Collisional excitation transfer between the potassium $4(2)P(3/2)$ and rubidium $5(2)P(1/2)$ levels.

Eugene S. Hrycyshyn

University of Windsor

Follow this and additional works at: https://scholar.uwindsor.ca/etd

Recommended Citation

Hrycyshyn, Eugene S., "Collisional excitation transfer between the potassium $4(2)P(3/2)$ and rubidium $5(2)P(1/2)$ levels." (1966). Electronic Theses and Dissertations. 6428.
https://scholar.uwindsor.ca/etd/6428

This online database contains the full-text of PhD dissertations and Masters' theses of University of Windsor students from 1954 forward. These documents are made available for personal study and research purposes only, in accordance with the Canadian Copyright Act and the Creative Commons license—CC BY-NC-ND (Attribution, Non-Commercial, No Derivative Works). Under this license, works must always be attributed to the copyright holder (original author), cannot be used for any commercial purposes, and may not be altered. Any other use would require the permission of the copyright holder. Students may inquire about withdrawing their dissertation and/or thesis from this database. For additional inquiries, please contact the repository administrator via email (scholarship@uwindsor.ca) or by telephone at 519-253-3000ext. 3208.
COLLISIONAL EXCITATION TRANSFER
BETWEEN THE POTASSIUM $4^2P_{3/2}$ AND RUBIDIUM $5^2P_{1/2}$ LEVELS

by

Eugene S. Hrycyshyn

A Thesis
Submitted to the Faculty of Graduate Studies through the Department of Physics in Partial Fulfillment of the Requirements for the Degree of Master of Science at the University of Windsor

Windsor, Ontario
1966
ABSTRACT

Sensitized fluorescence in rubidium vapour induced by inelastic collisions with excited potassium atoms was investigated in order to determine the cross sections for the inelastic collisions leading to excitation transfer between the resonance states of potassium and rubidium atoms. An absorption technique was used to determine the partial pressures of the rubidium and potassium vapours in the K - Rb mixture. The partial pressure of potassium was kept below 2 x 10^{-5} torr to prevent the imprisonment of the K resonance radiation. The collision cross section for the excitation transfer process \( Q_{21}' \) (\( K^2P_{3/2} \rightarrow Rb^2P_{1/2} \)) was found to be 5.7 \( \AA^2 \) and a comparison with the cross sections for Rb - Cs collisions indicates that the same type of interaction governs the energy transfer induced by Rb - Cs and K - Rb collisions.
ACKNOWLEDGMENTS

I would like to thank Dr. L. Krause for his guidance throughout the past year and for the hours spent in correction of the original manuscript.

Acknowledgments are due to Mr. W. Eberhart for his construction of the fluorescence cell and for the completion of many other tasks which constantly arose, to Mr. W. Grewe who manufactured the cryostat and other pieces of apparatus and to Mr. D. Cox who maintained the electronics equipment in top condition.

I am very grateful to Dr. B. Kibble who has offered valuable assistance and to Mr. D. McGillis who in the past year has given helpful suggestions and prepared some of the drawings for this thesis.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vii</td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. THEORETICAL</td>
<td>3</td>
</tr>
<tr>
<td>III. DESCRIPTION OF THE APPARATUS</td>
<td>9</td>
</tr>
<tr>
<td>IV. EXPERIMENTAL PROCEDURE</td>
<td>18</td>
</tr>
<tr>
<td>V. RESULTS AND DISCUSSION</td>
<td>22</td>
</tr>
<tr>
<td>(i) The Experimental Results</td>
<td>22</td>
</tr>
<tr>
<td>(ii) Discussion of the Results</td>
<td>29</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>36</td>
</tr>
<tr>
<td>VITA AUCTORIS</td>
<td>38</td>
</tr>
</tbody>
</table>
### LIST OF TABLES

<table>
<thead>
<tr>
<th></th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Preliminary Measurements of the Transmissions of the Filters</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>Extinction Coefficients in Pure Rubidium Vapour for the $7948 , \text{Å}$ Component</td>
<td>23-24</td>
</tr>
<tr>
<td>3</td>
<td>Extinction Coefficients in a K - Rb Mixture for the Rb $7948 , \text{Å}$ Resonance Line</td>
<td>25-26</td>
</tr>
<tr>
<td>4</td>
<td>Fluorescent Intensity Ratios in a K - Rb Mixture</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>Cross Sections for Inelastic Collisions between Unlike Alkali Atoms</td>
<td>32</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Energy Level Diagram showing Sensitized Fluorescence in Rb Induced by Collisions with K Atoms in their 4(^2)P(_3/2) States</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>Schematic Arrangement of the Apparatus</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>The Fluorescence Cell</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>Cell in Main Oven</td>
<td>13</td>
</tr>
<tr>
<td>5</td>
<td>The Temperature Controller</td>
<td>16</td>
</tr>
<tr>
<td>6</td>
<td>The Front Part of the Fluorescence Cell with the Ray Diagram of the Scheme Used in the Determinations of the Extinction Coefficients</td>
<td>20</td>
</tr>
<tr>
<td>7</td>
<td>The Variation with Density of the Extinction Coefficients for Pure Rubidium Vapour</td>
<td>27</td>
</tr>
<tr>
<td>8</td>
<td>The Variation with Temperature of the Extinction Coefficients for Pure Rubidium Vapour and for a Potassium-Rubidium Mixture</td>
<td>28</td>
</tr>
<tr>
<td>9</td>
<td>A Plot of the Intensity Ratio ( n_{21} ) Against the Partial Pressure of Rubidium</td>
<td>31</td>
</tr>
<tr>
<td>10</td>
<td>A Plot of the Cross Sections for Rb - Cs and K - Rb Collisions Against the Reciprocals of the Energy Defects Raised to the Power 2.1</td>
<td>35</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

When a mixture of potassium and rubidium vapour is irradiated with one component of the potassium or rubidium doublet, the fluorescent light will consist of the component present in the incident light (resonance fluorescence) as well as those components which arise as a result of transfer of excitation energy by collisions (sensitized fluorescence). R. W. Wood\textsuperscript{1,2} first observed sensitized fluorescence in pure sodium vapour and later, Wood and Mohler\textsuperscript{3} and Lochte-Holtgreven\textsuperscript{4} studied sodium-inert gas mixtures. Sensitized fluorescence in potassium, rubidium and their mixtures was studied by Thangaraj\textsuperscript{5} while Seiwert\textsuperscript{6}, Hoffmann and Seiwert\textsuperscript{7}, and Bunke and Seiwert\textsuperscript{8} investigated sodium, potassium and caesium respectively. All the above authors worked at high alkali vapour densities, where the resonance fluorescence is subject to multiple absorptions and re-emissions. This effect, known as radiation diffusion, radiation imprisonment or multiple scattering, in effect increases the lifetime of the excited state. Theoretical corrections have been made to account for radiation diffusion; Thangaraj\textsuperscript{5} employed Milne's\textsuperscript{9} theory and Seiwert\textsuperscript{10,11} adapted the theory of Holstein\textsuperscript{12}.

