}} = \frac{2\pi}{k^2} \sum \frac{(2L+1)(\sin^2 \eta_L^+ + \sin^2 \eta_L^-)}{L} \)

The diffusion cross-section takes on the slightly simpler form

\begin{equation}
Q_D = \frac{2\pi}{k^2} \sum \frac{(L+1)[\sin^2 (\eta_L^+ - \eta_{L-1}^-) + \sin^2 (\eta_{L+1}^+ - \eta_L^-)]}{L}.
\end{equation}

These expressions were used to calculate cross-sections at high energies and the results were compared with expressions 15 and 16.
Calculation of the scattering phase shifts \( \eta^\pm_L \) and thus the cross-sections is straightforward provided the interaction potentials \( V_+(R) \) and \( V_-(R) \) are known. The most recent theoretical calculations of the \( \text{He}(2^3S_1) - \text{He}(1^1S_0) \) interaction have been carried out by Matsen and co-workers and their results are shown in Figure 13\(^2^{22,23,24} \). The qualitative features of the interaction \( V_-(R) \), the potential minima and repulsive maxima, were first predicted by Buckingham and Dalgarno (1952)\(^2^{21} \) and the existence of the repulsive interaction has been well established experimentally. The height and position of the repulsive barriers, 0.36 eV and 0.14 eV at 3.5 \( a_o \) and 4.5 \( a_o \) for \( V_+(R) \) and \( V_-(R) \), determined by Matsen and co-workers is considered to be the most accurate to date. In order to carry out calculations of the scattering cross-sections it was convenient to construct relatively simple analytic forms for \( V_+(R) \) and \( V_-(R) \). The interaction potentials are divided arbitrarily into short-range \( V_{SR}^\pm(R) \) and long-range \( V_{LR}^\pm(R) \) parts corresponding to \( R < R_o \) and \( R \geq R_o \), respectively. For this calculation a convenient choice of \( R_o \) was 6 \( a_o \). The short-range potential \( V_{SR}^-(R) \) was represented by a Morse potential joined to a repulsive Gaussian form centered at about 4\( a_o \); the position of the potential maximum suggested by Matsen et al. For all
Figure 13  He($2^3S_1$) - He($1^1S_0$) interaction potentials calculated by Greenawalt and Matsen, and Matsen and Scott; as adjusted by Klein, Greenawalt and Matsen.
the energies of interest in this investigation (i.e. \( T \leq 300^\circ K \)) the cross-sections were found to be quite insensitive to the detailed nature of the short-range potentials. This is not surprising, since for \( T = 300^\circ K \), the repulsive barrier is still five times greater than \( kT \) and quite broad, thus preventing the penetration of scattered waves into the short-range potential region. One might expect the occurrence of resonances due to the presence of quasi-bound states inside the barrier. Buckingham and Dalgarno discussed this point and indicated that such resonances would be extremely narrow. Because of the unimportance of the short-range potentials in this investigation, the detailed analytic forms are omitted. At \( R = R_o \), taken to be \( 6a_o \), the short-range potentials are joined smoothly onto the long-range potentials, which are represented as

\[
\begin{align*}
V_{L\!R}^- (R) &= \alpha R^2 \exp (-\beta R) - (C/R^6) \\
V_{L\!R}^+ (R) &= V_{L\!R}^+ (R) + \gamma \exp (-\zeta R)
\end{align*}
\]

(19) \[ R \geq R_o \]

