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SENSITIZED FLUORESCENCE IN POTASSIUM VAPOUR

by

I. H. Brockman, B. E.

A Thesis Presented in Partial Fulfilment  
of the Requirements for the Degree of  
Master of Science

The Faculty of Graduate Studies  
Assumption University of Windsor

1961

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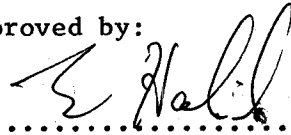
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### ABSTRACT

Sensitized fluorescence of potassium vapour was investigated to determine the cross-sections for collisions of a second kind occurring between potassium and potassium, potassium and helium, and potassium and argon atoms. The experiments involved the use of an idealized fluorescence tube and the application of a red-sensitive photomultiplier tube. Corrections for effects due to the imprisonment of radiation were made by extrapolating the results to zero pressure. The following values were obtained:  $Q_1 (4^2P_{1/2} \rightarrow 4^2P_{3/2}) = 95 \times 10^{-14} \text{ cm}^2$  and  $Q_2 (4^2P_{3/2} \rightarrow 4^2P_{1/2}) = 83 \times 10^{-14} \text{ cm}^2$  for potassium-potassium collisions;  $Q_1 = 1.54 \times 10^{-14} \text{ cm}^2$  and  $Q_2 = 1.04 \times 10^{-14} \text{ cm}^2$  for potassium-helium collisions, and  $Q_1 = 3.55 \times 10^{-14} \text{ cm}^2$  and  $Q_2 = 3.02 \times 10^{-14} \text{ cm}^2$  for potassium-argon collisions.

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I am also grateful to Mrs. S. Allon for drafting the diagrams and figures in this thesis.

## INTRODUCTION

Resonance Fluorescence in Potassium

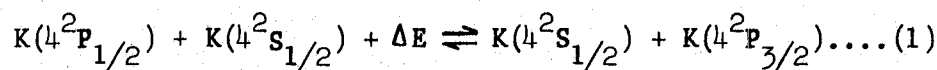
When light from a potassium spectral lamp is focussed on a tube containing potassium vapour at a pressure of about 0.01 mm Hg, a cone of red fluorescence may be observed, corresponding to the path of the light through the vapour. This effect is due to the potassium atoms which are being excited from the  $4^2S_{1/2}$  ground state to the  $4^2P_{1/2}$  and  $4^2P_{3/2}$  resonance levels and, in decaying back to the ground state, emit fluorescent light. This resonance fluorescence consists of two wavelength components, 7699Å and 7665Å, which are also present in the beam of incident light, corresponding to the  $4^2S_{1/2} \leftarrow 4^2P_{1/2}$  and  $4^2S_{1/2} \leftarrow 4^2P_{3/2}$  transitions respectively.

As the pressure of the potassium vapour is raised above 0.05 mm Hg, the fluorescence fills the whole volume of the tube and is known as 'volume fluorescence'. At vapour pressures above 0.30 mm Hg, the emission becomes confined to an intense fluorescent spot at the point where the exciting beam of light enters the vapour and is called 'surface fluorescence'.

Resonance fluorescence was first observed in sodium by R.W. Wood (1905) and in potassium by Nielsen and Wright (1930). The  $^2P_{1/2}$  and  $^2P_{3/2}$  resonance levels, which occur in all the alkali metal atoms (See Figure 1), become excited by means of the resonance radiation from the lamp and, in returning to their ground states, emit the fluorescent light. At higher vapour pressures the resonance radiation becomes imprisoned in the vapour with many re-emissions and reabsorptions of the light quantum taking place before the fluorescent light emerges from the tube; this causes the volume fluorescence to spread throughout the vapour. At still higher pressures the high absorption coefficient of the vapour causes the exciting radiation to be completely absorbed in the surface layer which then confines the fluorescence.

### Sensitized Fluorescence and Collisions of a Second Kind

If the beam of exciting light is passed through a monochromator so, that only one component of the resonance doublet is incident on the potassium vapour, both the components are still present in the fluorescent light. The appearance of the two resonance frequencies is due to inelastic collisions which occur between the excited and the unexcited potassium atoms and during which a radiationless transfer of excitation energy takes place. The energy transfer may be represented by the equation:

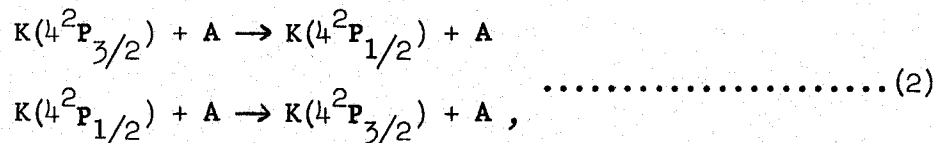


The above expression implies that translational kinetic energy may either be converted to excitation energy or may be liberated during a collision, depending on the direction of the process. The type of fluorescence, where the fluorescent radiation is of a different wavelength than the exciting radiation, is known as sensitized fluorescence. Although in this particular case the sensitizing agent is a potassium atom excited to one of the resonance levels by means of the appropriate component of the resonance doublet, a similar effect is frequently produced by having a mixture of two different atoms and irradiating it with a wavelength appropriate to one of them. The other atoms will become excited during collisions and will radiate their own wavelength provided that the energy gap between the two levels of the two atoms is not too large. Mercury vapour has been used in this way to sensitize fluorescence in thallium (Cario and Franck 1922, 1923), zinc (Winans, 1927), sodium (Beutler and Josephy 1929) and other metallic vapours. In the case represented by equation (1), the energy interval  $\Delta E$  equals  $57\text{cm}^{-1}$  whereas the mean translational kinetic energy of the potassium atoms at  $200^\circ\text{C}$  amounts to  $495\text{cm}^{-1}$ . For sodium the energy gap  $\Delta E$  is even smaller ( $17\text{cm}^{-1}$ ).

The inelastic collisions during which the energy transfer occurs, are known as collisions of a second kind. The term, collisions of a second kind, has been originally postulated by Klein

and Rosseland (1921) and applied to collisions between excited atoms and slow electrons, in the course of which the atomic excitation energy is transferred to the electrons as translational kinetic energy. Franck extended this definition to collisions between excited and unexcited atoms, during which an exchange of excitation and kinetic energy takes place. In contrast, collisions of a first kind are exciting or ionizing collisions between fast electrons and slow atoms.

Sensitized fluorescence may also be induced by adding inert gases to the potassium or sodium vapour. The collisions of a second kind, which then produce the energy transfer, occur between the excited alkali atoms and the inert gas atoms in their ground states according to the equations



where the argon atoms possess different kinetic energies before and after the collisions.

Sensitized fluorescence in sodium was first studied by Wood (1912, 1914) and in somewhat greater detail by Wood and Mohler (1918). Lochte-Holtgreven (1928) measured the intensities of the sodium 'D' lines in fluorescence using pure metallic vapour and vapour-gas mixtures. More recently Seiwert (1956c) used modern experimental methods in his work on sodium and sodium-argon mixtures in order to resolve discrepancies between the results of Wood and Mohler (1918) and those of Lochte-Holtgreven (1928). Thangaraj (1948) studied the sensitized fluorescence of potassium and rubidium vapours and of potassium-rubidium mixtures, and Hoffmann and Seiwert (1961) investigated the sensitized fluorescence in potassium vapour.

Investigations of sensitized fluorescence in alkali vapours provide a useful method for the study of collisions of a second kind between atoms and their efficiency with respect to the transfer of energy. The resonance doublet levels in these atoms are

far removed from their other energy states and, therefore, only the transitions between the ground and resonance states are involved during the collisions. Studies of collision processes of this kind yield information in the form of collision cross-sections which are a convenient means of assessing a collision. The cross-section gives a measure of the distance of approach between the atoms, at which a transfer of energy may occur and it also can be regarded as a criterion of the efficiency of the collision in effecting the energy transfer. The transfer of excitation energy in an atomic collision is most probable and the cross-section is largest when the energy interval  $\Delta E$  between the two levels is least (J. Franck, 1929). This phenomenon is due to a quantum mechanical resonance between the two closely lying energy levels and it has been demonstrated by Beutler and Josephy (1929) in their experiments with mercury-sensitized fluorescence in sodium vapour. A theoretical treatment of this resonance has been given by Kallmann and London (1929) and by Morse and Stueckelberg (1931).

All the experimental studies of resonance fluorescence and sensitized fluorescence in alkali metal vapours had to contend with the problem of diffusion of radiation. As the vapour pressures reach finite values and the resonance radiation becomes imprisoned in the vapour, the light quantum undergoes many emissions and absorptions before leaving the fluorescence vessel. This increases the apparent life time of the excited states and tends to give an artificially high value for the collision cross-sections.

The analogy between this transport of radiation and the process of diffusion has been brought out by Compton (1923) who applied ordinary diffusion theory to problems involving radiation. His theory has been further refined by Milne (1926) and a rather different treatment of the problem was given by Holstein (1947), who defined it in terms of a probability of a light quantum passing through a given layer of vapour without being absorbed. Although neither theory can be easily applied to experimental

problems involving sensitized fluorescence, Holstein's theory was recently adapted by Seiwert (1956a, b) who used it in his studies of sensitized fluorescence of sodium and potassium (Hoffmann and Seiwert, 1961). All the applications of the theories dealing with the diffusion of radiation have involved a number of fundamental assumptions and simplifications which necessarily affected the accuracy of the final answers.

The present investigation aims to obviate the necessity of correcting for radiation-diffusion effects by theoretical means. With an improved design of the fluorescence tube and working in regions of low pressure and low fluorescent intensities it is hoped that the diffusion effects, which tend to produce spurious values of collision cross-sections, may be considerably reduced if not altogether eliminated.

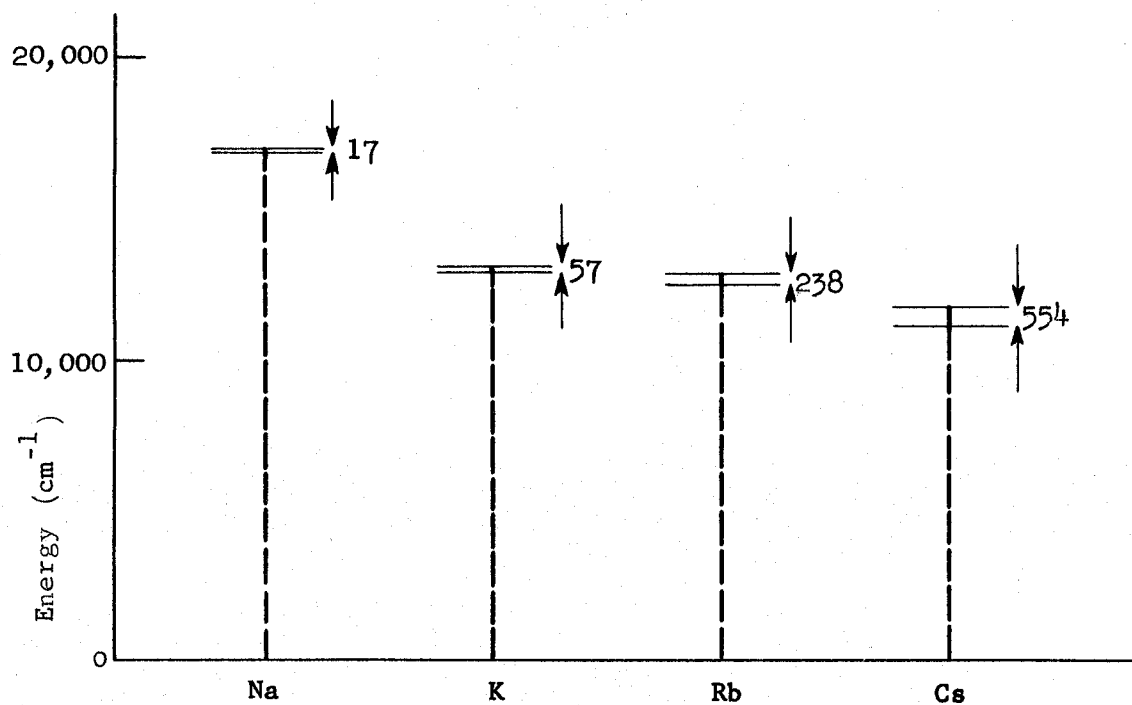


Fig. 1. Resonance energy levels in atoms of alkali metals. The zero energy line denotes the ground  $^2S_{1/2}$  states of the atoms and the broken lines indicate transitions from the ground states to the  $^2P_{1/2}$  and  $^2P_{3/2}$  resonance states.