In recent years, experiments have been conducted at extremely low alkali vapour densities where diffusion of radiation is
virtually absent. Chapman and Krause\textsuperscript{13} studied both pure potassium and potassium-inert gas mixtures while Czajkowski and Krause\textsuperscript{14} investigated pure caesium cross sections followed by caesium-inert gas cross sections by Czajkowski, McGillis and Krause\textsuperscript{15}. Accurate results have also been obtained for pure rubidium and rubidium-inert gas systems by Rae and Krause\textsuperscript{16} and Pitre, Rae and Krause\textsuperscript{17} respectively.

Thus far, only one investigation dealing with a mixture of two metals at low vapour densities has been performed. Czajkowski, McGillis and Krause\textsuperscript{18} studied a rubidium-caesium mixture and obtained total cross sections for inelastic collisions between excited rubidium atoms and ground state caesium atoms. In the present investigation, a rubidium-potassium mixture was studied. In principle, the processes which can be observed may be represented by the following equation:

\begin{equation}
K(4^2P_j) + Rb(5^2S_{1/2}) \rightleftharpoons K(4^2S_{1/2}) + Rb(5^2P_j) + \Delta E,
\end{equation}

where \( J = 1/2 \) or \( 3/2 \) and \( \Delta E \) is the energy defect between a particular pair of \( 2P \) states in potassium and rubidium. For the forward process, the energy defect \( \Delta E \) is converted into relative kinetic energy of the colliding atoms, whereas in the reverse process, \( \Delta E \) is supplied by the colliding partners.
II. THEORETICAL

The processes that occur when the mixture of potassium and rubidium vapours is irradiated continuously with the K 7665 Å component are depicted in Fig. 1. The solid arrows denote the primary process which gives rise to sensitized fluorescence in rubidium, and the broken arrows show some of the secondary reactions by which sensitized fluorescence can also be produced.

The various reactions may be represented by the following equations:

\[ (2) \quad \text{K}(^{2}S_{1/2}) + h\nu_{2} \xrightarrow{s} \text{K}(^{2}P_{3/2}) \]

\[ (3) \quad \text{K}(^{2}P_{3/2}) + \text{Rb}(^{2}S_{1/2}) \xrightarrow{Z_{22'}} \text{K}(^{2}S_{1/2}) + \text{Rb}(^{2}P_{3/2}) \]

\[ (4) \quad \text{K}(^{2}P_{3/2}) + \text{Rb}(^{2}S_{1/2}) \xrightarrow{Z_{21'}} \text{K}(^{2}S_{1/2}) + \text{Rb}(^{2}P_{1/2}) \]

\[ (5) \quad \text{K}(^{2}P_{3/2}) \xrightarrow{(T_{2})^{-1}} \text{K}(^{2}S_{1/2}) + h\nu_{2} \]

\[ (6) \quad \text{Rb}(^{2}P_{3/2}) \xrightarrow{(T_{2}')^{-1}} \text{Rb}(^{2}S_{1/2}) + h\nu_{2} \]

\[ (7) \quad \text{Rb}(^{2}P_{1/2}) \xrightarrow{(T_{1}')^{-1}} \text{Rb}(^{2}S_{1/2}) + h\nu_{1} \]

\[ (8) \quad \text{K}(^{2}P_{3/2}) + \text{M}(^{2}S_{1/2}) \xrightarrow{Z_{21}} \text{K}(^{2}P_{1/2}) + \text{M}(^{2}S_{1/2}) \]
Fig. 1. Energy level diagram showing sensitized fluorescence in Rb induced by collisions with K atoms in their $4^2P_{3/2}$ states. The $s$ coefficient denotes excitation by the absorption of photons, the $(\tau)^{-1}$ coefficients refer to spontaneous radiative decay and the $Z$ coefficients to radiationless transfer of energy by inelastic collisions. The primary processes are represented by solid arrows.
where $s$ is the number of potassium atoms excited per second from the $4^2S_{1/2}$ to the $4^2P_{3/2}$ state, $M$ is either a potassium or rubidium atom in the ground state, $\tau_1$, $\tau_2$, $\tau_1'$, and $\tau_2'$ are the average lifetimes of the $4^2P_{1/2}$, $4^2P_{3/2}$, $5^2P_{1/2}$ and $5^2P_{3/2}$ states in potassium and rubidium respectively, and $Z_{22}'$, $Z_{21}'$, $Z_{21}$, $Z_{12}'$, and $Z_{11}'$ are collision numbers representing the numbers of collisions per excited atom per second which give rise to radiationless energy transfer.

Several of the above processes may be neglected because of their relatively small probability. At K pressures of $10^{-5}$ torr, the mixing of the two $4^2P$ levels by collisions produces a ratio of about $10^{-5}$ of sensitized-to-resonance fluorescent intensities. Thus, processes (8) and (9) are negligible as compared to (2) and (5), and processes (10) and (11) are negligible in comparison with (3) and (4).

It should be pointed out that processes leading to collisional mixing of the two $5^2P$ states of rubidium, represented by the collision numbers $Z_{12}'$ and $Z_{21}'$ in Fig. 1, are omitted in equations (2) - (11) since the ratio of sensitized-to-resonance fluorescent intensities of $10^{-6}$ at rubidium vapour pressures of $10^{-5}$ torr make the observation of these
events impossible.