These analytic forms were suggested by Buckingham and Dalgarno to be representative of their potentials for large nuclear separation. It was found that the potential \( V_{L\!R}^- \) as calculated by Matsen et al. could be represented in this manner also, but, in this case, the potential difference
(parameters $\mathfrak{r}$ and $\mathfrak{z}$) is uncertain. The Matsen group calculated the $^3\Sigma^+_g$ interaction twice, using first a 5 and then a 50 term wave function. Upon comparing these results with their estimate of the $^3\Sigma^+_u$ interaction in the long range region, it was found that their $v^{LR}_+$ (5 term) crosses the $v^{LR}_-$ at roughly $R = 7a_0$. On the other hand their $v^{LR}_+$ (50 term) does not exhibit this crossing. It was decided to represent the Matsen potentials in a non-crossing manner (i.e. Eqs. 19) and the parameters $\mathfrak{r}$ and $\mathfrak{z}$ were determined from the difference $v^{LR}_+$ (5 term) $-$ $v^{LR}_-$ at $R = 5$ and $6a_0$ (just before the curves cross). This does not significantly effect the calculation of diffusion and total cross-sections because, at long range, $V_+ - V_- \ll V_-$. However, the excitation-transfer cross-section is very sensitive to the difference between the two potentials $v^{LR}_\mathfrak{r}(R)$ and, since this difference is uncertain in the case of the Matsen et al. potentials, a meaningful comparison between experiment and theory is not possible. Table III contains the sets of parameters used to represent the potentials of both Buckingham and Dalgarno, and Matsen and co-workers.

Included in Eqs. 19 is a term $-C/R^6$ of the Van der Waals type. It is true that at quite large separations where dispersion forces are dominant, $C$ should correspond
Table III

Parameters, in atomic units, used in conjunction with Equation 19 for representing the theoretical predictions of Buckingham and Dalgarno, and Matsen and co-workers of the He(2$^3S_1$) – He(1$^1S_0$) interaction for nuclear separations greater than 6$\alpha_0$.

<table>
<thead>
<tr>
<th></th>
<th>Buckingham and Dalgarno</th>
<th>Matsen and co-workers</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>0.07117</td>
<td>0.0198</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1.125</td>
<td>0.89</td>
</tr>
<tr>
<td>$C$</td>
<td>0, 20, 30</td>
<td>0.00</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>10.307</td>
<td>1.54 $^\dagger$</td>
</tr>
<tr>
<td>$\Upsilon$</td>
<td>1.73</td>
<td>1.43 $^\ddagger$</td>
</tr>
</tbody>
</table>

* The calculations of Buckingham and Dalgarno did not include correlation effects and these authors suggested the addition of a Van der Waals term with a coefficient of the order of 20 a.u.. Later, Dalgarno and Kingston calculated this coefficient and found 30 a.u. $^{31}$. The calculations of Matsen et al. include some correlation effects but the amount is not known, and their potentials can be represented accurately with $C = 0$.

** Interaction potentials calculated by Greenawalt and Matsen, and Matsen and Scott; as adjusted by Klein, Greenawalt and Matsen $^{22,23,24}$.

$^\dagger$ See text for explanation of these two parameters.
to the correct Van der Waals coefficient, having a value of about 30 a.u. It should be emphasized, however, that at smaller separations, where atomic wave functions begin to overlap appreciably, the expressions for $V_{LR}^{\pm}(R)$ should be considered as a whole, and C loses its meaning as the Van der Waals constant. Thus if the cross-sections are found to depend most strongly on such intermediate nuclear separa-
tions, C should be taken as a free parameter, which if non-zero allows the potentials to become attractive at some large value of R. The effects of including a term of the Van der Waals type in the long-range potential functions have been examined and the results are discussed in Section V.
V. **Comparison Between Experiment and Theory**

The diffusion cross-sections \( Q_D(k) \) calculated for \( k^2 \) between 0.0125 and 20 are shown in Figure 14. Curve 1 results from the long range potentials determined by Matsen and co-workers. Curves 2, 3 and 4 result from the potentials calculated by Buckingham and Dalgarno with a term of the Van der Waals type included; the coefficient of this term was 0, 20 and 30 a.u. \( a_o^6 \) respectively. The remaining curves, labeled with the notation \( V_\beta (R = 6a_o) \); \( \beta \), are pertinent to the experimental results and will be discussed shortly.