II

THEORETICAL

In order to represent the statistical rate of energy transfer in atomic collisions it is convenient to define a cross-section for the collisions under consideration. The process of energy transfer depends on the relative kinetic energy  $E$  of the colliding atoms and the total cross-section at a given temperature,  $Q(T)$ , may be defined as

$$Q(T) = \int_0^{\infty} q(E) f_T(E) dE, \dots\dots\dots (3)$$

where  $E$  is the relative kinetic energy of the colliding atoms,  $q(E)$  is the cross-section for a collision between two atoms whose relative kinetic energy lies between  $E$  and  $E + dE$  and  $f_T(E)dE$  is the probability, that at a temperature  $T$  the kinetic energy of the relative motion of the colliding atoms will lie between  $E$  and  $E + dE$ . From Maxwell-Boltzmann statistics,

$$f_T(E)dE = \frac{2\sqrt{E}}{\sqrt{\pi}(kT)^{3/2}} \exp(-\frac{E}{kT})dE, \dots\dots\dots (4)$$

where  $k$  is the Boltzmann constant.

It is also expedient to define a collision number  $Z(T)$  which represents the average number of collisions per atom and per second, during which energy transfer occurs:

$$Z(T) = N\sqrt{2/M} \int_0^{\infty} q(E)\sqrt{E} f_T(E) dE . \dots\dots\dots (5)$$

$M$  is the reduced mass of the colliding atoms and  $N$  is the density of the atoms in the ground state which approximately equals the overall density (atoms/cm<sup>3</sup>).

On the whole,  $Q(T)$  and  $Z(T)$  vary in a similar manner with the temperature  $T$  as does  $q(E)$  with the kinetic energy  $E$ . Thus, to a good approximation, the following relation can be obtained from equations (3) and (5):

$$Q(T) = \frac{Z(T)}{Nv_r}, \dots\dots\dots (6)$$

where  $v_r$ , the average relative velocity of the colliding atoms, is given by:

$$v_r = \sqrt{\frac{8kT}{\pi M}} .$$

Equation (6) defines the effective collision cross-section  $Q(T)$  in terms of the collision number  $Z(T)$  which in turn can be obtained from experimental observations.

If potassium vapour at low pressure be irradiated with one wavelength component of the resonance doublet causing sensitized fluorescence, and it is assumed that the fluorescent radiation emerges from the vapour without further reabsorption, the system may be considered to exist in a dynamic equilibrium represented by the following equations (Seiwert, 1956c):

$$-\frac{1}{\tau_1} n_1 - Z_1 n_1 + Z_2 n_2 + S_1 = 0 \dots\dots\dots (7a)$$

$$-\frac{1}{\tau_2} n_2 - Z_2 n_2 + Z_1 n_1 = 0 , \dots\dots\dots (7b)$$

where  $n_1$  is the density of the atoms excited to the first resonance level ( $4^2P_{1/2}$ ) by means of the 7699A radiation,

$n_2$  is the density of the atoms excited to the second resonance level ( $4^2P_{3/2}$ ) by collisions with the atoms in the  $4^2P_{1/2}$  state,

$Z_1$  and  $Z_2$  are collision numbers corresponding to the transitions  $1 \rightarrow 2$  ( $4^2P_{1/2} \rightarrow 4^2P_{3/2}$ ) and  $1 \leftarrow 2$  ( $4^2P_{1/2} \leftarrow 4^2P_{3/2}$ ) respectively,

$S_1$  is the number of atoms per sec and  $\text{cm}^3$  excited by the incident radiation (7699A) from the ground state to the first ( $4^2P_{1/2}$ ) resonance state,

$\tau_1$  and  $\tau_2$  are the average life times of the two excited resonance states.

A similar set of equations can be written, which corresponds to the equilibrium obtained when the vapour is irradiated with the second component of the resonance doublet (7665A):

$$-\frac{1}{\tau_2} n_2 - Z_2 n_2 + Z_1 n_1 + S_2 = 0 , \dots\dots\dots (8a)$$



$$-\frac{1}{\tau_1} n_1 - Z_1 n_1 + Z_2 n_2 = 0 \dots\dots\dots (8b)$$

By a suitable rearrangement of equations (7b) and (8b), two further equations may be obtained:

$$\frac{Z_1}{Z_2 + 1} = \frac{\frac{1}{\tau} n_2}{\frac{1}{\tau} n_1} = \frac{I_2}{I_1} = \eta_2 ; \dots\dots\dots (9a)$$

$$\frac{Z_2}{Z_1 + 1} = \frac{\frac{1}{\tau} n_1}{\frac{1}{\tau} n_2} = \frac{I_1}{I_2} = \eta_1 \dots\dots\dots (9b)$$

Since the two average lifetimes,  $\tau_1$  and  $\tau_2$  may be considered very nearly equal to one another, a simplification was made by putting  $\tau_1 = \tau_2 = \tau$ .

The equations (9a) and (9b) define the intensity ratios of the two resonance components present in the fluorescent light:

$\eta_1 = \frac{I_1}{I_2}$ , when the fluorescence is excited with the second component (7665A) and  $\eta_2 = \frac{I_2}{I_1}$ , when the fluorescence is excited by

means of the first component (7699A). These equations may be solved for  $Z_1$  and  $Z_2$ , yielding:

$$Z_1 (4^2P_{1/2} \rightarrow 4^2P_{3/2}) = \frac{1}{\tau} \frac{1 + \eta_1}{\eta_2 - \eta_1} \dots\dots\dots (10a)$$

$$Z_2 (4^2P_{1/2} \leftarrow 4^2P_{3/2}) = \frac{1}{\tau} \frac{1 + \eta_2}{\eta_1 - \eta_2} \dots\dots\dots (10b)$$

The equations (10a, b) permit the calculation of the collision numbers from experimental data. These can then be substituted in equation (6) in order to obtain the corresponding collision cross-sections  $Q_1 (4^2P_{1/2} \rightarrow 4^2P_{3/2})$  and  $Q_2 (4^2P_{1/2} \leftarrow 4^2P_{3/2})$ .

It was assumed in the whole argument that no diffusion of radiation takes place in the vapour and that a photon is able to emerge from the vapour without undergoing further absorption. Any

imprisonment of radiation present would affect the lifetimes  $\tau$ . The effective lifetimes of the excited states would become very much greater and  $\tau_1$  would no longer equal  $\tau_2$ , as the absorption coefficients for the two resonance wavelengths differ from one another.

### III

#### THE APPARATUS

The arrangement of the apparatus is shown in Figure 2. It consists of a potassium spectral lamp (A), a monochromator (B), a fluorescence tube (C) and a recording spectrometer (E, H, K). The potassium resonance doublet (7665A and 7699A), emitted by the lamp, was resolved by the monochromator. The radiation was then condensed by means of the lens  $L_1$  into the fluorescence tube, which contained potassium vapour. Fluorescent light from the vapour, emitted normally to the incident beam, was focused by means of lenses  $L_2$  and  $L_3$  onto the entrance slit of a spectrometer, detected with a photomultiplier tube and recorded on a strip chart recorder.

#### The Light Source and the Monochromator

An Osram potassium spectral lamp was used to excite the fluorescence. It was operated at a current of 1.5 amps. A.C. supplied by a Variac and a constant voltage transformer. In order to obtain a maximal illumination of the monochromator optics the lamp was enclosed in a polished cylindrical metal reflector and placed directly in front of the entrance slit of the monochromator.

The grating monochromator, manufactured by Bausch and Lomb, has an effective aperture of  $F/4.4$ , a focal length of 500 mm. and produces a linear dispersion of 33 A/mm. The instrument contains a 600 line/mm. plane replica grating blazed at 7500 A and has an efficiency of 66% at this wavelength. Adequate resolution of the potassium doublet could be obtained with a slit width of 1.75 mm. at both the entrance and exit slits.

#### The Fluorescence Tube

The pyrex fluorescence tube, shown in Figure 3, was 8 cm. long and 3 cm. in diameter. The two end windows were made of polished pyrex plate 2 mm. thick. The side window was 1.5 cm. in diameter and 1 mm. thick, and was set into the tube as close to the front window as possible. This particular feature would make possible the direct observation of the fluorescent vapour, without having the light pass

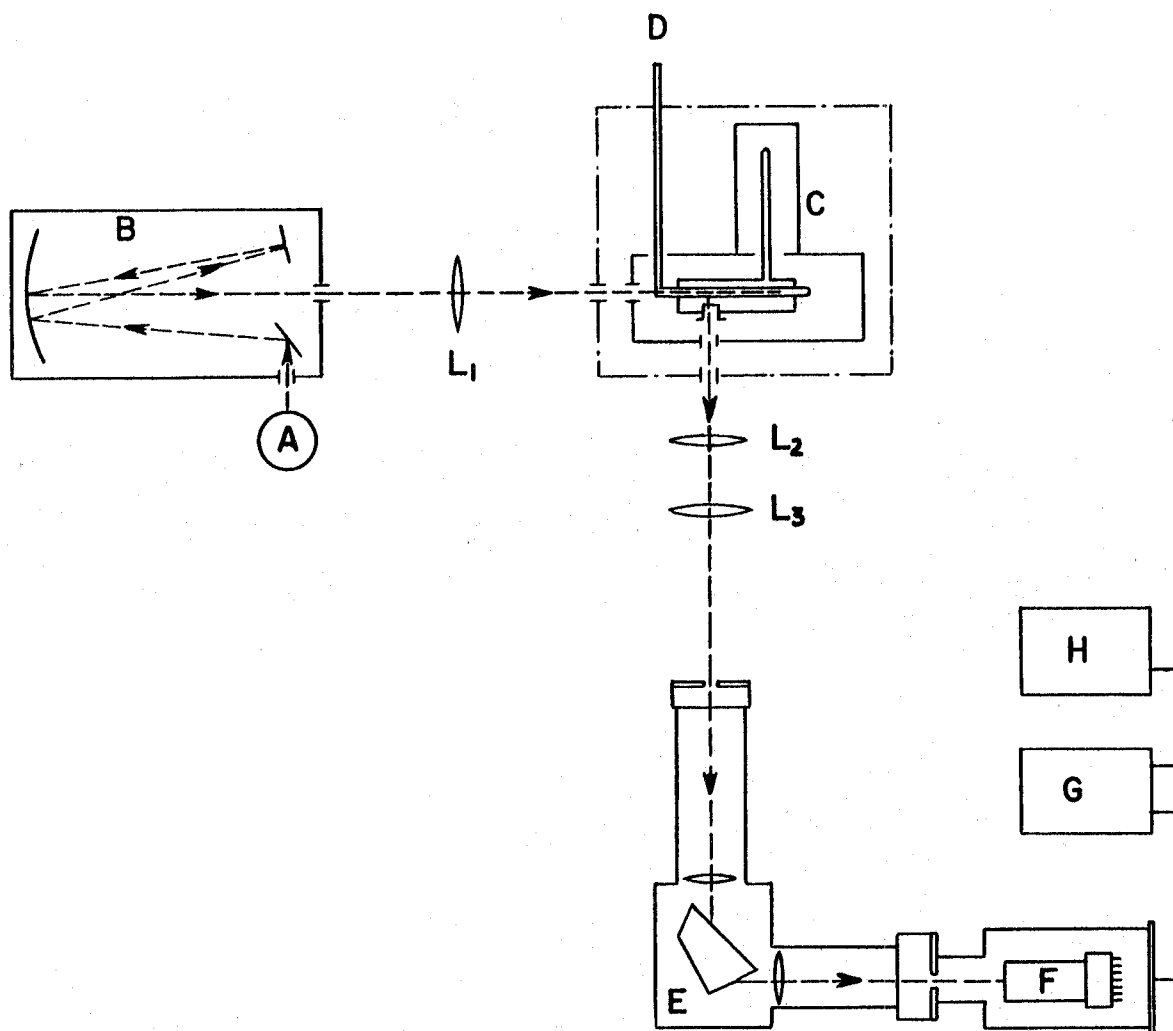


Fig. 2. Apparatus used in the studies of sensitized fluorescence. A - Osram spectral lamp; B - monochromator; C - oven with the fluorescence tube; D - connection to the vacuum and gas-filling system; E - spectrometer; F - photomultiplier; G - electrometer-amplifier; H - strip chart recorder.