If only the K 7665 Å component is used for excitation, this will result in optical excitation of the K$^2P_{3/2}$ level, spontaneous decay, and the primary collisional processes shown in Fig. 1. Assuming that the Rb - K vapour mixture exists in dynamic equilibrium, the following rate equations may be written:

\[
\frac{dN(4^2P_{3/2})}{dt} = s - N(4^2P_{3/2}) \left[ (\tau_2)^{-1} + Z_{22} + Z_{21} \right] = 0 ,
\]

\[
\frac{dN(5^2P_{3/2})}{dt} = Z_{22} N(4^2P_{3/2}) - (\tau_2')^{-1} N(5^2P_{3/2}) = 0 ,
\]

\[
\frac{dN(5^2P_{1/2})}{dt} = Z_{21} N(4^2P_{3/2}) - (\tau_1')^{-1} N(5^2P_{1/2}) = 0 ,
\]

where, for example, $N(4^2P_{3/2})$ denotes the density of $4^2P_{3/2}$ potassium atoms. Equations (13) and (14) yield:

\[
Z_{22}' = (\tau_2)^{-1} \mathcal{N}_{22}' \quad \text{and} \quad Z_{21}' = (\tau_2')^{-1} \mathcal{N}_{21}' ,
\]

where $\mathcal{N}_{22}'$ and $\mathcal{N}_{21}'$ represent the ratios of sensitized-to-resonance fluorescent intensities which are measured experimentally:

\[
\mathcal{N}_{22}' = \frac{I(7800 \ \text{Å})}{I(7665 \ \text{Å})} \quad \text{and} \quad \mathcal{N}_{21}' = \frac{I(7948 \ \text{Å})}{I(7665 \ \text{Å})} .
\]

If, instead, the K 7699 Å component is used for excitation, two further results are obtained:
\begin{align*}
(17) \quad Z_{12} &= (\tau_1)^{-1} \mathcal{N}_{12} \quad \text{and} \quad Z_{11} = (\tau_1)^{-1} \mathcal{N}_{11},
\end{align*}

where

\begin{align*}
(18) \quad \mathcal{N}_{12} &= \frac{I(7800 \text{ Å})}{I(7699 \text{ Å})} \quad \text{and} \quad \mathcal{N}_{11} = \frac{I(7948 \text{ Å})}{I(7699 \text{ Å})}.
\end{align*}

The reverse process, in which the rubidium atoms are initially excited and sensitized fluorescence in potassium results from collisional excitation, may also be observed. As in the previous case, similar expressions for the collision numbers are derived. Excitation with the Rb 7800 Å component yields:

\begin{align*}
(19) \quad Z_{22} &= (\tau_2')^{-1} \mathcal{N}_{22} \quad \text{and} \quad Z_{21} = (\tau_2')^{-1} \mathcal{N}_{21},
\end{align*}

where

\begin{align*}
(20) \quad \mathcal{N}_{22} &= \frac{I(7665 \text{ Å})}{I(7800 \text{ Å})} \quad \text{and} \quad \mathcal{N}_{21} = \frac{I(7699 \text{ Å})}{I(7800 \text{ Å})}.
\end{align*}

Excitation with the Rb 7948 Å component gives:

\begin{align*}
(21) \quad Z_{12} &= (\tau_1')^{-1} \mathcal{N}_{12} \quad \text{and} \quad Z_{11} = (\tau_1')^{-1} \mathcal{N}_{11},
\end{align*}

where

\begin{align*}
(22) \quad \mathcal{N}_{12} &= \frac{I(7665 \text{ Å})}{I(7948 \text{ Å})} \quad \text{and} \quad \mathcal{N}_{11} = \frac{I(7699 \text{ Å})}{I(7948 \text{ Å})}.
\end{align*}

By analogy with the gas kinetic cross section, the average total cross section for inelastic collisions leading to excitation transfer
from one alkali atom in state 'a' to another in state 'b', may be defined as

\[
Q_{ab} = \frac{Z_{ab}}{N_0 V_r},
\]

where \(N_0\) is the density of the ground state atoms belonging to the species which is not being excited and \(V_r\) is the average relative velocity of the two colliding atoms given by

\[
V_r = \sqrt{\frac{8kT}{\pi \mu}}.
\]

\(k\) is the Boltzmann constant, \(T\) the absolute temperature, and \(\mu\) the reduced mass of the two colliding partners.

Equation (23) indicates that the collision numbers \(Z\) (and, hence the intensity ratios, \(\mathcal{I}\)) should vary linearly with the vapour density. This fact may be used as a criterion for the reliability of the measurements and is valid only at very small \(\mathcal{I}\) values and very low vapour densities where radiation imprisonment is virtually absent.
III. DESCRIPTION OF THE APPARATUS

A schematic arrangement of the apparatus is shown in Fig. 2. Resonance lines emitted from an rf light source were separated by a grating monochromator in series with a set of interference filters. The monochromatic beam was then focused in a fluorescence cell enclosed in an electrically heated oven whose temperature was accurately controlled. Fluorescent light, observed at right angles to the incident beam, passed through a second set of filters and was focused on the photocathode of a photomultiplier tube. The photomultiplier current was registered by an electrometer amplifier and strip chart recorder or a counting train consisting of a preamplifier and a scaler.

The light source has been described elsewhere\textsuperscript{20}. The resonance radiation was emitted from a pyrex tube 9 cm long and 1.8 cm in diameter tapered at one end, which contained about 0.5 g of distilled alkali metal with 1.5 torr of argon as a carrier gas. The tube was placed in the tank coil of the rf oscillator with the tapered portion, containing the distilled metal, reaching down into a wire wound heater coil connected through a variac to a regulated power supply. The oscillator was of a push-pull variety operating in class C and functioned at 60 Mc/sec. A skin discharge was maintained and, with suitable adjustments of the temperature at the base of the lamp, the resonance lines
A  rf lamp
B  monochromator
L₁, L₂, L₃, L₄  condensing lenses
F₁, F₂  interference filters
F₃  neutral density filters
D  photomultiplier in the cryostat
E  electrometer and strip chart
C  recorder or counting train
    cell in main oven

Fig. 2.  Schematic Arrangement of the Apparatus
emitted were narrow, intense and only slightly self-reversed.