The diffusion cross-sections in Figure 14 must be averaged over the distribution function in Equation 9 before comparing with the experimental results. Using the definitions of \( k \) and \( g \) (Equations 9 and 11), the distribution function may be written in terms of \( k^2 \). This function is plotted also in Figure 14 for the temperatures of 1°K and 300°K in order to indicate the spread in the distribution relative to the calculated cross-sections. The diffusion cross-sections can be expressed in the form

\[
Q_D(k) = \sum_i A_i \exp(-a_i k^2) + \text{(constant)}; \ i = 1, 2, 3 \text{ and } 4
\]

to within 1% for \( k^2 \) between 0.0125 and 20, and the integration can then be carried out directly. Expression 20 ex-
Figure 14. Diffusion cross-section \( \Omega_{\text{e}}(k) \) in \( a_0^2 \) and distribution function for 1 and 300\( ^\circ \)K (arbitrary units) versus \( k^2 \).
tends the calculated cross-sections at both high and low $k^2$. The averaged diffusion cross-section at 300°K is over estimated slightly due to this extrapolation; however, this error is estimated to be less than 5% and the error at 1°K to be less than 1%.

The averaged diffusion cross-sections are compared with the experimental results in Figure 15. The interaction potentials of Buckingham and Dalgarno, and Matsen and co-workers predict diffusion cross-sections that are substantially greater than observed experimentally. The curve labeled by .002;1.6 corresponds to the repulsive interaction potentials (Equations 19) with $V_\text{r}(R = 6a_o) = .002$ a.u. and $\beta = 1.6 a_o^{-1}$ and $C = 0$. This particular long range interaction (choice of parameters) predicts diffusion cross-sections that agree very well with experiment. The two remaining curves, labeled .002;1.4 and .002;1.8, are included as potentials that bound the experimental uncertainties and also to indicate the sensitivity of the diffusion cross-section to $\beta$.

The long range interaction potentials corresponding to these diffusion cross-sections are shown in Figure 16. The boundaries of the hatched region correspond to the experimental uncertainties. These calculations indicate that the
Figure 15  Comparison between experimentally measured (△) and calculated diffusion cross-sections versus temperature.

BD0 and BD30 correspond to Buckingham and Dalgarno potentials with Van der Waals coefficient equal to 0 and 30 a.u. resp.
Figure 16  \( \text{He}(2^3S_1) - \text{He}(1^1S_0) \) interaction at long range resulting in cross-sections shown in Figures 14, 15, 17 and 18. Hatched region designates range of potentials that are consistent with the experimental diffusion cross-sections.
actual $^3\Sigma_u^+$ interaction potential curve for $R \geq 6a_0$ must lie within the hatched region in order to be consistent with the experimentally observed diffusion cross-sections. The position and width of this region indicate a substantial discrepancy between the theoretically predicted potential curves and the potential curves that are consistent with experiment. This discrepancy is understandable since the theoretical calculations were not expected to be particularly accurate at the large nuclear separations that are of interest here.

If the long range interaction has been determined accurately, then cross-sections calculated on the basis of these potentials can be expected to agree favorably with other experimental measurements. Rothe, Neynaber and Trujillo have measured the total $\text{He}^3(2^3S_1) - \text{He}^1(1^1S_0)$ scattering cross-section, $Q_{\text{total}}$, at relative velocities in the range 1000-3300 m/sec. Their method was a beam-gas attenuation experiment and the precision of the measurements was quoted as $\pm 10\%$. The results of this experiment are compared with total cross-sections calculated on the basis of the .002;1.4, 1.6, and 1.8 potential functions in Figure 17. The .002;1.6 potential predicts cross-sections that are in excellent agreement with these measurements and, as
Figure 17  He($2^3S_1$) - He($1^1S_0$) total scattering cross-section versus relative velocity. Curves 1 and 2 result from the potentials of Matsen et al., and Buckingham and Dalgarno, curves 3, 4 and 5 from the parameterized potentials with $V_0(R_0) = 0.002$ and $\beta = 1.4, 1.6$ and 1.8 $a_0^{-1}$ respectively. Data points measured by Rothe, Neynaber and Trujillo (ref. 34).
before, the 0.02;1.4, 1.8 potentials bound the experimental uncertainties. The total cross-section calculated from the potentials of Matsen et al., and Buckingham and Dalgarno are shown for comparison.