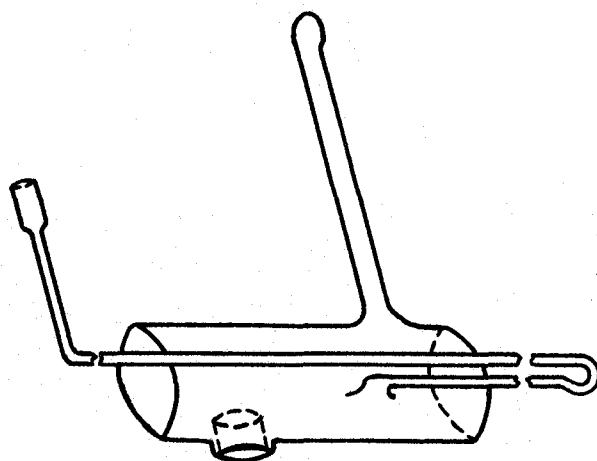


Fig. 3. The fluorescence tube.

through a layer of unexcited potassium atoms. It was hoped that the tube would be very nearly an ideal fluorescence tube, as described by Mitchell and Zemansky(1934). The fluorescence tube has a side arm, 35 cm. long and 6 mm. in diameter, which served to introduce the potassium sample and whose temperature would control the vapour pressure of the potassium in the tube. The tube was connected to the vacuum and gas filling system by means of a capillary 0.5 mm. in diameter and 38 cm. long. The purpose of the capillary was to prevent the loss of potassium vapour from the tube. This device, designed on the basis of mean free path calculations, proved to be so effective that after 100 hours of operation only a very slight trace of potassium penetrated through the capillary.

The fluorescence tube was clamped in the centre of an oven consisting of two parts. The main part, which contained the tube and the capillary, was heated by means of two heating strips rated at 300 watts each. In the oven walls there were three pyrex windows corresponding to the three windows of the tube. The side arm of the tube extended into another part of the oven (the side oven), heated by means of two heating strips rated at 200 watts each. The temperature of the side oven was maintained at about 20°C below that of the main oven; this prevented condensation of potassium vapour on the windows of the tube. Both parts of the oven were enclosed in a transite box lined with approximately 5 cm. of sintered glass insulation.

The voltages supplied to the two parts of the oven could be independently controlled by means of two Variac autotransformers. Fine

control of the temperature was maintained with Sunvic temperature controllers employing platinum resistance thermometers as sensing elements. With one of these controllers for each section, it was possible to maintain the temperature constant within  $0.5^{\circ}\text{C}$  over a two-day period.

Accurate temperature measurements were made with alumel-chromel thermocouples used in conjunction with a Leeds and Northrup precision potentiometer. The thermocouple junctions were cemented to the fluorescence tube and the side arm respectively. Both thermocouples had been calibrated against an N.R.C.-standardized platinum and platinum-rhodium thermocouple

The pressure of the potassium vapour was determined by the lower temperature of the side arm. The values of the vapour pressure, corresponding to the various temperatures, were calculated by means of an empirical equation which was developed by Ditchburn and Gilmour (1941) from a large amount of accumulated experimental data. The vapour pressure in mm. Hg is given by

$$\log_{10} P = \frac{-4552}{T} - 0.5 \log_{10} T + 8.795 ,$$

where T is the temperature in degrees K.

In order that reliable values of the vapour pressure could be obtained, the temperature of the side arm had to be known with reasonable accuracy. A check of the temperature distribution along the side arm revealed that the maximal variation amounted to less than  $1^{\circ}\text{C}$  over a distance of 12 cm. The corresponding error in the determination of the vapour pressure was negligible.

The arrangement of the vacuum and gas filling system is shown in Figure 4. A Kinney rotary pump in series with a C.E.C. oil diffusion pump was capable of producing a vacuum of less than  $10^{-5}$  mm. Hg. An Edwards Philani gauge was used for the measurement of the vacuum. The gauge employs a Philips head for pressures from  $10^{-5}$  to  $5 \times 10^{-3}$  mm. Hg and a Pirani head for pressures from  $5 \times 10^{-3}$  to 0.5 mm. Hg.

The inert gases were introduced into the system through a micro-metric needle valve thus making it possible to obtain desired gas pressures with a high degree of precision. Gas pressures were measured with

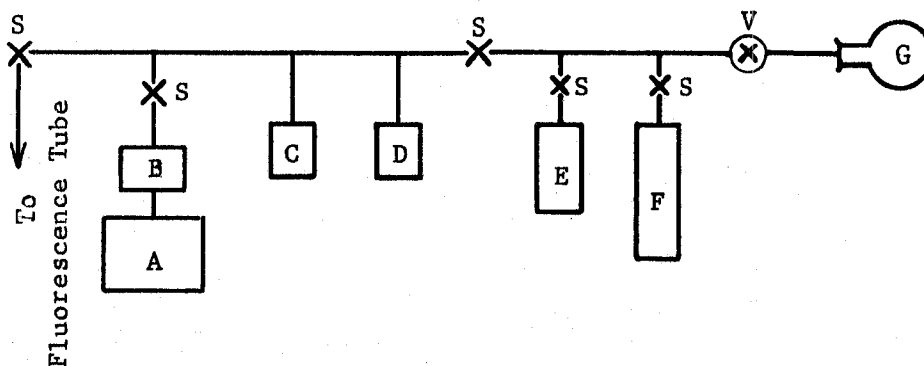


Fig. 4. A schematic diagram of the vacuum and gas-filling system. A - Kinney pump; B - oil diffusion pump; C - Pirani gauge head; D - Philips gauge head; E - oil manometer; F - mercury manometer; V - needle valve; G - gas bulb; S - stopcocks.

the Pirani head and with oil and mercury manometers.

#### The Recording Spectrometer

The spectrometer is a modification of the Hilger constant deviation prism instrument (model D187) which has an effective aperture of  $F/11$  and dispersion of  $166 \text{ \AA/mm.}$  at  $8000 \text{ \AA.}$  Its eyepiece was replaced by an exit slit followed by a vacuum cryostat containing a Dumont type 6911 photomultiplier tube which was used to detect the radiation. This tube has a current amplification of  $10^6$ . Because of the small amount of light being monitored, the signal to noise ratio had to be improved by cooling the tube with liquid air. A pyrex window, held in front of the phototube by means of an O-ring seal, prevented condensation of moisture on the surface of the tube. It was also necessary to place silica-gel drying agent in the phototube cavity and in the spectrometer. The voltage divider chain of the phototube (Figure 5) was placed in a separate chassis outside the cryostat, to prevent spurious electrical effects due to the cooling of the resistors. The phototube was operated at negative polarity to eliminate insulation problems; voltages up to  $-1800 \text{ V}$  were used. The output current from the phototube was amplified with a Victoreen electrometer amplifier (model VTE-2) and recorded with a Daystrom millivolt strip chart recorder.

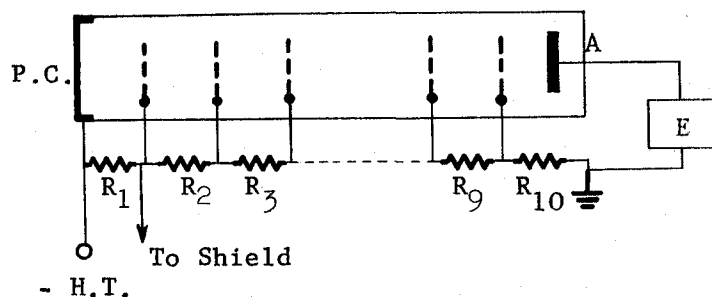


Fig. 5. Arrangement of the Photomultiplier circuit.  $R_1 = 800K$ ;  
 $R_2 - 9 = 270K$ ;  $R_{10} = 330K$ ; E - electrometer amplifier.

The intensity of the fluorescent light can be roughly calculated from the amplification of the electronic circuit. In the course of the experiments the electrometer amplifier was used at a setting corresponding to an input current of  $10^{-11}$  amp for a full scale deflection of the recorder. Assuming the rated phototube amplification of  $10^6$ , such a current would correspond to an emission of about 60 electrons/sec. The photocathode will emit one electron for each 50 photons incident at 8000 Å. Thus a full scale deflection of the recorder would be produced by a light flux of about 3000 photons/sec.

To facilitate the scanning of the spectrum, a synchronous motor was connected directly to the wavelength drum of the prism drive in the spectrometer. The motor, turning at a rate of  $1/2$  rev./hr., scanned the two resonance lines in about eight minutes. Although the two spectral lines are not strictly focused in one plane, it was found in practice that the exit slit could be set in a position, at which both the wavelengths, 7665 Å and 7699 Å, appeared to be in focus. The performance of this spectrometer was limited by its low dispersion and its straight entrance and exit slits, all of which considerably reduced its resolution and the light flux which could be passed through it.

#### The Preparation of Potassium Samples

Potassium metal (99% pure) was obtained from the A. R. MacKay



Company. To remove residual impurities, the metal was slowly vacuum-distilled through a series of four pyrex bulbs. Small quantities of potassium were then distilled into capsules of approximately 1/2 gram capacity and sealed off. The capsules were constructed with a thin-walled bulb at one end, to facilitate breaking under vacuum.

In order to introduce the potassium into the fluorescence tube, a capsule was placed, together with a steel breaker sealed in pyrex, in a tube connected by means of a constriction to the side arm of the fluorescence tube. The tube was sealed, the whole system evacuated, the capsule opened using the breaker and a magnet, and the potassium then distilled through the constriction into the side arm. Finally, the constriction itself was sealed off and excess tubing removed.

The pyrex, of which the fluorescence tube was made, had a tendency to assume a brown discolouration after being exposed to potassium vapour at high temperatures. This effect was temperature dependent and became very pronounced above  $260^{\circ}\text{C}$ . In order to maintain good transmission of the tube windows, it was necessary to rinse the tube periodically with distilled water which removed the brown deposit.

#### The Alignment of the Optical System

In order to eliminate the diffusion of radiation, the cone of exciting light was restricted to a thin layer near the side window of the fluorescence tube. The light from the monochromator was focused with a condensing lens so that the image of the exit slit was formed directly in front of the side window, with the cone of light just grazing the window surface. To accomplish this, the image of the monochromator slit was focused immediately outside the side window. Then the condensing lens was moved perpendicularly to the light path until the image and the light beam were properly positioned inside the tube. A positive alignment was assured by viewing the side window in the dark and observing when the incident light no longer produced reflections from it. Care was also taken to prevent the cone of light from being reflected at the walls of the tube. A tungsten filament lamp was used

for preliminary alignment and the location of the image was checked with a cathetometer; the location of the light cone in the tube is shown in fig. 6. To eliminate stray light from the inside of the oven, the tube was coated (except for the windows) with a thin layer of asbestos cement.

The spectrometer was focused for the 7665 Å to 7699 Å wavelength region with the Osram lamp placed directly in front of its entrance slit. The widths of the entrance and exit slits were both set at 0.075 mm. -- the highest value giving good resolution of the potassium doublet. Both the entrance and exit slits in the spectrometer are straight and do not compensate for the curvature of the spectral lines. In order to reduce the effect of this curvature on the resolution of the instrument, the length of the entrance slit was limited to 5.5 mm.

The fluorescent light emerging from the side window of the tube was condensed onto the slit of the spectrometer by means of the two lenses  $L_2$  and  $L_3$ . Their positions were calculated to illuminate fully the optics of the instrument. The final adjustments were made by obtaining the maximal signal from the photomultiplier tube.

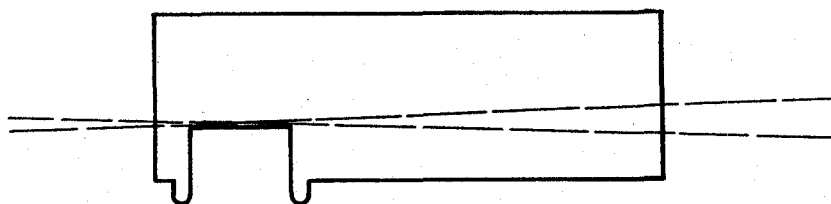


Fig. 6. Optical alignment of the fluorescence tube.

## IV

### RESULTS AND DISCUSSION

#### Energy Transfer in Potassium-Potassium Collisions

The potassium sample was introduced into the side arm of the fluorescence tube and the system was evacuated for a period of approximately fifteen hours, while the ovens were maintained at a temperature of 220°C. In this way, any gaseous impurities still present were removed from the walls of the fluorescence tube. The optical alignment was then completed and the electronic equipment allowed to warm up for at least one hour.

At the beginning of an experimental run, the oven temperatures were set and stabilized at about 160°C with the main oven at 20°C above the side oven. Each of the two resonance components in turn was made incident on the potassium vapour and the fluorescent light was scanned with the spectrometer. The fluorescence spectrum resulting from the excitation by each of the two resonance frequencies was scanned four times. The temperature of the oven was then raised to the next higher value and the procedure was repeated. A set of spectra at temperatures between 160° and 280°C was obtained in this way without interrupting the experiment.

The recorder maxima corresponding to each component of the spectrum were averaged and used to calculate the total fluorescent intensities and the intensity ratios  $\eta_1$  and  $\eta_2$  at each temperature. These values are given in Table I and selected profiles of fluorescence spectra corresponding to various temperatures are shown in Figure 7.