A Bausch and Lomb monochromator containing a 1200 line/mm grating blazed at 7500 Å in the first order was used to select one of the alkali resonance lines from the rf discharge. The instrument had an aperture of f/4.4, a focal length of 500 mm and a reciprocal dispersion of 16 Å/mm in the first order. The light intensity transmitted by the monochromator increased linearly with slit width and for a slit width of 1.50 mm gave a spectral purity of better than one part in 2000 for the potassium doublet and about one part in $10^4$ for the rubidium doublet. Since the tolerance of the filters to non parallel light was quite low, the transmissions of the wanted lines were measured in situ. Since the transmissions of unwanted lines are difficult to measure in situ, a preliminary experiment was conducted in which a parallel beam, monochromatic to about one part in $10^8$, was passed through each of the filters shown in table 1. The transmitted light was then focused on the photocathode of a photomultiplier tube whose current was amplified and registered by a strip chart recorder. Because of the different geometric conditions existing in the actual experiment where fluorescent light was resolved by the filters, the values quoted in table 1 give only a rough estimate of the expected resolution.
TABLE 1

Preliminary Measurements of the Transmissions of the Filters

<table>
<thead>
<tr>
<th>Serial Number</th>
<th>Transmission of 7665 Å</th>
<th>Transmission of 7699 Å</th>
<th>Transmission of 7800 Å</th>
<th>Transmission of 7948 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>10885</td>
<td>0.565*</td>
<td>0.001</td>
<td>0.007 x 10^{-3}</td>
<td>0.003 x 10^{-3}</td>
</tr>
<tr>
<td>10975</td>
<td>0.650*</td>
<td>0.001</td>
<td>0.009 x 10^{-3}</td>
<td>0.006 x 10^{-3}</td>
</tr>
<tr>
<td>10897</td>
<td>0.005 x 10^{-1}</td>
<td>0.565*</td>
<td>0.005 x 10^{-2}</td>
<td>0.004 x 10^{-2}</td>
</tr>
<tr>
<td>10972</td>
<td>0.001</td>
<td>0.710*</td>
<td>0.001 x 10^{-2}</td>
<td>0.001 x 10^{-3}</td>
</tr>
<tr>
<td>0074</td>
<td>0.002</td>
<td>0.005</td>
<td>0.690*</td>
<td>0.002</td>
</tr>
<tr>
<td>0075</td>
<td>0.003</td>
<td>0.008</td>
<td>0.700*</td>
<td>0.005</td>
</tr>
<tr>
<td>0065</td>
<td>0.002</td>
<td>0.004</td>
<td>0.005</td>
<td>0.755*</td>
</tr>
<tr>
<td>0038</td>
<td>0.002</td>
<td>0.003</td>
<td>0.002</td>
<td>0.745*</td>
</tr>
</tbody>
</table>

The values marked with an asterisk are transmissions of wanted lines as specified by the manufacturer.

The fluorescence cell, shown in Fig. 3, was designed with the intention of minimizing the reabsorption of both the exciting light and fluorescent radiation. This was accomplished by constructing the entrance and exit windows perpendicular to each other. Thus, the light from the monochromator could be directed so that the region under observation was well localized in the corner between the two windows. Care was taken to avoid reflections from either window and as a further precaution, the cell was coated with 'aquadag', a colloidal dispersion of graphite.

The side arm contained the alkali metal and its temperature controlled the vapour pressure within the main body of the cell. To
Fig. 3. The Fluorescence Cell

A entrance window
B exit window
C side arm
D capillary to vacuum system

Fig. 4. Cell in Main Oven

A cell
B side arm
C brass side oven controlling side arm temperature
D end window
E copper sheet
F heater wire
G capillary to vacuum

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
ensure this, the side arm was made about 4 cm long and 12 mm in diameter.\(^1\)

The cell was connected to the vacuum system by a capillary 2 mm in diameter which was large enough to ensure a hard vacuum within the cell, yet fine enough to prevent migration of the alkali vapour to the outside.

The fluorescence cell was enclosed in the main oven as shown in Fig. 4. The main oven was heated by two 8 ohm heating elements which were constructed from Chromel A heating wire (#26) covered with ceramic insulating beads and were mounted on the floor and top cover of a rectangular transite box. A copper sheet covering each element insured uniform heating and also shielded the cell from the glow. Windows at each end of the oven provided a means of admitting and viewing the incident light and a third window, situated on the front wall facing the detection equipment, provided an exit for the fluorescent light.

A side oven consisting of a brass cylinder on which was wound a length of Chromel A heating wire (resistance 8 ohms) snugly fitted the side arm which protruded from the back wall of the main oven. Where necessary, spacers of copper sheeting were wrapped around the side arm to ensure better thermal contact and uniform temperature throughout.

The heating elements of both main and side ovens were
connected to a temperature controller whose circuit diagram is shown in Fig. 5. The temperature of each oven was set by adjusting the bias level with a potentiometer at the base of the primary transistor connected in a grounded emitter configuration. Temperature changes in the oven produced proportional voltage variations across a thermistor which were amplified by a grounded emitter amplifier, and, the out of phase signal from the collector was fed into a current amplifier consisting of two emitter follower stages. The output current from the last stage was fed into the D.C. coils of a saturable reactor whose A.C. output supplied current to the ovens. A 20 ohm rheostat connected in parallel with the side oven allowed for finer control at low temperatures. In the region from 40°C to 150°C, the side and main ovens were maintained within ± 0.1°C and ± 1.0°C respectively.

The resonance lines in the fluorescent spectrum were resolved by a set of interference filters and were focused on the photocathode of a 16 dynode I.T.T. photomultiplier tube cooled in a liquid air cryostat. The S-1 (Ag-O-Cs) photocathode was 3 mm in diameter with maximum peak sensitivity varying slowly around 8000 Å. During the experiment, a Fluke 412B power supply operated at 1.8 kilovolts was connected to a resistive divider chain which gave a voltage drop of approximately 80 volts per dynode. The signal from the tube was fed either to a Victoreen VTE - 2 electrometer connected to a Philips strip chart recorder or a Philips counting train consisting of an amplifier and scaler.
Fig. 5. The Temperature Controller
An Edwards model EO - 2 diffusion pump filled with Dow Corning 704 pumping fluid, backed by a model 1SC50B rotary pump, was used to evacuate the fluorescence cell. This system, which included a liquid air trap, was capable of maintaining a vacuum of better than $10^{-7}$ torr. Protection from water and power failure was achieved by a relay system built around an FSM - 1 Flowtrol.
IV. EXPERIMENTAL PROCEDURE

The fluorescence cell was cleaned with dichromate cleaning solution and rinsed with distilled water before attaching it to the vacuum system through the side arm and capillary. The cell was then outgassed for several days at about 150°C under a vacuum of $10^{-7}$ torr. Two ampoules, containing 99.95% pure potassium and 99.99% pure rubidium respectively (supplied by the A. D. McKay Company of New York), which had been introduced into an extension of the side arm, were broken under vacuum and about 0.5 g of each metal was distilled into the side arm, which was then sealed off. Thermistors and chromel-alumel thermocouples were attached to the main body of the cell and to the side arm.