The excitation-transfer cross-section, defined in Equation 18, is particularly interesting because of its sensitivity to the difference in the potentials $V^L_R(R) - V^L'_R(R)$ as well as their separate values. This difference is represented by $\mathcal{R} \exp(-\mathcal{C} R)$ and the parameters $\mathcal{R} = 1.54$ a.u. and $\mathcal{C} = 1.43$ are chosen from the work of Matsen et al. but, as discussed, do not actually represent their results. A comparison between the calculated and measured excitation-transfer cross-sections will be a consistency check on the potentials previously determined from the diffusion data, and a particular check on the magnitude of the potential difference. In Figure 18 the averaged product of relative velocity and metastability exchange cross-section, obtained by Colegrove, Scheider and Walters in a He$^3$ optical pumping experiment, are compared with the calculations using the $V^L_R(R_o) = 0.002$ a.u., $\beta = 1.6$ potential. A comparison is also shown with the results obtained using the potentials of Buckingham and Dalgarno. The indicated agreement confirms the initial choice of $\mathcal{R}$ and $\mathcal{C}$. 
Figure 18  $\text{He}^3(2\,S_1) - \text{He}^3(1\,S_0)$ metastability exchange rate versus temperature. Curve 1 results from the parameterized potentials .002;1.6 (see text), curve 2 from the potentials of Buckingham and Dalgarno.
For all practical purposes the $\text{He}(2^3S_1)$-$\text{He}(1^1S_0)$ repulsive interaction at long range has been determined to an accuracy sufficient for the calculation of cross-sections appropriate to thermal energies. However, the effects of the Van der Waals force have been explicitly ignored since the $V^\text{LR}_-(R = 6a_0)$ potentials approach zero from a positive value at large $R$. It is generally agreed that this interaction must become attractive again at some very large nuclear separation due to the Van der Waals force. In the neighborhood of $2^\circ K$ the experimental diffusion cross-section appears to be roughly independent of temperature. This suggests that the repulsive interaction is cut off at large nuclear separations; perhaps by the Van der Waals interaction. The effects of adding a term of the form $(-C/R^6)$ to the repulsive interaction were studied and the results for the $0.002;1.4$ interaction are shown in Figure 19. This particular interaction is of interest because the net potential function tends toward the $0.002;1.6$ potential for $R$ between 6 and 9 $a_0$ as $C$ is increased, and thus the high temperature diffusion cross-sections are reproduced. The parameter $C$ should not be interpreted as the true Van der Waals coefficient, but rather is a term added on physical grounds in order to allow the potentials to have the expected weakly attractive behavior at very large nuclear separations.
Figure 19  The effect on the diffusion cross-section $Q_D(k)$ of adding a Van der Waals term ($-C/R^6$) to the .002;1.4 repulsive potential.
Increasing $C$ from zero has the expected effect of decreasing the low energy diffusion cross-sections and reducing the temperature dependence. However, as $C$ is increased further, this trend reverses and the diffusion cross-section becomes very large at low energies. Simultaneous with the sharp increase in $Q_D(k)$, the $L = 0$ phase shift goes through a multipole of $\pi/2$ suggesting that the shallow attractive potential well created by the Van der Waals term can support a bound state. Interaction potentials in the region of the Van der Waals potential well are shown in Figure 20. An approximate analysis of attractive potentials of this type (Appendix II) shows that the criteria for a bound state is roughly:

\[(21) \quad \frac{C}{R_1^4} \geq 3 \times 10^{-3} \text{ a.u. } a_o^2\]

where $R_1$ is the nuclear separation at which the potential energy goes through zero. In all cases the sharp changes in the low energy diffusion cross-section occurred with the passage of $n_o$ through a multiple of $\pi/2$ and were consistent with (21). This suggests that the observed variation of $Q_D(k)$ at low energies is the result of a bound state in the long range attractive well.