It can be seen that when fluorescence is excited by means of the 7665 Å radiation, the intensity of the exciting component present in the fluorescent light never exceeds the intensity of the component arising from the collisions. This is not so, when the fluorescence is excited with the 7699 Å radiation. The  $4^2P_{3/2}$  level of potassium, which emits the 7665 Å wavelength, has a statistical weight of four while the  $4^2P_{1/2}$  level, which emits the 7699 Å wavelength, has a

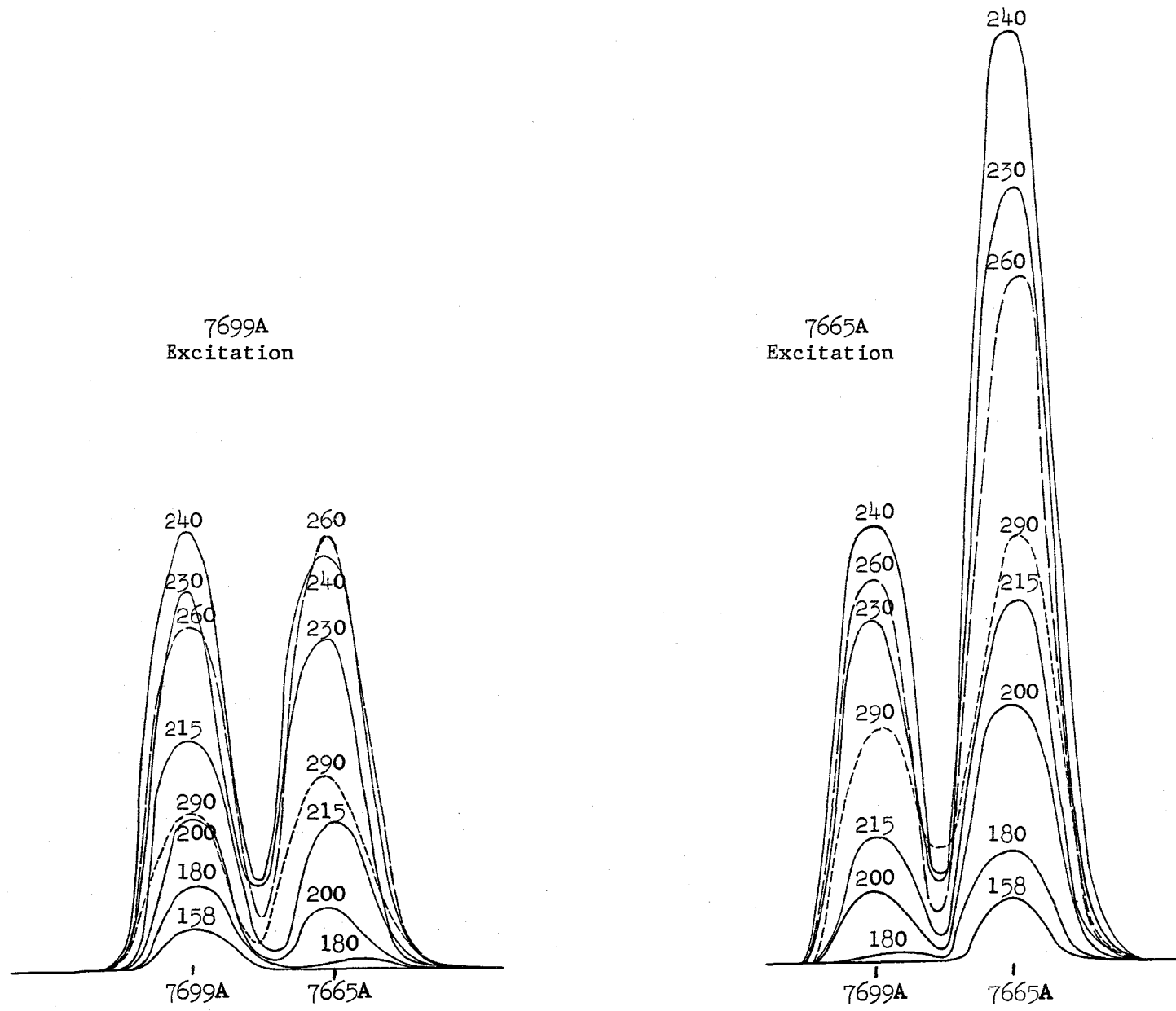


Fig. 7. Intensity profiles of the sensitized fluorescence spectra in potassium.

TABLE I  
 Intensities and intensity ratios in the fluorescence spectrum  
 of potassium

Temperature (°C)	Pressure (mm. Hg)	Excitation with 7699 Å radiation ( $I_1$ )		Excitation with 7665 Å radiation ( $I_2$ )	
		Total fluorescent intensity ( $I_1 + I_2$ )	$\eta_2 = \frac{I_2}{I_1}$	Total fluorescent intensity ( $I_1 + I_2$ )	$\eta_1 = \frac{I_1}{I_2}$
158	0.00083	0.140	0.00748	0.193	0.0217
169	0.00151	0.197	0.067	0.254	0.0554
180	0.00264	0.278	0.0986	0.383	0.0983
190	0.0040	0.417	0.197	0.648	0.156
200	0.0068	0.700	0.406 0.259	1.00	0.256 0.207 *
205	0.00856		0.357		0.275 *
210	0.0108	1.052	0.554 0.418	1.568	0.361 0.293 *
215	0.0133	1.194	0.630 0.694	1.692	0.358 0.432 *
220	0.0165	1.430	0.776 0.780	2.030	0.425 0.461 *
225	0.0205		0.884		0.477 *
230	0.0248	2.300	0.866 0.949	3.690	0.447 0.519 *
235	0.0303		1.010		0.524 *
240	0.0366	2.670	0.992 1.027	4.360	0.485 0.529 *
245	0.0444		1.092		0.555 *
250	0.0537	2.790	1.052 1.086	3.910	0.519 0.602 *
255	0.0650		1.152		0.602 *
260	0.0779	2.600	1.207 1.223	3.410	0.568 0.622 *
265	0.0926		1.232		0.643 *
270.5	0.1122	2.350	1.243	2.76	0.595
269.5	0.1085		1.246		0.638 *

TABLE I (cont'd)

Temperature (°C)	Pressure (mm. Hg)	Excitation with 7699 A radiation ( $I_1$ )		Excitation with 7665 A radiation ( $I_2$ )	
		Total fluorescent intensity ( $I_1 + I_2$ )	$\eta_2 = \frac{I_2}{I_1}$	Total fluorescent intensity ( $I_1 + I_2$ )	$\eta_1 = \frac{I_1}{I_2}$
275	0.1300		1.237		0.662 *
280	0.1530	1.750	1.216 1.224	2.110	0.576 0.647 *
290	0.2180	1.120	1.331	1.300	0.540

\* Values from Run No. 1.

statistical weight of two. At increasing pressures, the ratio of the populations of these levels in the potassium vapour tends to approach the ratio of their statistical weights and the intensities of the two components are, of course, proportional to the populations of the levels from which they originate.

It is also apparent that the total fluorescent intensity varies with the pressure (and the temperature) of the potassium vapour, reaching a maximum at about 0.04 mm. Hg (or 240°C). This variation is shown in Figure 8. With both 7665 A and 7699 A as exciting radiation, the intensity increases rapidly and almost linearly at low pressures as more atoms become available for the processes of excitation and collision. The maxima of both curves correspond roughly to the onset of 'volume fluorescence' which causes a decrease in the intensity of the light emitted from the small section of the tube even though the total fluorescent output of the tube may still be increasing. The occurrence of volume fluorescence above 240°C was confirmed using an infrared image converter tube (Sniperscope). When both the curves are extrapolated to higher pressures they tend to converge and indicate low fluorescent inten-

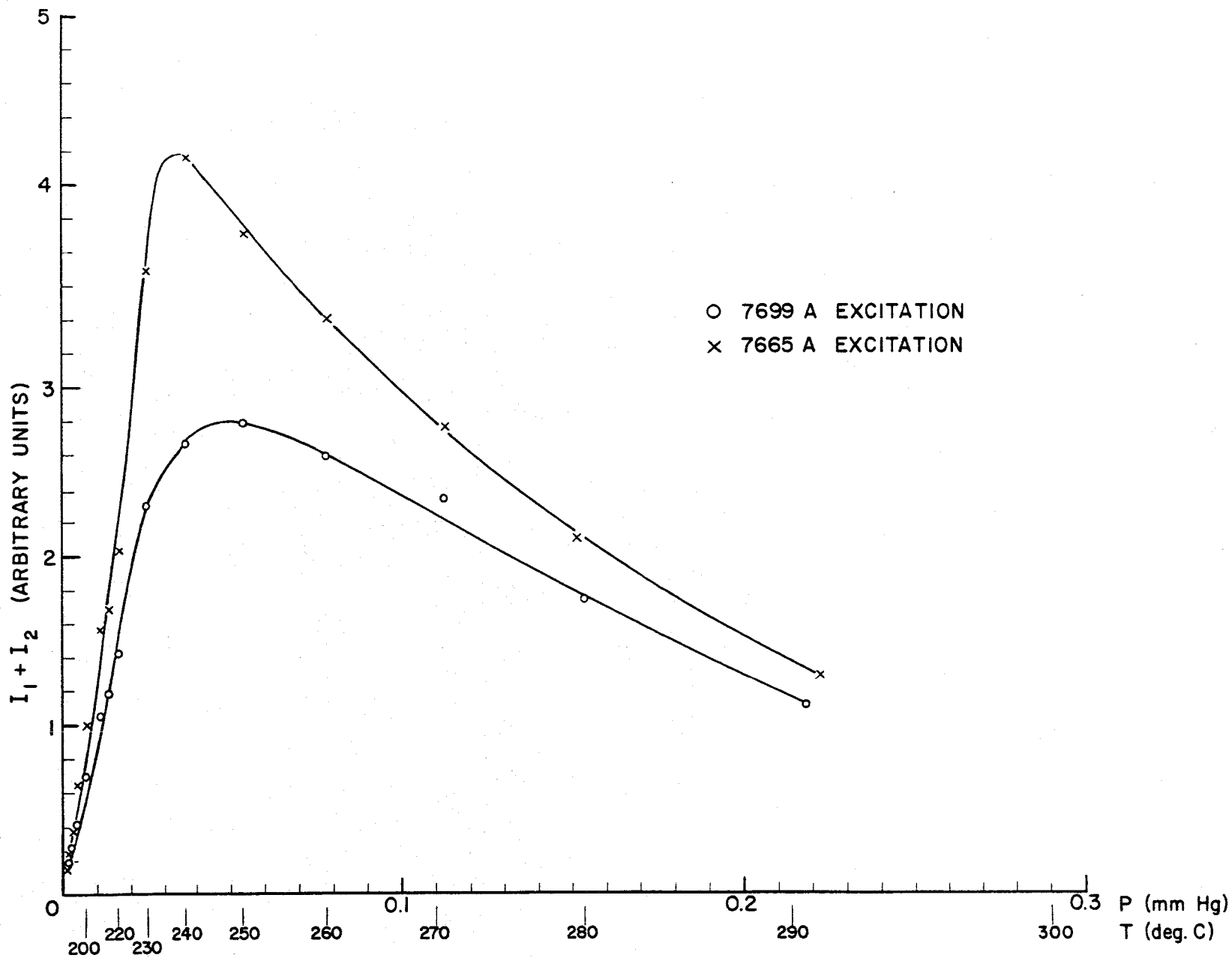


Fig. 8. The variation of the total fluorescent intensity with potassium pressure.

sities at temperatures above  $300^{\circ}\text{C}$ . At these temperatures 'surface fluorescence' becomes dominant because the exciting radiation is absorbed and re-emitted in a thin layer of vapour immediately adjacent to the front window of the tube, with practically none penetrating into the monitored segment.

The plots of the intensity ratios  $\eta_1$  and  $\eta_2$  against the potassium pressure are given in Figures 9 and 10, respectively. The graphs were obtained by drawing the best fitting curves through the experimental points. For the purpose of comparison, the results obtained by Thangaraj (1948) and Hoffmann and Seiwert (1961) are also included.

It might be expected from considerations of statistical weights, that, at increasing vapour pressures  $\eta_1$  and  $\eta_2$  should approach the values of 0.5 and 2 respectively. Although the two ratios do approach constant values, these values are not in agreement with the above prediction. It is likely that, in addition to the excitation and emission processes which would tend to establish the theoretical equilibrium, there are other competing processes taking place. In particular, quenching collisions and diffusion to the walls of the vessel would introduce an unknown factor into the equilibrium between the two states.