The calculation of the collision cross sections $Q_{ab}$ requires an accurate knowledge of the partial pressures of the alkali vapours over the experimental range of temperatures. Specifically, for the cross section $Q_{21'} (4^2P_{3/2} \rightarrow 5^2P_{1/2})$, the rubidium partial pressure was required. It has been shown by Rozwadowski and Lipworth\textsuperscript{22} that the usual vapour pressure - temperature formulae for a one component system are not applicable to a two component system. This was also shown by Czajkowski, McGillis and Krause\textsuperscript{18} who further verified Seiwert's\textsuperscript{23} contention that the partial pressure of one component depended on the composition of the mixture and could be represented by

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
the formula

\[ P_i = \gamma_i P_0 \]

where \( P_i \) is the partial pressure of one alkali metal in the mixture, 
\( P_0 \) is the vapour pressure of the pure metal at the same temperature, 
and \( \gamma_i \) is its mole fraction (ratio of the number of gram-atoms of the metal to the total number of gram-atoms present in the mixture). In the present situation, the mole fraction may be defined as

\[ \gamma_i = \frac{n(Rb)}{n(Rb) + n(K)} = \frac{1}{1 + \frac{n(K)}{n(Rb)}} \]

where \( n(Rb) \) and \( n(K) \) are the numbers of gram-atoms of rubidium and potassium in the mixture.

To determine the partial pressure of rubidium vapour in the Rb - K mixture, a method shown to be valid by Czajkowski, McGillis and Krause\(^{18} \) was used. This method is depicted in Fig. 6 which shows the incident beam passing through the fluorescence cell. The image of the monochromator exit slit, which was initially positioned in the corner formed by the exit and entrance windows, was moved back and forth along the axis of observation by laterally displacing the lens \( L_2 \) in Fig. 1 through a distance \( d = 1 \) mm by means of a micrometric device precisely calibrated with a cathetometer. The extinction coefficient \( K \) was then calculated from the Beer-Lambert law:

\[ K = \frac{\ln I_0 - \ln I}{d} \]
Fig. 6. The Front Part of the Fluorescence Cell with the Ray Diagram of the Scheme Used in the Determinations of the Extinction Coefficients.
where $I_0$ and $I$ are the fluorescent intensities corresponding to $d = 0$ and $d$ which is large compared to the 0.05 mm wide image of the monochromator exit slit. From a plot of the extinction coefficient against temperature for pure rubidium and rubidium in the K-Rb mixture, $\chi_1$ was obtained so that equation (24) could be employed in determining the partial pressure of rubidium vapour.

The vapour pressure of pure rubidium was taken from a temperature-vapour pressure plot given by Nesmeyanov. Actually, at vapour densities where the mean free path is much greater than the diameter of the tube, the vapour pressure in the main body of the cell is given by $P' = P \sqrt{T'/T}$. $P$ and $T$ are the pressure and temperature respectively of the vapour in the side arm and $P'$ and $T'$ are the corresponding quantities in the fluorescence cell. It was assumed, however, that since the side arm was short and wide, the two pressures would be equal.
V. RESULTS AND DISCUSSION

(i) The Experimental Results

The experimental values of the extinction coefficients \( K \) at various side oven temperatures, obtained by excitation of pure rubidium vapour and rubidium atoms in the K - Rb mixture, are shown in tables 2 and 3 respectively. These results were obtained with at least 4 independent runs to assure reproducibility. A plot of the extinction coefficients for pure rubidium vapour against the atomic density of rubidium, shown in Fig. 7, is linear at low vapour pressures. The linear region extends to \( 4 \times 10^{11} \text{ atoms/cm}^3 \) which corresponds to a temperature of 67°C. This determines the temperature range in which the mole fraction \( Y_1 \) may be calculated.

Plots of the extinction coefficients against temperature for both pure rubidium and the K - Rb mixture are shown in Fig. 8. From these curves, the temperature (and hence the vapour pressure) of pure rubidium was read off, corresponding to a given value of the extinction coefficient for rubidium in the mixture; this gives the partial pressure of rubidium vapour at a specified temperature of the mixture. Direct comparison of the partial pressure of rubidium in the mixture with the vapour pressure of pure rubidium at the same temperature yields \( Y_1 \).

Twelve such determinations gave \( Y_1 = 0.547 \pm 0.008 \) where .008 is the
TABLE 2