The experimental diffusion data are consistent with the addition of a term of the Van der Waals type to the long
Figure 20  Attractive potential well in the $\text{He}(^3S_1) - \text{He}(^1S_0)$ interaction at long range due to Van der Waals attraction. Van der Waals coefficient in a.u. $a_0^6$. 

$V(R)$ in $10^{-6}$ a.u. 

$R(a_0)$ 

$C = 0$ 

$C = 10$ 

$C = 20$ 

$C = 30$
range interaction. However, the data are not extensive enough nor is this analysis of the proper nature to accurately determine the Van der Waals coefficient. It is indeed surprising to note that a bound state could exist at large nuclear separations; particularly since the conditions for a bound state seem to be fulfilled when C is of the order of the previous estimates of the Van der Waals coefficient\textsuperscript{31}. 
Summary and Conclusions

The He(2\(^3S_1\)) - He(1\(^1S_0\)) interaction has been investigated for nuclear separations in excess of 6\(a_0\). The repulsive interaction potentials corresponding to the \(3\Sigma_g^+\) and \(3\Sigma_u^+\) molecular symmetries were expressed in terms of parametric functions that exhibit the qualitative features of the previous theoretical predictions of this interaction. The parameters were varied until the calculated diffusion cross-sections were in agreement with the experimentally measured values over the range of temperature of 1\(^\circ\)K to 300\(^\circ\)K. It was then shown that the resulting repulsive potential functions predict total and excitation-transfer cross-sections in agreement with previous and independent experimental measurements. The results of this investigation are summarized in Figure 21 in which the cross-sections \(Q_D\), \(Q_{\text{total}}\), \(Q_{\text{elastic}}\) and \(Q_{\text{trans}}\) are shown for \(k^2\) between 0.0125 and 10. All these cross-sections have been calculated on the basis of the .002;1.6 repulsive long range interaction (see text), and are in good agreement with the presently available experimental data.

While such a procedure cannot be expected to give a unique determination of the interaction potentials, it has been possible to demonstrate that the previous theoretical
Figure 21  Cross-sections calculated on the basis of the He(2^3S_1) - He(1^1S_0) interaction that best fits the experimentally measured diffusion cross-section between the temperatures of 1^0K and 300^0K.
results have substantially overestimated this repulsive interaction in the long-range region. This investigation indicates that the interaction potential remains repulsive for nuclear separations as large as 9.5 to 10 \( a_0 \). Beyond this a weak attractive character, due to the Van der Waals force, is more consistent with the lowest temperature diffusion measurements. This analysis cannot yield a definite value of the Van der Waals coefficient; however, it was noted that a Van der Waals coefficient in the range of the previous theoretical estimates may result in a long-range attractive potential well that can support a bound state.
Appendix I

In Part II - Section II the experimentally observed He($2^3S_1$) lifetimes are related to the diffusion coefficient D by solving the diffusion equation. The relation

$$D = \frac{\mathcal{L}^2}{\tau},$$

where $\tau$ is the measured lifetime, and the diffusion length $\mathcal{L}^2 = (r_o/\pi)^2$, with $r_o$ the inside radius of the spherical containers, results from requiring the He($2^3S_1$) concentration $M(r,t)$ to be zero at the walls. The boundary condition $M(r_o,t) = 0$ is not strictly correct, although, as will be shown, in most cases its use introduces a negligible error. The physically correct condition is a requirement on the behavior of the diffusion flux at $r_o$. If the He($2^3S_1$) atom-wall collisions were 100% effective in de-excitation of the metastable atoms, then the proper restriction is that the diffusion flux in the negative radial direction be zero at the surface. This has the effect of changing the diffusion length in a manner equivalent to changing $r_o$ to $r_o + \Delta$, where $\Delta$ is of the order of a mean free path $\lambda$.