If the higher energy level of potassium,  $4^2\text{P}_{3/2}$ , had a somewhat greater tendency to lose energy through such processes, than the  $4^2\text{P}_{1/2}$  level, this would produce an increase in  $\eta_1$  and a decrease in  $\eta_2$  from their theoretical values. This is the trend of the results obtained in the course of this investigation and it makes the postulated mechanism plausible. The effect would be further enhanced by the greater tendency of the 7665 Å radiation to become 'imprisoned' in the vapour, as its absorption coefficient is about twice as large as the absorption coefficient of the 7699 Å wavelength.

There is a significant discrepancy between the experimental results presented here and those of Hoffmann and Seiwert (1961). This should be ascribed to the large effect of the diffusion of radiation in his system, the design of which did not approximate the 'ideal fluorescence tube' of Mitchell and Zemansky (1934). Additional effects were produced by Seiwert's inability to resolve the



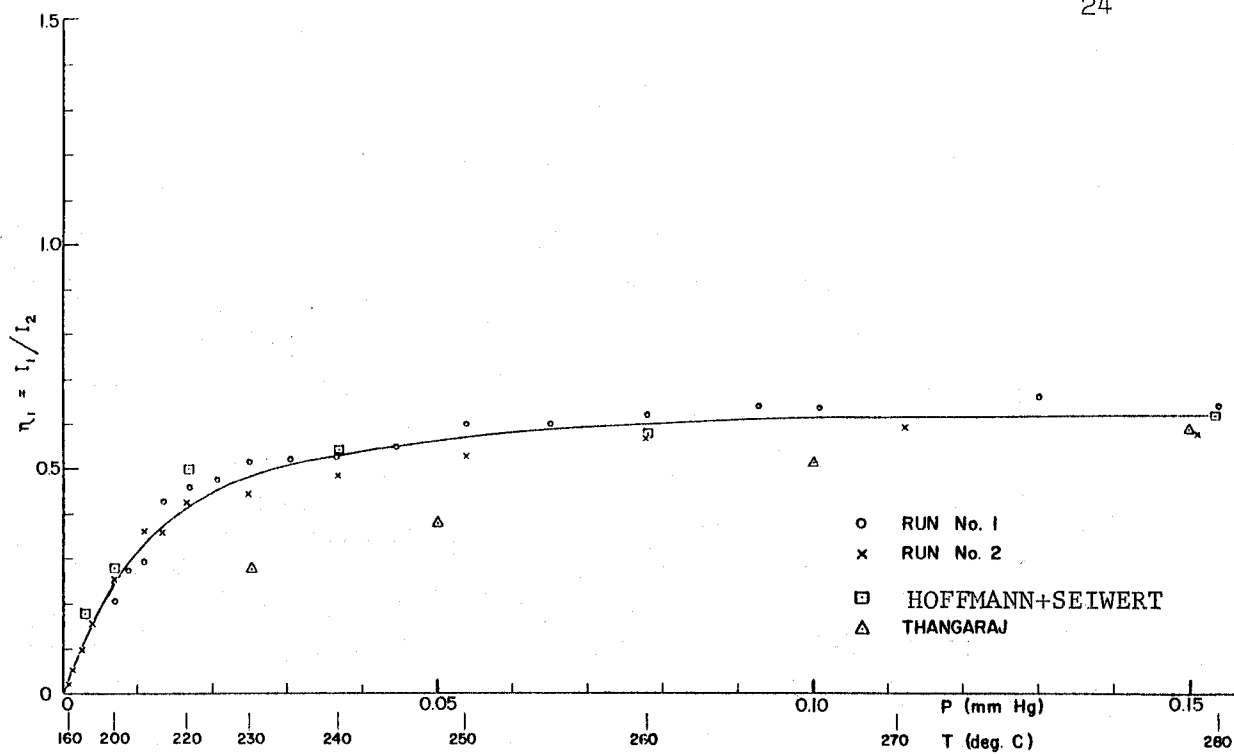


Fig. 9. The variation of  $\eta_1$  with potassium pressure.

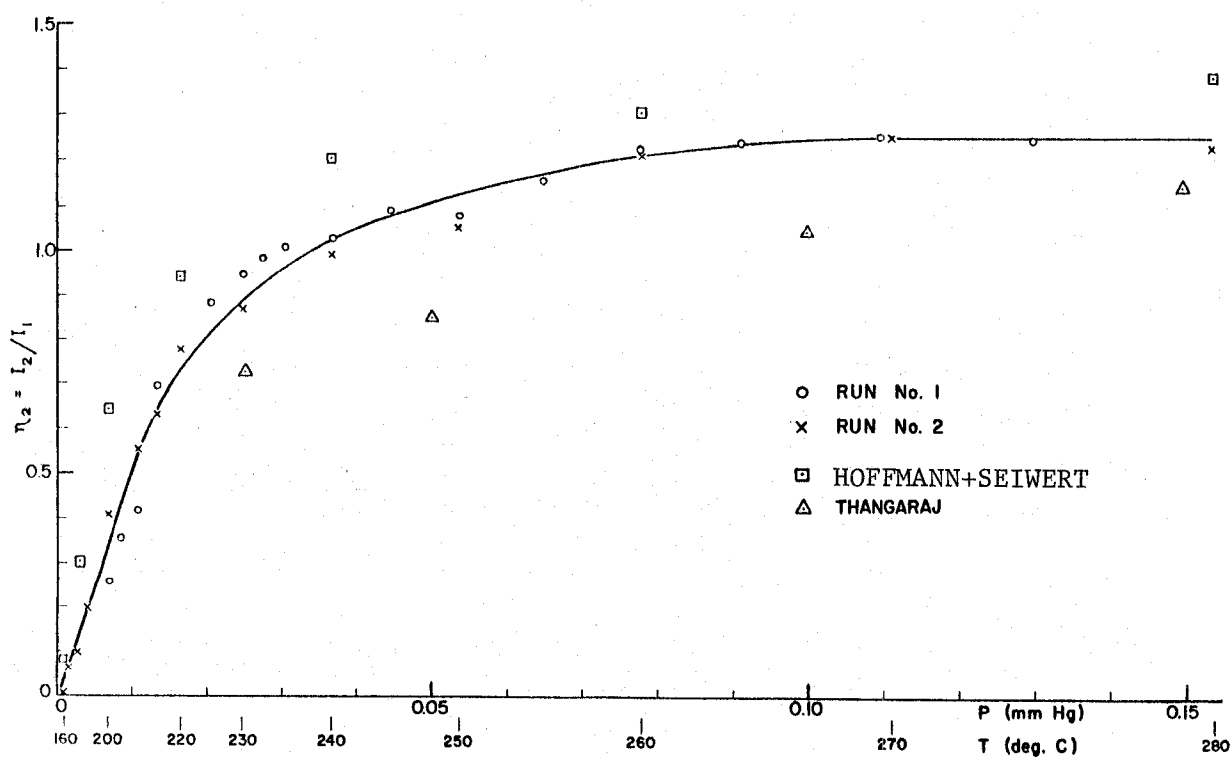


Fig. 10. The variation of  $\eta_2$  with potassium pressure.

two resonance components in the exciting beam.

Thangaraj's (1948) experiments were carried out under completely different conditions. He investigated the surface fluorescence of potassium, in which the diffusion of radiation assumes a prominent role.

The values of  $\eta_1$  and  $\eta_2$  for a number of vapour pressures were read off the curves in Figures 9 and 10, and substituted in equations 10a and 10b from which the collision cross-sections  $Q_1 (4^2P_{1/2} \rightarrow 4^2P_{3/2})$  and  $Q_2 (4^2P_{3/2} \rightarrow 4^2P_{1/2})$  were then calculated, using  $\gamma = 2.6 \times 10^{-8}$  seconds (Landolt and Börnstein 1950); the results are given in Table II.

TABLE II

Cross-sections for collisions of a second kind between potassium atoms

Temperature (°C)	Pressure (mm. Hg)	$Q_1 \times 10^{-13}$ ( $4^2P_{1/2} \rightarrow 4^2P_{3/2}$ )	$Q_2 \times 10^{-13}$ ( $4^2P_{3/2} \rightarrow 4^2P_{1/2}$ )
270	0.1097	21.3	14.6
260	0.0779	26.0	17.0
250	0.0537	24.9	17.2
240	0.0366	24.8	17.0
235	0.0303	25.1	17.1
230	0.0248	25.3	17.2
220	0.0165	24.8	17.2
215	0.0133	23.4	16.3
210	0.0108	21.5	15.4
200	0.0068	18.2	13.3
190	0.0040	15.2	12.0
180	0.00264	13.6	11.1
169	0.00151	12.0	10.1
158	0.00083	10.9	9.2
145	0.00040	10.2	8.8
134	0.00020	9.8	8.3

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The collision cross-sections thus obtained include a small contribution arising from the diffusion of radiation which tends to increase their values. So far in this investigation, no attempt has been made to correct for these effects. If, however, the collision cross-sections are plotted against the pressure of potassium as shown in Figure 11, they are found to decrease with pressure in a regular manner. A straightforward extrapolation to zero pressure yields two intercepts which correspond to  $Q_1 = 95 \times 10^{-14} \text{ cm}^2$  and  $Q_2 = 83 \times 10^{-14} \text{ cm}^2$ . These values represent the true cross-sections for collisions of a second kind taking place under conditions where no radiation diffusion is possible. A comparison with the results obtained by Thangaraj (1948) and Hoffmann and Seiwert (1961) is given below.

Source	$Q_1$	$Q_2$
This investigation	$95 \times 10^{-14} \text{ cm}^2$	$83 \times 10^{-14} \text{ cm}^2$
Thangaraj	$3.3 \times 10^{-14} \text{ cm}^2$	$1.65 \times 10^{-14} \text{ cm}^2$
Hoffmann+Seiwert	$1.2 \times 10^{-14} \text{ cm}^2$	$0.6 \times 10^{-14} \text{ cm}^2$

The large discrepancies between the results of this research on the one hand and those of Thangaraj and Seiwert on the other are due to several factors. The previously mentioned differences in experimental methods and results would necessarily have an effect. Most of the differences, however, must be due to a treatment of the experimental results which was entirely different from that employed here.

Both Thangaraj and Seiwert introduced corrections into their calculations of collision cross-sections, in order to eliminate the considerable effects of the diffusion of radiation. These effects manifest themselves by an effective increase in the lifetimes  $\tau$  of the excited states, as the radiation becomes imprisoned in the vapour. The effective lifetimes at any pressure may be obtained by applications of the existing theories of radiation diffusion and used in the calculations of the collision cross-sections.

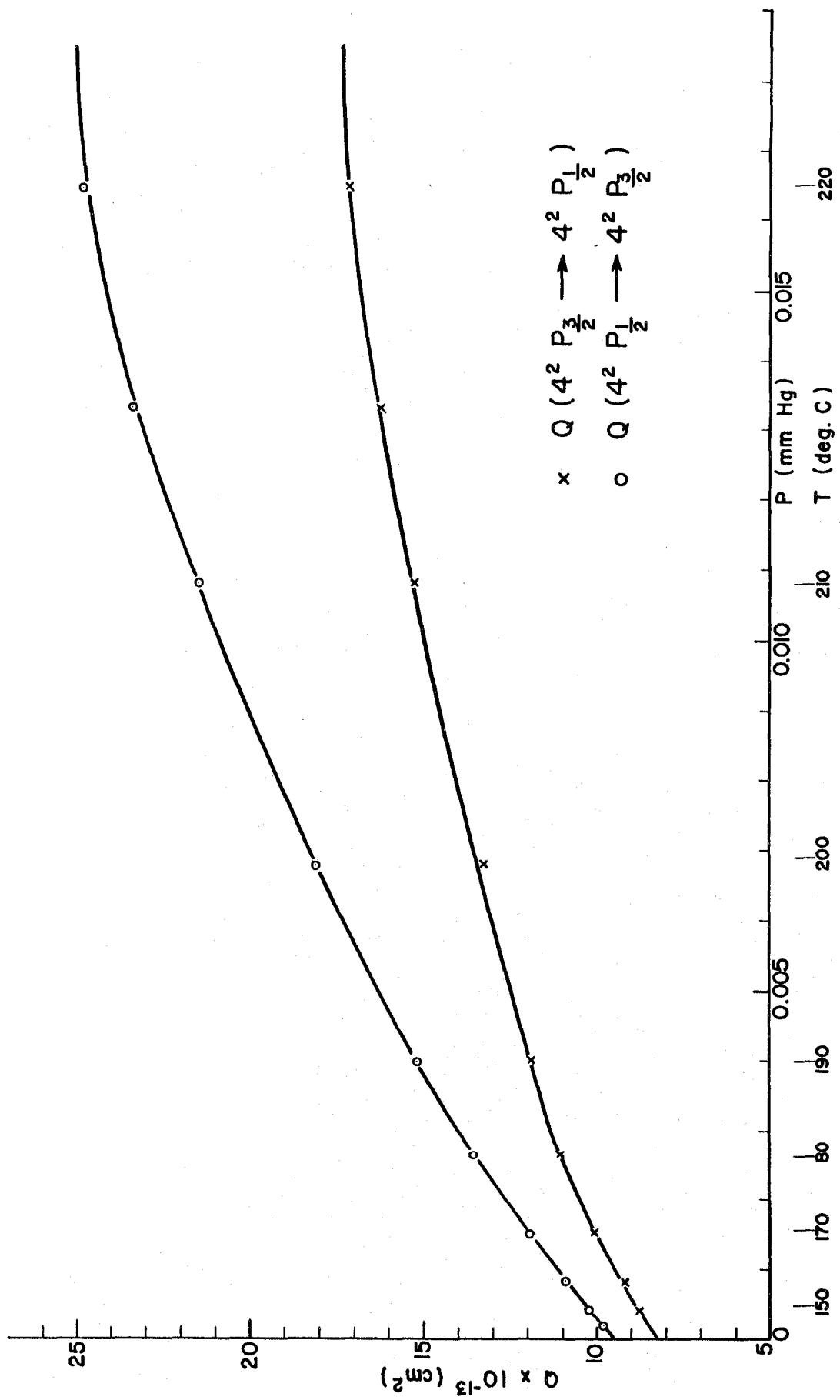


Fig. 11. The variation of cross-sections for potassium-potassium collisions with vapour pressure. 27