Extinction Coefficients in Pure Rubidium Vapour for the 7948 Å Component

<table>
<thead>
<tr>
<th>S. O. Temp °C</th>
<th>M. O. Temp °C</th>
<th>V. Pressure Torr</th>
<th>Density Atoms/cc</th>
<th>Ext. Coeff. K cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>44.3</td>
<td>57.5</td>
<td>2.05 x 10⁻⁶</td>
<td>5.99 x 10¹⁰</td>
<td>1.17 x 10⁻¹</td>
</tr>
<tr>
<td>46.8</td>
<td>62.6</td>
<td>2.60 x 10⁻⁶</td>
<td>7.49 x 10¹⁰</td>
<td>1.56 x 10⁻¹</td>
</tr>
<tr>
<td>49.6</td>
<td>64.3</td>
<td>3.38 x 10⁻⁶</td>
<td>9.67 x 10¹⁰</td>
<td>1.77 x 10⁻¹</td>
</tr>
<tr>
<td>50.4</td>
<td>61.0</td>
<td>3.64 x 10⁻⁶</td>
<td>1.05 x 10¹¹</td>
<td>1.89 x 10⁻¹</td>
</tr>
<tr>
<td>50.7</td>
<td>61.0</td>
<td>3.73 x 10⁻⁶</td>
<td>1.08 x 10¹¹</td>
<td>1.96 x 10⁻¹</td>
</tr>
<tr>
<td>52.4</td>
<td>60.5</td>
<td>4.35 x 10⁻⁶</td>
<td>1.26 x 10¹¹</td>
<td>2.49 x 10⁻¹</td>
</tr>
<tr>
<td>53.5</td>
<td>64.2</td>
<td>4.80 x 10⁻⁶</td>
<td>1.37 x 10¹¹</td>
<td>2.77 x 10⁻¹</td>
</tr>
<tr>
<td>56.2</td>
<td>70.0</td>
<td>6.10 x 10⁻⁶</td>
<td>1.72 x 10¹¹</td>
<td>3.52 x 10⁻¹</td>
</tr>
<tr>
<td>58.0</td>
<td>71.3</td>
<td>7.20 x 10⁻⁶</td>
<td>2.02 x 10¹¹</td>
<td>3.63 x 10⁻¹</td>
</tr>
<tr>
<td>58.9</td>
<td>74.5</td>
<td>7.75 x 10⁻⁶</td>
<td>2.16 x 10¹¹</td>
<td>4.02 x 10⁻¹</td>
</tr>
<tr>
<td>61.5</td>
<td>73.2</td>
<td>9.56 x 10⁻⁶</td>
<td>2.67 x 10¹¹</td>
<td>4.88 x 10⁻¹</td>
</tr>
<tr>
<td>61.6</td>
<td>81.0</td>
<td>9.65 x 10⁻⁶</td>
<td>2.63 x 10¹¹</td>
<td>4.60 x 10⁻¹</td>
</tr>
<tr>
<td>63.0</td>
<td>81.5</td>
<td>1.08 x 10⁻⁵</td>
<td>2.94 x 10¹¹</td>
<td>5.45 x 10⁻¹</td>
</tr>
<tr>
<td>63.4</td>
<td>81.2</td>
<td>1.12 x 10⁻⁵</td>
<td>3.06 x 10¹¹</td>
<td>5.35 x 10⁻¹</td>
</tr>
<tr>
<td>64.0</td>
<td>74.0</td>
<td>1.19 x 10⁻⁵</td>
<td>3.31 x 10¹¹</td>
<td>6.02 x 10⁻¹</td>
</tr>
<tr>
<td>64.1</td>
<td>82.5</td>
<td>1.20 x 10⁻⁵</td>
<td>3.26 x 10¹¹</td>
<td>5.92 x 10⁻¹</td>
</tr>
<tr>
<td>67.0</td>
<td>78.0</td>
<td>1.52 x 10⁻⁵</td>
<td>4.18 x 10¹¹</td>
<td>7.42 x 10⁻¹</td>
</tr>
<tr>
<td>67.5</td>
<td>86.0</td>
<td>1.58 x 10⁻⁵</td>
<td>4.25 x 10¹¹</td>
<td>7.51 x 10⁻¹</td>
</tr>
</tbody>
</table>

(Table continued on next page)
Table 2 - Extinction Coefficients in Pure Rubidium Vapour for the 7948 Å Component (continued)

<table>
<thead>
<tr>
<th>S. O. Temp °C</th>
<th>M. O. Temp °C</th>
<th>V. Pressure Torr</th>
<th>Density Atoms/cc</th>
<th>Ext. Coeff. K cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>68.8</td>
<td>86.0</td>
<td>1.76 x 10⁻⁵</td>
<td>4.73 x 10¹¹</td>
<td>8.43 x 10⁻¹</td>
</tr>
<tr>
<td>68.8</td>
<td>81.5</td>
<td>1.76 x 10⁻⁵</td>
<td>4.79 x 10¹¹</td>
<td>8.25 x 10⁻¹</td>
</tr>
<tr>
<td>69.1</td>
<td>85.5</td>
<td>1.81 x 10⁻⁵</td>
<td>4.87 x 10¹¹</td>
<td>8.98 x 10⁻¹</td>
</tr>
<tr>
<td>71.3</td>
<td>85.2</td>
<td>2.15 x 10⁻⁵</td>
<td>5.81 x 10¹¹</td>
<td>9.80 x 10⁻¹</td>
</tr>
<tr>
<td>73.5</td>
<td>89.0</td>
<td>2.60 x 10⁻⁵</td>
<td>6.94 x 10¹¹</td>
<td>1.10</td>
</tr>
<tr>
<td>76.0</td>
<td>90.3</td>
<td>3.15 x 10⁻⁵</td>
<td>8.38 x 10¹¹</td>
<td>1.22</td>
</tr>
<tr>
<td>77.5</td>
<td>96.5</td>
<td>3.55 x 10⁻⁵</td>
<td>9.27 x 10¹¹</td>
<td>1.32</td>
</tr>
<tr>
<td>80.8</td>
<td>94.8</td>
<td>4.45 x 10⁻⁵</td>
<td>1.17 x 10¹²</td>
<td>1.40</td>
</tr>
</tbody>
</table>

S. O. side oven
M. O. main oven

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
### TABLE 3

**Extinction Coefficients in a K - Rb Mixture**

for the Rb 7948 Å Resonance Line

<table>
<thead>
<tr>
<th>S. O. Temp (°C)</th>
<th>M. O. Temp (°C)</th>
<th>Ext. Coeff. (K cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>56. 2</td>
<td>71. 2</td>
<td>1.82 x 10⁻¹</td>
</tr>
<tr>
<td>56. 3</td>
<td>70. 9</td>
<td>1.53 x 10⁻¹</td>
</tr>
<tr>
<td>56. 9</td>
<td>76. 8</td>
<td>2.24 x 10⁻¹</td>
</tr>
<tr>
<td>60. 3</td>
<td>78. 5</td>
<td>2.39 x 10⁻¹</td>
</tr>
<tr>
<td>61. 8</td>
<td>79. 0</td>
<td>2.66 x 10⁻¹</td>
</tr>
<tr>
<td>64. 2</td>
<td>82. 5</td>
<td>3.54 x 10⁻¹</td>
</tr>
<tr>
<td>66. 2</td>
<td>80. 0</td>
<td>4.11 x 10⁻¹</td>
</tr>
<tr>
<td>67. 3</td>
<td>82. 0</td>
<td>4.78 x 10⁻¹</td>
</tr>
<tr>
<td>70. 2</td>
<td>88. 0</td>
<td>5.45 x 10⁻¹</td>
</tr>
<tr>
<td>70. 8</td>
<td>83. 5</td>
<td>5.64 x 10⁻¹</td>
</tr>
<tr>
<td>72. 3</td>
<td>88. 0</td>
<td>6.67 x 10⁻¹</td>
</tr>
<tr>
<td>72. 8</td>
<td>86. 6</td>
<td>6.49 x 10⁻¹</td>
</tr>
<tr>
<td>74. 2</td>
<td>89. 5</td>
<td>7.23 x 10⁻¹</td>
</tr>
<tr>
<td>76. 8</td>
<td>92. 8</td>
<td>8.34 x 10⁻¹</td>
</tr>
<tr>
<td>77. 0</td>
<td>93. 0</td>
<td>9.26 x 10⁻¹</td>
</tr>
<tr>
<td>78. 7</td>
<td>88. 0</td>
<td>9.35 x 10⁻¹</td>
</tr>
<tr>
<td>80. 0</td>
<td>94. 9</td>
<td>1.01</td>
</tr>
</tbody>
</table>