For the sample pressures in this experiment $\lambda/r_o \ll 1$ and the error is negligible. However, the probability of de-excitation during a wall collision may not be unity and this could effect the interpretation of the experimental
measurements. For reflective walls, the boundary condition is

\[ \left| J_-(r_o) \right| / \left| J_+(r_o) \right| = R \quad \text{the reflection} \]

coefficient with

\[ J_-(r) = [M(r,t) \bar{v}/4 + (\bar{v}/6) \text{d}M/\text{dr}] \quad (-\hat{r}) \]

\[ J_+(r) = [M(r,t) \bar{v}/4 - (\bar{v}/6) \text{d}M/\text{dr}] \quad (+\hat{r}) \]

and

\[ J(r,t) = J_+ + J_- = -\bar{v}/3 \text{d}M/\text{dr} = -D \text{d}M/\text{dr} . \]

In the fundamental diffusion mode (with spherical symmetry)

\[ M(r,t) = B/r \sin(r/\lambda) \exp(-Dt/\lambda^2) . \]

Using the above solution and imposing the boundary conditions it follows that

\[ \tan(r_o/\lambda) = \frac{-(\lambda/3\lambda)(1+R)}{(1-R)/2-\lambda(1+R)/3r_o} . \]

The right hand side may be expanded to first order in \( \lambda/r_o \) and the result is

\[ \tan(r_o/\lambda) = -[2\lambda(1+R)/3r_o(1-R)] \frac{r_o}{\lambda} . \]

The expansion is valid provided the term in the brackets is small and, if this is true, \( r_o/\lambda = \pi-\delta \) where \( \delta \) is also much less than \( 1 \). In this case \( \tan(\pi-\delta) \approx -\delta \), and
\[ \delta = \left[ \frac{2\lambda (1+R)}{3 \gamma_0 (1-R)} \right] (\pi-\delta) \]

and the diffusion length becomes

\[ (1/\mathcal{L})^2 = (1/\mathcal{L}_1)^2 \left[ 1-4\lambda (1+R)/3r_0 (1-R) \right] \]

where \( \mathcal{L}_1 \) is the diffusion length with the boundary condition \( M(r_0,t) = 0 \). The lowest experimental helium density was 0.57 torr at room temperature and, using the total cross-section as measured by Rothe et al., the mean free path at room temperature is roughly \( 3.0 \times 10^{-3} \) cm. \( r_0 \) is about 2.5 cm. Thus in order for the effects of reflections at the walls to constitute a 5% error in \( D \) over the \( M(r_0,t) = 0 \) boundary condition, \( R \) would have to be greater than 0.94. This is considered to be an unreasonably high reflection coefficient and it may be concluded that the effects of reflections are unimportant. Although the actual reflection coefficient is not known, if such effects were important, they would increase the discrepancy between the previous theoretical calculations and experimental measurements of diffusion cross-sections.
Appendix II

The existence of bound states in weakly attractive potentials has been of considerable interest in the past. In particular Kilpatrick, Keller and Hammel have considered the He-He ground state interaction from the point of view of calculating second virial coefficients\(^{35}\). This interaction is essentially a hard core repulsion with a long-range attractive well due to the Van der Waals force. They find that agreement with the experimental data can be achieved with any one of a small group of similar potentials. Some of these interaction potentials can support a bound state; however, the second virial coefficient is insensitive to the existence of stationary states in this case and thus the question of whether the He-He interaction has a low-lying discrete level is still open. It is of interest to note that the He\(^3\)-He\(^3\) interaction cannot support a bound state due to the smaller reduced-mass of the system. A similar weakly attractive potential occurs when the Van der Waals force is added to the long-range repulsive He\((2^3S_1)\)-He\((1^1S_0)\) interaction. Although the nuclear separations of interest are greater than in the He-He ground state interaction, the potential minima are comparable due to the
larger electric polarizability of the He(2^3S_1) atom. Since the diffusion cross-sections calculated in Part II indicate the presence of a bound state at reasonable values of the Van der Waals coefficient, it is reasonable to consider this problem from the stationary state point of view in order to determine a criteria for the existence of bound states. Due to the sharp decrease of the long-range repulsive interaction, Figure 20, this weak attractive interaction can be approximated by a hard core repulsive barrier plus an additional \(-C/R^6\) attraction. After separating Schroedinger's equation in spherical coordinates and assuming the angular momentum is zero \((L = 0)\), we desire the solution to the differential equation for the radial wave function \(\psi(R)\):

\[
A(1) \quad (-\hbar^2 / 2m) \frac{d^2 U(R)}{dR^2} - \left(\frac{C}{R^6}\right) U(R) = E U(R)
\]

with \(\psi(R) = U(R)/R\)