Thangaraj used Milne's (1926) theory and Seiwert employed Holstein's (1947) treatment, which he adapted (Hoffmann and Seiwert 1961) to his particular experimental conditions. Neither theory lends itself easily to being used for the purpose of calculating collision cross-sections and both authors were forced to make important assumptions about the geometry of their systems and values of absorption coefficients, and use mathematical approximations. The method of extrapolating an experimental curve to zero pressure does not present such problems and is much more likely to yield acceptable results. This was manifestly shown by Webb and Messenger (1929) and by Garrett (1932) who carried out experimental determinations of the lifetimes of the  $6^3P_1$  level of mercury at various vapour pressures. As the pressure became very small and the diffusion of radiation disappeared, the lifetime assumed a constant value. A comparison with Milne's theory indicated that the theory much overestimates the effects of radiation diffusion. Similar work on the lifetimes of helium atoms was carried out by Heron, McWhirter and Rhoderick (1954).

It might be of interest to compare the collision cross-sections obtained here with the values calculated on the basis of classical kinetic theory which are of the order of  $10^{-15} \text{ cm}^2$ . The higher values obtained experimentally imply that it is not necessary for the atoms to 'touch' in order that transfer of energy might take place.

Kallmann and London (1929) have treated the problem of interaction between two excited atoms almost in resonance with one another using techniques of classical quantum mechanics. They derived an expression giving cross-sections for collisions of a second kind:

$$q = 0.960 \pi \left( \frac{\mu_1 \mu_2}{\Delta E} \right)^{2/3}$$

where  $\mu_1$  and  $\mu_2$  are the dipole moments of the two states between which dipole transitions are allowed and  $\Delta E$  is the energy separation between them.

This equation yields a value  $7.5 \times 10^{-14} \text{ cm}^2$  which, however, should be considered in the light of the fact that the theory does not

allow either for electron spin or for the velocity-dependence of the cross-sections.

Energy Transfer in Collisions between Potassium  
and Inert Gas Atoms

When increasing quantities of an inert gas are added to potassium vapour, the collisions between the potassium and the gas atoms become correspondingly more frequent. The first excited states of the inert gas atoms lie considerably higher than the  $4^2P$  states of potassium and, therefore, no quenching of fluorescence occurs. The mean translational energy of the atoms is however sufficient to cause a transfer from the  $4^2P_{1/2}$  state to  $4^2P_{3/2}$  (and vice versa) during the collisions between the excited atoms of potassium and atoms of the inert gases. Thus an increase in inert gas pressure would enhance the transfer of energy between the two resonant states. The inert gas would also act as a buffer preventing the potassium atoms from diffusing to the walls of the tube and there losing their energy. This buffer action should cause an increase in the total fluorescent intensity.

Spectroscopically pure helium and argon, obtained from the Linde Company, were selected to study the collisions between the atoms of potassium and inert gases; argon has a mass nearly equal to that of potassium and helium has a very much smaller mass. In order to maintain a reasonable level of fluorescent intensity, a potassium pressure of 0.0086 mm. Hg (200°C) was chosen. At this pressure energy transfer due to potassium-potassium collisions was already noticeable.

With the system lined up and adjusted in the usual manner, carefully controlled amounts of the inert gases were admitted to the fluorescence tube by means of a micrometric needle valve. The fluorescence spectrum excited by each component of the resonance doublet in turn was scanned four times with the spectrometer. The total fluorescent intensities and the intensity ratios  $\eta$  corresponding to the various pressures are given for helium in Table III and for argon in Table IV.

TABLE III

Fluorescent intensities and intensity ratios  
for a potassium-helium mixture

Helium Pressure (mm. Hg)	Excitation with 7699 A Radiation ( $I_1$ )		Excitation with 7665 A Radiation ( $I_2$ )	
	Total fluorescent intensity ( $I_1+I_2$ )	$\eta_2 = \frac{I_2}{I_1}$	Total fluorescent intensity ( $I_1+I_2$ )	$\eta_1 = \frac{I_1}{I_2}$
0	0.681	0.410 0.428	1.00	0.256 0.255 *
0.0053		0.566		0.346 *
0.013	0.710	0.604	1.028	0.375
0.019		0.613		0.365 *
0.029		0.636		0.383 *
0.048	0.680	0.690	1.012	0.401
0.075		0.725		0.398 *
0.100	0.582	0.723	0.804	0.399
0.115		0.743		0.412 *
0.253		0.790		0.427 *
0.506	0.643	0.867	0.990	0.463
0.723		0.911		0.478 *
1.012	0.816	0.941	1.175	0.497
1.157		1.002		0.515 *
1.410		1.006		0.533 *
1.70		1.035		0.536 *
1.99		1.095		0.528 *
2.21	1.088	1.104	1.680	0.558 *
2.46		1.139		0.543 *
3.07	1.341	1.174	1.916	0.585
4.05		1.191		0.598 *
4.85	1.563	1.228	2.200	0.621
6.62		1.241		0.617 *
10.00		1.275		0.622 *

TABLE III (cont'd)

Helium Pressure (mm. Hg)	Excitation with 7699 A Radiation ( $I_1$ )		Excitation with 7665 A Radiation ( $I_2$ )	
	Total fluorescent intensity ( $I_1+I_2$ )	$\eta_2 = \frac{I_2}{I_1}$	Total fluorescent intensity ( $I_1+I_2$ )	$\eta_1 = \frac{I_1}{I_2}$
10.12	2.09	1.298	3.37	0.641
20.0	3.01	1.381	4.22	0.682
40.0	3.54	1.394	4.99	0.698
46.0		1.364		0.686 *
81.0	4.08	1.372	5.27	0.702
162.0	4.34	1.395	5.43	0.715
173.0		1.370		0.702 *
327.0	4.10	1.412	5.86	0.707

\* Run No. 2.

A plot of the total fluorescent intensities against the pressure of helium is shown in Figure 12 and the corresponding relationship for argon is given in Figure 13. In the case of both helium and argon the total intensity increases with pressure, but, unlike with potassium vapour alone, there are no maxima present in the curves. This is readily explained by the absence of volume or surface fluorescence. The intensity values reached are also considerably greater, indicating the effect of the buffer action of the gases. As might be expected, argon atoms are more efficient in this respect.

The graphs of the intensity ratios  $\eta_1$  and  $\eta_2$  against the pressure of helium are given in Figures 14 and 15 respectively,



TABLE IV

Fluorescent intensities and intensity ratios  
for a potassium-argon mixture

Argon Pressure (mm. Hg)	Excitation with 7699 A Radiation ( $I_1$ )		Excitation with 7665 A Radiation ( $I_2$ )	
	Total fluorescent intensity ( $I_1+I_2$ )	$\eta_2 = \frac{I_2}{I_1}$	Total fluorescent intensity ( $I_1+I_2$ )	$\eta_1 = \frac{I_1}{I_2}$
0	0.529	0.269	1.00	0.162
0.0106	0.638	0.325	1.003	0.177
0.045	0.648	0.461	1.050	0.276
0.095	0.818	0.497	1.195	0.319
0.47	1.090	0.727	1.474	0.443
1.080	1.450	0.843	1.932	0.569
2.03	1.730	0.959	2.13	0.642
3.07	1.960	0.963	2.33	0.671
4.96	2.26	0.999	2.89	0.750
10.0	3.07	1.056	3.90	0.792
20.5	3.77	1.092	4.83	0.826
40.0	4.76	1.090	6.34	0.859
81.0	6.05	1.057	7.50	0.895
159.0	6.20	1.102	6.77	0.875
314.0	7.94	1.104	9.72	0.877
573.0	8.53	1.102	10.58	0.919
720.0	9.02	1.060	11.58	0.899

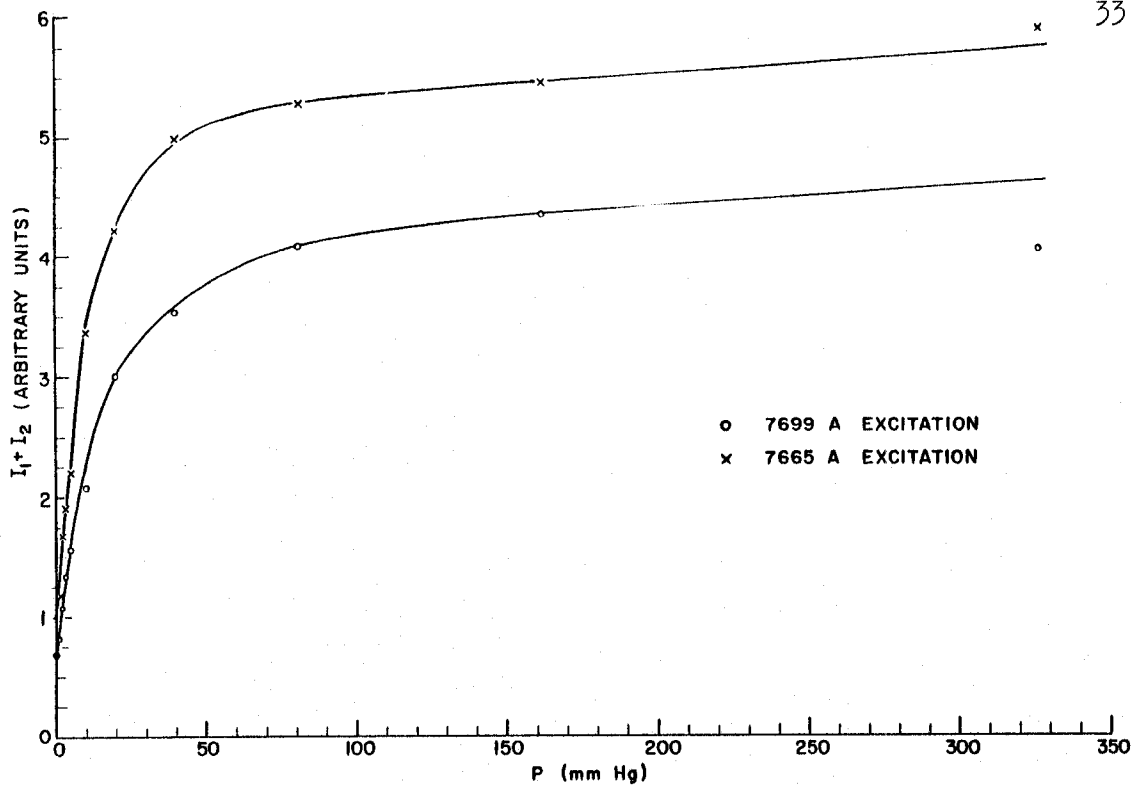


Fig. 12. A plot of total fluorescent intensity against helium pressure.