(Table continued on next page)
Table 3 - Extinction Coefficients in a K - Rb Mixture for the Rb 7948 Å
Resonance Line (continued)

<table>
<thead>
<tr>
<th>S. O. Temp °C</th>
<th>M. O. Temp °C</th>
<th>Ext. Coeff. K cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>80.5</td>
<td>94.9</td>
<td>1.05</td>
</tr>
<tr>
<td>81.8</td>
<td>95.0</td>
<td>1.14</td>
</tr>
<tr>
<td>84.0</td>
<td>100.5</td>
<td>1.20</td>
</tr>
<tr>
<td>86.4</td>
<td>100.5</td>
<td>1.35</td>
</tr>
<tr>
<td>88.7</td>
<td>112.0</td>
<td>1.50</td>
</tr>
</tbody>
</table>

S. O. side oven
M. O. main oven
Fig. 7. The Variation with Density of the Extinction Coefficients for Pure Rubidium Vapour

\[ \frac{\rho}{\ln \frac{1}{1 - \ln I}} = k \]
Fig. 8. The Variation with Temperature of the Extinction Coefficients for Pure Rubidium Vapour and for a Potassium-Rubidium Mixture
average deviation. Substitution into equation (24) yields the expression
\[ P_1 = 0.547 P_0, \]
which was used to determine the partial pressure of rubidium vapour.

The fluorescent intensity ratios \( \frac{\mathcal{I}_{21'}}{\mathcal{I}_{21}} \) in table 4, represent the observed values which were measured, using filters, over 3 independent runs. Since the neutral density filter transmitted \( 7.07 \times 10^{-3} \) of the resonance fluorescence (7665 Å) and the two rubidium filters in series (#0065, #0038) transmitted \( 0.515 \) of the sensitized fluorescence (7948 Å), the true intensity ratios \( \mathcal{I}_{21}' \) were obtained from the relationship \( \mathcal{I}_{21}' = 1.37 \times 10^{-2} \frac{\mathcal{I}_{21}}{\mathcal{I}_{21}} \). The slight discrepancy between the observed transmission of the interference filters and that quoted by the manufacturer (0.552), is due to the imperfect collimation of the fluorescent light emitted from a finite volume within the cell. A graph of \( \mathcal{I}_{21}' \) against rubidium vapour pressure is shown in Fig. 9 and the total cross section \( Q_{21}' \) was calculated from the slope of the linear region using \( \tau = 2.71 \times 10^{-8} \) sec \(^{-2} \). This cross section is compared in table 5 with cross sections for Rb - Cs\(^{18} \) collisions.

(ii) Discussion of the Results

The graph in Fig. 9 does not pass through the origin but has a finite intercept caused by some transmission of the unwanted potassium resonance fluorescence through the interference filters. Table 1 shows the transmission of this unwanted line to be about \( 2 \times 10^{-3} \) for each of the filters (#0065, #0038). Since the conditions in the actual experiment...
### TABLE 4
Fluorescent Intensity Ratios in a K - Rb Mixture

<table>
<thead>
<tr>
<th>S. O. °C</th>
<th>M. O. °C</th>
<th>( \mathcal{N}_{21}^{\prime} ) ( 10^{-4} )</th>
<th>( \mathcal{N}_{21}^{\prime} ) ( 10^{-6} )</th>
<th>Rubidium Partial Pressure ( 10^{-5} ) torr</th>
</tr>
</thead>
<tbody>
<tr>
<td>78.6</td>
<td>97.2</td>
<td>3.03</td>
<td>4.16</td>
<td>2.12</td>
</tr>
<tr>
<td>82.1</td>
<td>98.6</td>
<td>3.23</td>
<td>4.43</td>
<td>2.79</td>
</tr>
<tr>
<td>83.9</td>
<td>97.5</td>
<td>3.25</td>
<td>4.46</td>
<td>3.20</td>
</tr>
<tr>
<td>86.2</td>
<td>98.6</td>
<td>3.28</td>
<td>4.52</td>
<td>3.83</td>
</tr>
<tr>
<td>89.3</td>
<td>103.2</td>
<td>3.46</td>
<td>4.75</td>
<td>4.81</td>
</tr>
<tr>
<td>91.0</td>
<td>106.0</td>
<td>3.60</td>
<td>4.93</td>
<td>5.47</td>
</tr>
<tr>
<td>93.3</td>
<td>108.5</td>
<td>3.65</td>
<td>5.00</td>
<td>6.43</td>
</tr>
<tr>
<td>94.9</td>
<td>106.0</td>
<td>3.82</td>
<td>5.25</td>
<td>7.11</td>
</tr>
<tr>
<td>95.8</td>
<td>106.0</td>
<td>4.05</td>
<td>5.55</td>
<td>7.60</td>
</tr>
<tr>
<td>98.2</td>
<td>108.7</td>
<td>3.92</td>
<td>5.42</td>
<td>9.00</td>
</tr>
<tr>
<td>99.75</td>
<td>111.3</td>
<td>4.25</td>
<td>5.83</td>
<td>9.96</td>
</tr>
<tr>
<td>102.1</td>
<td>116.0</td>
<td>4.80</td>
<td>6.59</td>
<td>1.19 \times 10</td>
</tr>
<tr>
<td>103.0</td>
<td>121.0</td>
<td>4.68</td>
<td>6.42</td>
<td>1.26 \times 10</td>
</tr>
<tr>
<td>104.7</td>
<td>119.8</td>
<td>5.02</td>
<td>6.89</td>
<td>1.40 \times 10</td>
</tr>
<tr>
<td>107.2</td>
<td>116.0</td>
<td>5.55</td>
<td>7.61</td>
<td>1.66 \times 10</td>
</tr>
<tr>
<td>109.3</td>
<td>121.2</td>
<td>6.38</td>
<td>8.75</td>
<td>1.90 \times 10</td>
</tr>
<tr>
<td>112.0</td>
<td>124.1</td>
<td>7.76</td>
<td>1.06 \times 10</td>
<td>2.27 \times 10</td>
</tr>
<tr>
<td>112.2</td>
<td>124.1</td>
<td>7.85</td>
<td>1.08 \times 10</td>
<td>2.33 \times 10</td>
</tr>
<tr>
<td>120.0</td>
<td>125.0</td>
<td>1.24</td>
<td>1.70 \times 10</td>
<td>3.72 \times 10</td>
</tr>
</tbody>
</table>