Tabulated solutions of Equation A(1) are not available. However, a reasonably equivalent problem can be constructed if

\[
A(2) \quad -\frac{C}{R^6} \rightarrow -A \exp(-aR)
\]

with the equivalence conditions
\[ A(3) \quad C/R_1^6 = A \exp(-aR_1) \quad \text{and} \quad \int_{R_1}^{\infty} C/R^6 dR = \int_{R_1}^{\infty} A \exp(-aR) dR. \]

\( R_1 \) is the nuclear separation at which the potential goes through zero. The equivalence conditions result in

\[ A(4) \quad a = 5/R_1 \quad \text{and} \quad A = (C \exp 5)/R_1^6 \]

Using the transformation of variables

\[ Z = (2/a) \left(2mA/h^2\right)^{1/2} \exp(-aR/2), \] Equation A(1) may be written in the form:

\[ A(5) \quad d^2U(Z)/dZ^2 + (1/Z) dU(Z)/dZ + \left[1+(2/a)^2 \left(2mE/h^2\right) (1/Z)\right] U(Z) = 0 \]

The solutions of A(5) are Bessel functions. Applying the boundary conditions: \( U(R) \to 0 \) as \( R \to \infty \) or \( U(Z) \to 0 \) as \( Z \to 0 \) and \( U(R) = 0 \) at \( R \leq R_1 \) or \( U(Z) = 0 \) at \( Z \geq Z_1 \), \( (2/a) \left(2mA/h^2\right)^{1/2} \exp(-aR_1/2) \), then the solutions are \( J_v(Z) \) where the index

\[ A(6) \quad v = -(2/a)^2 \left(2mE/h^2\right). \]

For bound states \( E \leq 0 \). Thus the criteria for a bound state is that \( Z_1 \) is large enough for at least one solution of A(5) to have a positive index, or, in other words, \( Z_1 \) is greater than the first zero of \( J_0(Z) \) which is roughly \( Z = 2.4 \). Using the definition of \( Z \), the criteria for the
existence of a bound state is

$$A(7) \quad (2/5) \frac{2}{R_1} (2mC/h^2R_1^6) \geq 5.74 \text{ erg cm}^2$$

and in atomic units this becomes

$$A(8) \quad \frac{C}{R_1^4} \geq 4.9 \times 10^{-3} \text{ a.u. } a_o^2$$

This criteria for a bound state is based on the approximations discussed and as such can be expected to give only approximate results. A comparison of Equation A(8) with the theoretical results of Kilpatrick, Keller, and Hammel, Table AI, indicates that the number on the right-hand-side of this expression should be more like $2.9 \times 10^{-3} \text{ a.u. } a_o^2$. This probably results from the fact that the $-C/R_1^6$ potential is of somewhat longer range than the exponential equivalent as given by Equations A(2) and A(3).
The He(1\(^1\)S\(_0\))–He(1\(^1\)S\(_0\)) potentials considered by Kilpatrick, Keller and Hammel are labeled MR1 through MR5 and are of exp-six type:

\[ V(r) = \frac{\epsilon}{(1-6/\alpha)} \left[ (6/\alpha) \exp \frac{\alpha}{1-r/r_m} - \left( \frac{r_m}{r} \right)^6 \right] . \]

\( \alpha \) determines the hardness of the core, \( \epsilon \) is the position of the potential at the minimum, and \( r_m \) is the position of the minimum. \( C \) is the Van der Waals coefficient and \( R_1 \) is the nuclear separation at which the potential goes through zero; both are determined indirectly.
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