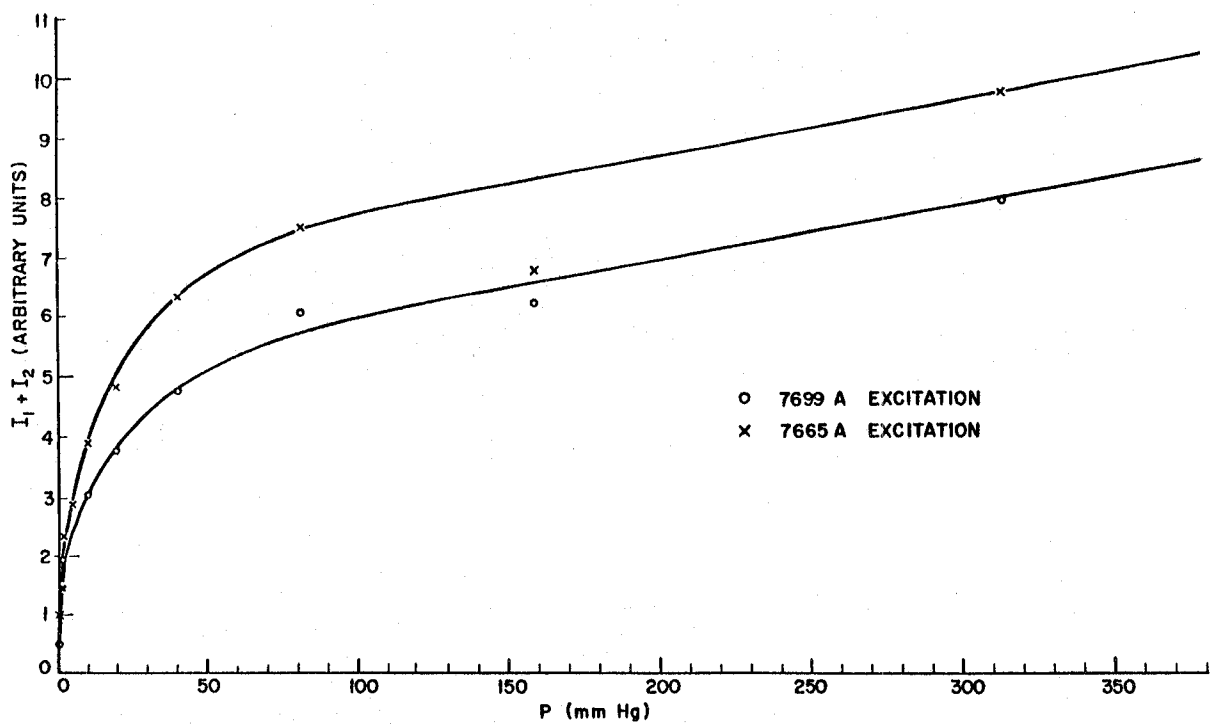


Fig. 13. A plot of total fluorescent intensity against argon pressure.

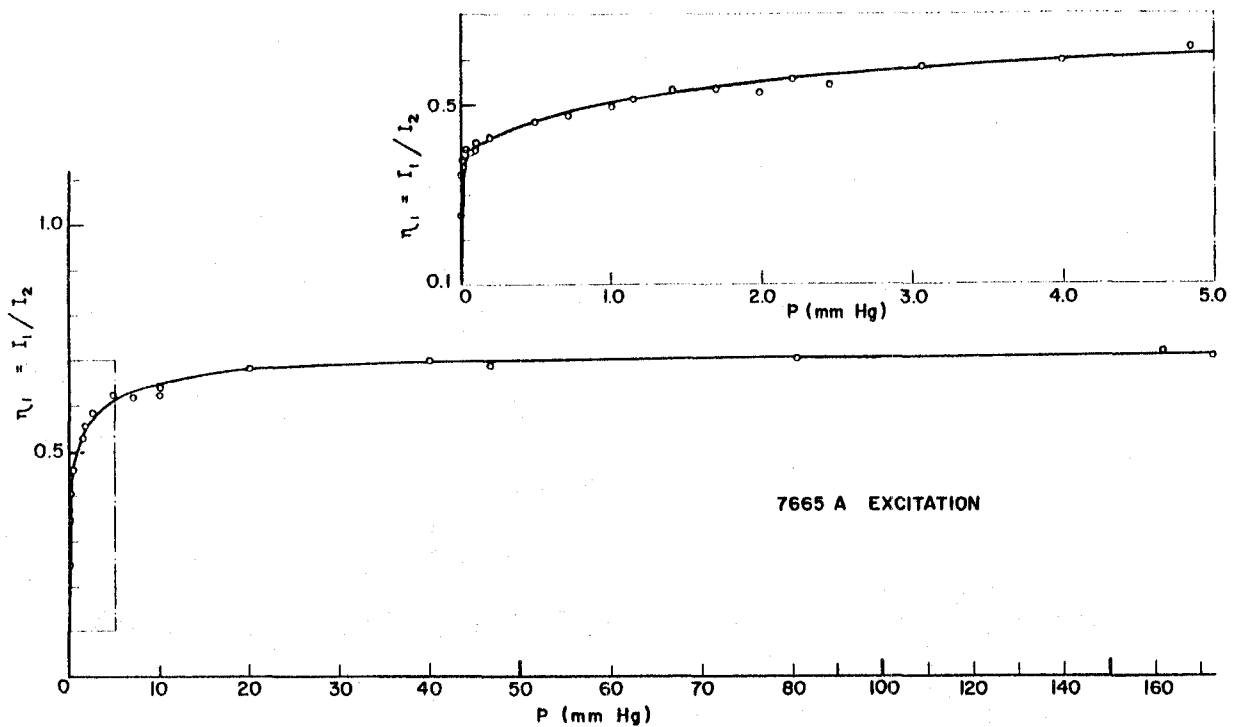


Fig. 14. Variation of  $\eta_1$  with the pressure of helium. The insert shows a magnified portion of the graph near the origin.

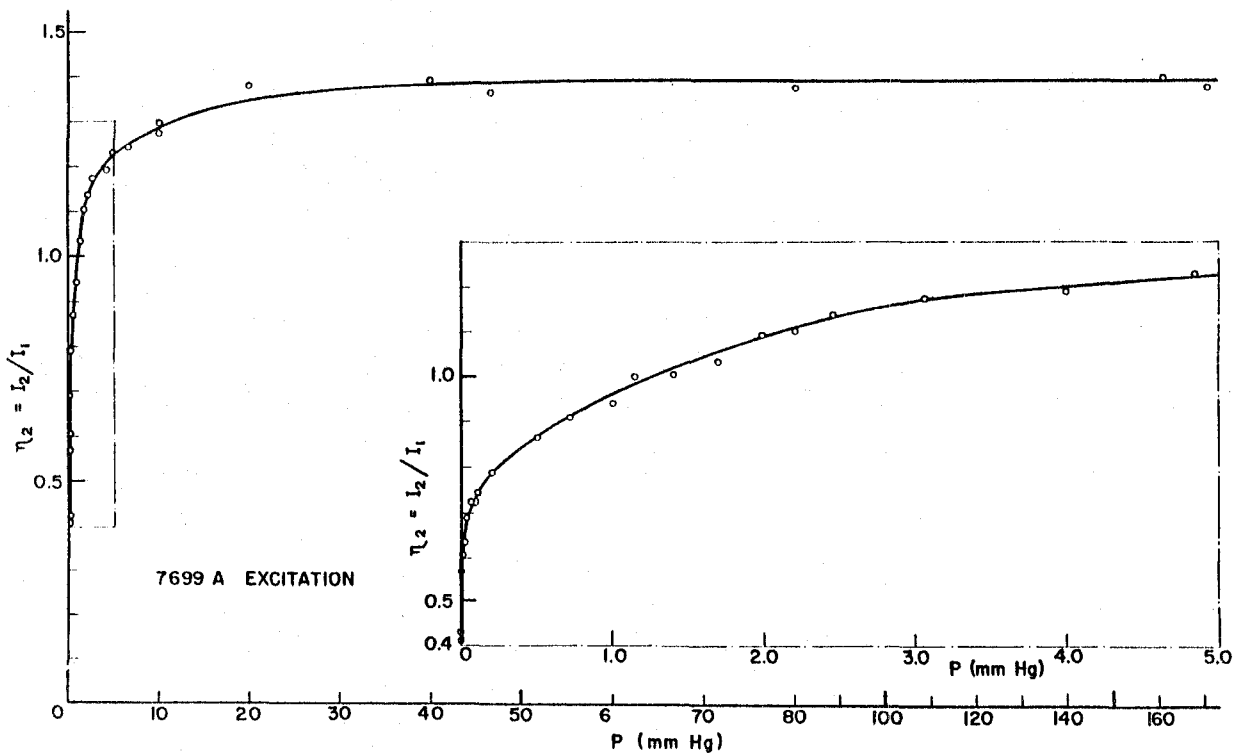


Fig. 15. Variation of  $\eta_2$  with the pressure of helium. A magnified portion of the graph near the origin is shown in the insert.

and the corresponding plots for argon appear in Figures 16 and 17. Each of these figures contains a magnified section of the graph showing its detail at very small gas pressures.

As with potassium alone, values of  $\eta_1$  and  $\eta_2$  for various pressures were read off the graphs and used in equations 10a and 10b to calculate the cross-sections between potassium and inert gas atoms, corresponding to the transfers  $4^2P_{1/2} \rightarrow 4^2P_{3/2}$  and  $4^2P_{1/2} \leftarrow 4^2P_{3/2}$ . The results for helium are given in Table V.

TABLE V

Cross-sections for collisions of a second kind  
between potassium and helium atoms

Helium Pressure (mm. Hg)	$Q_1 \times 10^{-14}$ ( $4^2P_{1/2} \rightarrow 4^2P_{3/2}$ )	$Q_2 \times 10^{-14}$ ( $4^2P_{1/2} \leftarrow 4^2P_{3/2}$ )
0	22.7	15.7
0.100	15.6	10.6
0.20	9.16	6.59
0.30	6.70	4.32
0.50	4.64	3.17
0.70	3.73	2.54
0.900	3.26	2.23
1.20	2.88	1.97
1.50	2.63	1.78
2.00	2.37	1.61
2.50	2.22	1.51
3.00	2.08	1.42
3.50	1.98	1.35
4.00	1.88	1.29
4.50	1.82	1.25
5.00	1.77	1.21
6.00	1.68	1.17
8.00	1.55	1.07
10.00	1.47	1.03
12.00	1.45	1.01

TABLE V (cont'd)

Helium Pressure (mm. Hg)	$Q_1 \times 10^{-14}$ ( $4^2P_{1/2} \rightarrow 4^2P_{3/2}$ )	$Q_2 \times 10^{-14}$ ( $4^2P_{3/2} \rightarrow 4^2P_{1/2}$ )
14.00	1.39	.97
16.00	1.36	.96
18.00	1.37	.96
20.00	1.36	.95
30.00	1.27	.90

It can be seen in Figure 18 that when there is no helium present in the system, all the collisions occur between potassium atoms and the cross-sections are those for potassium-potassium collisions at the appropriate temperature (200°C). As the pressure of helium is increased, the probability of collisions between potassium and helium becomes overwhelming and, at higher pressures, the cross-sections reach approximately constant values appropriate to helium-potassium collisions. (It is assumed that in the region of higher pressures the cross-sections include no contributions arising from potassium-potassium collisions.) There is also a certain tendency for the cross-sections to decrease slightly with increasing pressures which can most likely be ascribed to a pressure effect. Assuming this effect to be proportional to the pressure, an extrapolation of the linear portions of the graphs to zero pressure should yield the true values of  $Q_1$  and  $Q_2$ . The values thus obtained are:

$$Q_1 (4^2P_{1/2} \rightarrow 4^2P_{3/2}) = 1.54 \times 10^{-14} \text{ cm}^2$$

$$Q_2 (4^2P_{3/2} \rightarrow 4^2P_{1/2}) = 1.04 \times 10^{-14} \text{ cm}^2$$

The corresponding results for argon, which were obtained by means of an identical procedure are:

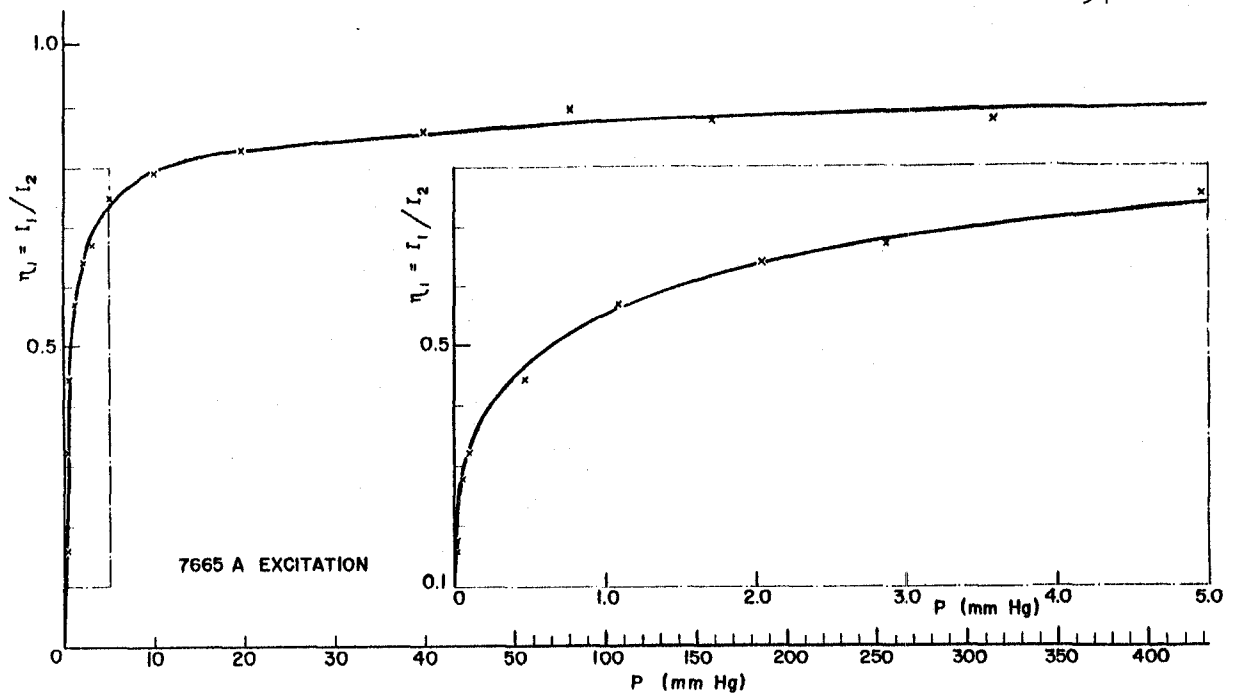


Fig. 16. A plot of  $\eta_1$  against the pressure of argon. A magnified section of the graph near the origin is shown in the insert.

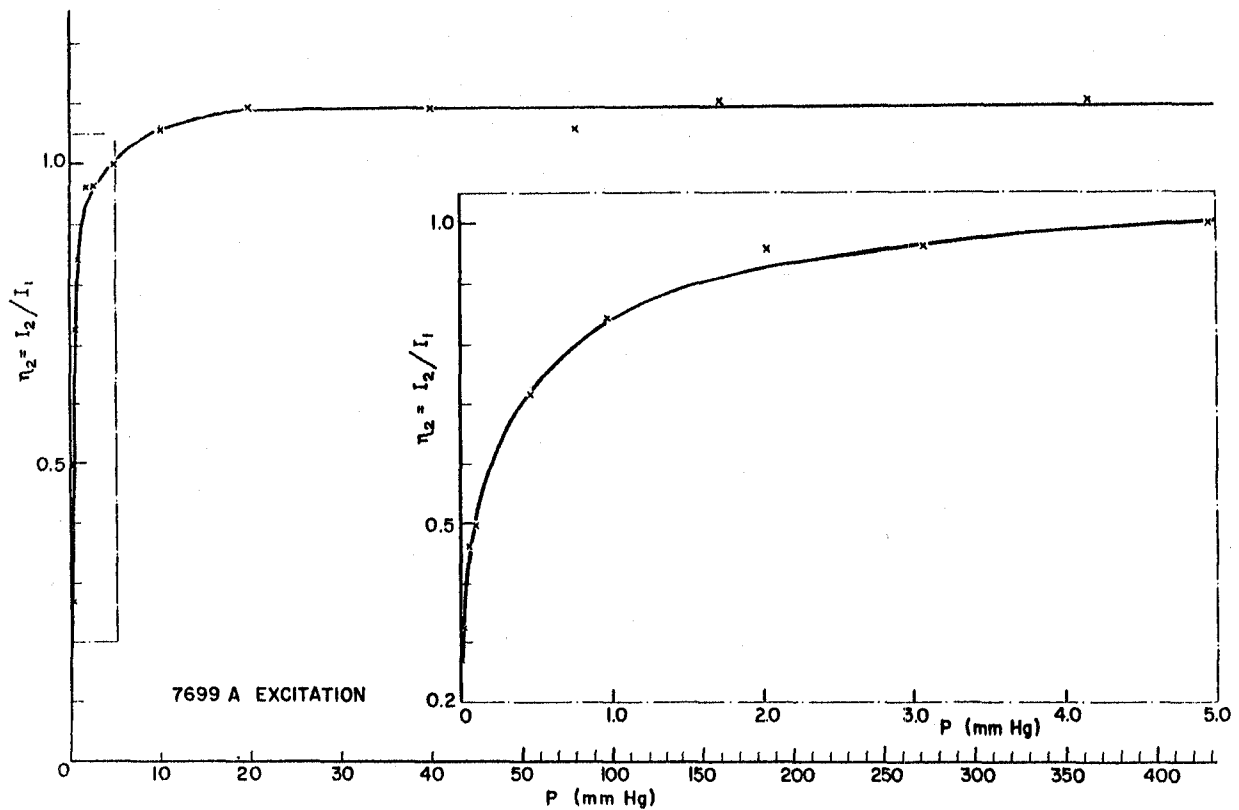


Fig. 17. A plot of  $\eta_2$  against argon pressure. The insert shows a magnified section of the plot near the origin.

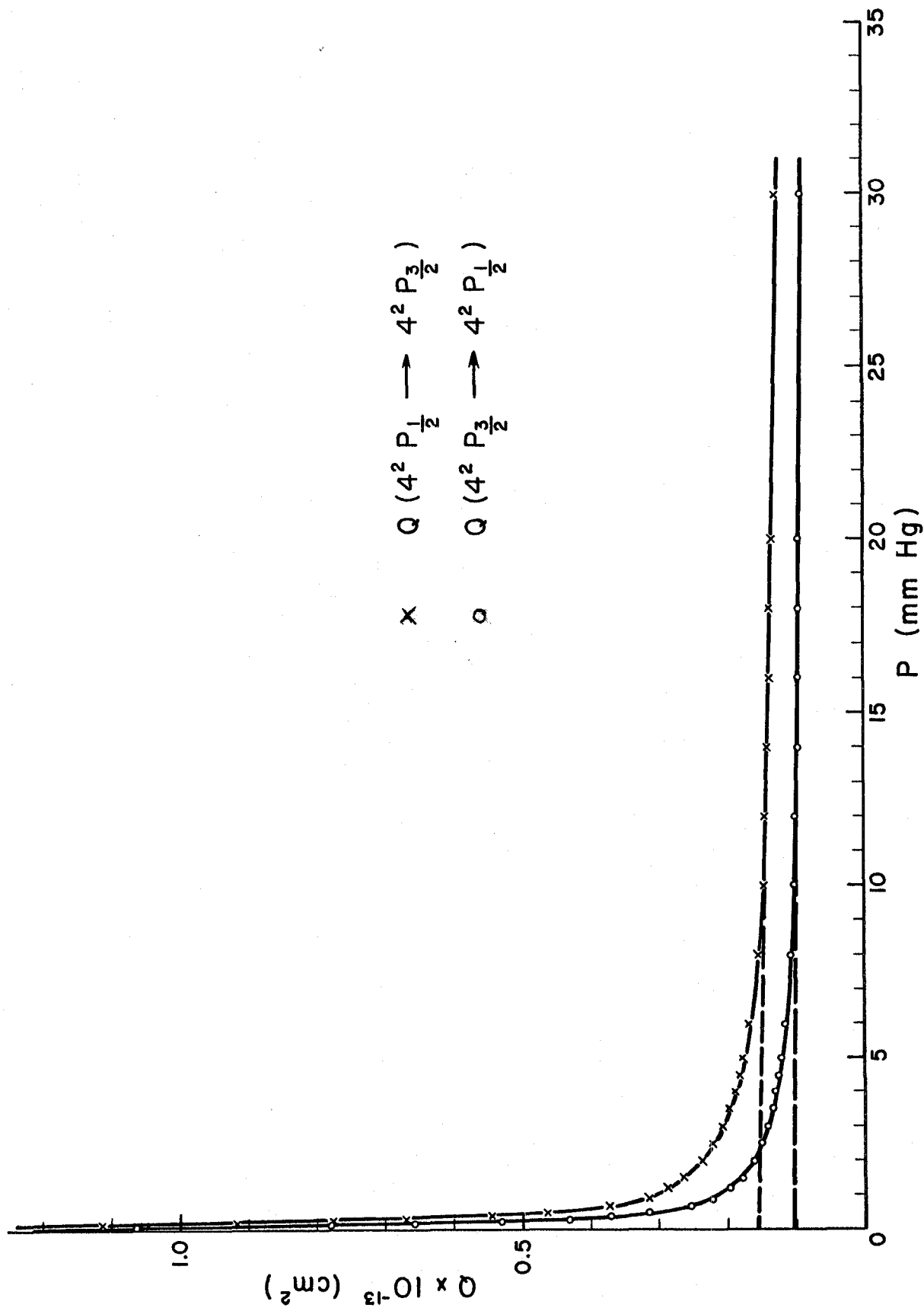


Fig. 18. The variation of cross-sections for potassium-helium collisions with helium pressure.

$$Q_1 (4^2P_{1/2} \rightarrow 4^2P_{3/2}) = 3.55 \times 10^{-14} \text{ cm}^2$$

$$Q_2 (4^2P_{3/2} \rightarrow 4^2P_{1/2}) = 3.02 \times 10^{-14} \text{ cm}^2$$

The cross-sections for both helium and argon are considerably smaller than those for potassium-potassium collisions corresponding to the same transitions. A similar effect has been observed by Seiwert (1956c) in the case of sodium-sodium and sodium-argon interactions.

As might be expected, the cross-sections for argon are larger than those for helium. The collision cross-sections are velocity dependent (Equation 6) and the velocity of a helium atom is greater than that of an argon atom at the same temperature, giving a smaller cross-section.

If values of the cross-sections are viewed as a measure of the classical efficiency of the collisions with respect to the transfer of energy, then these values would also have a reasonable relationship to each other. It is likely that a collision between argon (atomic mass 39.9) and potassium (atomic mass 39.1) would be more efficient than a collision between potassium and helium which has an atomic mass of 4.



## CONCLUSIONS

In the course of this research, the cross-sections for collisions of a second kind between potassium and potassium atoms were determined by a procedure involving an extrapolation of the results to zero vapour pressure. This method provides a satisfactory way of eliminating effects due to the imprisonment of radiation in the vapour, which tends to increase the effective lifetimes of the excited states.

The values  $Q_1 (4^2P_{1/2} \rightarrow 4^2P_{3/2}) = 95 \times 10^{-14} \text{ cm}^2$  and  $Q_2 (4^2P_{3/2} \rightarrow 4^2P_{1/2}) = 83 \times 10^{-14} \text{ cm}^2$  are considerably larger than

those quoted by Thangaraj (1948) and Hoffmann and Seiwert (1961), who obtained their results using theories for the diffusion of radiation in conjunction with their experimental observations.

The reliability of the extrapolation procedure depends critically on the availability of measurements in the region of low vapour pressure of potassium. Further experiments, which will utilize improved apparatus will extend the range of the measurements to still lower pressures than were employed in this investigation. A final corroboration of the results should be obtained by a direct experimental determination of the average lifetimes of the two resonance states at various vapour pressures.

Using a similar method, the collision cross-sections for collisions between potassium and helium and potassium and argon atoms corresponding to the transitions  $4^2P_{1/2} \rightarrow 4^2P_{3/2}$  and vice versa, were determined for the first time. These values are smaller than those for potassium-potassium collisions and their mutual relationship might be plausibly explained on the basis of the law of conservation of momentum. Further verification will be obtained from experiments with other inert gases, which will be performed at low potassium vapour pressures.

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## VITA AUCTORIS

The candidate for the Master of Science Degree was born in Humboldt, Saskatchewan on January 8, 1935 and spent his childhood on a farm. His elementary schooling was obtained from the Humboldt Separate School. From 1949 to 1953 he attended the Benedictine boarding school of St. Peter's College, Muenster, Saskatchewan, acquiring his senior matriculation. In 1953 he entered the University of Saskatchewan on an entrance scholarship and completed one year of pre-medical studies before transferring to the College of Engineering to embark on a course of studies in Engineering Physics, from which he graduated in 1958. Following graduation he joined the Federal Department of Transport to take a course in Meteorology. In the fall of 1958 he joined the Engineering faculty of Assumption University of Windsor and completed one lecture course from Wayne State University. The following year the candidate registered as a part time student in Assumption University advancing toward a Masters Degree in Physics.