S. O. side oven
M. O. main oven

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Fig. 9. A Plot of the Intensity Ratio $\tilde{\eta}_{21}'$ Against the Partial Pressure of Rubidium
### TABLE 5

Cross sections for inelastic collisions between unlike alkali atoms

<table>
<thead>
<tr>
<th>Collision Partners</th>
<th>Collision cross section</th>
<th>Value ($\AA^2$)</th>
<th>Energy defect $\Delta E$ cm$^{-1}$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb - Cs</td>
<td>$Q_{12}'(5^2P_{1/2} \rightarrow 6^2P_{3/2})$</td>
<td>$1.5 \pm 0.4$</td>
<td>847</td>
<td>Czajkowski, McGillis, Krause$^{18}$</td>
</tr>
<tr>
<td>Rb - Cs</td>
<td>$Q_{11}'(5^2P_{3/2} \rightarrow 6^2P_{1/2})$</td>
<td>$0.5 \pm 0.1$</td>
<td>1401</td>
<td>Czajkowski, McGillis, Krause$^{18}$</td>
</tr>
<tr>
<td>Rb - Cs</td>
<td>$Q_{22}'(5^2P_{3/2} \rightarrow 6^2P_{3/2})$</td>
<td>$0.9 \pm 0.2$</td>
<td>1084</td>
<td>Czajkowski, McGillis, Krause$^{18}$</td>
</tr>
<tr>
<td>Rb - Cs</td>
<td>$Q_{21}'(5^2P_{3/2} \rightarrow 6^2P_{1/2})$</td>
<td>$0.3 \pm 0.1$</td>
<td>1638</td>
<td>Czajkowski, McGillis, Krause$^{18}$</td>
</tr>
<tr>
<td>Rb - K</td>
<td>$Q_{21}'(4^2P_{3/2} \rightarrow 5^2P_{1/2})$</td>
<td>$5.7 \pm 0.9$</td>
<td>466</td>
<td>This investigation</td>
</tr>
</tbody>
</table>
were different from those prevailing during the determination of the filter transmissions, the value quoted in table 1 is only useful in that it suggests the possibility of a finite intercept in the \( n - P \) graph. It has been shown previously\(^{16,19}\) that this intercept is given by

\[
\frac{1}{\beta} = \delta
\]

where \( \delta \) is the transmission of the interference filters to resonance fluorescence and \( \beta \) is their transmission to sensitized fluorescence.

The intercept of \( 3.7 \times 10^{-6} \), taken from Fig. 9, yields the transmission of the interference filters to the unwanted line equal to \( 1.9 \times 10^{-6} \), which is of the same order as the value quoted in table 1. In the absence of radiation trapping, the parameters \( \delta \) and \( \beta \) are independent of vapour density and the slope of the straight line is unaffected. The departure from linearity at higher pressures is due to the increase in the effective lifetime of the \( ^2P_{3/2} \) state caused by the imprisonment of the potassium resonance radiation. It was estimated from Fig. 9, that nonlinearity and thus radiation trapping sets in at about \( 101^\circ C \). Again, assuming Seiwert's\(^{23}\) contention, \( P_2 = \gamma_2 P_0 \), where \( P_2 \) in this case is the partial pressure of potassium vapour in the mixture and

\[
\gamma_2 = \frac{n(K)}{n(K) + n(Rb)} = \frac{1}{1 + \frac{n(Rb)}{n(K)}} = 0.453
\]

this temperature corresponds to a partial potassium vapour pressure of \( 1.0 \times 10^{-5} \) torr, in exact agreement with the result obtained by Chapman and Krause\(^{13}\) with pure potassium vapour. It thus appears that the mole fraction \( \gamma_1 \) remained constant over at least the range...
of temperatures defined by the linear portion of the $\frac{\partial}{\partial t} - P$ plot. This result provides further indication that Seiwert's contention is applicable to the conditions of this experiment.

According to Franck's rule\textsuperscript{26}, the cross sections $Q_{ab}$ should have the following dependence on the energy defect $\Delta E$: $Q_{ab} = \frac{k}{(\Delta E)^\alpha}$ where $k$ is a proportionality constant. Czajkowski, McGillis and Krause\textsuperscript{18} found $\alpha = 2.1 \pm 0.1$ for Rb - Cs collisions. Fig. 10 is a plot of all the cross sections in table 5 against $(\Delta E)^{-2.1}$ and it may be seen that the cross section $Q_{21}'$ for K - Rb collisions, obtained in this investigation, obeys the same relationship. Chapman and Krause\textsuperscript{13} showed that for collisions between identical atoms $\alpha = 0.9 \pm 0.2$. Hence, it appears that the mechanism governing energy transfer between identical alkali atoms is different than for dissimilar atoms. Further investigation of excitation transfer in K - Rb collisions which is now in progress, should provide additional insight into this problem.
Fig. 10. A Plot of the Cross Sections for Rb - Cs and K - Rb Collisions Against the Reciprocals of the Energy Defects Raised to the Power 2.1
BIBLIOGRAPHY


VITA AUCTORIS

I was born on January 21st, 1941 in Kirkland Lake, Ontario where I attended primary and secondary schools. Upon graduation in 1959, I attended the University of St. Michael's College in Toronto, where I graduated in 1963 from a General Science course with a mathematics major. In 1963, I registered as a special student in Arts and Science at the University of Windsor and in 1964 enrolled in the Faculty of Graduate Studies to work toward a Master Degree in Physics.